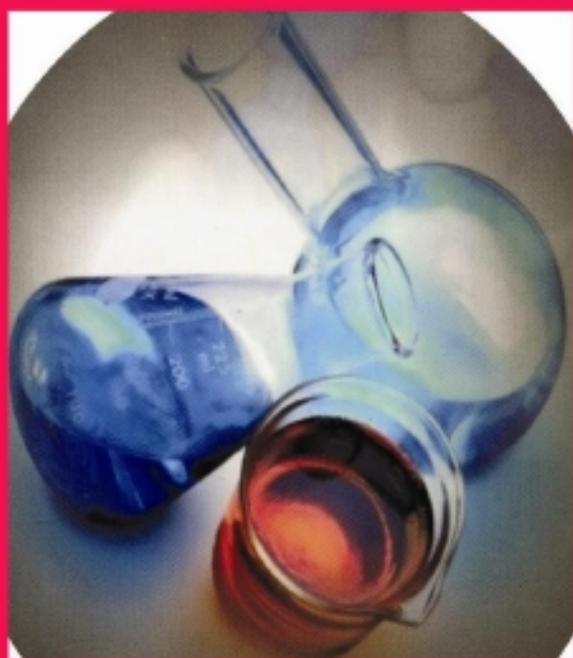


ADVANCED PHYSICAL CHEMISTRY EXPERIMENTS



PRAGATI PUBLICATIONS

Pragati's

**ADVANCED
PHYSICAL CHEMISTRY
EXPERIMENTS**

Dr. J.N. Gurtu

M.Sc., Ph.D.

Former Principal

Meerut College, Meerut

Amit Gurtu

B.Tech., P.G.D.M.



PRAGATI PRAKASHAN

PRAGATI PRAKASHAN

Educational Publishers

Head Office :

PRAGATI BHAWAN

240, W. K. Road, Meerut-250 001

SMS/Ph : (0121) 2643636, 6544642, 6451644

Tele/Fax : (0121) 2640642

Regd. Office :

New Market, Begum Bridge, Meerut-250 001

Phone : (0121) 2661657

Revised and Enlarged Edition : 2008

ISBN : 978-81-8398-527-7

CONTENTS

1. IMPORTANT FACTS IN EXPERIMENTAL CHEMISTRY	1-10
2. ERROR ANALYSIS AND STATISTICAL DATA ANALYSIS	11-25
3. ELECTRONICS	26-73
1. To measure the resistance with a multimeter.	26
2. To measure the output voltage of the audio signal generator with the help of CRO.	27
3. To become familiar with CRO.	29
4. To use a Wheatstone bridge for the accurate measurement of resistance.	31
5. To study the charge and discharge of a capacitor through a resistor.	32
6. To study the response characteristics of RC network	35
7. To study the response characteristics of LR network.	36
8. To verify the Kirchoff's current law (KCL).	37
9. To verify the Kirchoff's voltage law (KVL).	38
10. (1) To obtain Lissajous pattern on the CRO screen by feeding two sine-wave voltage from two signal generators.	
(2) To measure the frequency and phase shift by Lissajous pattern.	40
11. To determine the V-I characteristics of a given diode in :	42
(a) Forward biased mode/junction. (b) Reverse biased mode/junction.	
12. To use the clamping and clipping circuits.	44
13. To study half-wave and a full-wave rectifier circuit with and without capacitor filter and determine the ripple factor.	45
14. To determine the common base and common emitter characteristics of a transistor.	49
15. To design and construct the differential amplifier.	54
16. To :	
(i) Trace the circuit diagram of single stage transistor amplifier	
(ii) Measure the O point collector current and collector-to-emitter voltage.	
(iii) Measure the maximum signal which can be amplified by the amplifier without having clipped output.	
(iv) Measure the voltage gain of the amplifier at 1 kHz	
(v) Measure the voltage gain of the amplifier for different values of load resistance.	56
17. To study the introduction of an operational amplifier as a voltage follower.	58
18. To design operational amplifier as inverting and non-inverting amplifier.	59
19. To find the integration and differentiation with operational amplifier.	60
20. To study operational amplifier in (a) inverting mode (summing amplifier) (b) non-inverting mode (c) integrator (d) differentiator (e) difference amplifier.	61
21. To determine the energy band gap of a semiconductor (germanium) using four probe method.	66
22. To study the characteristics of an integrating and differentiating circuits.	70
23. To observe wave-forms and to measure amplitude, frequency and phase with a cathode ray oscilloscope.	71

4. MOLECULAR WEIGHT OF VOLATILE LIQUIDS **74-83**

1. To determine the molecular weight of the volatile liquid (chloroform, acetone, methanol) by Victor Meyer's method. 76
2. To determine the composition of a binary mixture of liquids by Victor Meyer's method. 80
3. To determine the solubility of CS_2 in CH_3OH at room temperature. 80
4. To find out the molecular weight of the given liquid by steam distillation method. 81
5. To determine the vapour pressure of chlorobenzene by steam distillation. 83

5. CRYOSCOPY (DEPRESSION IN FREEZING POINT) **84-101**

1. To find out the molecular weight of the given solute in water by depression in freezing point method. 86
2. To find out the concentration of the given solution of urea in water. 89
3. To find the molecular weight of sulphur, α -naphthol and biphenyl by freezing point method using naphthalene as solvent. 90
4. To find out the degree of dissociation of calcium nitrate. Also find its van't Hoff factor. 91
5. To find out the pH of the given 0.1N oxalic acid solution. 92
6. To find out the degree of association of benzoic acid in benzene. 93
7. To find out the degree of hydrolysis of the given substance, say CH_3COONa in 0.5M solution. 93
8. To study the formation of complex ions in solution of mercuric iodide in potassium iodide solution. 94
9. To find out the molecular weight of the given substance by Rast's Camphor method. 96
10. To determine the relative strength of acids. 96
11. To determine the dissociation constant of acetic acid in aqueous solution near 0°C . 97
12. To determine the latent heat of fusion per gram of ice (L_f) 97
13. To determine van't Hoff factor and find the apparent degree of association of benzoic acid and acetic acid in 1M and 0.5M solutions of benzene, near the freezing point of the liquid. 97
14. To analyse cryoscopically a given mixture of urea and glucose. 98
15. To determine K_f value of a given solvent. A solute of known molecular weight is provided. 98
16. To verify the formula of the complex salts like $\text{K}_2\text{S}_2\text{O}_8$, $\text{K}_4\text{Fe}(\text{CN})_6$ cryoscopically. 98
17. To determine the mean activity coefficient of an electrolyte (NaCl) in dilute solution by cryscopic measurements. 99

6. EBULLIOSCOPY (ELEVATION OF BOILING POINT) **102-109**

1. To find the molecular weight of the given solute in water by elevation of boiling point method. 104
2. To find out the concentration of the given solution of urea in water by elevation in boiling point method. 105
3. To find out the degree of dissociation of an electrolyte. Also find its van't Hoff factor. 106
4. To find out the ebullioscopic constant of water by taking a known substance. 107
5. To find out the molecular weight of a solute by Cottrell's method. 108

- | | |
|---|-----|
| 6. To determine the latent heat of evaporation. | 109 |
| 7. To determine the pH of an acid, say oxalic acid (or malonic acid). | 109 |
| 8. To study the association of organic acids and hydroxy compounds in benzene and other solvents. | 109 |

7. VISCOSITY **110-121**

- | | |
|--|-----|
| 1. To find the relative and absolute viscosity of the given liquid at the room temperature. | 114 |
| 2. To find the concentration of the given mixture, consisting of two liquids A and B by viscosity measurements. | 115 |
| 3. To find out the temperature coefficient for the given liquid. | 116 |
| 4. To determine the influence of temperature on viscosity. | 118 |
| 5. To calculate the molecular weight of a high polymer by means of viscosity measurements. | 118 |
| 6. To determine by viscosity method, whether the following pairs of liquids form molecular compounds or not :
(a) Water and ethyl alcohol. (b) Methyl alcohol and ethylidene chloride. (c) Nitric acid and chloroform. (d) Benzene and ethyl alcohol. | 120 |
| 7. To study the variation of viscosity with composition of the mixture of water and ethanol. | 120 |
| 8. To determine the viscosity of different mixtures of benzene and nitrobenzene and also test the validity of Kendall's equation. | 121 |

8. SURFACE TENSION **122-145**

- | | |
|---|-----|
| 1. To find the surface tension of the given liquid by drop weight method at room temperature. | 126 |
| 2. To find the composition of the given mixture of two components A and B. | 127 |
| 3. To find out the surface tension of the given liquid by single capillary rise method. | 128 |
| 4. To find out the surface tension of the given liquid by double capillary rise method. | 129 |
| 5. To find out the surface tension of CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ <i>n</i> -hexane at room temperature and hence calculate the atomic parachors of C, H and O. | 130 |
| 6. To find out the parachor of a solid in a given solvent by double capillary rise method, assuming the mixture law to hold good. | 131 |
| 7. To find out the molecular surface energy and the association factor of $\text{C}_2\text{H}_5\text{OH}$. | 132 |
| 8. To find out the parachor of a solid (say <i>p</i> -dichlorobenzene) in a given solvent (say benzene) by double capillary rise method, assuming the mixture law to hold good. | 134 |
| 9. To find out the molecular surface energy and the association factor of ethyl alcohol. | 135 |
| 10. To study the change of surface tension of a mixture of ethanol and water with composition by torsion balance method. | 138 |
| 11. To find the surface excess or molar surface area by using Gibb's adsorption equation | 142 |
| 12. To determine the critical miscelle concentration of soap. | 142 |
| 13. To show that surface activity of alcohol increases with chain length. | 143 |
| 14. To determine the interfacial tension between benzene and water at room temperature and test the validity of Antonoff's rule. | 144 |
| 15. To compare the cleansing powers of two samples of detergents supplied to you. | 144 |

9. VAPOUR PRESSURE OF LIQUIDS **146–151**

1. To determine the vapour pressure of a pure liquid, say benzene at a series of temperature and also determine the heat of vaporisation of liquid. 147
2. To determine the vapour pressure of water at different temperatures using Smith and Menzies apparatus. 148
3. To determine the vapour pressure of benzene at different temperatures by Ramsay-Young apparatus. Also determine latent heat of vaporisation. 149
4. To study the variation of vapour pressure of a liquid (benzene) using an isoteniscope. 151

10. SOLUBILITY **152–167**

1. To determine the solubility of a given salt at room temperature and also draw its solubility curve. 154
2. To find out the heat of solution of a substance, say oxalic acid by solubility method. 156
3. To determine the solubility of an organic acid at 40° and at a temperature lower than the room temperature. 157
4. To determine the solubility product of Ca(OH)_2 at room temperature. 158
5. To study the variation of the solubility of AgBrO_3 in KBrO_3 solution and to determine the solubility product of AgBrO_3 . 159
6. To study the effect of ionic strength on the solubility of CaSO_4 and so determine its thermodynamic solubility product and mean ionic activity. 150
7. To study the variation of solubility of potassium hydrogen tartrate with ionic strength using a salt having a common ion and thereby determine the mean ionic activity coefficients. 162
8. To determine the solubility of oxygen in water at room temperature. 164
9. To study the influence of the addition of various substances on the solubility of solutes. 165
10. To study the effect of concentration of an electrolyte such as KCl , NaCl , Na_2SO_4 , K_2SO_4 on the solubility of an organic acid (benzoic acid or salicylic acid) at room temperature. 165
11. To study the variation of solubility of Ca(OH)_2 in NaOH solution and also to determine its solubility product. 166

11 TRANSITION TEMPERATURE **168–174**

1. To find out the transition temperature of Glauber's salt by dilatometric method 169
2. To find out the transition temperature of Glauber's salt by solubility method. 171
3. To find out the transition temperature of Glauber's salt by thermometric method. 172
4. To determine the transition temperature of double chloride of copper and potassium. 174
5. To determine the transition of temperature of mercuric iodide. 174
6. To determine the transition temperature of sulphur system. 174

12. PARTITION COEFFICIENT **175–191**

1. To find out partition coefficient of I_2 between CCl_4 and H_2O . 176
2. To find out the partition coefficient of benzoic acid between C_6H_6 and water. 178
3. To find out the dimerisation constant of benzoic acid in benzene medium. 180

4.	To find out the equilibrium constant for the tri-iodide formation, $I_2 + I^- = I_3^-$	182
5.	To study the complex formation and find the formula of silver ammine complex by partition method.	185
6.	To find the formula of complex cuprammonium ion or study the complex formation between $CuSO_4$ and NH_3 solution.	187
7.	To determine the partition coefficient of succinic acid between water and ether.	189
8.	To determine the molecular weight of succinic acid in benzene by determining its partition coefficient with water.	190
9.	Study the partition of salicylic acid or picric acid between water and benzene and between water and chloroform.	190
10.	Find out the dimerisation constant of phthalic acid in a suitable solvent of your choice.	190
11.	Find out the partition coefficient of acetic acid between water and cyclohexane or butanol.	191
12.	Find out the molecular state of benzoic acid in benzene and water.	191

13. COLLOIDS 192-201

1.	To prepare colloidal solutions of As_2S_3 , Sb_2S_3 and $Fe(OH)_3$.	193
2.	To find out the precipitation values of As_2S_3 sol by using monovalent, bivalent and trivalent cations. Also test the validity of Schulze-Hardy law and Freundlich's adsorption isotherm.	195
3.	To investigate the nature of charge on particles in a given colloidal solution and determine their electrophoretic velocity and zeta potential.	198
4.	To find out the precipitation values of a number of active ions for a ferric hydroxide solution.	200
5.	To find out the effect of electrolytes on the viscosity of a gelatin gel.	200
6.	To find out the effect of concentration of an electrolyte on the viscosity of a gelatin gel.	200
7.	To study the effect of gelatin solution on the precipitation values of $NaCl$ and $BaCl_2$ for silver sol.	200
8.	To study the protective action of a hydrophilic colloid (such as starch, gelatin) on the precipitation of lyophobic sols.	201
9.	To study the mutual coagulation of As_2S_3 solution and $Fe(OH)_3$ solution and determine the optimum ratio for precipitation.	201

14. ADSORPTION 202-209

1.	Study the adsorption of acetic acid on charcoal and prove the validity of Freundlich's adsorption isotherm and Langmuir's adsorption isotherm.	202
2.	To determine the surface area of the given powdered catalyst sample by means of BET adsorption isotherm.	204
3.	To study the adsorption of iodine from alcoholic solution on charcoal.	208
4.	To study the adsorption of oxalic acid on charcoal and test the validity of Langmuir's and Freundlich's adsorption isotherm.	209
5.	To study the effect of temperature on adsorption.	209
6.	To study the adsorption of certain dyes such as methyl violet, picric acid or malachite green on charcoal.	209

15. PHASE EQUILIBRIUM 210-226

1.	To draw the mutual solubility curve of two immiscible liquids and find out the C.S.T. of phenol-water system	210
----	--	-----

2. Plot a graph for the miscibility temperature of mixture of 5 ml of 80% phenol and 5 ml of water in presence of 0.0 to 1.0% NaCl in aqueous layer in steps of 0.2% and find the amount of NaCl in the given solution of NaCl of unknown percentage. 212
3. Determine the compositions and the amounts of the layers obtained by mixing 55g of C₆H₅OH and 45 g of H₂O at any temperature. 213
4. Study the boiling point-composition curve for the binary liquid mixture of two miscible liquids. 214
5. Study the boiling point-composition curves for binary liquid mixtures. 215
6. Study the boiling point-composition curves for systems of binary liquid mixtures. 216
7. Draw a phase diagram for lead and tin and from it find out the melting points of the two components. Find the eutectic temperature also. 216
8. To determine the phase diagram of naphthalene and diphenyl system. 219
9. To determine the freezing point diagram of o-nitrophenol and p-toluidine system. 219
10. To construct a phase diagram for a two component system by plotting cooling curves for mixtures of different compositions. 219
11. To obtain the phase diagram for water-ethanol-benzene system at room temperature. 221
12. To study the mutual solubility and determine the upper and lower consolute temperatures of (a) nicotine-water system (b) glycerol-m-toluidine system. 223
13. To study the mutual solubility of triethyl amine-water system and find the critical solution temperature. 223
14. Construct a phase diagrams for : (a) urea (m. pt. 132°C) and phenol (m. pt. 43°C) system, (b) α-naphthyl-amine-phenol system. 223
15. Determine the freezing point curve of picric acid-benzene system. 223
16. To obtain a solubility curve for a ternary system of liquids, say water-acetic acid-chloroform system. 224
17. To study the influence of impurity on a ternary mixture. 226
18. To study the miscibility curve of a ternary system at different temperatures, by taking water-acetic acid- benzene. 226
19. Construct the phase diagram of three component system containing ethanol, benzene and water. 226

16. THERMOCHEMISTRY

227-246

1. To find the water equivalent of the calorimeter and also find out the heat of dilution of H₂SO₄. 229
2. To find out the heat of neutralisation of NaOH and HCl. 230
3. To determine the heats of neutralization of two acids, e.g., HCl and CH₃COOH and hence their relative strength. 233
4. To find the heats of reaction for the reactions :
 - (a) $\text{HC}_2\text{O}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C}_2\text{O}_4 + \text{OH}^-$
 - (b) $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^-$ 233
5. To determine the basicity of a polybasic acid of molecular weight 126. Also obtain the heat of neutralisation for the different stages of neutralisation. 234
6. To find out the heat of neutralisation of HAc by NaOH and from it also calculate the heat of ionisation of HAc. 235
7. To find out the heat of solution of a given substance. 236
8. To determine integral heats of dilution of H₂SO₄ starting with 10M acid and going down to 5M acid in the order 9M, 8M, 7M, 6M. 237
9. To determine the heats of formation of MgO and ZnO calorimetrically. 238

10. To determine the enthalpy change for the precipitation of a mole of Cu or Ag by Zn, Fe or Mg powder.	239
11. To find out the heat of precipitation of AgI.	240
12. To determine the fuel value of the given fuel by using a bomb calorimeter.	241
13. To determine the heat of hydration of anhydrous copper sulphate.	243
14. To determine the heat of hydration of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$).	244
15. To determine the heat of solution at various temperatures.	244
16. To determine the integral heat of solution of a salt at two concentrations and hence the integral heat of dilution.	244
17. To determine the heat of neutralisation of acetic acid by ammonium hydroxide.	245
18. To determine the heat of precipitation of BaSO_4 .	245
19. To determine the heat of transition of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ by calorimetry.	246

17. REFRACTOMETRY

247–255

1. To find out the refractive index of the given liquid and also find its molecular refractivity.	249
2. To find out the molecular refractivities of three liquids A, B and C. Also calculate the composition of the liquid C, which is a mixture of two liquids A and B.	250
3. To find out the atomic refractivities of C, H and O, by taking methyl acetate, ethyl acetate and n-hexane as the experimental liquids.	251
4. To determine the molecular refractivity of a solid.	252
5. To determine the refractive indices of a series of solutions of KCl and hence determine the compositions of the unknown solution of the salt.	253
6. To study the variation of refractive index with composition of mixtures of carbon tetrachloride and ethyl acetate.	253
7. You are provided with two liquids 1 and 2 and their mixtures 3 and 4. By means of a refractometer find the compositions of 3 and 4.	254
8. To determine the molar refractions of ethyl acetate, propyl acetate and butyl acetate and show the constancy of the contribution to the molar refraction made by $-\text{CH}_2$ group.	254
9. To determine molar refractivity of ethyl acetate, methyl acetate, ethylene chloride and chloroform and calculate the atomic refractivities of C, H and Cl. The density of each liquid can be measured experimentally or seen from the table.	254
10. To measure refractometrically average polarizability of some of the common solvents.	255
11. To calculate the value of optical exaltation.	255

18. CHEMICAL KINETICS

256–293

1. To find the velocity constant of the hydrolysis of methyl acetate catalysed by an acid.	264
2. To determine the order of saponification of ethyl acetate with NaOH.	266
3. To compare the strength of two acids say hydrochloric acid and sulphuric acid, used in equal concentration for the hydrolysis of methyl acetate.	268
4. To study the reaction kinetics of decomposition of benzene diazonium chloride in the temperature range 90°C to 60°C . Calculate the rate constant also.	269
5. To study the reaction between acetone and iodine in presence of acids.	270
6. To study the kinetic characteristics of iodination of acetone using a colorimeter.	273
7. To find out the order of reaction between potassium bromate and potassium iodide.	274

8. To find out the rate constant and order of reaction between hydrogen peroxide and hydroiodic acid.	275
9. To find out the velocity constant of the reaction between potassium persulphate and potassium iodide. Also calculate the activation energy and the influence of ionic strength on the rate constant.	277
10. To study the kinetics of iodine clock reaction.	280
11. To study the oxidation of iodide ions by H_2O_2 as an iodine clock reaction.	281
12. To study the kinetics of bromination of phenol by bromide-bromate mixture in an acid medium as a clock reaction.	283
13. To study the effect of change in ionic strength of solution on the kinetics of the reaction $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$.	285
14. To study the kinetics of depolymerisation of diacetone alcohol by means of a dilatometer.	287
15. To study the decomposition of hydrogen peroxide catalysed by iodide ion.	288
16. To find out the order of reaction of the hydrolysis of cane sugar.	290
17. To study the kinetics of bromination of acetone in presence of acid as catalyst.	290
18. To determine the relative strength of HCl , HNO_3 and H_2SO_4 by studying the kinetics of hydrolysis of methyl acetate.	290
19. To determine the relative strength of monochloroacetic acid (4N) and trichloroacetic acid (4N) by studying the kinetics of hydrolysis of methyl acetate or cane sugar.	290
20. To determine the degree of hydrolysis of urea hydrochloride (A) by studying the hydrolysis of methyl acetate by an acid and A.	290
21. To find out the order of reaction between sodium thiosulphate and ethyl bromoacetate.	290
22. To find out the order of reaction between chromic acid and oxalic acid.	291
23. To find out the effect of adding an indifferent electrolyte to the system of potassium persulphate and potassium iodide.	291
24. To study the reaction between potassium persulphate and potassium iodide in presence of an excess of latter.	291
25. To investigate the velocity of muta-rotation of α -D-glucose in water polarimetrically.	291
26. To study the autocatalytic reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ ions catalysed by Mn^{2+} ions.	292
27. To determine the temperature coefficient of hydrolysis of methyl acetate and its energy of activation.	293

19. TRANSPORT NUMBER

294-301

1. To determine the transport numbers of Ag^+ and NO_3^- ions in solution of AgNO_3 by Hittorf's method.	294
2. To find out the transport number of K^+ and Cl^- ions by moving boundary method.	298
3. To determine the transport numbers of copper and sulphate ions in 0.5 M solution of copper sulphate by Hittorf's method.	300
4. To determine the transport number of silver and chloride ions by moving boundary method.	301
5. To determine the transport number of chloride ions in a solution of 0.5N HCl by moving boundary method.	301

20. POLARIMETRY

302-312

1. To find the specific rotation and molecular rotation of cane sugar polarimetrically and also find the concentration of the unknown solution.	307
---	-----

2. To find out the order of reaction and velocity constant for the inversion of cane sugar by acids.	309
3. Find out the percentage of d-sugar and d-tartaric acid in a given solution polarimetrically.	310
4. To determine the specific rotation of turpentine oil, tartaric acid.	311
5. To determine the relative strength of acids.	311
6. To determine the specific rotation of camphor in benzene or carbon tetrachloride.	311
7. To determine the intrinsic rotation of a solution of cane sugar polarimetrically.	311
8. To study the influence of solvent on the optical rotation of a solute.	312
9. To study the influence of added impurity on the rotation of a solute.	312

21. CONDUCTIVITY

313–336

1. To find out the cell constant of the cell and find out the equivalent conductivity of a solution of barium chloride at various dilutions. Also infer the results obtained.	321
2. To determine the dissociation constant of HAc and verify the Ostwald's dilution law.	322
3. To find out the equivalent conductivity of strong electrolytes at different dilutions and from them also find out the equivalent conductivity of a weak electrolyte at infinite dilution.	325
4. To determine the equivalent conductivity of a strong electrolyte at several concentrations and verify the applicability of Debye-Huckel-Onsagar equation.	327
5. To determine the basicity of an acid, say citric acid conductometrically.	327
6. To find the solubility and solubility product of a sparingly soluble salt, say barium sulphate conductometrically.	328
7. To determine the degree of hydrolysis and hydrolysis constant of ammonium chloride at room temperature.	330
8. To determine the order of reaction of the saponification of ethyl acetate by NaOH. Also determine the rate constants at different temperatures and from them calculate the energy of activation of the reaction.	331
9. To study the kinetics of hydrolysis of a tertiary aliphatic halide conductometrically.	334
10. To compare relative strengths of different acids say acetic acid and monochloroacetic acid.	336
11. To determine the basicity of tartaric acid, oxalic acid etc.	336
12. To find out the degree of dissociation and dissociation constant of monochloroacetic acid.	336
13. To study the kinetics of ionisation of nitroethane in presence of pyridine in 80% alcohol solution.	336

22. CONDUCTOMETRIC TITRATIONS

337–350

1. To find out the strength of HCl solution by titrating it against standard NaOH solution conductometrically.	338
2. To find out the strength of given NH_4OH by titrating it against HCl solution conductometrically.	339
3. To find out the strength of the given HAc solution by titrating it against NaOH solution conductometrically.	340
4. To determine the strength of a moderately strong acid (like salicylic acid, mandelic acid or malonic acid) in the given solution conductometrically.	341
5. To find out the strength of HCl and HAc in a mixture of both by titrating it against NaOH solution conductometrically.	343
6. To estimate oxalic acid by carrying out suitable conductometric titrations in the following solutions :	

(a) A solution of pure oxalic acid	(b) A solution of oxalic acid and HCl	
(c) A solution of oxalic acid and CH_3COOH		345
7. To estimate conductometrically HNO_3 and H_2SO_4 in a mixture of both the acids.		345
8. Titrate a given mixture of H_2SO_4 , HAc and CuSO_4 against 0.1M NaOH solution conductometrically.		346
9. To determine the strength of acetic acid by titration with ammonium hydroxide.		346
10. To determine the strength of boric acid by titrating it with sodium hydroxide.		346
11. To perform the conductometric titration between a salt and alkali (or acid), e.g., between magnesium sulphate and barium hydroxide (Displacement titration).		347
12. To study the complex formation between two species, e.g., potassium iodide and mercuric iodide.		347
13. To study the conductometric titration of a Lewis acid (stannic chloride) with a Lewis base (benzophenone) in a non-aqueous medium (thionyl chloride).		347
14. To determine the strength of silver nitrate by titration with sodium chloride or potassium thiocyanate (precipitation titration).		348
15. To titrate a given solution of phenol with NaOH.		348
16. A commercial sample of vinegar is suspected of having H_2SO_4 . Show conductometrically if it is so and estimate the impurity of mineral acid, if present.		349
17. To estimate conductometrically sodium acetate and ammonium chloride in 50 ml of a mixture of both.		349
18. To estimate conductometrically the quantities of HCl and NH_4Cl in a given mixture.		349
19. To estimate conductometrically NH_4OH and NH_4Cl in their mixture.		349
20. To titrate 10 ml of 0.1 N KI solution after dilution to 150 ml with 0.1 N $\text{Hg}(\text{ClO}_4)_2$ solution. Repeat the titration with 0.05 M HgCl_2 solution.		349
21. To find out the concentration of H_2SO_4 , HCl and HClO_4 in a given mixture by conductometric titration.		350
22. To determine the strength of NaOH and NH_4OH in a given solution by titrating it against HCl.		350

23. pH TITRATIONS

351-359

1. To find out the strength of the given hydrochloric acid solution by titrating it against NaOH. Use a pH meter.	353
2. To find out the strength of HCl and CH_3COOH in a mixture of both by titrating it against NaOH solution. Use a pH meter	354
3. To determine the pH of a given solution with indicators.	354
4. To determine the pH of a given solution by comparator method or buffer solution method.	356
5. To find out the strength of acetic acid by titrating it against sodium hydroxide.	357
6. To find out the strength of ammonia solution by titrating it against acetic acid solution.	357
7. To find out the strength of ammonia solution by titrating it against hydrochloric acid.	358
8. To find out the strength of borax solution by titrating it against hydrochloric acid.	359
9. To find out the strength of sodium carbonate solution by titrating it against hydrochloric acid.	359
10. To find out the dissociation constants of a polybasic acid, say phosphoric acid by titrating it against sodium hydroxide solution.	359

1. To determine the electrode potentials of copper and zinc electrodes in 0.1M and 0.01M solutions and calculate SEP of these electrodes. 368
2. To find out the strength of HAC by titrating it against NaOH potentiometrically. Also calculate the dissociation constant of the acid using quinhydrone electrode. 370
3. (a) To determine the mean ionic activity coefficients of hydrochloric acid solution at different concentrations.
(b) To study the effect of ionic strength on mean activity coefficient of hydrochloric acid in a given solution. 374
4. To find the mean ionic activity coefficients in a solution of zinc chloride. 377
5. To determine the transport numbers in HCl and $ZnSO_4$ solutions potentiometrically. Use 0.01M and 0.1M HCl and 0.1M and 0.5M $ZnSO_4$ solutions. 378
6. To find the strengths of HCl and CH_3COOH in a given mixture potentiometrically. 380
7. To determine the transport numbers of Ag^+ and NO_3^- ions in solutions of $AgNO_3$ in the concentration range 0.01M to 0.1M (Mean activity coefficients of silver nitrate in 0.01M and 0.1M solutions are 0.89 and 0.73). 380
8. To find out the strength of the given ferrous ammonium sulphate solution (approximate strength N/10) by titrating it against potassium dichromate solution potentiometrically. Also find the redox potential of the ferrous-ferric system. 381
9. To find out the strength of the given ferrous ammonium sulphate solution by titrating it with 0.1N $KMnO_4$ solution potentiometrically. Also find the redox potential of $Fe^{2+} - Fe^{3+}$ system. 382
10. To find out the dissociation constants of phosphoric acid by titrating it with a standard solution of NaOH. Use a hydrogen electrode. 384
11. To find out the strength of cobalt sulphate solution by titrating it against a standard solution of potassium ferricyanide potentiometrically. 386
12. To find out the strength of the given halide solution by titrating it against a standard $AgNO_3$ solution, potentiometrically. 388
13. To find out the strength of a mixture of halides by titrating it against $AgNO_3$ solution potentiometrically. 389
14. To determine the hydrolysis constant of aniline chloride by e.m.f. method. 390
15. To determine the solubility and solubility product of a sparingly soluble salt potentiometrically. 391
16. To determine the valency of mercurous ions potentiometrically. 392
17. To determine the heat of reaction, equilibrium constant and other thermodynamic functions for the reaction $Zn + Cu^{2+} = Zn^{2+} + Cu$, potentiometrically 393
18. To determine the equilibrium constant for the formation of complex ion $[Ag(NH_3)_2]^+$ potentiometrically. 394
19. To find out the composition of zinc ferrocyanide precipitate on adding zinc sulphate to acidified potassium ferrocyanide solution, potentiometrically. 395
20. To titrate a solution of silver nitrate with potassium chloride by the differential titration technique. 396
21. To titrate ferrous ammonium sulphate solution with potassium dichromate solution potentiometrically using a bimetallic electrode pair. 397
22. To titrate iodine solution with sodium thiosulphate by the dead stop end point or polarisation method. 397
23. To find out the strength of KI or KBr solution (approximate strength N/10) by titrating it against silver nitrate solution. 399

24. To find out the strength of KI and KBr (or KCl and KBr) solutions (approximate strength N/10) in a given mixture by titrating against silver nitrate solution. 399
25. To find out the strength of KI, KBr and KCl solution (approximate strength N/10) in a given mixture by titrating it against silver nitrate solution. 399
26. To find out the strength of KCNS solution by titrating it against silver nitrate solution. 399
27. To determine the standard oxidation potential of $\text{Fe}(\text{CN})_6^{4-} - \text{Fe}(\text{CN})_6^{3-}$ system. 400
28. To determine potentiometrically the thermodynamic functions for the reactions :
 (i) $\text{Zn (s)} + \text{Pb}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Pb (s)}$
 (ii) $\text{Pb (s)} + 2\text{AgCl (s)} \rightarrow \text{PbCl}_2 (\text{s}) + 2\text{Ag (s)}$ 400
29. To titrate 0.1 M solutions of oxalic acid, malonic acid and tartaric acid against 0.1 M NaOH solution potentiometrically. 400

25. COLORIMETRY

401–428

1. To determine iron in the given sample of water (or determine the concentration of the unknown solution) using Duboscq colorimeter. 405
2. To verify Beer's law for solutions of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ using absorptionmeter and determine concentrations in their solutions of unknown concentration. 407
3. To test the validity of Beer-Lambert's law using photo electric absorptionmeter and to determine the unknown concentration of the solution. 408
4. To scan a spectral absorption curve of a given substance using a spectrophotometer (Bausch-Lomb Spectronic-20 colorimeter) and also determine the wavelength of maximum absorption. 409
5. To obtain the calibration curve for a given compound and verify the Beer-Lambert's law and determine the known concentration of the compound. 410
6. Obtain a spectral absorption curve of a given substance using a spectrophotometer and also find the wavelength of maximum absorption. 410
7. To determine the phosphate concentration in a soft drink. 411
8. To determine the composition of a binary mixture containing say $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 spectrophotometrically. 412
9. To find the composition of ferric ions–thiocyanate complex by Job's method. 414
10. To study the complex formation between Fe(III) and salicylic acid and to find the formula and stability constant of the complex. 415
11. To study the formation of complex formed between nickel ion and o-phenanthroline by Job's method. 417
12. To determine the dissociation constant of phenolphthalein colorimetrically. 417
13. To determine the ionisation constant of bromophenol blue. 419
14. To titrate a solution of 0.1N NaOH against approximately 0.1N HCl spectrophotometrically. 421
15. To find out the strength of the given ferric ammonium sulphate solution by using EDTA solution spectrophotometrically. 421
16. To find the strength of CuSO_4 solution by titrating it with EDTA spectrophotometrically. 422
17. To titrate ferrous ammonium sulphate with potassium permanganate solution spectrophotometrically. 422
18. To determine the concentrations of Cu(II) and Fe(III) solution photometrically by titrating it with EDTA. 423
19. To determine simultaneously arsenic (III) and antimony (IV) in a mixture by spectrophotometric titration. 424

- | | |
|---|-----|
| 20. To study the kinetics of decomposition of the complex formed between sodium sulphate and sodium nitroprusside spectrophotometrically and also to determine the order and rate constant of the reaction. | 424 |
| 21. To determine colorimetrically the order and energy of activation for the decomposition of violet coloured complex of ceric ions and N-phenyl anthranitic acid. | 425 |
| 22. To study the decomposition of oxalic acid in a solution photosensitised by uranyl sulphate. | 427 |
| 23. To determine the composition of a binary mixture of aurine and crystal violet spectrophotometrically. | 427 |
| 24. To determine the composition of a binary solution containing N-butylacetanilide and benzyl benzoate in 95% ethanol, photometrically. | 428 |
| 25. To test the validity of Beer's law for a solution of CuSO_4 and also determine λ_{max} . | 428 |
| 26. To find out the concentration of CuSO_4 solution using Duboscq colorimeter. | 428 |

26. POLAROGRAPHY AND AMPEROMETRY (Current-Potential Relationships)

429–452

- | | |
|---|-----|
| 1. To study the variation of diffusion current with concentration, and also to construct a wave height-concentration curve for cadmium ion. | 438 |
| 2. To plot a polarogram for a mixture of Cd^{2+} , Zn^{2+} and Mn^{2+} ions. | 439 |
| 3. To plot current-voltage curves for 0.05M and 0.01M solutions of copper sulphate and sulphuric acid using bright platinum electrodes. | 443 |
| 4. To study the polarogram of the solution of supporting electrolyte with and without the elimination of dissolved oxygen. | 444 |
| 5. To plot a polarogram for a mixed solution of Cd^{2+} , Zn^{2+} and Mn^{2+} ions in 0.1M KCl. | 444 |
| 6. To determine the half-wave potential of Zn^{2+} and Cd^{2+} ion in 0.1M KCl solution. | 445 |
| 7. To find the formation constant of copper glycinate complex polarographically. | 446 |
| 8. To carry out the following amperometric titrations : | |
| (a) A solution of lead nitrate in potassium nitrate against potassium dichromate solution. | |
| (b) A solution of potassium sulphate against lead nitrate. | |
| (c) A solution of $\text{Ba}(\text{NO}_3)_2$ in KNO_3 against $\text{K}_2\text{Cr}_2\text{O}_7$. | 447 |
| 9. To determine nickel in solution by amperometric titration with dimethyl glyoxime. | 448 |
| 10. To titrate amperometrically bismuth, lead and calcium in solution with EDTA. | 449 |
| 11. To determine the formula and stability constant of a metal ion complex (lead oxalate complex). | 450 |

27. CHROMATOGRAPHY

453–478

- | | |
|---|-----|
| 1. To separate a mixture of sudan red and sudan yellow by adsorption on silica gel column. | 462 |
| 2. To separate a mixture of methylene blue and fluorescein (sodium salt) on an alumina column. | 463 |
| 3. To separate a mixture of 2 : 4 dinitrophenyl hydrazones by adsorption chromatographic technique. | 463 |
| 4. To separate a mixture of <i>o</i> and <i>p</i> -nitroanilines on an alumina column. | 464 |
| 5. To study the isolation of ions of inorganic substances by paper chromatography. | 465 |

6. To study the separation of organic acids by one dimensional paper chromatography. 465
7. To study the separation of amino acids by one and two dimensional paper chromatography. 466
8. To differentiate common sugars by paper chromatography and to analyse their mixture. 467
9. To demonstrate the separation of inorganic ions by paper chromatography. 468
10. To demonstrate the separation of dyes (azobenzenes) by thin layer chromatography. 471
11. To analyse a mixture of components, say *q*- and *p*-nitroanilines by TLC technique. 472
12. To prepare free acid or base from the salt of an organic acid (say sodium citrate) or base (as aniline hydrochloride) using cation and anion exchange resins. 473
13. To determine the concentration of a salt solution by ion exchange chromatography 474
14. To determine the composition of a solution containing an acid and its salt (sodium acetate) and acetic acid. 475
15. To study the separation of inorganic cations by paper electrophoresis. 476
16. To study the separation of amino acids in a mixture by paper electrophoresis. 477
17. To determine the iso-electric point of glutamic acid by paper electrophoresis. 477
18. To check up by column or TLC technique whether the following inks consist of single or multiple mixtures of dyes:
(a) Royal blue, (b) Red, (c) Blue black, (d) Black. 478
19. To separate components of chlorophyll by ascending paper chromatography. 478

28. DIPOLE MOMENT AND MAGNETIC SUSCEPTIBILITY **479–489**

1. To determine the dipole moment of the given liquid. 481
2. To determine the magnetic susceptibility of Mohr's salt at room temperature and also calculate its magnetic moment. 488

29. EQUILIBRIUM AND DISSOCIATION CONSTANTS **490–499**

1. To determine the equilibrium constant of the esterification reaction between acetic acid and ethanol. 492
2. To determine the equilibrium constant of the following reversible reaction :

$$2\text{Ag}^+ + \text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ag}_2\text{SO}_4(\text{s}) + \text{Ca}^{2+}$$
 493
3. To determine the equilibrium constant of the keto-enol tautomerism of ethyl acetoacetate. 495
4. To determine the dissociation constant of picric acid by studying its distribution between benzene and water. 497

30. GAS ANALYSIS **500–503**

1. To determine carbon dioxide, carbon monoxide, oxygen and nitrogen in the sample of flue gas provided to you, using a simple Orsat set up. 500

APPENDIX **504–516**

1

IMPORTANT FACTS IN EXPERIMENTAL CHEMISTRY

[I] CONCENTRATION OF SOLUTION

A homogeneous mixture of two or more substances is called a solution. The concentration of a dissolved substance (solute) in a solution is determined by its amount contained in a definite weight (or volume) of the solvent (or solution). The concentration of a solution can be expressed in a number of following different ways:

[A] Expressing Concentration in Physical Units

(1) **In terms of percentage composition** : It is expressed by the number of weight units (g) of the solute in 100 weight units (g) of the solution. For example, 10% aqueous glucose solution contains 10 g of glucose in 100 g of solution. For preparing this solution, 10 g of glucose is dissolved in 90 g of water to form 100 g of solution.

(2) **In terms of weight of solute per unit volume (litre or dm³) of solution** : In such a case, we can express 1 g of glucose per dm³ of the solution, i.e., 1 g of glucose is dissolved in water and the total volume is made 1000 cm³ or 1 litre of solution.

(3) **By weight of solute per weight of solvent** : For example, 5 g of NaCl in 100 g of water.

(4) **In terms of parts per million (ppm)** : This is usually used for solutions when the substance is present in a very small amount. It is defined as,

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 10^6$$

[B] Expressing Concentration in Chemical Units

(1) **In terms of normality** : Normality (N) of a solution is defined as the number of gram equivalent weight of the solute in one litre (dm³) of the solution. For example, 1*N* solution of sodium chloride (eq. wt. = 58.5) contains $1 \times 58.5 = 58.5$ g of sodium chloride in 1 litre (dm³) of the solution. Similarly, 0.1*N* solution of oxalic acid (eq. wt. = 63) contains $0.1 \times 63 = 6.3$ g of oxalic acid in 1 litre (dm³) of the solution .

(2) **In terms of molarity** : Molarity (M) of a solution is defined as the number of moles of the solute in 1 litre (dm³) of the solution. For example, 0.2*M* solution of oxalic acid (mol. wt. = 126) contains $0.2 \times 126 = 25.2$ g oxalic acid in one litre (dm³) of solution.

(3) In terms of molality : Molality (m) of a solution is defined as the *number of moles of the solute per kilogram (1000 g) of the solvent*. For example, 1 m solution of glucose (mol. wt. = 180) contains $1 \times 180 = 180$ g of glucose in 1 kg (1000 g) of water.

(4) In terms of mole fraction or mole percent : Mole fraction of a substance in a solution is defined as the *number of moles of that substance divided by the total number of moles of all the substances in the solution*. The sum of the mole fractions of all the components in a solution is always unity. In a binary solution,

$$\text{Mole fraction of solute} = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

Similarly,

$$\text{Mole fraction of solvent} = \frac{\text{Moles of solvent}}{\text{Moles of solute} + \text{Moles of solvent}}$$

For example, if a solution contains 1 mole of A and 2 moles of B, then mole fraction of A will be $\frac{1}{1+2} = \frac{1}{3}$. Similarly, mole fraction of B will be $\frac{2}{1+2} = \frac{2}{3}$.

[III] CALIBRATION OF WEIGHTS

The accuracy of weighing depends on the accuracy of the weights used even with the use of a sensitive and accurate balance. Normally, the weights deteriorate by using them for a long time in a chemical laboratory. Even in costly weight sets, errors of quite appreciable degree are sometimes found. So, it becomes necessary to determine the errors in the weights, *i.e.*; to calibrate the weights before carrying out accurate weighing. Therefore, for the calibration of weights, the following two methods are used :

(1) Method using standardised weights : If a complete set of standardised weights is available, the calibration can be easily carried out by weighing the individual weights against the standardised ones by the method of substitution to eliminate the error which might creep in due to inequality of balance arms.

In order to calibrate the weights by the substitution method, place the standard weight on the left hand scale pan and adjust a tare on the right hand scale pan. For the exact balancing, use a rider (It is always advisable to use the rider in the middle of the arm by keeping an extra 5 mg weight on the left hand pan throughout the whole operation of calibration). Replace the standard weight by the weight to be calibrated and obtain the same rest point by moving the rider, if necessary. In this way, a relation between the standard weight and the weight to be calibrated can easily be found. Similarly, other weights can be compared.

(2) Kohrausch's method : When only one set of unstandardised weights is given, the weights can be calibrated with respect to one another, taking one of the weights (*e.g.*, 50 g) as an arbitrary standard. Although the calibration is in terms of relative mass, not absolute mass, but this relative calibration serves the purpose in several chemical usages, such as volumetric and gravimetric analysis.

This method consists in comparing each weight in the set in turn with a suitable selection of others. So, in a set of brass weights of 50, 20', 20'', 10, 5, 2', 2'', 1 g (the sign ' and '' distinguish duplicates), the 50g can be compared with (20' + 20'' + 10)g, 20', with 20''g, 20''g, with 10 + 5 + 2' + 2'' + 1g, 10g with

(5 + 2' + 2'' + 1)g and so on upto 10 mg. The 10 mg weight can be compared by placing a rider on 10th mark on the balance arm. Let $a_1, a_2, a_3, \dots g$ etc. be the small differences determined very accurately using a rider between normally equal collection of weights. Then we have the following simultaneous equations :

$$50 = 20' + 20'' + 10 + a_1 \quad \dots (1)$$

$$20' = 20'' + a_2 \quad \dots (2)$$

$$20'' = 10 + 5 + 2' + 2'' + 1 + a_3 \quad \dots (3)$$

$$10 = 5 + 2' + 2'' + 1 + a_4 \quad \dots (4)$$

.....

.....

$$0.05 = 0.02' + 0.02'' + 0.01 + a_{n-3} \quad \dots (n-3)$$

$$0.02' = 0.02'' + a_{n-2} \quad \dots (n-2)$$

$$0.02'' = 0.01 + \text{rider on the } 10^{\text{th}} \text{ mark} + a_{n-1} \quad \dots (n-1)$$

$$0.01 = \text{Rider on the } 10^{\text{th}} \text{ mark} + a_n \quad \dots (n)$$

For (n + 1) weights (including the rider) there will be n equations. For the sake of calculation, take 0.01 g as a temporary internal standard and the equations are then solved as follows :

From equations (n) and (n - 1), we get

$$0.02'' = 2 \times (0.01) + a_{n-1} - a_n$$

On substituting the value of (0.02'') in equation (n - 2), we get

$$0.02' = 2 \times (0.01) + a_{n-1} - a_n + a_{n-2}$$

This procedure may be adopted upto 50 g weight.

The numerical a values with their proper sign are summed up step-by-step and apparent weight of each piece is calculated in terms of (0.01) piece and the results are tabulated. Then the different values are converted taking 50 g weight as standard instead of 0.01 g piece.

Suppose, the apparent wight of 50 g piece is found to be 50.0124 g. In order to standardise the various weights with reference to 50 g piece as the internal standard multiply the apparent weight of each piece by $\frac{50}{50.0124}$.

[III] CLEANING OF VOLUMETRIC APPARATUS

All the volumetric apparatus, *e.g.* pipette, burette, volumetric flasks etc must be perfectly clean, free from dust and greasy impurities. If the apparatus is dirty, unreliable results are liable to be obtained. The cleanliness of a glass vessel can be easily tested by filling it with distilled water and then pouring it out. If an unbroken film of water remains on the walls, the vessel is clean, the formation of droplets shows the presence of impurities which means that the vessel needs cleaning.

Following methods can be adopted for cleaning the glass apparatus.

(a) Soak the apparatus in warm solution (about 10%) of soap or detergent for nearly 20-25 minutes. Wash it with tap water, then with HCl and finally with distilled water.

Or, (b) Soak the vessel in cleaning mixture (equal volumes of concentrated H₂SO₄ and saturated solution of Na₂Cr₂O₇ or K₂Cr₂O₇, (preferably the former) for

a few hours. Pour off the mixture and wash the apparatus thoroughly with tap water and finally with distilled water. Preserve the cleaning mixture for subsequent use.

Or, (c) Soak the apparatus in a mixture of concentrated sulphuric acid and nitric acid. Pour off the mixture and wash the apparatus thoroughly with tap water and then with distilled water. This method is very efficient for cleaning very dirty and greasy apparatus.

After cleaning, the apparatus may be dried by rinsing it with a little acetone alcohol and then passing a current of warm air filtered through the cotton wool plug. *It must be noted that the volumetric apparatus should never be dried in an oven, because the volume of the apparatus is likely to change on heating.* Apparatus made of pyrex or borosilicate glass may be dried in an oven at 100–120°C.

[IV] CALIBRATION OF VOLUMETRIC APPARATUS

Now-a-days, all the volumetric apparatus are calibrated in cm^3 (one thousandth part of a litre. 1 litre = 1000 ml = 1000.028 cm^3) at room temperature (average) of 20°C. For ordinary purposes, the volume marked on the apparatus by the manufacturer may be treated as reliable. Moreover, in relative measurements, such as double titrations, any error in the volume, if present, gets cancelled. However, for accurate work, even small error must be determined and hence the apparatus must be calibrated.

(1) **Calibration of volumetric flask :** Weigh accurately a thoroughly cleaned and dried flask on a balance. Fill the flask with air-free distilled water (water boiled and then cooled) so that the lower edge of the meniscus stands at the fixed mark of the neck. Remove any drop of water above the mark by a piece of filter paper. Dry the outer surface and weigh the flask again. After having calculated the weight of water contained in the flask upto the mark obtain the true volume of the vessel from the following table. In case the error is appreciable, etch a new ring on the neck.

Table-1. Apparent specific weight and apparent specific volume of water weighed in air.

Temp. (°C)	Apparent weight of 1 cm^3 of water (g)	Volume corresponding to an apparent weight of 1 g of water (cm^3)	Temp. (°C)	Apparent weight of 1 cm^3 of water (g)	Volume corresponding to an apparent weight of 1 g of water (cm^3)
10	0.9986	1.0013	18	0.9976	1.0024
11	0.9985	1.0014	19	0.9974	1.0026
12	0.9984	1.0015	20	0.9972	1.0028
13	0.9983	1.0017	21	0.9970	1.0030
14	0.9982	1.0018	22	0.9967	1.0033
15	0.9981	1.0019	23	0.9965	1.0035
16	0.9979	1.0021	24	0.9963	1.0037
17	0.9977	1.0023	25	0.9960	1.0040

(2) Calibration of pipettes : Calibration of a pipette can be done by weighing the water it delivers from the fixed mark. Thoroughly clean the pipette to be calibrated by *cleaning mixture* and then wash it with tap water and finally with distilled water. Suck the air-free distilled water into the pipette upto the mark and transfer it by keeping it almost upright, into a previously weighed small flask. When the water stops running, allow the pipette to drain for about 12-15 second, touch the tip of the pipette against the side of the flask so as to remove the last drop of water which collects at the tip. Determine the weight of water so run out by weighing the flask again. From the weight of water, calculate the true volume of the pipette from table-1.

(3) Calibration of burettes : Burettes are generally calibrated by means of Ostwald's method with the help of a small pipette (capacity 10 cm^3), the volume of which has been accurately determined. Alternately, it can be calibrated as follows:

First, clean the burette, which is to be calibrated with '*cleaning mixture* and wash it with tap water and finally with distilled water. Then fill the cleaned burette with air-free distilled water, taking care that no air bubble remains in the jet of the burette. Clamp it in vertical position and deliver 1 cm^3 water from zero mark in a previously weighed small flask. Determine the weight of water delivered by weighing the flask again. Withdraw successively 1 cm^3 water and weigh the flask after each delivery. From the weights of 1, 2, 3, ..., 10 cm^3 etc from the burette, calculate the correct volumes. Tabulate the corrections (differences) corresponding to 1, 2, 3,, 50 cm^3 . Now plot a graph between the burette readings as abscissa (X-axis) and corrections as ordinates (Y-axis), taking positive corrections above and the negative corrections below the abscissa axis.

[V] PREPARATION OF STANDARD SOLUTIONS

A solution whose concentration is known is called a *standard solution*. Such a solution can be prepared by dissolving a known amount of the solute in a known amount of solvent or in a known volume of the solution. This method of preparing the standard solution is restricted only to substances of primary standard, *i.e.*, substances whose concentration is exactly known and which does not change with time, *e.g.*, oxalic acid, $\text{K}_2\text{Cr}_2\text{O}_7$, AgNO_3 , CuSO_4 etc. Such a procedure cannot be adopted for substances of secondary standard, *i.e.*, substance whose concentration changes with time, *e.g.*, sodium hydroxide, sodium thiosulphate etc. or substance whose concentration is not exactly known, *e.g.*, HCl , HNO_3 , H_2SO_4 , NH_4OH etc. The standard solution of such substances can be obtained by preparing first a solution (known as stock solution) of concentration higher than that required (about 1.5–2.0 times concentrated) by approximate weighing or taking the required volume by means of a graduated pipette and then standardising it by titration. Then a solution of particular concentration (on dilution side) can be prepared by dilution of the stock solution (using the formula $N_1V_1 = N_2V_2$). Standard solutions of some substances of secondary standard can be prepared as follows :

(1) Standard solution of caustic soda (200 cm³ 0.1 N) : We know that sodium hydroxide is hygroscopic in nature, so it is always contaminated with water. Hence, its standard solution cannot be prepared by dissolving a weighed amount in a known volume of solution. A solution of higher concentration (stock solution) is first prepared by approximate weighing and it is then standardised with a standard solution of oxalic acid (primary standard). A standard solution of any desired strength (less than that of stock solution) can be prepared easily by proper dilution of the stock solution.

The amount of NaOH required to prepare 200 cm³ of 0.1M solution = $\frac{40 \times 200}{1000} \times 0.1 = 0.8$ g. Dissolve about 1.5 g of NaOH in 200 cm³ water. Prepare 100 cm³ of standard solution (0.1 N) of oxalic acid by accurate weighing ($\frac{63 \times 100}{1000} \times 0.1 = 0.63$ g). Titrate 20 cm³ of the acid solution with alkali using phenolphthalein as an indicator. The exact strength of the alkali is thus found by using the formula, $N_1V_1 = N_2V_2$. Let the concentration be 0.1754 N. Then the volume of the alkali required to prepare 200 cm³ 0.1 N solution of NaOH may be calculated as,

$$0.1754N \times V_1 = 0.1N \times 200$$

or
$$V_1 = \frac{0.1N \times 200}{0.1754N} = 114.02 \text{ cm}^3$$

By means of a calibrated burette take 114.02 cm³ of the alkali (NaOH) into a 200 cm³ measuring flask and make the solution upto the mark. This gives 0.1 N solution of NaOH. Similarly, solutions of other alkalis, such as KOH *etc.* can be prepared.

(2) Standard solutions of acids, e.g., HCl, H₂SO₄, HNO₃ etc. (Suppose 200 cm³ 0.1 N HCl solution is to be prepared) : The concentration of concentrated solution of different acids, e.g., HCl, H₂SO₄, HNO₃, CH₃COOH *etc.* is approximately known. For preparing a standard solution of any desired concentration, a stock solution of some nearly known concentration about 1.5 to 2 times higher than the concentration of the standard solution required, is prepared. Its exact concentration is then determined by titrating it with a standard solution of NaOH. The solution of any required concentration (dilute one) can then be prepared by proper dilution of the stock solution.

For preparing 200 cm³ of 0.1N HCl solution, the volume of concentrated HCl (~ 11.6N) required will be given by,

$$11.6N \times V_1 = 0.1N \times 200$$

or
$$V_1 = \frac{0.1N \times 200}{11.6} = 1.7 \text{ cm}^3 \text{ (approx)}$$

By means of a graduated pipette take about 3 to 4 cm³ of concentrated HCl and dilute it to 200cm³. Titrate the acid solution with a standard alkali and find

the exact concentration of the stock solution. Suppose the correct concentration is found to be $0.1876N$. The volume of stock solution to be diluted to 200 cm^3 is

$$0.1876N \times V_1 = 0.1N \times 200$$

or
$$V_1 = \frac{0.1N \times 200}{0.1876} = 106.6\text{ cm}^3$$

Take 106.6 cm^3 of the acid solution in a 200 cm^3 measuring flask and make the solution upto the mark to get the desired solution of HCl. Similarly, standard solutions of H_2SO_4 , HNO_3 , CH_3COOH etc. can be obtained.

(3) Standard solution of ammonium hydroxide : Suppose 1000 cm^3 of $0.1N$ solution is to be prepared. The strength of concentrated solution of ammonia available in the laboratory is nearly $14.8N$. The volume of concentrated solution of ammonia required is thus

$$V_1 = \frac{0.1N \times 1000}{14.8N} = 6.7\text{ cm}^3 \text{ (approximately)}$$

Dilute about 15 cm^3 of concentrated ammonia to about 1000 cm^3 . (The bottle of ammonia should be properly cooled in a bath of ice, before it is opened). Standardise the above ammonia solution by titrating it with a standard HCl solution, say $0.1N$, using methyl orange, as an indicator. Suppose the concentration of ammonia solution is nearly $0.25N$. The volume of stock solution to be diluted to 1000 cm^3 is,

$$0.25N \times V_1 = 0.1N \times 1000$$

or
$$V_1 = \frac{0.1N \times 1000}{0.25N} = 400\text{ cm}^3$$

Now take 400 cm^3 of the stock solution and dilute it with distilled water to make the solution up to 1000 cm^3 mark to get the solution of desired concentration.

Table-2. Concentration of aqueous solutions of common acids and ammonia

Reagent	Normality of concentrated solution	Molarity of concentrated solution	Volume required to make 1 dm^3 $0.1N$ solution (approximately cm^3)
Hydrochloric acid	11.6	11.6	8.6
Sulphuric acid	17.8	35.6	2.8
Nitric acid	15.4	15.4	6.5
Acetic acid	17.4	17.4	5.8
Phosphoric acid	43.8	14.6	2.3
Ammonia	14.8	14.8	8.6

(4) Standard solutions of KMnO_4 and $\text{Na}_2\text{S}_2\text{O}_3$: First, solutions of KMnO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ (concentration higher than required) are prepared. KMnO_4 solution is standardised by titrating it with a standard oxalic acid solution (self indicator). The $\text{Na}_2\text{S}_2\text{O}_3$ (hypo) solution is standardised with standard copper sulphate solution iodometrically, using starch solution as an indicator. The

standard solution on the dilution side can be obtained by proper dilution of the stock solution.

(5) Preparation of a mixture of two miscible liquids, composition in mole fraction being known : The mole fraction of each liquid is multiplied by the respective molecular weights and the amount so obtained is mixed to get the required mixture. If the densities of the liquids are known, their volumes to be mixed can be calculated by dividing the above amounts by their respective densities. Suppose M_1 and M_2 are the molecular weights and d_1 and d_2 are the densities (in g cm^{-3}) of the two liquids. Let the respective mole fractions of the liquids be x_1 and x_2 . The amounts (m_1 and m_2) of the liquids to be mixed will be :

$$m_1 = M_1 x_1 \text{ g} \quad ; \quad m_2 = M_2 x_2 \text{ g}$$

The respective volumes will be given by,

$$V_1 = \frac{M_1 x_1}{d_1} \text{ cm}^3 \quad ; \quad V_2 = \frac{M_2 x_2}{d_2} \text{ cm}^3$$

So, to prepare the required mixture of the two liquids mix either m_1 and m_2 g or V_1 and V_2 cm^3 of liquids 1 and 2, respectively. If a mixture of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ (respective mole fractions being 0.4 and 0.6) is to be prepared then,

$$\begin{aligned} \text{Amount of methyl alcohol} &= 0.4 \times 32 = 12.8 \text{ g} \\ &= \frac{12.8}{0.75} \approx 17.1 \text{ cm}^3 \text{ at } 20^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \text{Amount of ethyl alcohol} &= 0.6 \times 46 = 27.6 \text{ g} \\ &= \frac{27.6}{0.79} \approx 34.9 \text{ cm}^3 \text{ at } 20^\circ\text{C} \end{aligned}$$

So mix 12.8 g (or 17.1 cm^3) of methyl alcohol and 27.6 g (or 34.9 cm^3) of ethyl alcohol or multiples of these amounts to obtain the desired mixture.

THERMOSTAT (OR TEMPERATURE CONTROL DEVICE)

Several physical properties such as osmotic pressure, vapour pressure, rate constant, equilibrium constant, surface tension, viscosity etc. depend on temperature and hence their values must be measured at a known temperature controlled to within $\pm 0.01^\circ\text{C}$. Ice bath (ice in equilibrium with water at 0°C), mixture of crushed ice with salts (freezing mixtures), liquid nitrogen at its normal boiling point (77.2K or -195.8°C), dry ice-acetone bath, solid carbon dioxide in equilibrium with CO_2 vapours at 1 atmosphere ($\sim 78.5^\circ\text{C}$) are some low temperature baths.

An important method of obtaining temperature control is to use a thermo-sensing device with a feedback system to control the input of heater or refrigerator to a bath such that the temperature is maintained to any desired arbitrary value within a narrow range. Such a device is known as a **thermostat**. It consists mainly of the following different parts :

- (i) Bath, (ii) Stirrer, (iii) Heater or refrigerator, (iv) Thermo-regulator and (v) Relay.

(1) **Bath** : It consists of a large rectangular tank of suitable size. The most commonly used size is 45 cm deep and 45 × 75 cm in horizontal area. The bath is made up of glass or stainless steel metal with glass windows on two or more sides. The tank is filled with water for temperatures upto ~ 70 to – 80°C or a suitable oil such as heavy cylinder oil up to ~ 300°C or silicone oil for still higher temperatures.

(2) **Stirrer** : To provide a good stirring of the liquid in the tank, a metallic stirrer or a centrifugal liquid circulation driven by an electric motor is used.

(3) **Heater or refrigerator** : To heat the bath, an electric heater of suitable wattage is used. For more accurate work, an auxiliary heater is also provided. If two heaters are used, one may be constantly switched on and the other is intermittent under the control of a thermoregulator or both may be intermittent depending upon their power rating. If a thermostat working at low temperatures is required, then a refrigerating device instead of a heater is used. The thermostat is then known as a **cryostat**.

(4) **Thermo-regulator** : A thermo-regulator or a thermo-sensing element is a thermometric instrument which provides an electric signal. For laboratory temperature control, the most commonly used devices are *off-on thermo-switch type*.

Four types of devices based on the principle of thermo-switch viz. (a) toluene bulb regulator, (b) vapour-liquid type regulator, (c) mercury-in-glass regulator and (iv) bi-metallic strips type regulator, are commonly used.

Fig. (1) shows a toluene bulb regulator. It consists of a J-type glass tube having a bulb at its one end and a capillary at the other. The bulb is filled with toluene (a liquid of large thermal expansion coefficient) in contact with mercury ending as a capillary column. A mercury reservoir is connected by means of a side tube having a stopcock to the main mercury column. For making electric contacts, two platinum wires are used, one Pt. wire is directly inserted into the main mercury column by fusion through the glass, while the other to mercury meniscus in the capillary when temperature has attained the desired value. The regulator is set to the desired temperature either by lowering or raising the central wire in the capillary using a screw or by adjusting the height of the mercury column.

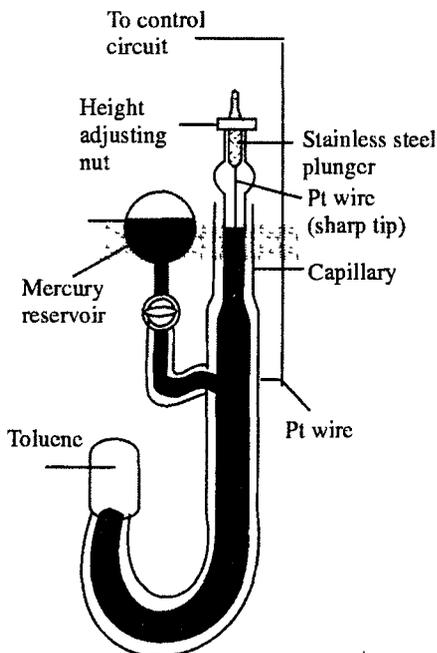


Fig. 1 : Toluene thermo-regulator

Fig. (2) shows a vapour-liquid type regulator in which the bulb is partly filled with a liquid in equilibrium with its saturated vapour and partly with mercury. The liquid is so chosen as to have a boiling point close to the desired temperature.

In a mercury-in-glass thermo-regulator, the bulb is filled completely with mercury. A bimetallic strip type regulator is useful only where the temperature regulation better than 1° is not required. This type of regulator is commonly used for temperature control in electric ovens used in laboratory.

(5) Relay : It is an electronic or electromechanical device which 'makes' or 'breaks' the electrical circuit of heater or refrigerator. In electromechanical relay, an electromagnet gets energised when its circuit is closed through the thermoregulator. The electromagnet attracts a piece of soft iron which then breaks the circuit of the heater. When the circuit of the relay is broken through the regulator and temperature falls below the desired value due to heat losses, the piece of iron is released by the electromagnet which then makes the circuit of the heater.

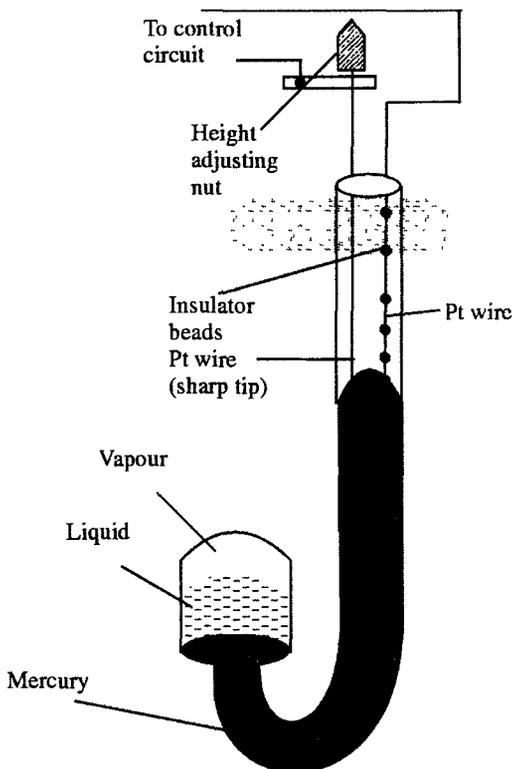


Fig. 2 : Vapour-liquid thermo-regulator



2

ERROR ANALYSIS AND STATISTICAL DATA ANALYSIS

The function of the analyst is to obtain a result as near to the true value as possible by correct application of the analytical procedure used. The level of confidence that the analyst may enjoy in his results will be very small unless he has knowledge of the accuracy and precision of the method used as well as is aware of the sources of error which may be introduced. Quantitative analysis is not simply a case of taking a sample, carrying out a single determination and then claiming that the value so obtained cannot be refuted. It also requires a sound knowledge of the chemistry involved, of the possibilities of interferences from other ions, elements and compounds as well as the knowledge of the statistical distribution of values.

[I] TYPES OF ERRORS

The errors which affect an experimental result may conveniently be classified into systematic and random errors.

(A) Systematic (determinate) errors : These are errors which can be avoided, or whose magnitude can be determined. The most important of them are:

(1) *Operational and personal errors* : These are due to factors for which the individual analyst is responsible and are not, in any way, connected with the method or procedure : they form part of the 'personal equation' of an observer. These errors are mostly physical in nature and occur when sound analytical technique is not followed, e.g., mechanical loss of materials in various steps of analysis; underwashing or overwashing of precipitates; ignition of precipitates at incorrect temperatures; insufficient cooling of crucibles before weighing; allowing hygroscopic materials to absorb moisture before or during weighing; and use of reagents containing harmful impurities.

Personal errors may arise from the constitutional inability of an individual to make certain observations accurately. So, some persons are unable to judge colour changes sharply in visual titrations, which may result in a slight overstepping of the end point.

(2) *Instrumental and reagent errors* : These arise from the faulty construction of balances, the use of uncalibrated or improperly calibrated weights, graduated glasswares, and other instruments; the attack of reagents upon glassware, porcelain, etc., resulting in the introduction of foreign materials; volatilisation of platinum at very high temperatures; and the use of reagents containing impurities.

(3) *Errors of method* : These errors originate from incorrect sampling and from incompleteness of a reaction. In gravimetric analysis, errors may arise due to

appreciable solubility of precipitates, co-precipitation, and post-precipitation, decomposition, or volatilisation of weighing forms on ignition, and precipitation of substances other than the intended ones. In titrimetric analysis, errors may occur due to failure of reactions to proceed to completion, occurrence of induced and side reactions, reaction of substances other than the constituents being determined, and a difference between the observed end point and the stoichiometric equivalence point of a reaction.

(4) *Additive and proportional errors* : The absolute value of an additive error is independent of the amount of the constituent present in the determination, e.g., loss in weight of a crucible in which a precipitate is ignited, and errors in weights. The presence of this error is shown by taking samples of different weights.

The absolute value of a proportional error depends upon the amount of the constituent. Thus a proportional error may arise from an impurity in a standard substance, which leads to an incorrect value for the molarity of a standard solution. Other proportional errors may not vary linearly with the amount of the constituent, but will at least show an increase with the amount of constituent present. One example is the ignition of aluminium oxide at 1250°C, the aluminium oxide is anhydrous and virtually non-hygroscopic; ignition of various weights at an appreciably lower temperature will show a proportional type of error.

(B) Random (indeterminate) errors : These errors arise due to the slight changes that occur in successive measurements made by the same observer with the greatest care under as nearly identical conditions as possible. They are due to causes over which, the analyst has no control, and which, in general, are so intangible that they are incapable of analysis. If a *sufficiently large number of observations* is taken, it can be shown that these errors lie on a curve of the type as shown in fig (1). An inspection of this error curve shows: (a) small errors occur more frequently than large ones : and (b) positive and negative errors of the same numerical magnitude are equally likely to occur.

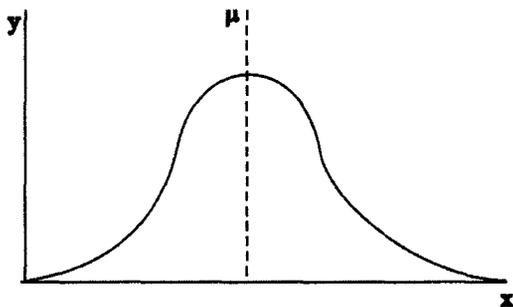


Fig : 1

[II] MINIMISATION OF ERRORS

Systematic errors can often be materially minimised by one of the following methods.

(1) *Calibration of apparatus and application of corrections* : All instruments (weights, flasks, burettes, pipettes, etc.) should be calibrated, and necessary corrections should be applied to the original measurements. In some cases, where an error cannot be eliminated, it is possible to apply a correction for the effect that it produces. Thus, an impurity in a weighed precipitate may be determined and its weight deducted.

(2) *Running a blank determination* : This consists in carrying out a separate determination, the sample being omitted, under exactly the same experimental

conditions as are used in the actual analysis of the sample. The object is to find out the effect of the impurities introduced through the reagents and vessels, or to determine the excess of standard solution necessary to find the end-point under the conditions met within the titration of the unknown sample. A large blank correction is undesirable, because the exact value then becomes uncertain and the precision of the analysis is reduced.

(3) *Running a control determination* : This consists in carrying out a determination under as nearly as possible identical experimental conditions upon a quantity of a standard substance which contains the same weight of the constituent as is contained in the unknown sample. The weight of the constituent in the unknown can then be calculated from the expression :

$$\frac{\text{Result found for standard}}{\text{Result found for unknown}} = \frac{\text{Weight of constituent in standard}}{w}$$

where w is the weight of the constituent in the unknown.

In this connection, it must be pointed out that standard samples which have been analysed by a number of skilled analysts are commercially available. These include certain primary standards (sodium oxalate, potassium hydrogenphthalate, arsenic(III) oxide, and benzoic acid) and ores, ceramic materials, irons, steels, steel-making alloys, and non-ferrous alloys.

(4) *Use of independent methods of analysis* : In some cases, the accuracy of a result may be established by carrying out the analysis in an entirely different manner. Thus, iron may first be determined gravimetrically by precipitation as iron(III) hydroxide after removing the interfering elements, followed by ignition of the precipitate to iron(III) oxide. It may then be determined titrimetrically by reduction to the iron(II) state, and titration with a standard solution of an oxidising agent, such as potassium dichromate or cerium (IV) sulphate. Another example that may be mentioned is the determination of the strength of solution of hydrochloric acid both by titration with a standard solution of a strong base and by precipitation and weighing as silver chloride. If the results obtained by the two radically different methods are concordant, it is highly probable that the values are correct within small limits of error.

(5) *Running parallel determinations* : These serve as a check on the result of a single determination and show only the precision of the analysis. The values obtained for constituents which are present in not too small an amount should not vary among themselves by more than three parts per thousand. If larger variations are observed the determinations must be repeated until satisfactory concordance is obtained. Duplicate and at most triplicate, determinations should suffice. It must be understood that good agreement between duplicate and triplicate determinations does not justify the conclusion that the result is correct; a constant error may be present. The agreement merely shows that the accidental errors, or variations of the determinate errors, are the same, or nearly the same, in the parallel determinations.

(6) *Standard addition* : A known amount of the constituent being determined is added to the sample, which is then analysed for the total amount of constituent present. The difference between the analytical results for samples with and without the added constituent gives the recovery of the amount of added

constituent. If the recovery is satisfactory our confidence in the accuracy of the procedure is enhanced. The method is usually applied to physico-chemical procedures such as spectrophotometry and polarography.

(7) *Internal standards* : This method is of particular value in spectroscopic and chromatographic determinations. It involves adding a fixed amount of a reference material (the internal standard) to a series of known concentrations of the material to be measured. The ratios of the physical value (absorption or peak size) of the internal standard and the series of known concentrations are plotted against the concentration values (abscissa). This should give a straight line. Any unknown concentration can then be determined by adding the same quantity of internal standard and finding where the ratio obtained falls on the concentration scale.

(8) *Amplification methods* : In determinations in which a very small amount of material is to be measured this may be beyond the limits of the apparatus available. In these cases, if the small amount of material can be reacted in such a way that every molecule produces two or more molecules of some other measurable material, the resultant amplification may then bring the quantity to be determined within the scope of the apparatus or method available.

(9) *Isotopic dilution* : A known amount of the element being determined, containing a radioactive isotope, is mixed with the sample and the element is isolated in a pure form (usually as a compound), which is weighed or determined by other methods. The radioactivity of the isolated material is measured and compared with that of the added element : the weight of the element in the sample can then be calculated.

[III] ACCURACY

The accuracy of a determination may be defined as the *concordance between it and the true or most probable value*. It follows, therefore, that systematic errors cause a constant error (either too high or too low) and thus affect the accuracy of a result. For analytical methods there are two possible ways of determining the accuracy as follows.

(1) **Absolute method** : A synthetic sample containing known amounts of the constituents in question is used. Known amounts of a constituent can be obtained by weighing out pure elements or compounds of known stoichiometric composition. These substances of primary standards, may be available commercially or they may be prepared by the analyst and subjected to rigorous purification by recrystallisation, etc. The substances must be of known purity. The test of the accuracy of the method under consideration is carried out by taking varying amounts of the constituent and proceeding according to specified instructions. The amount of the constituent must be changed because the determinate errors in the procedure may be a function of the amount used. The difference between the mean of an adequate number of results and the amount of the constituent actually present, usually expressed as parts per thousand, is a measure of the accuracy of the method in the absence of foreign substances.

The constituent in question will usually have to be determined in the presence of other substances, and it will, therefore, be necessary to know the effect of these upon the determination. This will require testing the influence of a large number of elements, each in varying amounts. The scope of such tests may be limited by considering the determination of the component in a specified range of concentration in a material whose composition is more or less fixed both with

respect to the elements which may be present and their relative amounts. It is desirable, however, to study the effect of as many foreign elements as possible. In practice, it is mostly found that separations will be required before a determination can be made in the presence of varying elements; the accuracy of the method is likely to be largely controlled by the separations involved.

(2) **Comparative method** : Sometimes, as in the analysis of a mineral, it may be impossible to prepare solid synthetic samples of the desired composition. It is then necessary to resort to standard samples of the material in question (mineral, alloy, ore, etc) in which the content of the constituent sought has been determined by one or more supposedly 'accurate' methods of analysis. This comparative method involving secondary standards, is clearly not altogether satisfactory from the theoretical standpoint, but is nevertheless very useful in applied analysis.

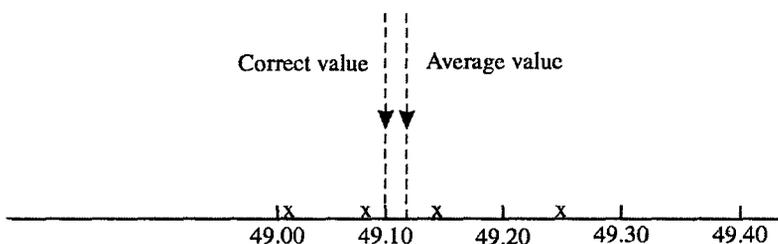
If several fundamentally different methods of analysis for a given constituent are available, e.g., gravimetric, titrimetric, spectrophotometric or spectrographic, the agreement between at least two methods of essentially different character can usually be accepted as indicating the absence of an appreciable systematic error in either (a systematic error is one which can be evaluated experimentally or theoretically).

[IV] PRECISION

Precision may be defined as the *concordance of a series of measurements of the same quantity*. Accuracy expresses the correctness of a measurement, and precision the 'reproducibility' of a measurement. Precision always accompanies accuracy, but a high degree of precision does not imply accuracy. This may be illustrated by the following example.

A substance was known to contain 49.10 ± 0.02 per cent of a constituent A. The results obtained by two analysts using the same substance and the same analytical method were as follows.

Analyst (1) % A 49.01; 49.25; 49.08; 49.14



The arithmetic mean is 49.12% and the results range from 49.01% to 49.25%.

Analyst (2) % A 49.40; 49.44; 49.42; 49.42.

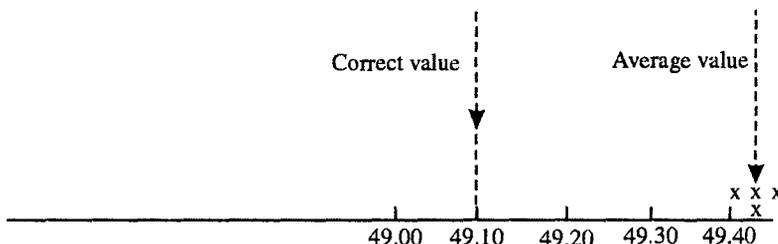


Fig. 2

The arithmetic mean is 49.42% and the results range from 49.40% to 49.44%.

We can summarise the results of the analysis as follows :

(a) The values obtained by Analyst 1 are accurate (very close to the correct result), but the precision is inferior to the results given by Analyst 2. The values obtained by Analyst 2 are very precise but are not accurate.

(b) The results of Analyst 1 face on both sides of the mean value and could be attributed to random errors. It is apparent that there is a constant (systematic) error present in the results of Analyst 2.

Precision was previously described as the reproducibility of a measurement. However, the modern analyst makes a distinction between the terms '**reproducible**' and '**repeatable**'. On further consideration of the above example :

(c) If Analyst 2 had made the determinations on the same day in rapid succession, then this would have been defined as 'repeatable' analysis. However, if the determinations had been made on separate days when laboratory conditions may vary, this set of results would be defined as '**reproducible**'. Therefore, there is a distinction between a within-run precision (repeatability) and a between-run precision (reproducibility).

[V] STATISTICAL TREATMENT FOR ERROR ANALYSIS

Suppose that a sample is analysed by two different methods, each repeated several times, and that the mean values obtained are different. Statistics, of course, cannot say which value is "right," but there is a prior question in any case, namely, "is the difference between the two values significant?" It is possible simply by the influence of random fluctuations to get two different values using two methods; but it is likewise possible that one (or even both) of the methods are subject to a determinate error. There is a test, using Student's t , that will tell (with a given probability), whether it is worthwhile to seek an assignable cause for the difference between the two means. It is clear that the greater the scatter in the two sets of data, the less likely it is that differences between the two means are real.

(a) **Null hypothesis** : The statistical approach to this problem is to set up the so-called **null hypothesis**. This hypothesis states, in the present example, that the two means are identical.

(b) **Student's t-test** : This is a test used for small samples, its purpose is to compare the mean from a sample with some standard value and to express some level of confidence in the significance of the comparison. The t -test gives a *yes* or *no* answer to the correctness of the null hypothesis with a certain confidence such as 95 or 99%. The procedure is as follows :

Suppose a sample has been analysed by two different methods, yielding means \bar{x}_1 and \bar{x}_2 and standard deviations s_1 and s_2 ; n_1 and n_2 are the number of individual results obtained by the two methods. The first step is to calculate a t value using the formula.

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

(This procedure presupposes that s_1 and s_2 are the same; there is a test for this, noted below). Second, enter a t table at a degree of freedom given by $(n_1 + n_2 - 2)$ and at the desired probability level. If the value in the table is greater than the t

calculated from the data, the null hypothesis is substantiated; *i.e.*, \bar{x}_1 and \bar{x}_2 are the same with a certain probability. If the t value in the table is less than the calculated t , then by this test the null hypothesis is incorrect and it might be profitable to look for a reason to explain the difference between \bar{x}_1 and \bar{x}_2 .

(c) **F-Test** : If s_1 and s_2 are really different, a much more complicated procedure, which is not discussed here, must be used. Usually, in analytical work involving methods that would, by ordinary commonsense, be considered comparable, s_1 and s_2 are about the same. A test is available for deciding whether a difference between s_1 and s_2 is significant. This is the *variance-ratio* or *F-test*. The procedure is simple : Find the ratio $F = s_1^2/s_2^2$, placing the larger s value in the numerator so that $F > 1$, then go to a table of F values. If the F value in the table is less than the calculated F value, then the two standard deviations, are significantly different, otherwise they are not. Some sample F values are given in Table-1 for a probability level of 95%. The F -test may be used to determine the validity of the simple t -test described here, but it may also be of interest in its own right to determine whether two analytical procedures yield significantly different precision.

Table-1. F values at the 95% probability level

$n - 1$ for smaller s^2	$n - 1$ for larger s^2					
	3	4	5	6	10	20
3	9.28	9.12	9.01	8.94	8.79	8.66
4	6.59	6.39	6.26	6.16	5.96	5.80
5	5.41	5.00	2.05	4.21	4.74	4.56
6	4.76	4.53	4.39	4.28	4.06	3.87
10	3.71	3.48	3.33	3.22	2.98	2.77
20	3.10	2.87	2.71	2.60	2.35	2.12

Sometimes it may be of interest to compare the two results, one of which is considered a priori to be highly reliable. An example of this might be a comparison of the mean \bar{x} of several analyses of an NBS sample with the value certified by the National Bureau of Standards. The goal would be not to pass judgment upon the Bureau, but to decide whether the method employed gave results that agreed with the Bureau's. In this case, the Bureau's value is taken as μ in the equation defining Student's t , and a t value is calculated using \bar{x} , n , and s for the analytical results at hand. If the calculated t value is greater than that in the t table for $(n - 1)$ degrees of freedom and the desired probability, then the analytical method in question gives a mean value significantly different from the NBS value; otherwise, difference in the two values would be attributable to chance alone.

The following examples indicate the foregoing points.

Example 1 : A sample of soda ash (Na_2SO_3) is analysed by two different methods giving the following results for the percentage of Na_2CO_3 :

Method 1	Method 2
$\bar{x}_1 = 42.34$	$\bar{x}_2 = 42.44$
$s_1 = 0.10$	$s_2 = 0.12$
$n_1 = 5$	$n_2 = 4$

(a) Are s_1 and s_2 significantly different? Apply the variance-ratio or F -test.

$$F = \frac{s_2^2}{s_1^2} = 1.44$$

Consult table-1 under column $(n - 1) = 3$ (since $s_2 > s_1$) and row $(n - 1) = 4$, finding $F = 6.59$. Since $6.59 > 1.44$, the standard deviations are not significantly different.

(b) Are the two means significantly different? Calculate a t value (either s_1 or s_2 may be used):

$$t = \frac{|42.34 - 42.44|}{0.10} \sqrt{\frac{5 \times 4}{5 + 4}}$$

$$t = 1.491$$

Consult table-1 at degree of freedom $n_1 + n_2 - 2 = 7$, finding t for the 95% probability level = 2.365. Since $1.491 < 2.365$, the null hypothesis is correct and the difference is not significant.

Example 2 : A chemist analyses a sample of iron ore furnished by the Bureau of Standards and obtains the following results. $\bar{x} = 10.52$, $s = 0.05$, $n = 10$. The Bureau's value for this sample is 10.60% Fe. Are the results significantly different?

Calculate t from the equation,

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

$$10.60 = 10.52 \pm \frac{t \times 0.05}{\sqrt{10}}$$

$$t = 5.06$$

In table-1, at degrees of freedom = 9 and 95% probability level $t = 2.262$. Since $5.06 > 2.262$, the results are significantly different from the Bureau's value.

[VI] CRITERIA FOR REJECTION OF AN OBSERVATION

Sometimes a person performing measurements is faced with one result in a set of replicates which seems to be out of line with the others, and he then must decide whether to exclude this result from further consideration. This problem is encountered in beginning analytical chemistry courses, later in physical chemistry laboratory work, and even in advanced research, although hopefully with lessening frequency as the student progresses. It is a generally accepted rule in scientific work that a measurement is to be automatically rejected when it is known that an error was made; this is a determinate situation with which we are not concerned here. It should be noted that it is incorrect (but all too human) to reject results which were subject to known errors only when they appear to be discordant. The only way to avoid an unconscious introduction of bias into the measurements is to reject every result where an error is known to be made, regardless of its agreement with the others. The problem to which we address ourselves here is a different one: How do we decide whether to throw out a result which appears discordant when there is no known reason to suspect it?

If the number of replicate values is large, the question of rejecting one value is not an important one; first, a single value will have only a small effect upon the

mean, and second, statistical considerations give a clear answer regarding the probability that the suspected result is a member of the same population as others. On the other hand, a real dilemma arises when the number of replicates is small. The divergent result exerts a significant effect upon the mean, while at the same time there are insufficient data to permit a real statistical analysis of the status of the suspected result.

Many different recommendations that have been promulgated by various writers attest to the conclusion that the question of rejecting or retaining one divergent value from a small sample really cannot satisfactorily be answered. Some of the more widely recommended criteria for rejection are considered below, and the student is referred to the excellent discussion by Blaedel, et. al. and interesting brief commentaries by Laitinen and Wilson.

In the first place, it is necessary to decide how large the difference between the suspected result and the other data must be before the result is to be discarded. If the minimum difference is made too small, valid data may be rejected too frequently; this is said to be an "*error of the first kind.*" On the other hand, setting the minimum difference too high leads to "*errors of the second kind,*" viz., too frequent retention of highly erroneous values. The various recommendations for criteria of rejection steer one course or another between the Scylla and Charybdis of these two types of errors, some closer to one and some closer to the other.

The *2.5 d rule* is applied as follows :

1. Compute the mean and the average deviation of the "good" results.
2. Find the deviation of the suspected result from the mean of the "good" ones.

If the deviation of the suspected result from the mean of the "good" ones is at least 2.5 times the average deviation of the "good" results, then reject the suspected result. Otherwise retain it.

Strictly, the limit for rejection is too low with the *2.5 d rule*. Valid data are rejected too often (errors of the first kind). The degree of confidence often quoted for the rule is based upon large sample statistics extended to small samples without proper compensation.

The *4d rule* is used in the same manner as the *2.5 d rule* above. This rule likewise leads to errors of the first kind, although obviously not so frequently. There is no statistical justification for using either the *2.5d* or the *4d* rule, although both are widely recommended. It should be noted that these rules are meant to apply to the rejection of only one result from a group of four to eight, not to one out of three, or two out of five, etc.

Q-test : The *Q-test*, described by Dean and Dixon,* is statistically correct, and it is very easy to apply. When the *Q-test* calls for rejection, confidence is high (90%) that the suspected result was indeed subject to some special error. Using the *Q-test* for rejection, errors of the first kind are highly unlikely. However, when applied to small sets of data (say, three to five results), the *Q-test* allows rejection only of results that deviate widely, and hence leads frequently to errors of the second kind (retention of erroneous results). Thus, the *Q-test* provides excellent justification for the rejection of grossly erroneous values, but it does not eliminate the dilemma with suspicious but less deviant values. The reason for this, of course, is that with

* R.B. Dean and W. J. Dixon., *Anal. Chem.* 23, 636 (1951).

small samples only crude guesses of the real population distribution are possible, and thus sound statistics lends assurance only to the rejection of widely divergent results.

The Q -test is applied as follows :

- (1) Calculate the range of the results.
- (2) Find the difference between the suspected result and its nearest neighbour.
- (3) Divide the difference obtained in step 2 by the range from step 1 to obtain the rejection quotient, Q .
- (4) Consult the table of Q values. If the computed value of Q is greater than the value in the table, the result can be discarded with 90% confidence that it was indeed subject to some factor which did not operate on the other results.

Some Q values are given in Table-2.

Table-2. Values of rejection quotient, Q

Number of observations	$Q_{0.90}$
3	0.90
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

The following example illustrates the application of the above tests.

Example 3 : Four results obtained for the normality of a solution are 0.1014, 0.1012, 0.1019 and 0.1016. Apply the above tests to see if the 0.1019 result can be discarded.

- (a) Compute the mean and average deviation of the three "good" results :

Results	Deviations (ppt)
0.1014	0.0
0.1012	2.0
<u>0.1016</u>	<u>2.0</u>
Average : 0.1014	Average : 1.3

- (b) Compute the deviation of the suspected result from the mean of the three "good" results:

$$0.1019 - 0.1014 = 0.0005 \text{ or } 5.0 \text{ ppt}$$

Using the 2.5 d rule,

$$2.5 \times 1.3 = 3.3 < 5.0 \text{ (discard)}$$

Using the 4.0 d rule,

$$4.0 \times 1.3 = 5.2 > 5.0 \text{ (do not discard)}$$

Using the Q -test,

$$Q = \frac{0.1019 - 0.1016}{0.1019 - 0.1012}$$

$$Q = \frac{0.0003}{0.0007}$$

$$Q = 0.43$$

Since $Q < 0.76$ (table-2) so do not discard.

As noted above, the Q -test affirms the rejection of a value at a confidence level of 90%. Willingness to reject a result with less confidence would make possible a Q -test which allowed retention of fewer deviant values (errors of the second kind). While this appears superficially attractive, there are valid reasons for conservatism in rejecting measurements. Actually, low confidence levels (say 50%) are scarcely meaningful when only a small number of observations is involved. Further, although to many students in introductory courses laboratory measurements are only exercises, it must be remembered that the collection of data is a scientific enterprise with a purpose, and the matter must be discussed as though it were important. The worker who has carefully conceived his measurement and executed it painstakingly, and who has reason to hope that the outcome will be significant, will not quickly throw his work away. He will be more likely to repeat the measurement until the dilemma of the discordant result has evaporated through the operation of two factors: Dilution of any one result by all the other results will lessen its significance, and, as the number of observations increases, statistical evaluation of the suspected result will become more meaningful.

A sort of compromise between outright rejection and the retention of a suspected value is sometimes recommended, viz., reporting the median of all the results rather than a mean either with or without the deviant value. The median is influenced by the *existence* of one discordant result, but it is not affected by the extent to which the result differs from others. For a sample containing three to five values, Blaedel et al. recommend testing the suspected value with the Q -test and rejecting it if the test allows this; if not, the median is reported rather than the mean. Some writers, e.g., Wilson, recommend that the highest and lowest values both be rejected and the mean of the others reported: "The best procedure to use depends on what is known about the frequency of occurrence of wild values, on the cost of additional observations, and on the penalties for the various types of error. In the absence of special arguments, the use of the interior average would appear to be a good practice. It may be noted that this interior average and the median are necessarily identical in the special case where there are just three results.

[VII] CONTROL CHARTS

The control chart method was originally developed as a system for keeping track of quality during large-scale manufacturing operations. Often a production run is too large to permit individual inspection of each item (say, razor blades or ball bearings), and in some cases the quality test is destructive (as in measuring the stress required to break an object) and hence cannot be applied to each specimen produced by a company. In such cases, some sort of spot-checking of a

few of the samples coming off the production line is necessary, and judgment is required to decide whether the manufacturing process is under control or whether a costly shutdown is justified in order to seek the cause of a deviation from the specifications in the tested results. The control chart method has also proved useful in keeping track of the performance of analytical methods in busy laboratories where the same types of samples are repeatedly analysed day after day over long periods of time. The method tends to distinguish with a high degree of efficiency definite trends or periodically recurring anomalies from random fluctuations. The control chart method can be discussed only briefly here. The interested reader is referred to books on the subject and several briefer discussions.

Let us suppose that a company manufactures some chemical material, and that as part of the quality control program, the analytical laboratory performs each day a certain analysis on samples bled from the plant output, perhaps for percent water in the product. Let us further suppose that the laboratory checks its water determination each day by running a standard sample of known water content through the analytical procedure. We are interested here to know how the control chart for the laboratory analysis is set up and used. The plant could also use a control chart method, based upon the laboratory reports, for monitoring the quality of the product but here we are concerned with the laboratory's checking its own analytical method.

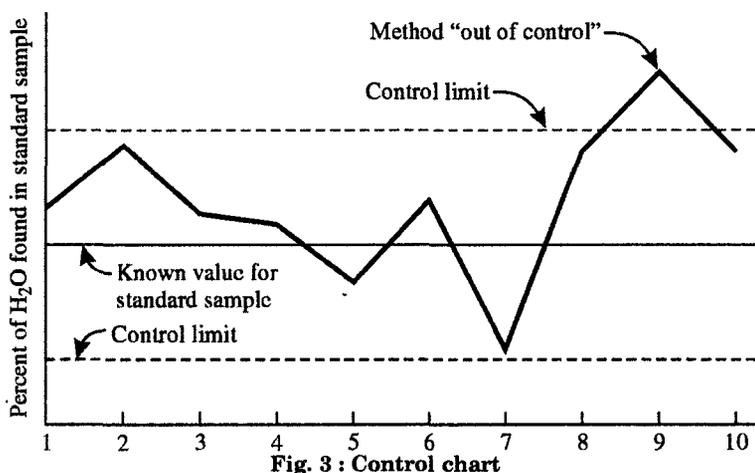


Fig. 3 : Control chart

The control chart for the analysis is set up as follows (see fig. 3). The percent water in the standard sample is indicated on the chart by a horizontal line. The standard sample is analysed every day, and the average of five weekly results is plotted, week after week, on the chart. Also placed on the chart are the *control limits*. Analytical results falling outside these limits are considered to result from the operation of some definite factor which is worth investigating and correcting. When results fall within the limits, the method is "*under control*," and fluctuations are only random and indeterminate. (The analogous conclusion with a production control chart is that, when samples test outside the control limits, there is justification for shutting down the process and looking for the trouble.) Clearly, the control limits must be set in an arbitrary manner; one must decide how large must be the probability of an assignable cause for a deviant result before he is willing

to say that something is wrong with the analysis. It seems usual in practice to set the control limits at the expected value $\pm 3s$; there is no fundamental aspect of probability theory demanding this, but apparently experience has shown that these are sound limits economically as a basis for action. Sometimes two sets of control limits are placed on the chart, "inner limits" at about $\pm 2s$ to warn of possible trouble, and "outer limits" of $\pm 3s$ demanding a corrective step. (Actually, the chances are 1 in 20 that an observation subject only to random scatter will lie outside limits of $\pm 1.96\sigma$; 99.7% if a group of results should fall within the $\pm 3\sigma$ limits unless a definite cause is operating on the analysis). If the analysis is one that has been performed many times, the laboratory may have a value for s which is a good estimate of σ . Otherwise, the control limits can be established temporarily on the basis of an s value obtained from a few results, and then adjusted later as more data become available. Parallel control charts for ranges, standard deviations, etc., may be employed to help the laboratory personnel keep track of the precision of an analytical method.

[VIII] CORRELATION AND REGRESSION

When using instrumental methods it is often necessary to carry out a calibration procedure by using a series of samples (standards) each having a known concentration of the analyte to be determined. A **calibration curve** is constructed by measuring the instrumental signal for each standard and plotting this response against concentration. Provided the same experimental conditions are used for the measurement of the standards and for the test (unknown) sample, the concentration of the latter may be determined from the calibration curve by graphical interpolation.

There are two statistical tests that should be applied to a calibration curve :

- (a) to ascertain if the graph is linear, or in the form of a curve;
- (b) to evaluate the best straight line (or curve) throughout the data points.

Correlation coefficient : In order to establish whether there is a linear relationship between two variables x_1 and y_1 Pearson's correlation coefficient r is used.

$$r = \frac{n \sum x_1 y_1 - \sum x_1 \sum y_1}{\sqrt{[n \sum x_1^2 - (\sum x_1)^2] [n \sum y_1^2 - (\sum y_1)^2]}} \quad \dots(1)$$

where n is the number of data points.

The value of r must lie between + 1 and - 1; the nearer it is to + 1, or in the case of negative correlation to - 1, then the greater is the probability that a definite linear relationship exists between the variables x and y . Values of r that tend towards zero indicate that x and y are not linearly related (they may be related in a non-linear fashion).

Although the correlation coefficient r would easily be calculated with the aid of a modern calculator or computer package, the following example will show how the value of r can be obtained.

Example 4 : *Quinine may be determined by measuring the fluorescence intensity in 1 M H₂SO₄ solution. Standard solutions of quinine gave the following fluorescence values. Calculate the correlation coefficient r .*

Concentration of quinine (x_1)	0.00	0.10	0.20	0.30	0.40 $\mu\text{g ml.}$
Fluorescence intensity (y_1)	0.00	5.20	9.90	15.30	19.10 arbitrary units

The terms in equation (1) are found from the following tabulated data.

x_1	y_1	x_1^2	y_1^2	$x_1 y_1$
0.00	0.00	0.00	0.00	0.00
0.10	5.20	0.01	27.04	0.52
0.20	9.90	0.04	98.01	1.98
0.30	15.30	0.09	234.09	4.59
0.40	19.10	0.16	364.81	7.64
$\Sigma x_1 = 1.00$	$\Sigma y_1 = 49.5$	$\Sigma x_1^2 = 0.30$	$\Sigma y_1^2 = 723.95$	$\Sigma x_1 y_1 = 14.73$

Therefore,

$$(\Sigma x_1)^2 = 1.000; (\Sigma y_1)^2 = 2450.25, n = 5$$

Substituting the above values in equation (1),

$$r = \frac{5 \times 14.73 - 1.00 \times 49.5}{\sqrt{(5 \times 0.30 - 1.000)(5 \times 723.95 - 2450.25)}} = \frac{24.15}{\sqrt{584.75}} = 0.9987$$

Hence, there is a very strong indication that a linear relation exists between fluorescence intensity and concentration (over the given range of concentration).

It must be noted, however, that a value of r close to either + 1 or - 1 does not necessarily confirm that there is a linear relationship between the variables. It is a sound practice first to plot the calibration curve on graph paper and ascertain by visual inspection if the data points could be described by a straight line or whether they may fit a smooth curve.

The significance of the value of r is determined from a set of tables (See table-3). Consider the following example using five data ($x_1 y_1$) points : From the table the value of r at 5 percent significance value is 0.878. If the value of r is greater than 0.878 or less than - 0.878 (if there is negative correlation), then the chance that this value could have occurred from random data points is less than 5 percent. The conclusion can, therefore, be drawn that it is likely that x_1 and y_1 are linearly related. With the value of $r = 0.998$, obtained in the example given above there is confirmation of the statement that the linear relation between fluorescence intensity and concentration is highly likely.

Table-3. Critical values of the correlation coefficient
 ρ ($\rho = 0.05$)

No. of data pairs (x, y)	Critical value
5	0.88
6	0.82
7	0.76
8	0.71
9	0.67
10	0.64
11	0.61
12	0.58

[IX] LINEAR REGRESSION ANALYSIS

Once a linear relationship has been shown to have a high probability by the value of the correlation coefficient (r), then the best straight line through the data

points has to be estimated. This can often be done by visual inspection of the calibration graph but in many cases it is a far better practice to evaluate the best straight line by linear regression (the method of least squares).

The equation of a straight line is

$$y = mx + c$$

where y , the dependent variable, is plotted as a result of changing x , the independent variable. For example, a calibration curve in atomic absorption spectroscopy would be obtained from the measured values of absorbance (y -axis) which are determined by using known concentrations of metal standards (x -axis).

To obtain the regression line 'y on x', the slope of the line (m) and the intercept on the y -axis (c) are given by the following equations.

$$m = \frac{n \sum x_1 y_1 - \sum x_1 \sum y_1}{n \sum x_1^2 - (\sum x_1)^2} \quad \dots (2)$$

and
$$c = \bar{y} - a\bar{x} \quad \dots (3)$$

where \bar{x} is the mean of all values of x_1 and \bar{y} is the mean of all values of y_1

Example 5 : Calculate by the least squares method the equation of the best straight line for the calibration curve given in the previous example.

From example (4) the following values have been determined:

$$\sum x_1 = 1.00; \sum y_1 = 49.5; \sum x_1^2 = 0.30; \sum x_1 y_1 = 14.73; (\sum x_1)^2 = 1.000,$$

the number of points (n) = 5

The values of \bar{x} and \bar{y} are given by,

$$\bar{x} = \frac{\sum x_1}{n} = \frac{1.00}{5} = 0.2$$

and
$$\bar{y} = \frac{\sum y_1}{n} = \frac{49.5}{5} = 9.9$$

By substituting the values in equations (2) and (3),

$$m = \frac{5 \times 14.73 - 1.00 \times 49.5}{(5 \times 0.30) - (1.00)^2} = \frac{24.15}{0.5} = 48.3$$

and
$$c = 9.9 - (48.3 \times 0.2) = 0.24$$

So the equation of the straight line is

$$y = 48.3x + 0.24$$

If the fluorescence intensity of the test solution containing quinine was found to be 16.1, then an estimate of the concentration of quinine ($x \mu\text{g mL}^{-1}$) in this unknown could be

$$16.10 = 48.3x + 0.24$$

$$x = \frac{15.86}{48.30} = 0.328 \mu\text{g mL}^{-1}$$

The determination of errors in the slope m and the intercept c of the regression line together with multiple and curvilinear regression is beyond the scope of this book.

3

ELECTRONICS

EXPERIMENT No. 1

Object : *To measure the resistance with a multimeter.*

Apparatus : Multimeter, signal generator, power supply unit, resistors of assorted values, dry cell.

Theory : The multimeter is an instrument that can measure a.c. and d.c. voltage currents and resistances. It consists essentially of separate voltage, current and resistance measuring circuits. The meter movement is common to all the three circuits. A selector switch is provided to set up the required circuit for the desired measurement.

A multimeter is normally used to measure a.c. and d.c. voltages from 0 to 3000 V, a.c. and d.c. currents from 0 to 3 A and resistances from 0 to 20 M Ω . In a.c. ranges the measurements are possible from 40 Hz to 10 kHz. It is calibrated for a pure sine wave signal. When used as a voltmeter, the resistance of the meter is determined by its sensitivity expressed in ohm/volt and full scale voltages. While measuring resistance, never connect the meter terminals to an energized circuit. Also ensure that there is no parallel branch across the component you are measuring. When in doubt, disconnect one terminal of the component from the circuit. The measured value of a resistor can be compared with the value written on its body.

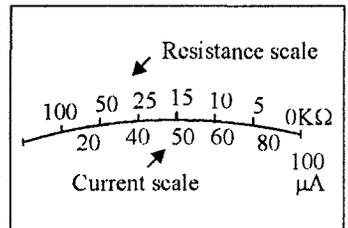


Fig. 1 : Resistance scale of a multimeter.

Resistance measurement : There are three methods commonly used for the measurement of resistances. These are as follows :

(i) We can connect the test piece in shunt with the meter. Then we determine the ability of the test piece to bypass current by this shunt path. Ohm-meters based on this principle are called *shunt type*. Such ohm-meters are suitable for the measurement of low value resistances.

(ii) We can connect the test piece in series with the meter. Then we determine the ability of the test piece to prevent current flow in the meter path. Ohm-meters using this principle are called *series type*.

(iii) The third alternative is to apply a known voltage across the test piece and then to determine the resulting current through it. The ratio of voltage to current

gives resistance. Ohm-meters using this principle are called *meggat type*. They are suitable for measurement of high value resistances, such as the insulation of a cable.

Procedure :

- (1) Set the function switch for ohm measurement.
- (2) Adjust the adjust control.
- (3) Now connect the unknown resistor to the test leads and read the value of resistance.
- (4) Select the range suitably so that the reading is in the upper half of the scale where the markings are not very crowded.
- (5) Similarly, read the value of resistance for other resistors.
- (6) Using colour code, find the value of resistance of these resistors.
- (7) Compare the measured value with the value found by using colour code.

Observations :

- (i) Voltage of the dry cell = V
- (ii) Voltage of d.c. supply = V
- (iii) Voltage of a.c. mains = V
- (iv) Maximum voltage obtainable from signal generator
= V

Resistance measurement

S.No.	Measured value	Value indicated in colour code	Tolerance indicated	Difference between measured value and given values
1.				
2.				
3.				
4.				
5.				

- Precautions :**
- (i) All the connections should be made tightly.
 - (ii) For accurate result, readings should be taken carefully.
 - (iii) Switch off after taking the readings.

EXPERIMENT No. 2

Object : To measure the output voltage of the audio signal generator with the help of CRO.

Theory : Both the CRO and the signal generator are important test instruments. The signal generator contains an oscillator and produces sine wave

voltage of adjustable frequency and magnitude. This voltage can be used for testing the performance of electronic circuits. The main purpose of CRO is to display wave shape. The heart of CRO is its cathode ray tube (CRT). To operate this CRT, the oscilloscope has a sweep (sawtooth) oscillator, deflection amplifier (horizontal and vertical), power supply circuit and a number of controls, switches and input terminals on the front panel. An electron beam produced by the electron gun in the CRT strikes the fluorescent screen. As a result, a bright spot is observed on the screen of the CRT. By applying voltage to the horizontal and vertical deflection plates (in the CRT), the beam is deflected in any desired direction. To display a voltage wave, it is connected to the vertical input of the oscilloscope. To the horizontal deflection plates, a sawtooth wave voltage is applied internally.

Circuit diagram : The circuit diagram for finding the output voltage of the audio signal generator with the help of CRO is shown in fig. (2).

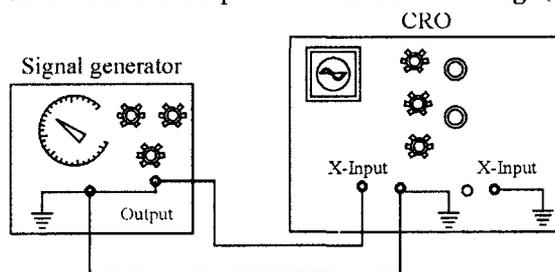


Fig. 2.

Procedure : Following steps are involved :

- (1) To measure the voltage of the signal generator, adjust the vertical amplifier sensitivity suitably, so as to get a sufficiently large display.
- (2) Read on the calibrated graticule, the vertical length of the display. This corresponds to peak-to-peak value of the signal.
- (3) Multiply this length by the sensitivity (in V/cm).
- (4) Divide this result by 252 which gives the rms value of the signal voltage.
- (5) Repeat the measurement procedure for two or three other values of output signal voltages.

Observations :

Measurement of voltage

S.No.	Signal generator output (measurement by a voltmeter)	Measurement on CRO		
		(p - p') value in cm	Sensitivity in V/cm	rms value

Result : The value of voltage by voltmeter (V_1) = ... Volt

The value of voltage by CRO (V_2) = ... Volt

$$\text{Error} = V_1 \sim V_2$$

- Precautions :** (i) All the connections should be tight.
(ii) For an accurate result readings should be taken carefully.
(iii) Switch off after taking the readings.

EXPERIMENT No. 3

Object : To become familiar with CRO.

Theory : Out of all the equipments/instruments available in laboratory, perhaps the most important and versatile is the cathode ray oscilloscope (CRO). It is primarily used for the display of wave-forms. It works as an ("eye") for the electronics engineer. With the help of CRO, one can see what is happening in each part of the electronic circuit.

A CRO is basically a very fast X-Y plotter. It displays an input signal versus another signal or versus time. The 'stylus' of this plotter is a luminous spot which moves over the display area in response to input voltages. The heart of the oscilloscope is the cathode ray tube (CRT). The rest of the instrument consists of circuitry necessary to operate the CRT. Now we shall discuss the construction and working of CRT.

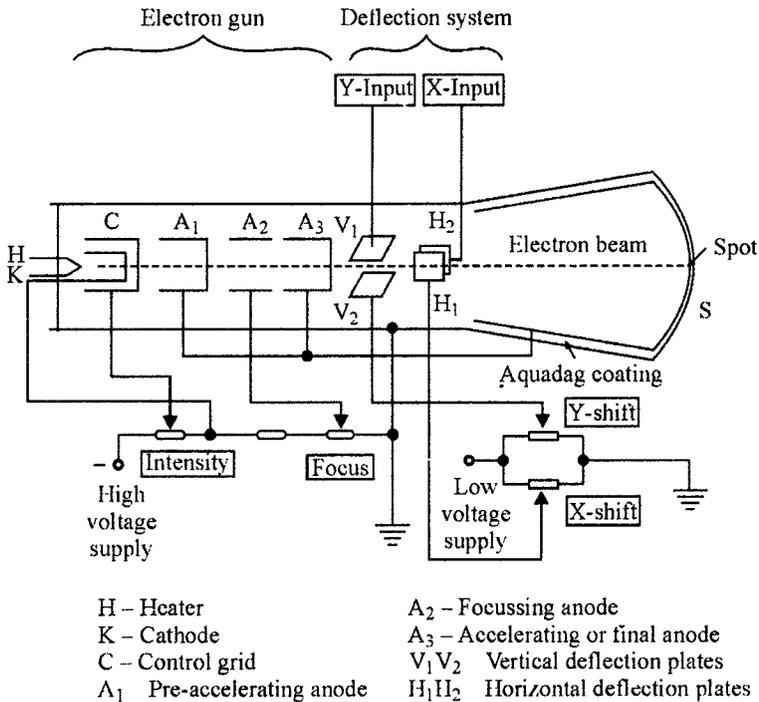


Fig. 3 : Schematic diagram of a CRT.

The schematic diagram of a cathode ray tube along with its control circuit is shown in fig. (3). It consists of basically three parts.

(i) **The electron gun :** The electron gun produces a sharply focussed beam of electrons, accelerated to a very high velocity.

(ii) **The deflection system** : This system deflects the electrons both in the horizontal and vertical planes electrostatically (or magnetically in TV tubes) in accordance with the wave-form to be displayed.

(iii) **The fluorescent screen** : When the electron beam impinges on the fluorescent screen it produces spots of visible light.

The three essential components of a CRT are put inside a highly evacuated funnel shaped glass envelope to a pressure of 10^{-5} mm of Hg. The large end of this tube is coated on the inside with a phosphor material. This material fluoresces when high velocity electrons strike it, converting the energy of the electrons into visible light, hence, the name fluorescent screen.

The electrons are emitted from a cathode which is in the form of a nickel cylinder coated with barium oxide and heated indirectly by passing current in the tungsten filament by a low tension battery. The cathode is surrounded by cylinder C and is called the control grid. The grid is maintained at a negative potential with respect to the cathode so that the electrons emitted from the cathode are repelled and are confined in a fine narrow beam. A fine pencil of electrons emerging from a narrow aperture in C is accelerated towards the anode A_1 as it is maintained at a high positive potential with respect to the cathode. The electron beam comes out in the form of a well defined and narrow fine beam through a hole in the anode A_1 . For further focussing of the beam there is another anode A_2 whose potential is so adjusted that the electron beam is focussed on the screen S . Thus, the last two electrodes of the electron gun provide an electron lens system for focussing the beam into a spot on the screen.

A sharp, well defined and controlled beam of electrons coming out of the anode passes between two pairs of metallic plates provided with an appropriate potential difference. The plates V_1 and V_2 of one pair are in vertical plane. The plates H_1 and H_2 of the other pair are in horizontal plane. The V -plates provide horizontal while H -plates the vertical deflection. The displacement of the spot on the screen is proportional to the intensity of the field producing deflection.

For the measurement with CRO, one of the pairs of the plates is connected to a circuit known as **time base**. This time base provides a sweep voltage of the form shown in fig. (4). It should be noted that without time base voltage, the visual display of applied voltage wave-form is impossible.

To obtain the visual display of the wave-form of the applied voltage it is essential to apply a.c. to one set of deflection plates say H - H plates and to the other set of deflection plates a time base voltage, which can be obtained by special electric circuit call **time base circuits**. When such a voltage is applied to the pair of V -plates

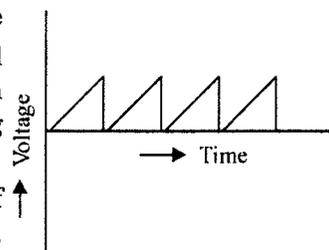


Fig. 4.

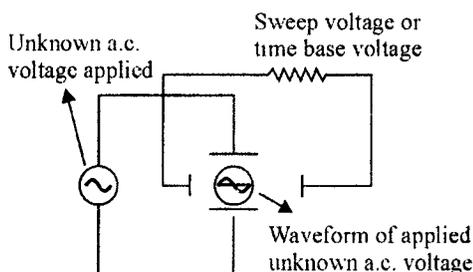


Fig. 5.

of CRO, the spot of light sweeps linearly across the screen in the horizontal direction and suddenly flies back to its starting point for the next sweep.

Hence, a horizontal line appears on the screen which is called **time base line**. This is the spot on the screen which moves up and down due to unknown a.c. voltage applied to the pair of V-plates and at the same time moves horizontally [fig. (5)]. One complete wave-form appears on the screen when the frequency of the time base equals the frequency of the applied a.c. voltage.

EXPERIMENT No. 4

Object : To use a Wheatstone bridge for the accurate measurement of a resistance.

Apparatus : Three resistances with known values, galvanometer, cell, one way key etc.

Theory : Wheatstone bridge principle states that four resistances *P, Q, R, S* are arranged to form a bridge. If galvanometer shows no deflection, the bridge is balanced. In that case,

$$\frac{P}{Q} = \frac{R}{S}$$

Circuit diagram : The circuit diagram is shown in fig. (6).

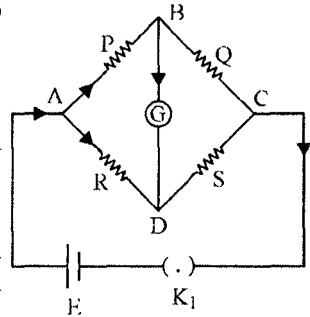


Fig. 6.

Procedure :

(1) Three known resistors *P, Q* and *R* are connected with unknown resistance (*S*) in such a way that they form a bridge.

(2) Connect the galvanometer between two points *B* and *D*.

(3) Use the cell of good quality according to circuit diagram.

(4) Give the current through the cell to circuit.

(5) Now select that value of current at which there is no deflection in the galvanometer.

(6) In case of no deflection in the galvanometer, then according to the Wheatstone bridge principle

$$\frac{P}{Q} = \frac{R}{S}$$

where *S* is unknown resistance.

$$\therefore S = \frac{R \cdot Q}{P}$$

Observations :

S.No.	P	Q	R	Deflection in galvanometer	S
1.	Null deflection
2.
3.
4.
5.

Result : The value of S for different values of P , Q and R will be given by,

$$S = R \cdot \frac{Q}{P} \Omega$$

After that check the resistance of S by multimeter and find the error.

- Precautions :** (i) The values of resistances P , Q and R should be well known.
(ii) The accurate value of resistance of the cell is also known.
(iii) The galvanometer should be of high quality.
(iv) All the wires should be tightly connected.
(v) Take the readings slowly.

EXPERIMENT No. 5

Object : To study the charge and discharge of a capacitor through a resistor.

Apparatus : Resistance (10 k Ω , 50 k Ω), capacitors (500 μ F, 1000 μ F), d.c. supply (15 volt, 25 mA), d.c. voltmeter (0–10 mA), toggle switches, stop watch.

Theory :

(1) For charging

The charging of a capacitor through resistor can be given by

$$q = q_0 (1 - e^{-t/RC})$$

where RC = time constant

q_0 = maximum charge acquired by the capacitor

The corresponding current equation is given by

$$i = \frac{dq}{dt} = \frac{q_0}{RC} (e^{-t/RC})$$

(2) For discharging

The discharge equation is

$$q = q_0 e^{-t/RC}$$

$$i = -i_0 e^{-t/RC}$$

where

$$i_0 = \frac{E}{R}$$

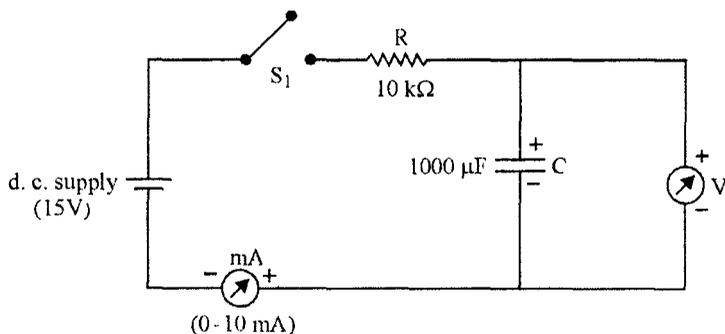


Fig. 7.

Procedure : (a) **For charging of capacitor**

- (1) Make a circuit diagram as shown in fig. (7) and keep switch S_1 open.

(2) Close switch S_1 and simultaneously start the stop watch.

(3) Reading in voltmeter will increase while reading in milliammeter will decrease.

(4) Record the reading of voltmeter and milliammeter after every 2 seconds till you get the maximum voltage and minimum current.

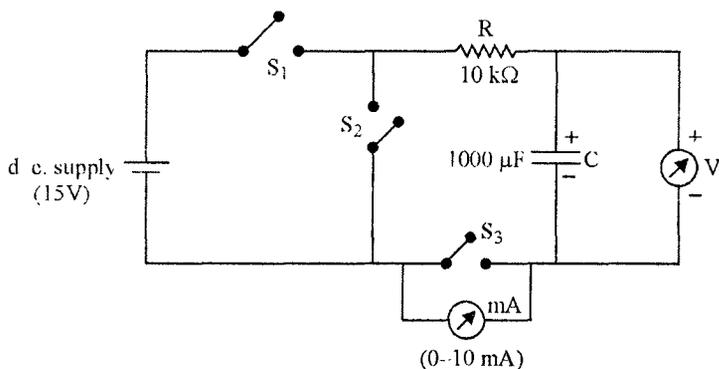


Fig. 8.

(5) Repeat the same process by changing R and C .

(b) For discharging of capacitor

(1) Make a circuit diagram as shown in fig. (8).

(2) Keep switches S_1 and S_2 open while switch S_3 be closed.

(3) Close S_1 till reading in voltmeter reaches maximum value.

(4) Then open and close S_2 (S_3 is already closed). Capacitor will start discharging across R . Take readings in voltmeter after every 2 second till reading becomes minimum.

(5) For discharge current, open S_2 . Again close S_1 so that reading in voltmeter reaches a minimum. Then open S_1 , open S_3 , and close S_2 . Reading in milliammeter will start increasing. Take its reading after every 2 seconds.

(6) Repeat the experiment by changing R and C .

Observations :

(a) For charging of capacitor

$$R = \dots \text{ ohm}$$

$$C = \dots \mu F$$

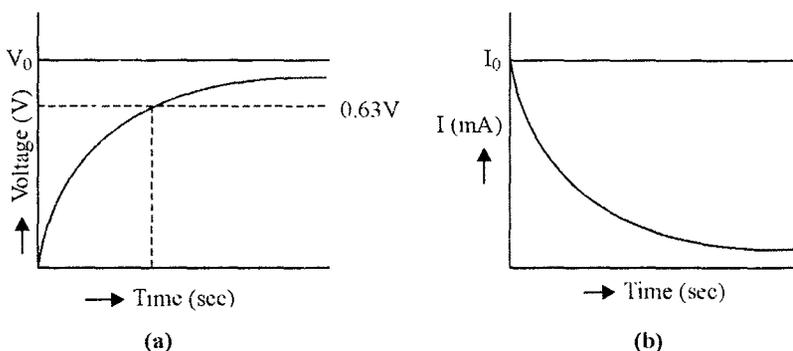
S.No.	Time (sec)	Voltage (volt)	Current (mA)
1.			
2.			
3.			
...			

(b) For discharging of capacitor

S.No.	Time (sec)	Voltage (volt)	Current (mA)
1.	...		
2.	...		
3.	...		
4.	...		
...	...		

Calculations :**(a) For charging of capacitor**

Plot a graph in voltage and time and another in current and time [Fig. 9(a), 9(b)].

**Fig. 9.**

If the maximum voltage reached is V_0 then time constant is the time corresponding to the point where the voltage is $0.63 V_0$. Compare it with theoretical value $\approx RC$.

(b) For discharging of capacitor

Plot one graph in voltage and time, and another in current and time. Find time constant which is the time corresponding to the point where voltage is $0.37 V$. Compare it with the theoretical value.

Result : Time constant of circuit from the graph = ... sec.

Theoretical value of time constant = ... sec.

Precautions :

- (i) Voltmeter and ammeter must have small test counts.
- (ii) Appropriate values of R and C , giving quite a good number of observations, should be used.
- (iii) All the connections should be tight.

EXPERIMENT No. 6

Object : To study the response characteristics of RC network.

Apparatus : a.c. voltmeter, a.c. ammeter, resistor, capacitor, connecting wire.

Theory : Consider an a.c. circuit containing a resistance capacitance C, connected in series as shown in fig. (10).

Impedance of the circuit

$$\begin{aligned} Z &= \sqrt{R^2 + X_C^2} \\ &= \sqrt{R^2 + \left(\frac{1}{\omega C}\right)^2} \end{aligned}$$

(i) Phase angle

$$\tan \phi = \frac{V_C}{V_R} = \frac{IX_C}{I.R} = \frac{X_C}{R}$$

$$\phi = \tan^{-1} \left(\frac{X_C}{R} \right)$$

or,

$$\phi = \tan^{-1} \left(\frac{1}{R\omega C} \right)$$

(ii) Average power

$$p = V_{rms} \cdot I_{rms} \cos \phi$$

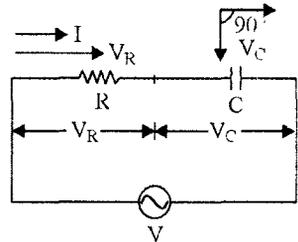


Fig. 10.

Procedure :

(1) Connect the resistor and capacitor in series with a.c. voltage according to fig. (10).

(2) Note the value of current flowing in a circuit through a.c. voltage source.

(3) Measure the voltage drop across resistor (V_R).

(4) Now measure the voltage drop across the capacitor (V_C).

(5) Find the value of impedance Z.

(6) Find the value of f by using the equation, $f = \frac{1}{2\pi C X_C}$.

(7) Phase angle, $\phi = \tan^{-1} \frac{V_C}{V_R}$

Observations :

S.No.	R	V_R	C	$V_C = \sqrt{V^2 - V_R^2}$	$X_C (= \frac{V_C}{I})$	$f = \frac{1}{2\pi C X_C}$	$\phi (= \tan^{-1} \frac{V_C}{V_R})$
1.							
2.							
3.							
4.							
5.							

Result : Frequency, $f = \frac{1}{2\pi C X_C} = \dots$ Hertz

Phase angle, $\phi = \tan^{-1} \frac{V_C}{V_R} = \dots$

Precautions :

- (i) Readings should be taken carefully.
- (ii) Use the resistor, capacitor and a.c. source of high quality.
- (iii) Connections should be tight.

EXPERIMENT No. 7

Object : To study the response characteristics of LR network.

Apparatus : a.c. voltmeter, a.c. ammeter, resistor, inductor, connecting wire.

Theory : Consider the a.c. circuit containing the inductor and resistance in series.

The impedance of the circuit

$$Z = \sqrt{R^2 + X_L^2}$$

$$Z = \sqrt{R + (\omega L)^2}$$

(i)Phase angle

$$\tan \phi = \frac{X_L}{R}$$

$$\phi = \tan^{-1} \left(\frac{X_L}{R} \right)$$

(ii)Average power

$$p = V_{\text{rms}} I_{\text{rms}} \cos \phi$$

Procedure :

(1) Connect the resistor and inductor in series with a.c. voltage according to fig. (11).

(2) Note the value of current flowing in a circuit through a.c. voltage source.

(3) Measure the voltage drop across R , i.e., V_R .

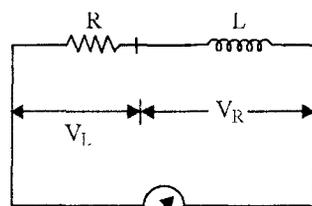
(4) Now measure the voltage drop across inductor L i.e., X_L .

(5) Find the value of impedance.

(6) Find the value of f by using the formula.

$$f = \frac{X_L}{2\pi L}$$

(7) Phase angle, $\phi = \tan^{-1} \left(\frac{X_L}{R} \right)$



$$V = V_0 \sin \omega t$$

Fig. 11.

Observations :

S.No.	R	V_R	L	X_L	$f = \frac{X_L}{2\pi L}$	$\phi = \tan^{-1} \left(\frac{X_L}{R} \right)$

Result : Frequency $(f) = \frac{X_L}{2\pi L}$

$$\phi = \tan^{-1} \left(\frac{X_L}{R} \right)$$

Precautions :

- (i) Readings should be taken carefully.
- (ii) All the connections should be tight.
- (iii) Use high quality equipments.

EXPERIMENT No. 8

Object : To verify the Kirchoff's current law (KCL).

Apparatus : Ammeter, rheostat, d.c. supply, connecting wire.

Apparatus details :

S. No.	Name of apparatus	Type	Range/ Rating	Quantity	Make	Remarks

Theory : The Kirchoff's current law states that *the algebraic sum of currents meeting at a junction of conductors is zero*. In other words, the sum of the current flowing away from a junction is equal to the sum of current flowing towards the junction. This law is illustrated in fig. (12) where six currents I_1, I_2, I_3, I_4, I_5 and I_6 are meeting at a junction. Assuming the currents entering into the junction as positive and currents leaving the junction as

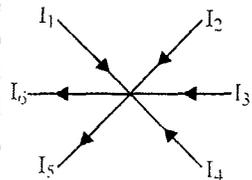


Fig. 12.

negative, we can take the algebraic sum, *i.e.*, all of these six currents and equate it to zero,

$$I_1 + I_2 + I_3 + I_4 - I_5 - I_6 = 0$$

Alternately, we can write KCL as the sum of currents flowing towards the junction to be equal to the sum of currents flowing away from the junction. Thus,

$$I_1 + I_2 + I_3 + I_4 = I_5 + I_6$$

Procedure : This experiment is performed in the following steps :

(1) Connect the different instruments and equipment as shown in the circuit of fig. (13).

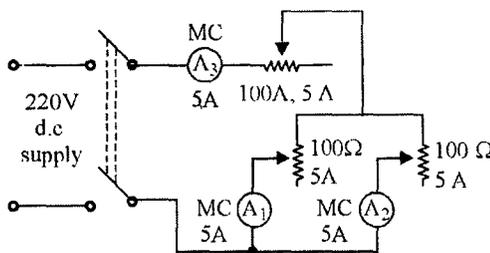


Fig. 13.

(2) Switch on the supply.

(3) Note down the readings of ammeters, A_1 , A_2 and A_3 .

(4) Change the settings of rheostats so as to get different readings in all the three ammeters. Note down the readings of all the ammeters. Check that the sum of readings of ammeters, A_1 and A_2 equals that of ammeter A_3 . Repeat the above procedure.

Observations : Record the observations as per the table given below :

S.No.	I_1 amp	I_2 amp	$I_3 = (I_1 + I_2)$
1.			
2.			
3.			

Calculations : Add the readings obtained from first and second ammeter and it should be equal to the reading of the third ammeter *i.e.*,

$$I_1 + I_2 = I_3$$

Results : As $I_1 + I_2 = I_3$, the Kirchoff's current law is verified, because the current of third ammeter is equal to the sum of currents of first and second ammeter.

Precautions : (i) All the connections should be tight.

(ii) Before operating, check the zero reading of instruments.

(iii) The direction of current should be connected properly.

EXPERIMENT No. 9

Object : To verify the Kirchoff's voltage law (KVL).

Apparatus : Voltmeter, ammeter, rheostats etc.

Apparatus details :

S.No.	Name of apparatus	Type	Range/ Rating	Quantity	Make	Remarks

Theory : According to Kirchoff’s voltage law, “the algebraic sum of voltage around a closed circuit or a loop is zero”.

$$\sum_{j=1}^k V_j = 0$$

The KVL can also be stated as “in any closed circuit, the algebraic sum of the products of current and resistance in each of the conductors is equal to the algebraic sum of the emf of the batteries”. The voltage rise is to be taken as positive, i.e., if we move from the negative terminal to the positive terminal, then it can be taken as positive. Similarly, voltage fall is to be taken as negative, i.e., from positive to negative terminal, the voltage is taken as negative.

Procedure : The experiment is to be performed in the following steps :

- (1) Connect the circuit as shown in fig. (14).

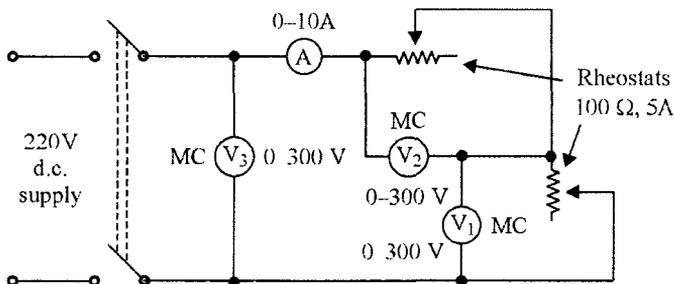


Fig. 14.

- (2) Switch on the d.c. supply.
- (3) Note the readings of ammeter and voltmeters.
- (4) Change the values of rheostats and repeat the step 3 times.
- (5) Each time check that ammeter does not read more than the current rating of the rheostats.
- (6) Switch off the d.c. supply.

Observations : Record the observations as per the following table.

S.No.	Current/ Amp	Voltage V ₁ (volts)	Voltage V ₂ (volts)	Voltage V ₃ (volts)	V ₁ + V ₂
1.					
2.					
3.					

Calculations : Add the voltages V_1 and V_2 recorded from first and second voltmeter and record the same in last column of the above table. Check that the voltage V_3 agrees well with the voltage $(V_1 + V_2)$ recorded in the last column.

Result : As the voltages V_3 and $(V_1 + V_2)$ are equal, Kirchoff's voltage law is verified.

Precautions : (i) All connections should be tight.

(ii) Before connecting the instruments, check their zero readings.

(iii) The terminals of the rheostats should be connected properly.

(iv) The current of ammeter should not exceed the current rating of the rheostats, at any time during the experiment.

EXPERIMENT No. 10

Object : (1) To obtain Lissajou's pattern on the CRO screen by feeding two sine-wave voltages from two signal generators.

(2) To measure the frequency and phase shift by Lissajou's pattern.

Apparatus : CRO, sine wave or other wave whose Lissajou's pattern is to be found, signal generator, connection wire etc.

Circuit diagram : The circuit diagram for measurement of frequency is the same as for voltage measurement and for phase difference as shown in fig. (15).

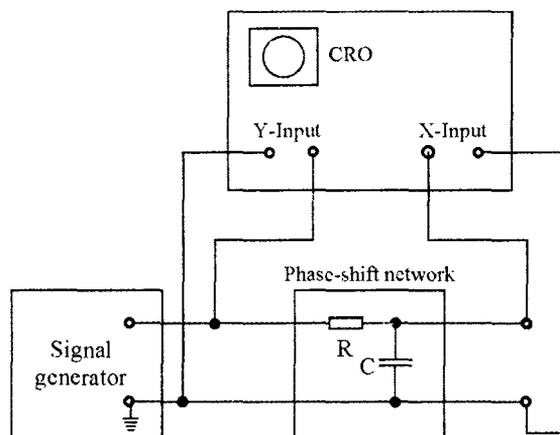


Fig. 15 : Circuit diagram for measuring phase difference.

Procedure : (A) For frequency measurement :

(1) Feed the unknown signal (taken from the signal generator) to the Y-input terminals.

(2) Take a standard signal generator, and connect its output to the X-input terminals of the CRO.

(3) Put the time base or horizontal amplifier knob at exit position.

(4) Change the frequency of the standard signal generator till you get the Lissajou's patterns.

(5) For various frequency ratios, the Lissajou's patterns are shown in fig. (16).

(6) The unknown frequency can be determined.

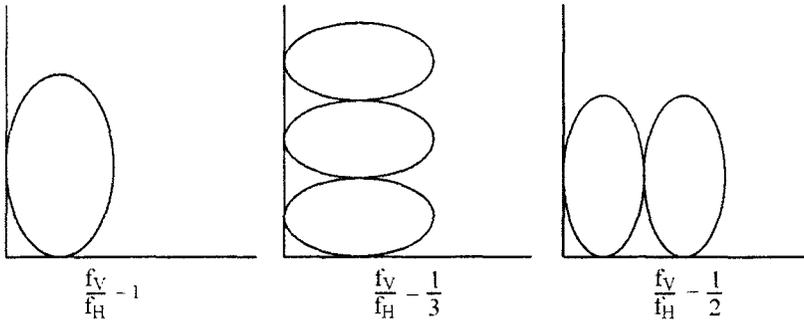


Fig. 16 : Lissajou's pattern for measurement of frequency.

(B) For phase difference between two waves :

- (1) Make connections as shown in fig. (15).
- (2) Put the time base control at exit position.

(3) Adjust the vertical and horizontal amplifier gains (sensitivities) so as to get an ellipse of suitable size as shown in fig. (17).

(4) Measure the lengths Y_1 and Y_2 (or X_1 and X_2).

(5) Calculate the phase difference between the two waves, by using the relation,

$$\sin \theta = \frac{Y_1}{Y_2} = \frac{X_1}{X_2}$$

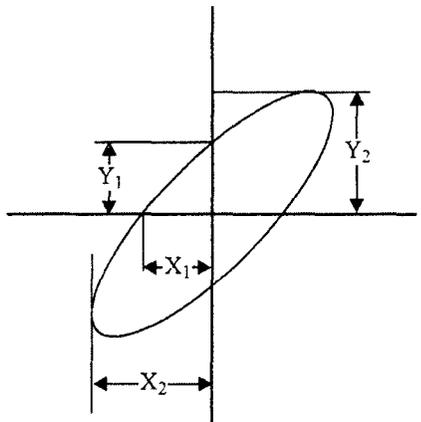


Fig. 17 : Lissajou's pattern for measurement of phase difference.

Observations :

(i) Measurement of frequency

S.No.	Frequency of signal generator	Measurement on CRO		
		Sensitivity in ms/cm	Time period	Frequency in kHz
1.				
2.				
3.				
4.				

(ii) Measurement of phase angle

$$Y_1 = \dots\dots \text{ cm}$$

$$Y_2 = \dots\dots \text{ cm}$$

$$\therefore \theta = \sin^{-1} \frac{Y_1}{Y_2} = \sin^{-1} (\dots\dots)$$

Precautions :

- (i) All the connections should be tight.

(ii) Take the readings when the Lissajou's figure is obtained on the CRO with sharp intensity .

(iii) Readings should be taken carefully.

EXPERIMENT No. 11

Object : To determine the V-I characteristics of a given diode in :

(a) Forward biased modeljunction.

(b) Reverse biased modeljunction.

Apparatus : Regulated power supply, resistors, d.c. milli- ammeter, d.c. micro-ammeter, d.c. voltmeter and connecting wires etc.

Apparatus details :

S.No.	Name of apparatus	Type	Range/ Rating	Quantity	Make	Remarks

Theory : When a *p*-type semi-conductor is joined to an *n*-type semiconductor, the electrons and holes in the region combine and result in a lack of carriers in the regions near the junction. The region of uncovered positive and negative ions is called the *depletion region*. The diode is a two-terminal device. The application of voltage across its terminal leaves three possibilities, viz., no bias ($V_d = 0V$), forward biased ($V_d > 0V$) and reverse biased ($V_d < 0V$). It may be noted that in the absence of an applied voltage ($V_d =$ zero bias voltage), the net flow of charge in any direction for a semiconductor diode is zero.

The V-I characteristics of a diode represent a curve between the external voltage applied across its terminals and the current that flows through the diode due to this applied voltage. There are two characteristics.

(a) Forward characteristic : When the positive terminal of the battery is connected to the *p*-type crystal and the negative terminal of the battery is connected to the *n*-type crystal, then the *p-n* junction is said to be **forward biased**. The potentiometer helps in varying the voltage across the diode as shown in fig. 18(a). The load resistance R_L is included in the circuit, so as to limit the current through the diode. It will be interesting to know that if excessive current is permitted to flow through a diode, it may get permanently damaged. A voltmeter is connected across the diode to measure the voltage whereas milli-ammeter measures current in the circuit.

Let us gradually increase the voltage in small steps of about 0.1 V and record the corresponding values of diode current. Now, if we plot a graph with voltage across the diode along the horizontal axis and diode current along vertical axis, we shall get a curve called the **forward characteristic** of *p-n* junction diode as shown in fig. (18 b).

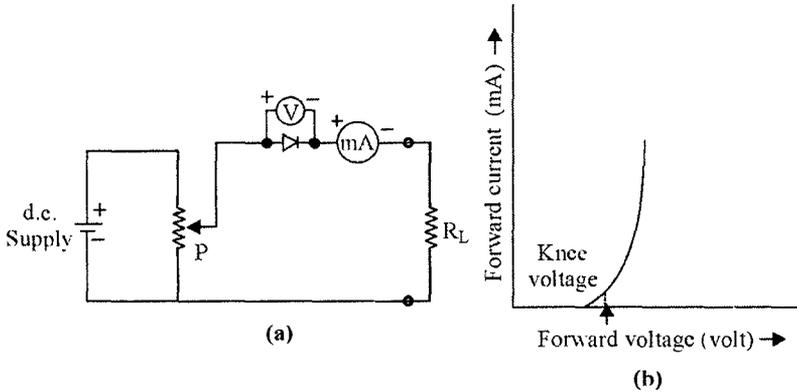


Fig. 18 : Semi-conductor diode in forward bias with V-I characteristic.

(b) Reverse characteristic : The circuit arrangement for obtaining the reverse characteristic of a diode is shown in fig. (19-a). This circuit is similar to that shown in fig. 18 (a), except for two changes, namely the diode terminals are reversed and the milli-ammeter is replaced by a micro-ammeter.

It may be noted that the negative terminal of the voltage source is connected to the anode of diode and positive terminal of the source is connected to cathode of a diode. Hence, the diode is reverse biased. The applied reverse voltage is gradually increased in suitable steps and the values of diode current are recorded at each step. Now, if we plot a graph with reverse voltage along the horizontal axis and the diode current along the vertical axis, we get a curve referred to as **reverse characteristic** of the diode as shown in fig. (19 b).

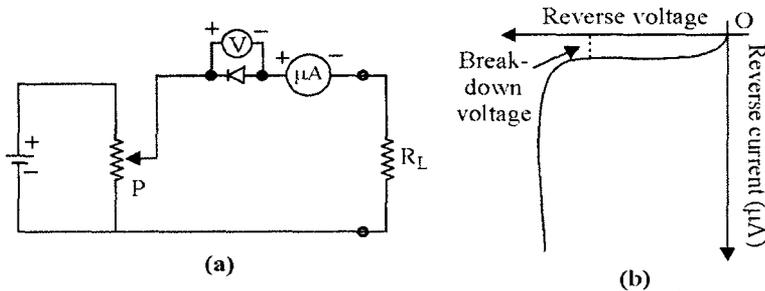


Fig. 19 : Semi-conductor diode in reverse bias with V-I characteristic.

A careful study of the reverse characteristic indicates that when the applied reverse voltage is below the breakdown voltage (V_{BR}), the diode current is small and remains constant. This value of current is called **reverse saturation current** (I_{sat}). It is of the order of nano-ampere for silicon diode and micro-ampere for germanium diode.

Circuit diagram :

Procedure :

For forward biasing

- (1) Make the connections as shown in circuit diagram of fig. (18 a).
- (2) Apply the variable voltage across the diode with the help of potentiometer in forward bias.

(3) Note down the corresponding current from milli-ammeter and voltage from voltmeter and repeat the process again.

(4) Plot a graph between forward voltage and forward current and calculate the forward static and dynamic resistances.

For reverse biasing

(1) Now connect the diode in reverse bias as shown in fig. (19 a) and apply the variable voltage at n -terminal of p - n junction diode.

(2) Note down the corresponding current from micro-ammeter and voltage from voltmeter and repeat the process again.

(3) Draw the curve between reverse voltage and reverse current.

(4) Calculate the static and dynamic resistances from the graph.

Observations :

S.No.	Forward bias		Reverse bias	
	Potential (V)	Current (mA)	Potential (V)	Current (μ A)

Calculations : Find the resistance in forward bias with the help of the graph.

The forward resistance or static resistance $= V/I \Omega$

$$R_{d.c.} = \dots \Omega$$

d.c. forward resistance or dynamic resistance, $R_{a.c.} = \Delta V/\Delta I \Omega$

$$R_{a.c.} = \dots \Omega$$

Result : Discuss the nature of the curve obtained for forward and reverse bias modes.

Precautions : (i) All connections should be tight.

(ii) All steps should be followed carefully.

(iii) Readings should be taken carefully.

(iv) Do not touch the live terminals.

(v) Assume a scale for V - I characteristics in forward and reverse biasing.

(vi) Never increase reverse biased voltage upto the breakdown voltage for an ordinary diode.

EXPERIMENT No. 12

Object : To use the clamping and clipping circuits.

Aparatus : Ammeter, p - n junction diode, battery, resistance of different values.

Procedure :

(A) For clipping circuit

(1) Build and test the signal peak clipper in fig. (20) and verify with PSpice result.

(2) Assume that V_i is 10 V peak to peak sine wave, V_{Bias} is 1.0 VDC, $R = 1K$. $D1$ is 1N400 series diode.

(3) Record the important break points (voltage V_i and time at the corners of the wave-form) in a table.

(4) Change V-Bias and observe the clipping points.

(5) As V_i is increased to higher values, note at what peak to peak does $D1$ begin to clip the negative peak.

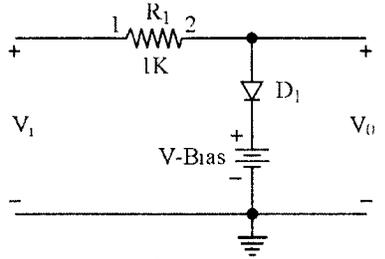


Fig. 20.

Design a clipping circuit as shown in fig. (21) so that the wave-form will be clipped at +3V and -6V. Build the circuit to show all work. Verify your design with PSpice.

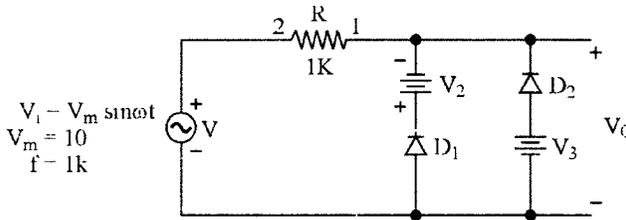


Fig. 21.

(B) For clamping circuit

(1) Build up the clamping circuit as shown in fig. (22) and capture the wave-form at V_0 to verify with PSpice result.

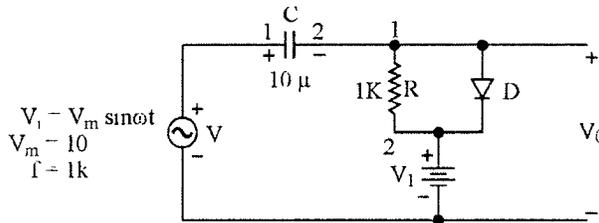


Fig. 22.

(2) Compare this wave-form to what you would expect if the diode was ideal [$V_f = 0$, R_f (forward resistance) = 0] by comparing it with ideal diode model theory. Observe the effects of changing V_1 .

- Precautions :** (i) The $p-n$ junction diode should be an ideal one.
 (ii) Do not have the loose wire.
 (iii) Take readings carefully.

EXPERIMENT No. 13

Object : To study the half-wave and a full-wave rectifier circuit with and without capacitor filter and determine the ripple factor.

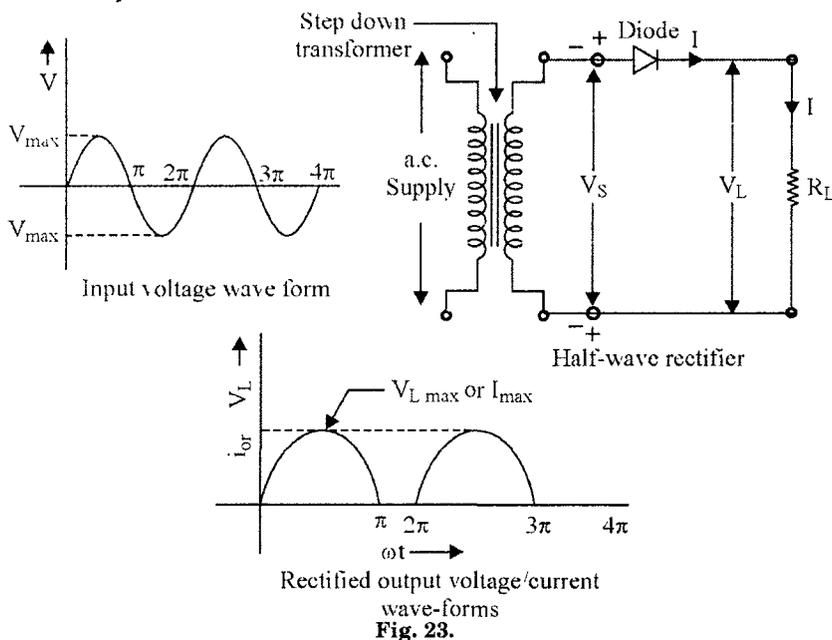
Apparatus : Semi-conductor diode, centre tapped transformer, switches, capacitor, load resistor, multimeter, connecting wires etc

Apparatus details :

S.No.	Name of apparatus	Type	Range/Rating	Quantity	Make	Remarks

Theory : Rectifier is a device which converts the sinusoidal a.c. voltage. A $p-n$ junction diode, which conducts when forward biased and practically does not conduct when reverse biased, can be used for rectification. The rectifier typically needs one, two or four diodes. Rectifier may be either half-wave or full-wave (centre tap or bridge) type.

When a single rectifier is placed in series with the load across an a.c. supply, as shown in fig. (23), it converts alternating voltage into uni-directional pulsating a.c. voltage, using one-half cycle of the applied voltage, the other half cycle being suppressed because it conducts only in one direction. Unless there is an inductance or battery in the circuit, the current will be zero for half the time. This is called **half-wave rectification**.



The half rectifier circuit using a semi-conductor diode with a load resistance R_L but no smoothing filter is given in fig. (23). The diode is connected in series with the secondary of the transformer and the load resistance R_L , the primary of the transformer is being connected to the a.c. supply mains.

In half-wave rectifiers, only one half cycle of the input is utilized but in full-wave rectifiers both half cycles of the input are utilized. Alternate half cycles

are inverted to give uni-directional load current. There are two types of full-wave rectifier circuits viz., (i) centre-tap rectifier and (ii) bridge rectifier.

In a centre-tap full-wave rectifier, the a.c. input is applied through a transformer, the anodes of the two diodes D_1 and D_2 (having similar characteristics) are connected to the opposite ends of the centre tapped secondary winding and two cathodes are connected to each other and are also connected through the load resistance R_L and back to the centre of the transformer as shown in fig. (24).

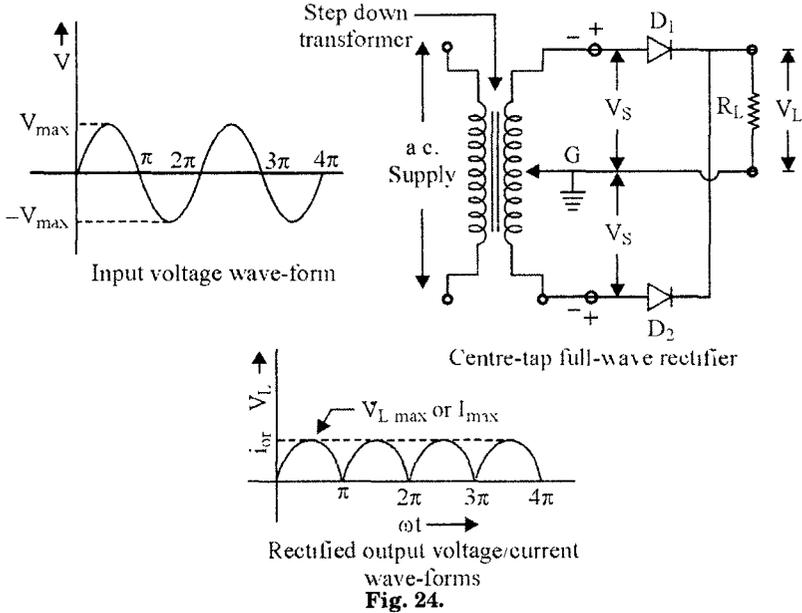


Fig. 24.

In the first half cycle assume that the tap of secondary winding is positive. The anode of diode D_1 is positive with respect to cathode and anode of diode D_2 is negative with respect to cathode. Thus, only diode D_1 conducts, being forward biased and current flows from cathode to anode of diode D_1 , through load resistance R_L and top half of the transformer secondary making cathode end of load resistance R_L positive. During the second half cycle of the input voltage, the polarity is reversed, making the bottom of the secondary winding positive with respect to center tap and thus diode D_2 is forward biased and diode D_1 is reversed biased. Consequently, during this half cycle of input only the diode D_2 conducts and current flows through the load resistance R_L and bottom of the transformer secondary making the cathode end of the load resistance R_L positive. Thus, the direction of flow of current through the load resistance R_L remains the same during both halves of the input supply voltage. Thus, the circuit shown in fig. (24) acts as full-wave rectifier.

The output voltage from a rectifier circuit has a pulsating character, i.e., it contains unwanted a.c. components along with d.c. components. To reduce the a.c. components from the rectifier output voltage, a filter circuit is required. Thus, "filter is a device which passes d.c. component to the load and blocks a.c. components of the rectifier output." Filter is typically constructed from reactive circuit elements such as capacitors/inductors and resistors. Commonly used filter circuits are as follows :

- (a) Series inductor filters (b) Shunt capacitor filters
 (c) Choke input filters (d) Capacitor input or π filters

The function of the capacitor filter may be viewed in terms of impedance. The large value capacitor C offers a low impedance shunt path to the a.c. components or ripples, but offers high impedance to the d.c. components. Thus, ripple gets bypassed through capacitor d.c. and only d.c. component flows through the low resistance R_L .

The pulsating output of a rectifier can be considered to contain a d.c. component and a.c. component called the **ripples**. The ripple current is undesirable and its value should be the smallest possible in order to make the rectifier effective.

The ripple voltage or current is measured in terms of the **ripple factor** which is defined as the ratio of the effective value of a.c. components of voltage (or current) present in the output from the rectifier to the average value of the output voltage (or current), i.e., ripple factor, (γ) is given by

$$\gamma = \sqrt{\left(\frac{V_{rms}}{V_{dc}}\right)^2 - 1}$$

The d.c. output voltage ($V_{d.c.}$) is given by

$$V_{d.c.} = \frac{\sqrt{2}}{\pi} V_{rms} \text{ (for half-wave rectifier)}$$

$$V_{d.c.} = \frac{2\sqrt{2}}{\pi} V_{rms} \text{ (for full-wave rectifier)}$$

Circuit diagram : The circuit diagram is shown in fig. (25). When switch S_1 is open the circuit behaves as a half-wave rectifier and when switch S_1 is closed the circuit behaves like a full-wave rectifier. Shunt capacitor C can be connected across load resistor R_L by closing switch S_2 and taking out from the circuit by opening the switch S_2 .

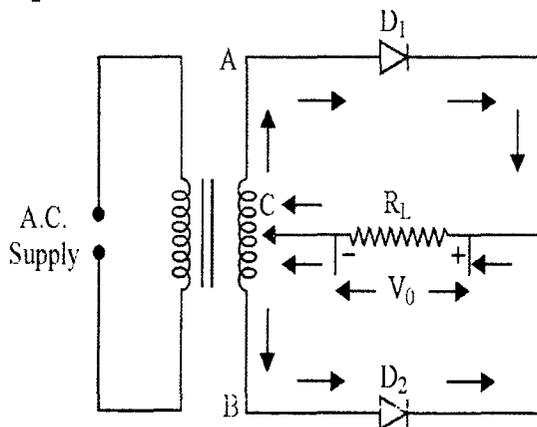


Fig. 25.

Procedure :

(1) The switches S_1 and S_2 are kept in open position. The circuit now behaves as a half-wave rectifier without capacitor filter. A.C. voltage across the secondary of the transformer in the circuit (i.e., half the secondary) and the d.c. voltage across the load resistor R_L are measured with a multimeter.

(2) A.C. voltage across the secondary of the transformer and the d.c. voltage across the load resistor R_L are measured with a multimeter.

(3) The process is repeated with switch S_1 closed and switch S_2 open (*i.e.*, full-wave rectifier without capacitor filter) and with both switches S_1 and S_2 closed (*i.e.*, full-wave rectifier with capacitor filter).

Observations :

S. No.	Parameters	Half-wave rectifier without capacitor filter	Half-wave rectifier with capacitor filter	Full-wave rectifier without capacitor filter	Full-wave rectifier with capacitor filter
1.	Voltage at the diode input V_{rms} in volt.				
2.	D.C. output voltage (measured), V_{dc} in volt.				
3.	D.C. output voltage (calculated), <i>i.e.</i> , V'_{dc} .				
4.	Ripple factor $\gamma = \sqrt{\left(\frac{V_{rms}}{V_{dc}}\right)^2 - 1}$				

Result : It is observed that the ripple factor is maximum in the case of half-wave rectifier (decreases by capacitor filter circuit) and is minimum in case of full-wave rectifier with capacitor filter circuit.

Precautions : (i) All connections should be tight.

(ii) Readings should be obtained carefully.

(iii) The peak value of applied voltage should be less than peak inverse voltage of diode.

EXPERIMENT No. 14

Object : To determine the common base and common emitter characteristics of a transistor.

Apparatus : P-N-P transistor, multi-range voltmeter and milliammeters (digital or analog), variable d.c. supply (0–24 V) and connecting leads etc.

Apparatus details :

S.No.	Name of apparatus	Type	Range/ Rating	Quantity	Make	Remarks

Theory : Basically, junction transistor is a 3-terminal, 2 $p-n$ junction, bi-polar, current controlled device. A junction consists of a silicon or germanium crystal in which a layer is sandwiched between two layers of other type semi-conductor (either p -type or n -type). So a BJT can be either NPN or PNP -type. Transistors have three separate regions (*i.e.*, emitter, base and collector) and two $p-n$ junctions (CB and EB junctions). For the working of transistor in active region, emitter base junction should be forward biased and collector base junction should be reverse biased. Transistor can be connected, in a circuit, in three configurations, *viz.*,

- (a) Common base CB configuration,
- (b) Common emitter CE configuration,
- (c) Common collector CC configuration.

If base is common in input and output circuit., transistor is said to be in **common base configuration**. Similarly, in the case of CE and CC configuration, emitter and collector are taken to be common between input and output circuits, respectively.

Characteristics of Transistor

(a) CB Configuration

We can determine two types of characteristics in CB configuration, one is input characteristic and another is output characteristic.

(i) **Input characteristics :** These characteristics are plotted between the input current and input voltage, *i.e.*, I_E and V_{EB} in case of CB configurations, keeping output voltage V_{CB} constant.

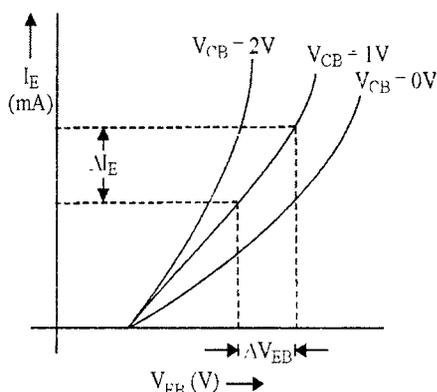


Fig. 26 : Input characteristics for CB configuration.

Dynamic input resistance, $r_1 = \frac{\Delta V_{EB}}{\Delta I_E}$, at constant V_{CB} .

The value of input resistance is very small, *i.e.*, of the order of a few ohm.

(ii) Output characteristics :

These characteristics are plotted between output voltage and output current, *i.e.*, V_{CB} and I_C , keeping input current (I_E) constant.

Dynamic output resistance :
 $r_o = \frac{\Delta V_{CB}}{\Delta I_C}$, at constant I_E .

The output resistance of CB configuration is of the order of several tens of kilo-ohm because the collector current changes very slightly with the change in V_{CB} .

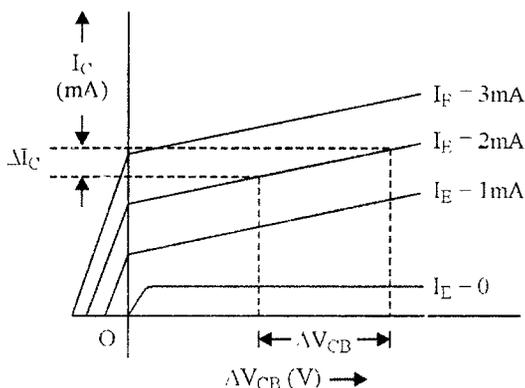


Fig. 27 : Output characteristics for CB configuration.

Current gain, $\alpha = \frac{\Delta I_C}{\Delta I_E}$, at constant V_{CB} .

The *current gain* or *current amplification factor* (α) is less than unity. The value of α can be increased (but not more than unity) by decreasing the base current. This is achieved by making the base thin and doping it lightly. The value of α lies from 0.9 to 0.99.

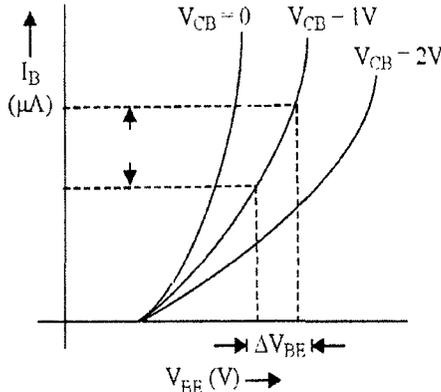


Fig. 28 : Input characteristics for CE configuration.

(b) CE Configuration

(i) **Input characteristics** : Input characteristics in *CE* configuration are plotted between V_{BE} and I_B , keeping V_{CE} constant.

Dynamic input resistance,

$$r_i = \frac{\Delta V_{BE}}{\Delta I_B}$$

(ii) **Output characteristics** : Input characteristics in *CE* configuration are plotted between V_{CE} and I_C , keeping I_B constant.

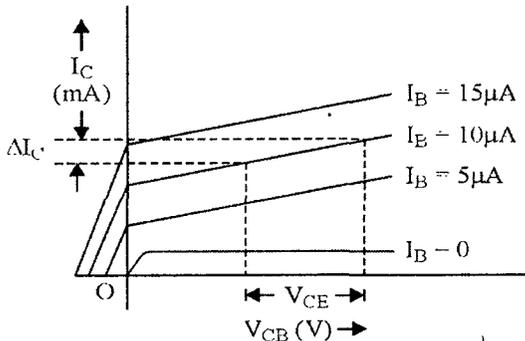


Fig. 29 : Output characteristics for CE configuration.

Dynamic output resistance,

$$r_o = \frac{\Delta V_{CE}}{\Delta I_C},$$

and current gain $\beta = \frac{\Delta I_C}{\Delta I_B}$, at constant V_{CE}

Circuit diagrams :**Procedure :****(a) Common base configuration****(1) Input characteristics :**

(i) Make the connections as shown in fig. (30).

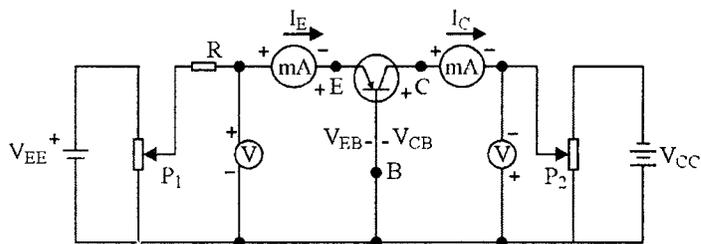


Fig. 30 : Common base configuration.

(ii) Set the output voltage constant.

(iii) Take the readings of input current I_E , increasing the input voltage, V_{EB} .

(iv) Repeat it at different values of output voltage V_{CB} and tabulate in observation table.

(2) Output characteristics :

(i) Make the connections according to the circuit of figure (30).

(ii) Fix the input current I_E .

(iii) Read the values of I_C , increasing the output voltage V_{CB} and tabulate in observation table.

(iv) Repeat this procedure at different values of input current I_E .

(b) Common emitter configuration**(1) Input characteristics :**

(i) Make the connections according to the circuit diagram [Fig. (31)].

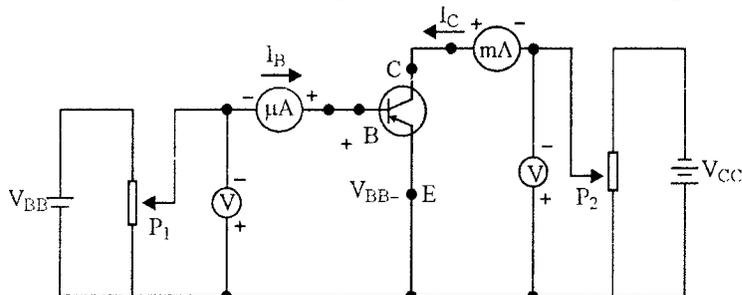


Fig. 31 : Common emitter configuration.

(ii) Firstly, set the output voltage V_{CE} .

(iii) Read the values of I_B , increasing V_{BE} and tabulate in the observation table.

(vi) Set V_{BE} at different values and repeat the above process.

(2) Output characteristics :

(i) Make a proper connection according to the circuit diagram [Fig. (31)].

(ii) Set the input current I_B .

(iii) Observe the value of I_C , increasing V_{CE} and tabulate in the observation table.

(v) Repeat this process, at different values of I_B .

Observations :

(a) Common base configuration

S.No.	Input characteristics			Output characteristics			
	Input voltage V_{EB} (volt)	Input current I_E (mA)		Output voltage V_{CB} (volt)	Output current I_C (mA)		
		$V_{CB} = \dots V$	$V_{CB} = \dots V$		$V_{CB} = \dots V$	$I_E = \dots \text{mA}$	$I_E = \dots \text{mA}$
1.							
2.							
3.							
...							
10.							

(b) Common emitter configuration

S.No.	Input characteristics			Output characteristics			
	Input voltage V_{BE} (volt)	Input current I_B (μA)		Output voltage V_{CE} (volt)	Output current I_C (mA)		
		$V_{CE} = \dots V$	$V_{CE} = \dots V$		$V_{CE} = \dots V$	$I_B = \dots \mu\text{A}$	$I_B = \dots \mu\text{A}$
1.							
2.							
3.							
...							
10.							

Note : Draw the characteristics on a graph paper.

Calculations : From the graph $r_i = \frac{\Delta V_{EB}}{\Delta I_E}$ (in CB) = ... Ω

$$r_o = \frac{\Delta V_{CB}}{\Delta I_C} \text{ (in CB) } = \dots \Omega$$

$$\alpha = \frac{\Delta I_C}{\Delta I_E} \Bigg|_{V_{CB} = \text{constant}} = \dots \Omega$$

$$r_i = \frac{\Delta V_{BE}}{\Delta I_B} \text{ (in CE) } = \dots \Omega$$

$$r_o = \frac{\Delta V_{CE}}{\Delta I_C} \text{ (in CE) } = \dots \Omega$$

$$\beta = \frac{\Delta I_C}{\Delta I_B} \Bigg|_{V_{CE} = \text{constant}} = \dots \Omega$$

Result : The input and output characteristics of *CB* and *CE* configurations of transistor are shown on the graph paper and from calculations :

- | | | |
|-------|----------------------------|--------------------------------------|
| (i) | Dynamic input, | $r_i = \dots \Omega$ (in <i>CB</i>) |
| | | $r_i = \dots \Omega$ (in <i>CE</i>) |
| (ii) | Dynamic output resistance, | $r_o = \dots \Omega$ (in <i>CB</i>) |
| | | $r_o = \dots \Omega$ (in <i>CE</i>) |
| (iii) | Current gain, | $\alpha = \dots$ (in <i>CB</i>) |
| | | $\beta = \dots$ (in <i>CE</i>) |

Precautions : (i) All connections should be tight.

(ii) Instruments should be of suitable range.

(iii) Readings should be taken carefully.

EXPERIMENT No. 15

Object : To design and construct the differential amplifier.

Apparatus : Transistor, current source, resistors, connecting wire etc.

Theory : Transistors Q_3 and Q_4 form the differential pair. Transistors Q_1 and Q_2 form the current source. Resistor R_b is used to set the bias current I_C . The output resistance of Q_2 , as determined by the early voltage V_A , becomes the current source resistance R_0 .

The transistors on IC LM 3086 have nominal values of $V_A = 100$, $V_A = 60$ and $V_B = 0.8$ V. However, in our calculations, we may take $V_A = \infty$ for Q_3 , Q_1 and Q_2 , since r_0 is large enough to be neglected for these transistors.

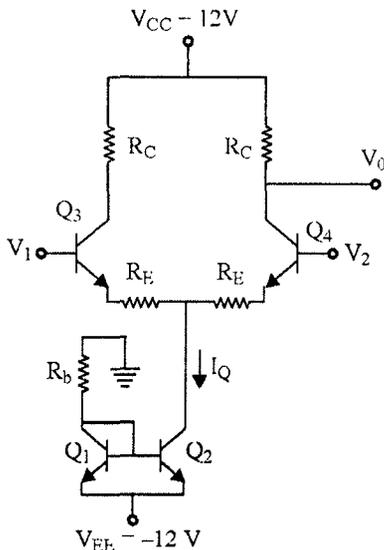


Fig. 32.

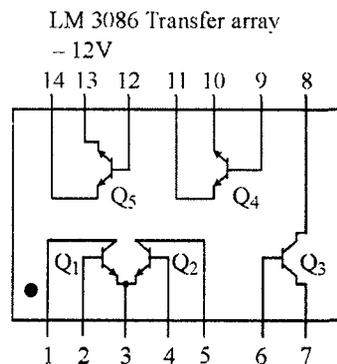


Fig. 33.

The design requirements are listed as follows :

	Min	Max
One-sided differential voltage gain $A_{d.dB}$	28 dB	30 dB
Differential-mode input resistance R_{id}	5 k Ω	
Output resistance R_{out}		4 k Ω
Quiescent output voltage V_{CEQ4}	+5V	+ 7V

(1) Design the differential amplifier and determine the values of R_C , R_E and R_b . Write the values of these resistors in the boxes provided after finishing your design.

R_C	R_E	R_b

Use standard resistor values for R_C and R_E . In the experiment R_b will be set using a variable resistor, and can have any value.

Standard resistor values : 10, 12, 15, 18, 22, 27, 33, 39, 47, 56, 68, 82 ($\times 10^3 \Omega$).

(2) Analyse your circuit using the resistor values in the previous part. Fill out the following table with the values found in your analysis.

Bias current, I_Q

Current source resistance, R_0

V_{CEQ4}

r_π

Differential voltage gain, A_d (linear scale)

Differential voltage gain, $A_{c.d.B}$ (dB scale)

Common-mode voltage gain, A_{cm} (linear scale)

Common-mode voltage gain, $A_{cm.dB}$ (dB scale)

Common-mode rejection ratio, $CMRR_{dB}$ (dB scale)

Differential-mode input resistance, R_{id}

Peak-to-peak undistorted output voltage swing.

Procedure : Construct differential amplifier that you have designed in the preliminary work section. Use transistors Q_3 and Q_4 (on the circuit diagram of LM 3086) as your differential part and use transistors Q_1 and Q_2 as the transistors for the current source. Note that pin 13 of LM 3086 should always be connected to the most negative voltage in your circuit (-12 V in this case) Use a 10 k Ω variable resistor for R_b , and use this resistor to adjust the bias current I_Q . (You can measure I_Q by measuring the voltage drop across the two collector resistors, while inputs are grounded) During your measurements, make sure that your oscilloscope is a.c. coupled.

(1) Measure V_{CEQ3} and V_{CEQ4} and verify that both transistors are active.

(2) Measure the common-mode gain. Connect V_1 and V_2 and connect both of these to the signal generator V_{in} . Set the output of the signal generator to be a sine-wave with an amplitude of ~ 1 V peak-to-peak at a frequency of 2 kHz. Plot

$V_o = V_{C4}$, V_{C3} , and V_{in} versus time on the same graph in this common mode configuration. Determine the one-sided common-mode gain $A_{cm} = V_o/V_{in}$. Compare this value with your calculations.

(3) Measure the differential-mode gain : To do this you would normally need two signal generators that are perfectly out of phase by π radian so that you could have $V_d/2$. Since this is difficult to do experimentally, you will measure the differential mode gain by applying a signal to only one input. The error on this measurement will be very small since the CMRR is large. Set $V_2 = 0$ by grounding the base of Q_1 . Connect the signal generator to V_1 . Set the output of the signal generator to be a sine-wave with an amplitude of 20 mV peak-to-peak at a frequency of 2 kHz. Plot $V_o = V_{C4}$, V_{C3} and V_{in} versus time on the same graph. Calculate the one-sided differential mode gain. Compare this value with your calculations.

(4) Measure the peak-to-peak undistorted (unclipped) output voltage swing.

(5) Observe the linearity of your amplifier by using the oscilloscope in the X-Y mode.

(6) Measure the differential-mode input impedance : To do this, connect a 4.7 k Ω resistor between the signal generator and the input and then measure the voltage division between this resistor and R_{id} to determine R_{id} .

EXPERIMENT No. 16

Object : To :

(1) Trace the circuit diagram of single-stage transistor amplifier.

(2) Measure the Q point collector current and collector-to-emitter voltage.

(3) Measure the maximum signal which can be amplified by the amplifier without having clipped output.

(4) Measure the voltage gain of the amplifier at 1 kHz.

(5) Measure the voltage gain of the amplifier for different values of load resistance.

Apparatus : Amplifier circuit, electronic multimeter, a.c. millivoltmeter, CRO etc.

Circuit diagram : The circuit diagram is as shown in fig. (34) typical values of the components are also given.

Theory : In the amplifier circuit shown in figure (34), the resistors R_1 , R_2 and R_E fix a certain Q point. The resistor R_E stabilizes it against temperature variations. The capacitor C_E bypasses the resistor R_E for the a.c. signal. As it offers very low impedance path for a.c., the emitter terminal is almost at ground potential. When the a.c. signal is applied to the base, the base-emitter voltage changes, because of which the base-current changes. Since collector current depends upon the base current, the collector current also changes. When this changing collector current passes through the load resistance R_C , an a.c. voltage is produced at the output. As the output voltage is much more than the input voltage, the circuit works as an amplifier circuit. The voltage gain (A_v) of this amplifier is given by the formula.

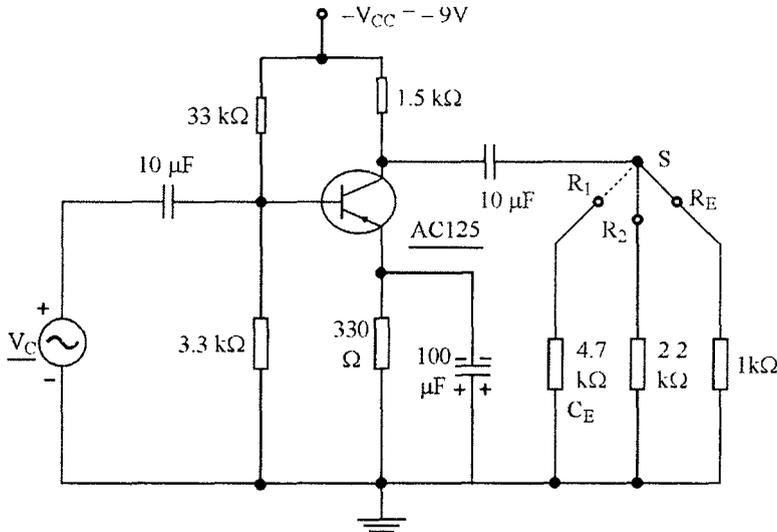


Fig. 34.

$$A_v = \frac{\beta R_{ac}}{r_{in}} \angle 180^\circ$$

where r_{in} is the dynamic input resistance, β is the current amplification factor, and R_{ac} is the a.c. load resistance in the circuit.

Procedure :

(1) Look at the circuit and draw it accordingly in your notebook. With the help of the colour code, find the value of every resistor. Note the values of capacitors also.

(2) Connect the d.c. supply V_{CC} (either with the regulated transistorized power supply or with IC power supply). Measure the d.c. voltage supplied.

(3) For the measurement of quiescent collector current, measure the voltage of collector terminal with reference to ground (V_C). Calculate the collector current by the formula

$$I_C = \frac{V_{CC} - V_C}{R_C}$$

Also measure V_{CE} , i.e., d.c. voltage between the collector and the emitter.

(4) Make sure that the transistor is operating in the active region by noting that V_{CE} is about half of V_{CC} . Feed a.c. signal at 1 kHz at the input of the amplifier. Observe the amplified output on the CRO. Increase the input signal till the output wave shape starts getting distorted. Measure this input signal. This is the maximum signal that the amplifier can amplify without giving distorted output.

(5) Now feed an a.c. signal that is less than the maximum signal handling capacity of the amplifier. Fix the frequency of the input signal at 1 kHz. Note the input and output voltages and calculate the voltage gain.

(6) Connect different load resistors and find the voltage gain of the amplifier for each.

Observations :(1) *Q point of the amplifier*

V_{CC}	V_C	$V_{CC} - V_C$	$I_C = \frac{V_{CC} - V_C}{R_C}$	V_{CE}
1.				
2.				
3.				

(2) Maximum signal that can be handled by the amplifier without introducing distortion = mV. Frequency of the input signal = 1 kHz.

(3) *Voltage gain of the amplifier*

S.No.	Load resistor	Input voltage	Output voltage	Gain = $\frac{V_o}{V_i}$
1.				
2.				
3.				

Result :(i) *Q point of the transistor is*

$$I_C = \dots\dots\dots \text{ mA}, V_{CE} = \dots\dots\dots \text{ V}$$

Since $V_{CE} \approx \frac{1}{2} V_{CC}$, the transistor is biased in active region.

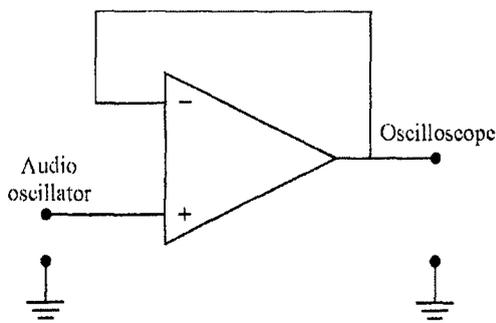
(ii) Maximum signal handling capacity of the amplifier (at 1 kHz) = mV.

(iii) The voltage gain reduces as the load resistance decreases.

EXPERIMENT No. 17**Object :** *To study the introduction of an operational amplifier as a voltage follower.***Apparatus :** Oscilloscope, power supply, audio oscillator assorted resistors and capacitor, operational amplifier potentiometer (variable resistor)**Circuit diagram :** It is shown in fig. (35).**Procedure :** A voltage follower is an amplifier whose closed loop gain is +1, i.e., a non-inverting, unity gain amplifier.

(1) On your protoboard, wire up the voltage follower, including its power supply connections, filter capacitors and offset null point.

(2) Set your function generator to the sine wave mode. Set its frequency to approximately 10 kHz, with an amplitude of approximately 1.0 V.

**Fig. 35 : Circuit diagram.**

(3) Connect the FG output and channel 1 of the oscilloscope between the follower input (In +) and ground.

(4) Connect channel 2 of the oscilloscope between the follower output and ground.

(5) Confirm that input and output amplitudes are equal.

(6) Slowly raise the amplitude of the input signal (V_i) and record the gain ($V_o \sim V_i$) as a function of (V_i). It is important to observe the output amplitude for which the gain deviates from unity; the point where the amplifier saturates.

Result : Thus, by the above procedure, it has been found that the gain deviates from unity, which means that the amplifier saturates.

Precautions : (i) All the connections should be tight.

(ii) Take the readings carefully.

(iii) Switch off, after getting the readings.

EXPERIMENT No. 18

Object : To design operational amplifier as inverting and non-inverting amplifier.

Apparatus : Power supply, audio oscillator, oscilloscope assorted resistors and capacitor, operational amplifier.

(A) Circuit diagram for inverting amplifier : It is shown in fig. (36).

Procedure : (1) Design an inverting amplifier with a closed loop gain of 10.

(2) Select the desired resistors and measure and record their values.

(3) Wire up this circuit on your protoboard, including power and null.

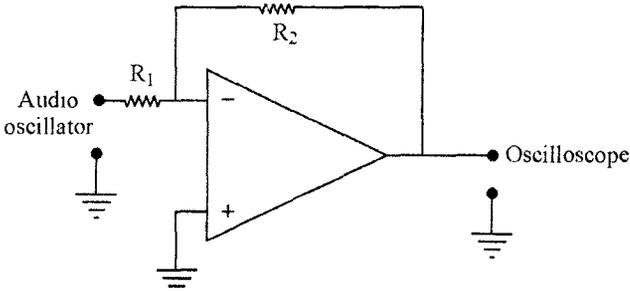


Fig. 36 : Circuit diagram for inverting amplifier.

(4) Keep its output amplitude well below the saturation point.

(5) Repeat these measurements for an amplifier with closed loop gain of 100.

(B) Circuit diagram for non-inverting amplifier : It is shown in fig. (37).

Procedure : (1) Design the non-inverting amplifier as shown in fig. (37) with a closed loop gain of 10.

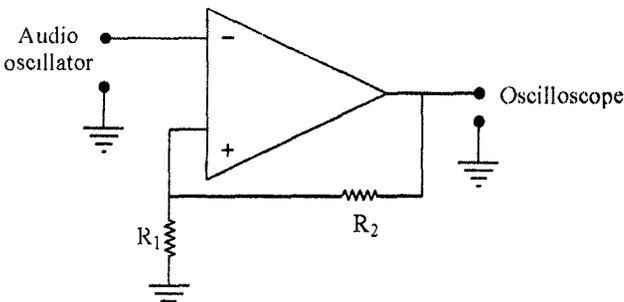


Fig. 37 : Circuit diagram for non-inverting amplifier.

- (2) Select the desired resistors and measure and record their values.
- (3) Wire up this circuit on your protoboard, including power and null.
- (4) Keep its output amplitude well below the saturation point.
- (5) Repeat these measurements for an amplifier with closed loop gain of 100.

Precautions : (i) Take all the readings carefully.

(ii) All the connections should be made tight.

(iii) Switch off, after getting the readings.

(iv) Do not touch the live wire.

EXPERIMENT No. 19

Object : To find the integration and differentiation with operational amplifier.

Apparatus : Power supply, audio oscillator, assorted resistors and capacitor, operational amplifier, oscilloscope etc.

Procedure :

(A) Integration

(1) Design a "standard" integrator and a "DC clamped integrator". Pick up a reasonably high value of RC , so that "high frequency", where the above expression is valid, is not too high. An $RC \sim 0.1$ sec is a possible choice (e.g., $R = 100$ k Ω . $C = 1$ μ F). Pick up an appropriate value for the clamping resistor R_L . On Bode diagrams, plot the expected transfer function.

(2) Measure and record the values of the resistor and capacitor that you will use, using the DMM and the capacitor bridge. Wire up the integrator on your protoboard (don't forget the offset null circuit).

(3) Connect a clip lead across the capacitor, so that $G(\omega) = 0$. Carefully compensate the amplifier offset. Remove one end of the clip lead from the capacitor. Retain the clip lead so that you can discharge the capacitor when needed.

(4) Set the function generator to the sine wave mode. Reduce its d.c. offset to as close to zero as possible.

(5) Set the frequency of the function generator to about 1 kHz. Set its output amplitude to about 0.5 V.

(6) Connect the output of the function generator between the integrator input and ground and across channel 1 of the oscilloscope.

(7) Connect the output of the integrator circuit to channel 2 of the oscilloscope.

(8) Measure and record the transfer function between about 1 kHz and 2 MHz.

(9) As mentioned above, even with a very small residual d.c. offset, the d.c. level under the a.c. output signal will slowly (or not so slowly) drift up to the saturation level. If you have done a good job in the offset compensation, you will have enough time to measure the transfer function at one frequency setting. Before taking the measurement at the next frequency, discharge the capacitor with your clip lead.

(10) Now connect resistor R_L in parallel with C to build a good d.c. clamped integrator. Again measure and record the transfer function as a function of frequency.

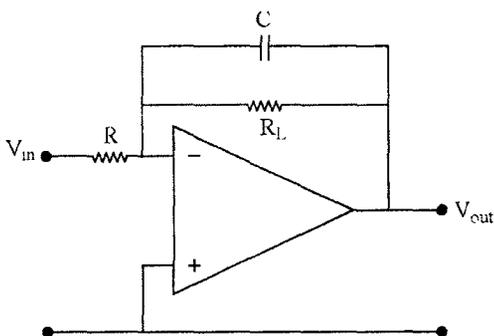


Fig. 38 : Circuit diagram.

(11) Discuss the agreement (or disagreement) between your predictions and your measurements.

(12) Now set up the function generator in the square wave mode, again with an amplitude of above 1V peak-to-peak. Sketch the input and output signals at several appropriate frequencies and discuss how well your circuit works as an integrator.

(B) Differentiation

Construct a differentiation circuit using a second 741 operational amplifier with $C_i = 0.01f$ and $R_f = 20\text{ k}\Omega$.

Connect the output of your integrator to the input of the differentiating circuit. Sketch the output and compare quantitatively with V_i , measured in part 2. In particular, calculate the output you would expect. (The output may have significant ringing present; if so, it may be eliminated by placing a $1\text{ k}\Omega$ resistor in series with the $0.1\text{ }\mu F$ capacitor).

Connect the signal from the pulse generator directly to the input of the differentiating circuit. Sketch quantitatively the output of V_o . You may again find it necessary to place $1\text{ k}\Omega$ resistor in series with the capacitor.

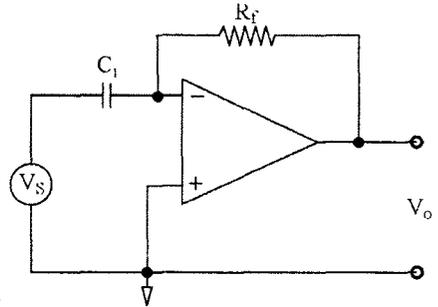


Fig. 39.

- Precautions :**
- (i) Do not touch the live wire.
 - (ii) All the connections should be tight.
 - (iii) Switch off, after getting the readings.
 - (iv) Take all the readings carefully.

EXPERIMENT No. 20

Object : To study operational amplifier in (a) inverting mode (summing amplifier) (b) non-inverting mode (c) integrator (d) differentiator (e) difference amplifier.

Apparatus : Op-amp, IC (741C); Two voltage regulated supplies of +12 volt and -12 volt for supplying voltage to the 7 and 4 terminals of Op-amp respectively; C R.O. with a facility to measure the amplitude of various wave-forms displayed

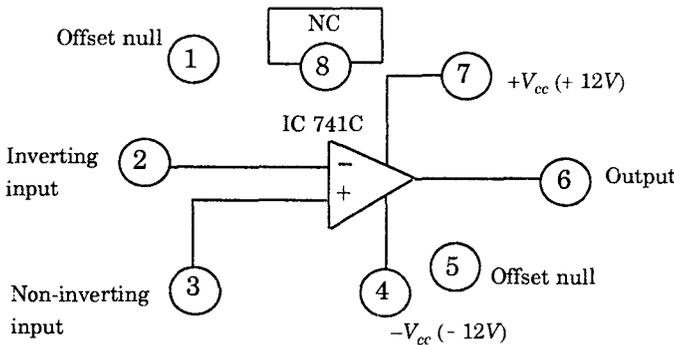


Fig. 40.

on screen in μV and mV . A V.T.V.M. and a millivoltmeter, various resistances and capacitances of values shown in the respective diagrams. Fixed positive d.c. voltage supplies V_1 , V_2 and V_3 to be used as input voltages of the Op-amp.

Base Connections of IC 741 C

Characteristics :

Ideal voltage gain = 2×10^5 (open loop gain)

Output impedance = 75 ohm

Input impedance = 2 meg. ohm

(A) Inverting Mode Summing Amplifier

Circuit and Theory : The circuit is shown in fig. (41). V_{id} is the input differential voltage. The output of the amplifier is given by

$$\begin{aligned} e_0 &= \text{Open loop gain} \times \text{Input differential voltage} \\ &= A_{OL} \times V_{id} \end{aligned}$$

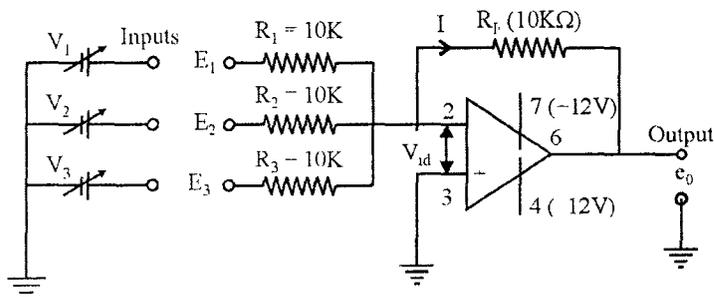


Fig. 41 : Inverting mode.

Since A_{OL} is almost infinite, V_{id} must be very small to have a finite output, e_0 . Thus, the point 2 in the circuit is virtually at ground potential.

$$\text{Current, } I_1 + I_2 + I_3 = \frac{e_1}{R_1} + \frac{e_2}{R_2} + \frac{e_3}{R_3}$$

As the current drawn by Op-amp is negligible, the sum of these currents flows through R_F , so that output is

$$\begin{aligned} e_0 &= -R_F \cdot I = -R_F \left(\frac{e_1}{R_1} + \frac{e_2}{R_2} + \frac{e_3}{R_3} \right) \\ &= -(e_1 + e_2 + e_3) = -(V_1 + V_2 + V_3), \end{aligned} \quad \dots (1)$$

if $R_1 = R_2 = R_3 = R_F$. Thus, output is the negative sum of the inputs *i.e.*, phase of output is reversed.

Procedure :

(1) Make connections as shown in fig. (41). Connect terminal 7 to +12 volt supply and 4 terminal to -12 volt supply. Terminal 2 is connected to input voltages. Keep $R_1 = R_2 = R_3 = R_F = 10 \text{ K}\Omega$. For input voltages use supply V_1 , V_2 and V_3 .

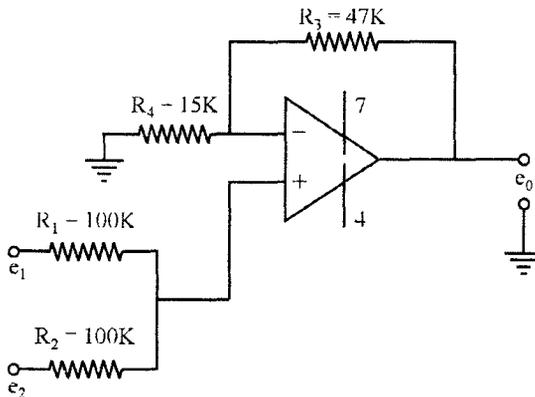
(2) Apply some values of V_1 , V_2 and V_3 . Measure them with the help of V.T.V.M. Measure output voltage, e_0 which will be reverse in polarity.

(3) Repeat the experiment by varying V_1 , V_2 and V_3 .

Observations :Calculated output, $e_0 = V_1 + V_2 + V_3$

$$R_1 = R_2 = R_3 = R_F = 10 \text{ K}\Omega$$

S.No.	Input (volt)	Output (volt)	Calculated output (volt)	Difference (volt)
1.	$V_1 = \dots$ $V_2 = \dots$ $V_3 = \dots$
2.	$V_1 = \dots$ $V_2 = \dots$ $V_3 = \dots$
3.	$V_1 = \dots$ $V_2 = \dots$ $V_3 = \dots$

Result : We observe that output is the negative sum of the inputs.**(B) Non- Inverting Mode****Fig. 42.****Circuit and Theory :** In this circuit, the input is given at non-inverting terminal. Output is in phase with the input. The circuit is shown in fig. (42).Output voltage, e_0 is given by,

$$e_0 = \left(1 + \frac{R_3}{R_4}\right) \left[e_1 \cdot \frac{R_2}{R_1 + R_2} + e_2 \cdot \frac{R_1}{R_1 + R_2} \right] \quad \dots(2)$$

For calculating the output, the above relation will be used and the result will be tabulated.

Procedure :

- (1) Refer to fig. (42). Keep $R_1 = R_2 = 100 \text{ K}\Omega$, $R_3 = 47 \text{ K}\Omega$ and $R_4 = 15 \text{ K}\Omega$. Use V_1 and V_2 for e_1 and e_2 inputs and measure them with V.T.V.M.
- (2) Measure the output, e_0 .
- (3) Repeat the experiment by changing the values of V_1 and V_2 .

Observations :

S.No.	Input (volt)	Output, e_0 (volt)	Calculated output e_0 , cf. equation (2), (volt)	Difference (volt)
1.	$V_1 = \dots$
	$V_2 = \dots$			
2.	$V_1 = \dots$
	$V_2 = \dots$			
3.	$V_1 = \dots$
	$V_2 = \dots$			

Result : Output e_0 is verified and is in phase with input.

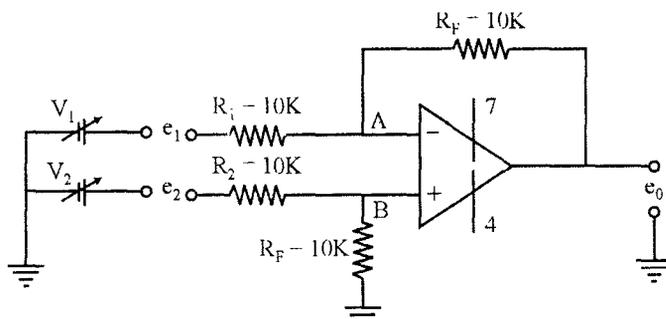
(C) Difference Amplifier

Fig. 43.

Circuit and Theory : Difference amplifier is used to find the difference between two signals. The output is given by

$$e_0 = \frac{R_F}{R_1} (e_2 - e_1)$$

If $R_F = R_1$ then

$$e_0 = (e_2 - e_1) \quad \dots (3)$$

Therefore, in this case, the circuit acts as a subtractor. The circuit is shown in fig. (43).

Procedure :

(1) Refer to fig. (43). Keep $R_1 = R_F = 10 \text{ K}\Omega$. Use V_1 and V_2 for e_1 and e_2 inputs. Measure their values with V.T.V.M.

(2) Measure output, e_0 , with V.T.V.M. Note if $V_1 > V_2$, output e_0 will be negative and if $V_1 < V_2$, output e_0 will be positive.

(3) Repeat the above steps for various values of V_1 and V_2 .

Observations :

S.No.	Input (volt)	Output, e_0 (volt)	Calculated output cf. equation (3), (volt)	Difference (volt)
1.	$V_1 = \dots$ $V_2 = \dots$
2.	$V_1 = \dots$ $V_2 = \dots$
3.	$V_1 = \dots$ $V_2 = \dots$

Result : We note that the circuit acts as a subtractor.

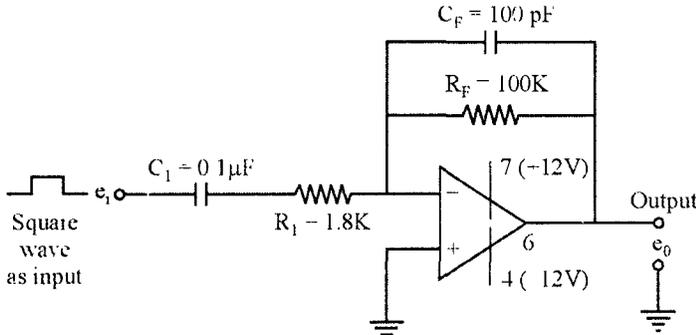
(D) Differentiator

Fig. 44.

Circuit and Theory : The output of this circuit is proportional to the differential of the input. Output is given by

$$e_0 = -R_F C_1 \frac{de_i}{dt} \quad \dots (4)$$

Time constant $R_F C_1$ should be low as compared to the period of input wave. The circuit diagram is shown in fig. (44).

Procedure :

- (1) Keep $R_1 = 1.8 \text{ K}\Omega$, $C_1 = 0.1 \text{ }\mu\text{F}$, $C_F = 100 \text{ pF}$, $R_F = 100 \text{ K}\Omega$.
- (2) Use square wave as input from an oscillator. See the wave-form on a C.R.O. Trace it.
- (3) Connect C.R.O. at output points and increase input from zero till you get a differentiated output on C.R.O. Do not increase input amplitude too much as it will saturate the Op-amp. Trace the differentiated output.

(4) Vary frequency of input square wave, trace it and again trace output also.

Observations and Result : Paste the input and output trace papers for various inputs.

(E) Integrator

Circuit and Theory : This circuit performs an integration over the input. Values of R_1 and C_F are chosen such that time constant $R_1 C_F$ is high as compared to the period of input square wave. The formula for the output, e_0 , is given by

$$e_0 = - \frac{1}{R_1 C_F} \int e_i dt \quad \dots (5)$$

where e_i is input voltage.

The circuit diagram is shown in fig. (45).

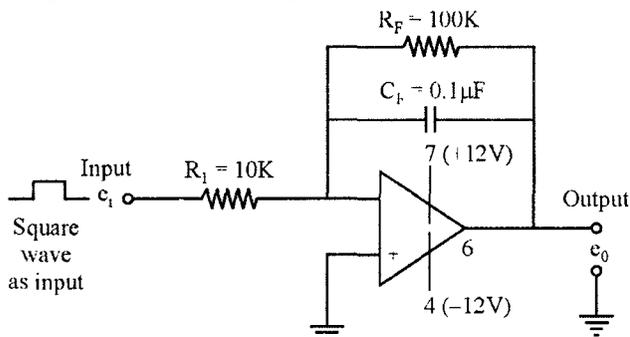


Fig. 45.

Procedure :

(1) Keep $R_1 = 10 \text{ K}\Omega$, $R_F = 100 \text{ K}\Omega$, $C_F = 0.1 \mu\text{F}$. Use square wave from an oscillator as input. Trace its wave-form on a trace paper by placing it on a C.R.O. screen.

(2) Connect C.R.O. to output points. Now increase input from zero to a value such that an integrated output is obtained on C.R.O. screen. Trace it on a paper.

(3) Use input wave of other frequencies. Trace input and corresponding output wave-forms on a paper by placing it on C.R.O. screen.

Observations and Result :

Paste all input and output wave-forms traced on a trace paper from C.R.O. screen. Output wave-forms show that input wave is integrated.

Sources of Error and Precautions :

(i) External connections to Op-amp 741C should be made to the correct pins; Inputs to pin 2 or 3, Supply + 12V to pin 7, - 12V to pin 4. Pin 6 is for output.

(ii) Input voltage level should not reach such a high value that Op-amp becomes saturated.

(iii) Various voltages applied to the pins of Op-amp should not exceed the rating values provided.

(iv) Power supply used for Op-amp should be electronically regulated.

EXPERIMENT No. 21

Object : To determine the energy band gap of a semiconductor (germanium) using four probe method.

Apparatus : Probes arrangement (it should have four probes, coated with zinc at the tips. The probes should be equally spaced and must be in good electrical

contact with the sample), sample (germanium or silicon crystal chip with nonconducting base), oven (for the variation of temperature of the crystal from room temperature to about 200°C), a constant current generator (open circuit voltage about 20V, current range 0 to 10 mA), millivoltmeter (range from 100 mV to 3V, electronic is better), power supply for oven, thermometer etc.

Theory :

The energy band gap, E_g , of semi-conductor is given by

$$E_g = 2k \frac{2.3026 \times \log_{10} \rho}{\frac{1}{T} \text{ (in K)}}, \text{ in eV.}$$

where k is Boltzmann constant equal to 8.6×10^{-5} eV/deg., and ρ is the resistivity of the semi-conductor crystal, given by

$$\rho = \frac{\rho_0}{f(W/s)} \quad \text{where } \rho_0 = \frac{V}{I} \times 2\pi s.$$

The function $f(W/s)$ refers to the table data given in calculations. s is the distance between probes and W is the thickness of semi-conducting crystal, V and I are the voltage and current across and through the crystal chip.

Procedure : Refer to fig. (46).

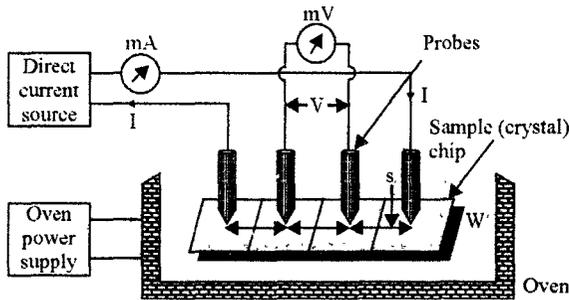


Fig. 46.

- (1) Connect one pair of probes to direct current source through milliammeter and the other pair to millivoltmeter.
- (2) Place the four probe arrangement in the oven. Fix the thermometer.
- (3) Switch on the constant current source and adjust current I , to a desired value, say 2 mA.
- (4) Connect the oven power supply and start heating.
- (5) Measure the inner probe voltage V , for various temperatures.

Observations :

- (i) Distance between probes (s) = ... mm
- (ii) Thickness of the crystal chip (W) = ... mm
- (iii) T and V for current (I) = ... mA (constant)

Table-1

S. No.	Temperature		Voltage V, in volt
	in 0°C	in K	
1	18	291	0.68
2	24	297	0.68
...
...	44	317	0.61
...
...	160	433	0.036

Calculations :

First, find resistivity, ρ , corresponding to temperature in K using the relation

$$\rho = \frac{\rho_0}{f(W/s)},$$

where

$$\rho_0 = \frac{V}{I} \times 2\pi s = \dots \text{ ohm cm.}$$

Corresponding to different values of V , there will be different values of ρ_0 . Find them after putting the values of I and s from the table. Find W/s and then corresponding to this value choose the value of the function $f(W/s)$ from table-2.

Table-2. Values for germanium crystal chip with non-conducting base.

W/s	f (W/s)
0.100	13.863
0.141	9.704
0.200	6.931
0.333	4.159
0.500	2.780
1.000	1.504
1.414	1.223
2.000	1.094
3.333	1.0228
5.000	1.0070
10.000	1.00045

If any (W/s) value is not found in the table then plot a graph in these (W/s) and $f(W/s)$ values. From the graph the desired value of $f(W/s)$ corresponding to any value of (W/s) can be found out.

After choosing $f(W/s)$, calculate the value of resistivity, ρ , for various values of ρ_0 , i.e., for various values of V which correspond to various values of temperature and tabulate as shown in table-3.

Table-3

Temperature, T, in K	Resistivity ρ , ohm cm.	$\frac{1}{T} \times 10^3$	$\log_{10} \rho$
291
297
...
433

Finally, plot a graph between $\left(\frac{1}{T} \times 10^3\right)$ as abscissa and $\log_{10} \rho$ as ordinate and the curve is obtained as shown in fig. (47). Find the slope of the curve which is given by,

$$\frac{AB}{BC} = \frac{\log_{10} \rho}{\left(\frac{1}{T}\right) \times 1000}$$

The energy band gap of semi-conductor (germanium) is given by

$$\begin{aligned} E_g &= 2k \times \frac{2.3026 \times \log_{10} \rho}{1/T} \\ &= 2k \times 2.3026 \times \frac{AB}{BC} \times 1000 \\ &= 2 \times 8.6 \times 10^{-5} \times 2.3026 \times \frac{AB}{BC} \times 1000 \text{ eV} \\ &= 0.396 \times \frac{AB}{BC} \text{ eV} \end{aligned}$$

Result : Energy band gap for semi-conductor (...)

$$E_g = \dots \text{ eV}$$

Standard result : $E_g = \dots \text{ eV}$ (for germanium, $E_g = 0.7 \text{ eV}$).

Sources of Error and Precautions :

(i) The resistivity of the material should be uniform in the area of measurement.

(ii) The surface on which the probes rest should be flat with no surface leakage.

(iii) The diameter of the contact between the metallic probes and the semi-conductor crystal chip should be small as compared to the distance between the probes.

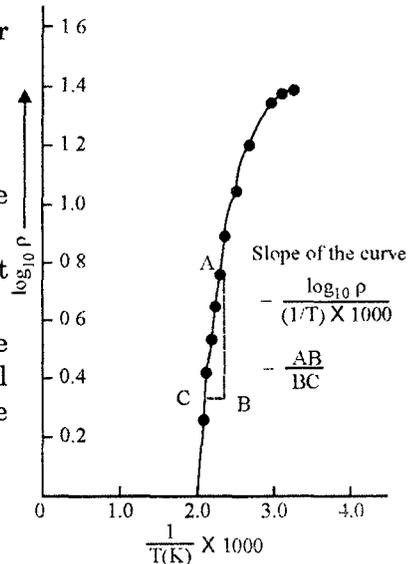


Fig. 47.

EXPERIMENT No. 22

Object : To study characteristics of an integrating and differentiating circuit.

Apparatus : Square wave generator (frequency range 100 c/s to 10,000 c/s), cathode ray oscilloscope, resistances $20\text{ K}\Omega$, $200\text{ K}\Omega$, capacitances $0.001\ \mu\text{F}$, $0.01\ \mu\text{F}$.

(A) **Integrating Circuit :** The circuit is shown in fig. (48).

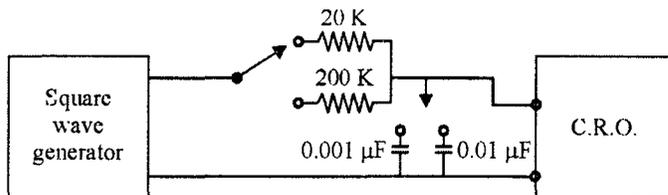


Fig. 48 : Integrating circuit.

Procedure :

(1) Switch on the square wave generator. Set the output to 1 k c/s and feed it to C.R.O. Adjust till the mark/space ratio is unity. That will correspond to a pulse width of 0.5 millisecond. Measure the peak to peak voltage of the input.

(2) Keep $C = 0.001\ \mu\text{F}$, $R = 20\text{ K}\Omega$

Integrated wave-form will appear on the C.R.O. screen. Trace it on a trace paper. Measure peak to peak voltage.

(3) Repeat the above procedure with,

$$C = 0.001\ \mu\text{F}, \quad R = 200\text{ K}\Omega$$

$$C = 0.01\ \mu\text{F}, \quad R = 20\text{ K}\Omega$$

$$C = 0.01\ \mu\text{F}, \quad R = 200\text{ K}\Omega$$

With each set, copy the trace from screen on a trace paper and measure peak to peak voltage. Tabulate the observations as follows :

C,R Values	Peak to peak voltage	Paste the trace paper
$C = 0.001\ \mu\text{F}$ $R = 20\text{ K}\Omega$	$\Delta E = \dots$ volt.	
$C = 0.001\ \mu\text{F}$ $R = 200\text{ K}\Omega$	$\Delta E = \dots$ volt.	
$C = 0.01\ \mu\text{F}$ $R = 20\text{ K}\Omega$	$\Delta E = \dots$ volt.	
$C = 0.01\ \mu\text{F}$ $R = 200\text{ K}\Omega$	$\Delta E = \dots$ volt.	

Conclusion : We observe that if time constant RC is very large as compared to the interval of the input signal then better integrated output wave is obtained. If, on the other hand, time constant RC is decreased, output wave-form approaches the rectangular wave-form.

(B) Differentiating Circuit : The circuit diagram is shown in fig. (49).

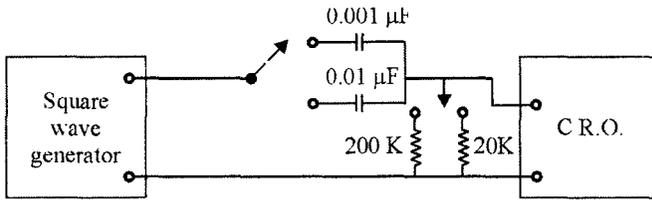


Fig. 49 : Differentiating circuit.

Proceed exactly in the same way as described earlier in the case of integrating circuit. Trace the wave-form for the following sets :

- $C = 0.001 \mu F,$ $R = 20 K\Omega$
- $C = 0.001 \mu F,$ $R = 200 K\Omega$
- $C = 0.01 \mu F,$ $R = 20 K\Omega$
- $C = 0.01 \mu F,$ $R = 200 K\Omega$

Measure peak to peak voltage of the differentiated wave in each case and tabulate as follows :

C,R Values	Peak to peak voltage	Paste the trace paper
$C = 0.001 \mu F$ $R = 20K\Omega$	$\Delta E = \dots$ volt.	
$C = 0.001 \mu F$ $R = 200K\Omega$	$\Delta E = \dots$	
$C = 0.01 \mu F$ $R = 20K\Omega$	$\Delta E = \dots$	
$C = .01 \mu F$ $R = 200K\Omega$	$\Delta E = \dots$	

Conclusion : We observe that if the time constant RC is small as compared to the interval of the input signal then better differentiated output wave is obtained. If, on the other hand, time constant RC is increased, output wave-form approaches the rectangular wave-form.

EXPERIMENT No. 23

Object : To observe wave-forms and to measure amplitude, frequency and phase with a cathode ray oscilloscope.

Apparatus : A.F. oscillator, an $R-C$ circuit and a cathode ray oscilloscope etc.

Circuit : The circuit is shown in fig. (50).

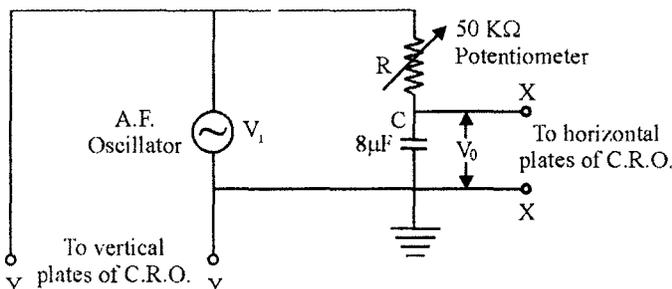


Fig. 50 : R.C. network with its connection with C.R.O. and A.F. oscillator.

Theory : Some controls on C.R.O. front panel are shown in fig. (51). On vertical scale divisions, use volt/div and find amplitude. On horizontal scale divisions, use time/div and find time and hence frequency.

Procedure :

(A) To measure output voltage, V_0 and frequency of input voltage

- (1) Connect A.F. oscillator to RC network.
- (2) Connect X—X terminals to the horizontal plates of C.R.O.
- (3) Use Int synchronisation control of C.R.O.
- (4) By adjusting the output of A.F. oscillator, V_i (both amplitude and frequency control terminals) and frequency of Int.Syn. terminal, obtain a stable wave-form [Fig. (52)] on the C.R.O. screen. Using VTVM, measure input voltage V_i .

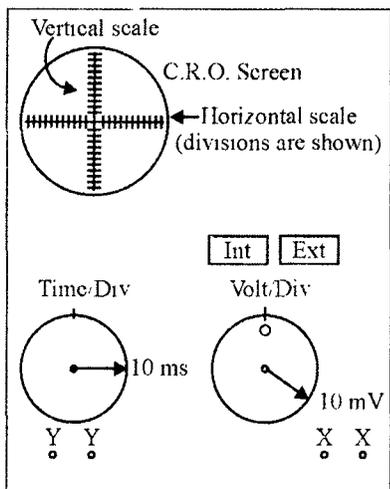


Fig. 51 : Front panel of C.R.O. :
Some control points.

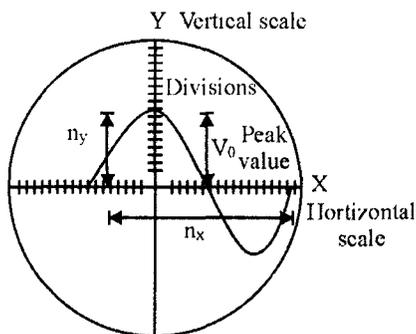


Fig. 52.

- (5) Read number of divisions in the peak value V_0 of voltage on the vertical scale of C.R.O. Using volt/div value find V_0 . For example, say volt/div indicator is at 10 mV and we get n_y division corresponding to V_0 on vertical scale then $V_0 = n_y \times 10 \text{ mV}$.

- (6) To measure the frequency, note the number of divisions on horizontal scale in one complete cycle of wave-form on the screen. Suppose number of divisions are n_x and (time/div) control indicator of C.R.O. is on 10 ms then period of wave is given by :

$$T = n_x \times 10 \text{ m sec. Then } (1/T) \text{ will give the frequency.}$$

(B) To measure phase angle, ϕ :

- (1) Cut off Int. Syn. control of C.R.O. and use Ext. Syn.
- (2) Connect X—X terminals to horizontal plates and Y—Y terminals to vertical plates of C.R.O. i.e., V_0 to horizontal and V_i to vertical plates.

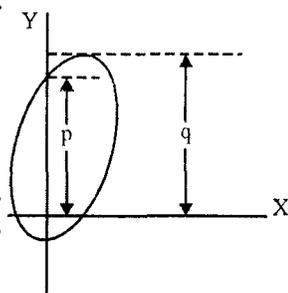


Fig. 53.

(3) A wave-form shown in fig. (53) is obtained. Measure p and q by noting number of divisions on vertical scale and then on multiplying by volt/div value.

(4) Find phase angle, $\phi = \tan^{-1} (p/q)$.

Experiment can be repeated for other frequencies of input voltage.

Observations :

A.F. oscillator frequency	Amplitude, V_0		Frequency, $f = 1/T$		Phase angle ϕ		
	n_y	$V_0 = n_y \times$ (volt/div) value	n_x	$T = n_x \times$ (time/div) value	p	q	$\phi =$ ($\tan^{-1} p/q$)
...
(f_1)							
...
(f_2)							

Result : (1) Amplitude : Theoretical value

$$V_0 = \frac{V_i}{\sqrt{1 + \omega^2 C^2 R^2}} = \dots \text{ volt}$$

(2) Frequency : Directly from A.F. oscillator scale = ... Hz

(3) Phase : Theoretical value, $\phi = \tan^{-1} (p/q) = \dots \text{ deg.}$

Precautions : (i) Do not keep the intensity of wave-form on the screen too high.

(ii) Use such a value of volt/div and time/div that nearly the full scales on C.R.O. screen are used. Wave-form should be large so as to be on full screen.

(iii) Reactance of capacitance, C , should be much smaller than the input impedance of C.R.O.



4

MOLECULAR WEIGHT OF VOLATILE LIQUIDS

The methods for molecular weight determination can be classified into two types :

1. Methods for substances which are either gaseous or volatile.
2. Methods for non-volatile substances. These methods include cryoscopic, ebullioscopic, lowering of vapour pressure, osmotic pressure etc.

Methods of Determining Molecular Weight of Volatile Substances.

The general principle for such determinations includes the finding of weight w , of a known volume v , of a gas or vapour. The temperature and pressure during the measurements are recorded. The pressure is corrected for aqueous tension of water, if the gas or vapour is collected over water. Knowing these data, the molecular weight of volatile substances or gases can be determined by using one of the following procedures.

(1) From vapour density data

Vapour density of a gas or vapour is defined as the *number of times a certain volume there of is heavier than the weight of an equal volume of hydrogen at the same temperature and pressure.*

If V ml of a gas or vapour at N.T.P. weighs W g, then

$$\text{Weight of 1 ml of vapour} = \frac{W}{V} \text{ g}$$

$$\begin{aligned} \text{Vapour density, V.D.} &= \frac{\text{Weight of certain volume of gas}}{\text{Weight of the same volume of hydrogen}} \\ &= \frac{W}{V} / 0.00009 \\ &= \frac{W}{0.00009 \times V} \end{aligned}$$

(\because 1 ml of hydrogen at N.T.P. weighs 0.00009 g)

$$\begin{aligned} \text{Molecular weight, } M &= 2 \times \text{V.D.} \\ &= 2 \times \frac{W}{0.00009 \times V} \end{aligned} \quad \dots (1)$$

(2) From Avogadro's law

We know that at N.T.P. 1 mole of every gas occupies a volume of 22.4 litres or 22400 ml. If W g of a volatile substance gives V ml of dry vapour at N.T.P., then according to Avogadro's law,

$$\text{Molecular weight, } M = \frac{W}{V} \times 22400 \quad \dots (2)$$

The experimental technique most often used for determining the molecular weight of volatile liquids is known as Victor Meyer's method.

Alternately, the molecular weight can be calculated from the equation,

$$PV = nRT = \frac{w}{M} RT \quad \dots (3)$$

where $V \text{ dm}^3$ is the volume of $w \text{ g}$ of the substance of molecular weight, M at temperature $T \text{ K}$ and pressure $P \text{ (atm)}$.

The determination of molecular weight by means of equations (1), (2) or (3) involves the measurement of the volume of a known mass of a gaseous substance at a given temperature and pressure. This method is particularly useful for the determination of molecular weight of gases and easily volatile organic compounds both solid and liquid, provided they do not undergo decomposition at temperature well above their boiling point.

We know that all real gases and vapours deviate more or less from ideal behaviour ($PV = nRT$). Therefore, for these substances, neither the Avogadro's hypothesis is strictly correct nor the volume of 1 mole of a gas at N.T.P. is exactly 22400 dm^3 . Due to this fact, equations (1), (2) and (3) do not hold good strictly for the real gases and vapour and give only an approximate molecular weight. An appropriate equation of state such as vander Waals equation should, therefore, be used for accurate determination. For 1 mole of a gaseous substance, vander Waals equation is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$\text{or } PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

where a and b are vander Waals constants. Neglecting the very small term $\left(\frac{ab}{V^2}\right)$ and replacing $\frac{1}{V}$ by its approximate equivalent $\frac{P}{RT}$, the above equation can be written as,

$$PV - Pb + \frac{aP}{RT} = RT$$

$$\text{or } V = \frac{RT}{P} + b - \frac{a}{RT} \quad \dots (4)$$

Thus, knowing the vander Waals constants, a and b ($a = 3P_c V_c^2$ and $b = \frac{V_c}{3}$, where P_c and V_c are critical pressure and critical volume), the volume V per mole of gaseous substances at pressure P and temperature T can be calculated more accurately from equation (4) than from ideal gas equation.

If $w \text{ g}$ of a gas or vapour occupies a volume v at pressure P and temperature T , then the molecular weight, M can be calculated from the relation,

$$M = \frac{wV}{v} \quad \dots (5)$$

Alternatively, for accurate results limiting vapour density obtained by extrapolating vapour density versus pressure curve to zero pressure must be used.

EXPERIMENT No. 1

Object : To determine the molecular weight of the volatile liquid (*chloroform, acetone, methanol*) by Victor Meyer's method.

Apparatus : Victor Meyer apparatus, graduated cylinder, barometer etc.

Theory : A known weight of a volatile liquid is heated and made to displace its own volume of air which is then collected and measured under known conditions of temperature and pressure. If it is assumed that the vapours of the liquid behave ideally, then the molecular weight of the liquid can be derived from the fact that 1 mole of a gas at N.T.P. occupies a volume of 22,400 ml.

Procedure : The Victor Meyer apparatus (fig. 1) consists of an inner tube A also known as Victor Meyer tube with a cylindrical bulb B at its lower end. The inner tube also known as *vaporizing tube* is connected to a side tube T for the exit of the displaced air or gas which is collected in the graduated cylinder C, by

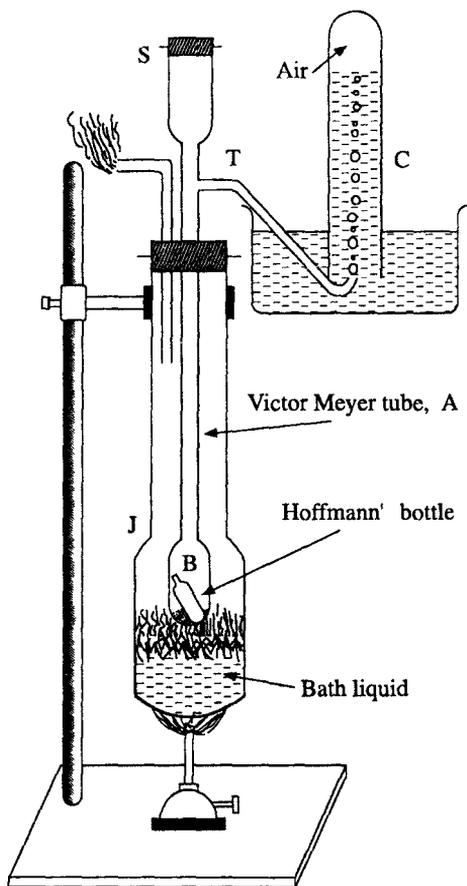


Fig. 1 : Victor Meyer apparatus

downward displacement of water. The tube *A* is closed at the top by means of a rubber stopper. The tube *A* is then enclosed within an outer jacket *J* consisting of a round bottomed flask with a very long neck (usually the outer jacket is made of metal). In this jacket, a liquid is taken whose boiling point is about 20° higher than that of the substance whose molecular weight is to be determined. The cylindrical bulb *B* is provided with some glass wool or sand in order to protect the Hoffmann bottle from breaking, when it is dropped in.

First, the vaporizing tube is cleaned and dried. The inner tube is then rubbercorked and one end of the delivery tube is immersed under water taken in a trough. The liquid (usually water) in the outer jacket is boiled. When the temperature becomes constant, *i.e.*, when no air bubbles escape from the delivery tube, a graduated tube *C*, filled with water is inverted over the end of the delivery tube.

Weigh out accurately a dried Hoffmann bottle and then again weigh it after filling its $3/4$ th with the experimental liquid. The cork of the tube *A* is removed slightly momentarily and the Hoffmann bottle is inserted in it. Since the temperature in the tube is very high as compared to the boiling point of the liquid, the latter vaporises rapidly and blows the stopper out of the Hoffmann bottle. The vapour of the liquid, rising up the tube, drives its own volume of air into the graduated tube *C*. When there is no further displacement, the graduated cylinder is removed, taking care that no water drops out while removing.

The graduated tube *C* is then placed in levelling jar full of water and the former is moved upward and downward in such a way that the level of water in the graduated tube is the same as that in the levelling jar (fig. 2). The volume of air is now noted. The atmospheric pressure is noted from the barometer, while the room temperature is noted by taking the temperature of water in the trough.

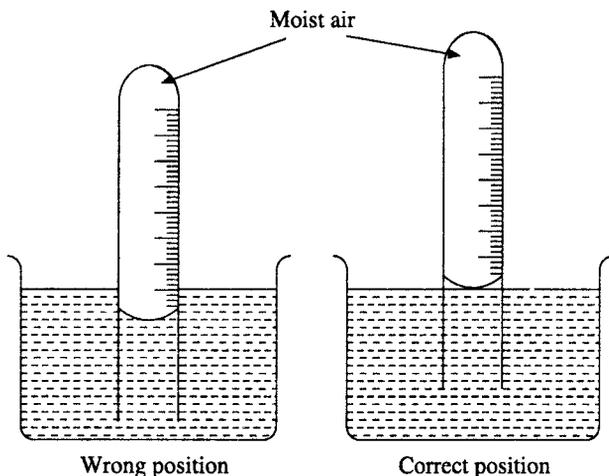


Fig. 2 : Measurement of volume of air

Observations : Weight of empty Hoffmann bottle = W_1 g

Weight of Hoffmann bottle + liquid = W_2 g

Volume of air collected = V ml (say)

Room temperature = $t^\circ\text{C}$

Atmospheric pressure = P mm

Aqueous tension of water at $t^\circ\text{C} = p$ mm

Calculations : Weight of the liquid taken = $(W_2 - W_1)$ g
= W g (say)

Pressure of dry air = $(P - p)$ mm

From gaseous equation we have,

$$\frac{P_1 V_1}{T_1} = \frac{P_0 V_0}{T_0}$$

(Experimental) (N.T.P.)

\therefore Volume (V_0) of dry gas at N.T.P. is given by,

$$V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0}$$

$$= \frac{(P - p)V}{(t + 273)} \times \frac{273}{760} \text{ ml} = v \text{ ml (say).}$$

Therefore, W g of the liquid in the vapor state occupies a volume of v ml at N.T.P.

\therefore Weight of the substance (or liquid) that would occupy a volume of 22,400 ml at N.T.P.

$$= \frac{W \times 22400}{v}$$

\therefore Molecular weight of the liquid

$$= \frac{22400 \times W}{v}$$

Result : The molecular weight of the given liquid = ...

Correction of aqueous tension : This correction is necessary as the air displaced from inside Victor Meyer's tube A due to evaporation of the liquid is the same as the atmospheric air. However, when the displaced air is collected over water, it gets saturated with water vapours. If the atmospheric pressure is P mm of Hg and aqueous tension is p mm of Hg; then true pressure of displaced air, if it were to occupy the same volume as the moist air and at the same temperature, would have been equal to $(P - p)$ mm of Hg. But it is an impossible situation that the atmospheric air should be absolutely dry. If the percentage of humidity in the atmosphere is x , then the correct pressure of air would be equal to,

$$\left[P - p \left(1 - \frac{x}{100} \right) \right] \text{ mm of Hg.}$$

Use of Hempel Gas Burette

The threeway tap Hempel gas burette is the most convenient device for measuring the volume of the air displaced from the inner tube. We proceed as follows for performing the experiment.

(1) Connect the side tube with gas burette using a piece of India rubber tubing as shown in figure (3). By means of another rubber tubing, connect the lower end of the burette to a water reservoir, which can be moved up and down along an iron stand.

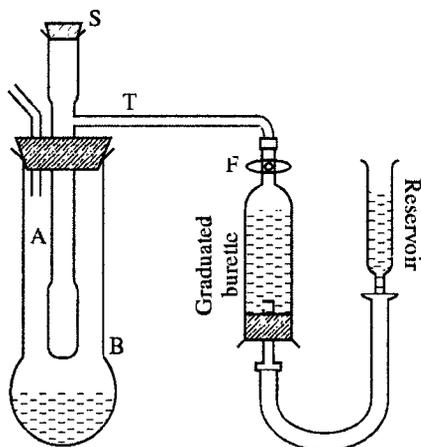


Fig. 3 : Hempel gas burette

(2) To check the apparatus for possible leaks, turn the threeway tap, F, to connect the burette to air. Lower the reservoir so that enough air enters into the burette. Then the burette is connected to the inner tube through the three-way tap and the reservoir is raised. The gas in the burette and in the inner tube gets compressed and any leak will be shown by the upward movement of water level in the burette. Check the fitting of stopper S, connection between the burette and the inner tube and the three-way tap. In case of any leakage, fit and tight them correctly.

(3) Heat the outer jacket and bring the liquid in it to boil. Connect the inner tube to air through the three-way tap so as to allow the expanded air to escape. After 10-15 minutes, when the liquid begins to boil, ensure that the inner tube has reached the steady temperature and the expulsion of the air is complete. To do this, equalise the levels in the burette and the water reservoir and connect the inner tube with the burette. In case the water level in the burette remains stationary, the steady temperature has been attained and the expulsion of air is complete at that temperature. If the level drops slowly, continue to heat the jacket till the level stands stationary. Equalise the levels again taking care that the level in the burette stands near the top but on the graduation. This is done by connecting the burette to air and raising the reservoir till the level reaches near the top. Connect again the inner tube to the burette and note the initial reading of the level in the burette after careful equalisation.

(4) Now remove the stopper, S and introduce a Hoffmann's bottle containing a weighed amount (~ 0.1 g) of the experimental liquid into the inner tube and immediately put the stopper properly so that there is no leakage through it. The air displaced by the vapour of the liquid from the inner tube is collected in the burette. Lower the reservoir so as to maintain atmospheric pressure in the burette and to minimise the leakage. When the level in the burette becomes stationary equalise the levels by lowering or raising the reservoir and close the tap. Disconnect the burette and take it away from the vicinity of the outer jacket. After the burette has reached the room temperature, equalise the levels again and note the final reading of the volume. The difference of the two readings gives the volume of the air displaced at room temperature and atmospheric pressure.

(5) Record the room temperature, atmospheric pressure from the barometer and the relative humidity, if possible.

Precautions : (1) The boiling point of the liquid taken in the vaporised tube should be at least 20°C higher than the boiling point of the liquid.

(2) The cork of the Hoffmann bottle should be loosely held, so that as soon as it is inserted in the tube A, it may open spontaneously.

(3) The Hoffmann bottle should not be filled more than 3/4th, otherwise if it is taken in a large quantity, the vapours of the liquid will displace all the air from the tube A and start passing through water where they will condense.

(4) Heating should be strong and uniform, otherwise water will pass from the trough into the tube A.

(5) While introducing the Hoffmann bottle, the cork of tube A should be slightly opened only for a very short period.

(6) For getting good results, the evaporation of the liquid should be as fast as possible. This minimises the error due the diffusion of vapour.

(7) The stopper, S, should be removed and the tip of the side tube should be taken out from water before the source of heating is removed, otherwise water will be sucked into the inner tube.

EXPERIMENT No. 2

Object : To determine the composition of a binary mixture of liquids by Victor Meyer's method.

Apparatus : Same as in experiment 1.

Theory : Consider a mixture of two volatile liquids A and B. Let d_A , d_B and d_M be the respective densities of liquids A, B and mixture of A and B. We know that the volume of vapour mixture is the sum of the separate volumes of vapours of both components, so,

$$\frac{w}{d_m} = \frac{w_A}{d_A} + \frac{w_B}{d_B} = \frac{w_A}{d_A} + \frac{(w - w_A)}{d_B}$$

or,

$$w_A = w \times \frac{d_A(d_B - d_m)}{d_m(d_B - d_A)}$$

$$\begin{aligned} \therefore \text{Composition of A by weight} &= \frac{w_A}{w} \times 100\% \\ &= \frac{d_A(d_B - d_m)}{d_m(d_B - d_A)} \times 100\% \quad \dots (1) \end{aligned}$$

Therefore, the composition of a binary mixture of volatile liquids can be determined by vapour density measurements.

Procedure : The vapour densities of volatile liquids A, B and mixture are determined by Victor Meyer's method, as described in experiment 1.

Calculations : The percentage composition by weight of liquid A is then calculated by means of equation (1). The value of w_B is calculated from the relation, $w_B = w - w_A$.

Result : The binary mixture contains ... % A and ... % B

Precautions : Same as described in experiment 1.

EXPERIMENT No. 3

Object : To determine the solubility of carbon disulphide in methyl alcohol at room temperature by vapour density method.

Apparatus : Same as in experiment no. 1.

Theory : The method consists in first determining the individual vapour densities of CS_2 and CH_3OH . Then both these substances are shaken together for sometime and the vapour density of the layer of the mixture is determined.

Procedure : The vapour densities of CS_2 and CH_3OH are determined as described in experiment 1. A pure sample of CS_2 is then mixed with pure CH_3OH in a stoppered conical flask and kept for about half an hour in a thermostat to attain the room temperature. The mixture is shaken thoroughly and then allowed to rest until the mixture separates into two layers.

A portion of the upper layer is carefully pipetted out. A small amount of it is carefully weighed in a Hoffmann's bottle and vapour density measured as usual.

Observations and Calculations : Calculate the relative amounts and hence the solubility of CS_2 in CH_3OH as in previous experiment. Similarly, determine the solubility of CH_3OH in CS_2 .

Result : The solubility of CS_2 in $\text{CH}_3\text{OH} = \dots \%$.

EXPERIMENT No. 4

Object : *To find out the molecular weight of a given liquid (benzene, toluene, nitrobenzene or aniline) by steam distillation method.*

Apparatus : Steam distillation apparatus, thermometer, graduated cylinder etc.

Theory : In case of completely or partially miscible liquids, since the addition of one liquid to the other does not change the properties of either liquid, each liquid exerts its own vapour pressure, irrespective of the other. Therefore, the total vapour pressure (P) above the mixture of two immiscible liquids will be the sum of the individual vapour pressure of the two liquids. Thus

$$P = p_A + p_B \quad \dots (1)$$

where p_A and p_B are the vapour pressures of the pure liquids A and B, respectively.

Since the boiling point of any system is the temperature at which its total vapour pressure becomes equal to the atmospheric pressure, so the mixture will boil at a temperature at which,

$$p_A + p_B = \text{Atmospheric pressure.}$$

This temperature is lower than the normal boiling point of either of the liquids alone. Therefore, *any mixture of two immiscible liquids will boil at a temperature lower than that at which any pure component of the mixture boils.* This mixture will continue to distill off at a constant temperature giving the two liquids in constant proportion in the distillate, as long as both the liquids are present in the distillation flask.

In steam distillation, one of the liquids is water. The relative proportion of the two liquids in the distillate can be calculated by assuming that the number of moles of each constituent liquid present in the vapour phase is proportional to its vapour pressure.

If n_A and n_B are the number of moles of each constituent liquid A and B in the vapour phase at the boiling point then,

$$\frac{n_A}{n_B} = \frac{p_A}{p_B}$$

where p_A and p_B are the respective vapour pressures.

If W_A and W_B are the actual weights of the two liquids in the distillate and m_A , m_B are their respective molecular weights, then,

$$\frac{p_A}{p_B} = \frac{W_A/m_A}{W_B/m_B}$$

or

$$\frac{W_A}{W_B} = \frac{p_A m_A}{p_B m_B} \quad \dots (2)$$

From equation (2), it is clear that the weights of the liquids in the distillate are in the ratio of their vapour pressure and molecular weight. The relative weights of the two liquids can be determined from their respective volumes in the distillate and their densities.

Procedure : Steam distillation apparatus (fig. 4) consists of a steam generating metal flask A. The mixture of liquids to be distilled is taken in a round bottomed flask B, which is clamped at an angle so as to prevent the solution from

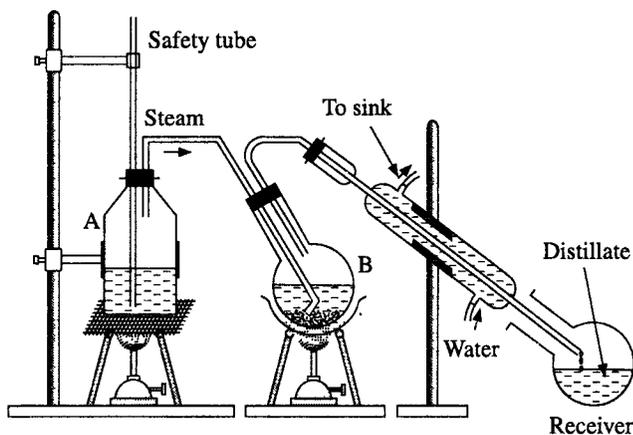


Fig. 4 : Steam distillation apparatus

being splashed into the condenser. The tube carrying steam from the flask A dips in the liquid in the flask B. The distillation flask B is kept heated or kept on a sand bath so as to avoid too much condensation of water into it. The vapours of the experimental liquid mixed with steam pass over and are condensed in the receiver.

Take 50 ml of water and 50 ml of the experimental liquid say aniline, in the flask B. Heat the flask B and pass steam into it. Record the mean temperature of distillation by noting the temperature at regular intervals of say 5/10 minutes. Adjust the rate of heating so that distillation proceeds at a rate of 1 drop every second. Reject the first 10 ml of the distillate and then collect about 35–40 ml of the distillate in a graduated cylinder, (graduated in tenths of a cm^3) called the receiver. Note that the collection must be stopped before the organic liquid is completely exhausted from the distillation unit. Record the volumes of organic liquid and water layers in the measuring cylinder. Also record the barometric pressure.

Observations : Volume of water collected = v_B ml

Volume of liquid collected = v_A ml

Temperature of distillation = $t^\circ\text{C}$

Atmospheric pressure = P mm

Calculations : Weight of liquid (W_A) collected = $d_A \cdot v_A$

Weight of water (W_B) collected = $d_B \cdot v_B$

where, d_A and d_B are the densities of the liquid and water, which can be seen from the standard table.

If vapour pressure (aqueous tension) of water at $t^\circ\text{C}$ is p_B , then,

Vapour pressure of liquid = $P - p_B = p_A$ (say).

The molecular weight (m_A) of the liquid is then calculated, as

$$m_A = \frac{W_A}{W_B} \cdot \frac{p_B m_B}{p_A}$$

The value of $m_B = 18$ (mol. wt. of water = 18).

Result : The molecular weight of the given liquid =

Precautions : (i) The distillation flask B should be continuously heated in order to avoid condensation of water vapours.

(ii) The distillation flask B should be clamped so as to prevent the solution from being splashed into the condenser.

EXPERIMENT No. 5

Object : To determine the vapour pressure of chlorobenzene by steam distillation.

Apparatus : Same as required in experiment 4.

Theory : According to equation (2), deduced in the theory of experiment 4, we have,

$$\frac{W_A}{W_B} = \frac{p_A m_A}{p_B m_B} \quad \dots (3)$$

where all letters have their usual significance. If P be the barometric pressure, then according to equation (1) of experiment 4, $P = p_A + p_B$ or $p_A = P - p_B$.

Thus from equation (3), we get,

$$\frac{W_A}{W_B} = \frac{(P - p_B) m_A}{p_B m_B}$$

Thus, from the determination of the composition of the distillate, *i.e.*, W_A/W_B , the vapour pressure of the given organic liquid, say chlorobenzene, p_B can be calculated.

Procedure, Observations and Calculations :

Same as described in experiment 4.

Result : The vapour pressure of chlorobenzene = mm.



5

CRYOSCOPY (Depression in Freezing Point)

Theory : When a dilute solution of a solute in a solvent is cooled, a temperature is reached at which the solid solvent begins to separate from the solution. This temperature at which separation begins, is known as the '*freezing point of the solution*'. In other words, it may be defined as the *temperature at which a particular solution is in equilibrium with solid solvent*.

The lowering of vapour pressure due to dissolution of a solute causes the solution to freeze at a lower temperature because at the freezing point (f. pt.) of a liquid, its vapour pressure becomes equal to the vapour pressure of its solid form which separates out, and is in equilibrium with the liquid phase. This solid form has a higher vapour pressure when it remains in equilibrium with the pure solvent at its freezing point. So, it may be concluded that the freezing point of a solution is lower than that of the pure solvent.

Solutions freeze at a temperature lower than that of the pure solvent. The difference in the temperature between the freezing point of the pure solvent and that of the solution is known as *depression in freezing point* (ΔT). The dependence of the depression in f. pt. on concentration was studied by earlier scientists Watson and Blagden. Beckmann (1888) was the person who placed the subject of '*cryoscopy*', the study of freezing points of solutions, on a solid experimental

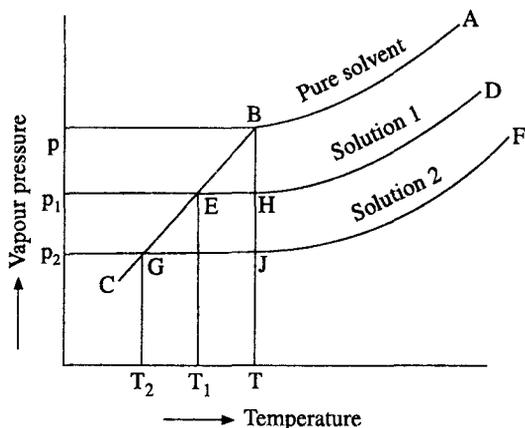


Fig. 1 : Temperature-vapour pressure curve

footing. The theoretical treatment of freezing point depression is primarily due to van't Hoff (1886). The depression in freezing point is a direct consequence of the lowering of vapour pressure of the solvent by a dissolved solute. To appreciate this, consider a temperature-vapour pressure curve, as shown in fig. (1).

Curves AB , BC , DE and FG are the vapour pressure- temperature curves of the pure liquid solvent, solid solvent, solution 1 and solution 2, respectively. Since the solutions are dilute, the two curves (DE and FG) may be taken to be nearly parallel straight lines. T , T_1 and T_2 represent the freezing points of the pure solvent, solution 1 and solution 2, respectively, *i.e.*, where the curves AB , DE and FG meet the vapour pressure curve BC of the solid solvent.

Consider similar triangles BEH and BGJ whereby,

$$\frac{BH}{BJ} = \frac{EH}{GJ}$$

$$\frac{p - p_1}{p - p_2} = \frac{T - T_1}{T - T_2}$$

or

where, p , p_1 and p_2 are the vapour pressure of pure solvent and the two solutions.

From the last equation, we have,

$$\frac{\Delta p_1}{\Delta p_2} = \frac{\Delta T_1}{\Delta T_2} \quad \dots (1)$$

where, Δp and ΔT terms indicate the lowering of V.P. and depression in f. pt., respectively. The subscripts 1 and 2 represent two dilute solutions 1 and 2. Therefore, from equation (1) we have $\Delta p \propto \Delta T$, *i.e.*, *lowering of vapour pressure is directly proportional to the depression in freezing point.*

Relation between ΔT and molecular weight of solute (m_1) : From Raoult's law for dilute solutions, we have,

$$\frac{p - p_1}{p} = \frac{n_1}{n_2} \quad \dots (2)$$

where, n_1 and n_2 are number of moles of the solute and solvent, respectively. If w_1 and w_2 are the weights of the solute and solvent of molecular weights m_1 and m_2 , respectively, then,

$$n_1 = \frac{w_1}{m_1} \quad \text{and} \quad n_2 = \frac{w_2}{m_2}$$

From equation (2),
$$\frac{\Delta p}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or
$$\Delta p = p m_2 \cdot \frac{w_1}{w_2 m_1} \quad \dots (3)$$

For a given solvent at its freezing point, p and m_2 are constants, hence from equation (3), we have,

$$\Delta p = \text{constant} \times \frac{w_1}{w_2 m_1}$$

or
$$\Delta p \propto \frac{w_1}{w_2 m_1}$$

Since $\Delta p \propto \Delta T$, we have,

$$\Delta T \propto \frac{w_1}{w_2 m_1} \quad \text{or} \quad \Delta T = k \cdot \frac{w_1}{w_2 m_1} \quad \dots (4)$$

where k is constant, known as **elevation constant**.

If $\frac{w_1}{m_1} = 1$ and $w_2 = 1$ g, then $k = \Delta T$.

Therefore, elevation constant may be defined as, **the depression in freezing point when 1 mole of a solute is dissolved in 1 g of the solvent.** But this is not practically possible. Hence, if we take,

$$\frac{w_1}{m_1} = 1 \text{ and } w_2 = 100 \text{ g}$$

then,
$$\Delta T = \frac{k}{100} = K \text{ or } K_{100}$$

where K is known as **molecular elevation constant.** Therefore, K may be defined as the **depression in freezing point produced by dissolving 1 mole of solute in 100 g of the solvent.** Equation (4) then reduces to,

$$\Delta T = \frac{100 K w_1}{w_2 m_1} \quad \dots (5)$$

If,
$$\frac{w_1}{m_1} = 1 \text{ and } w_2 = 1000 \text{ g}$$

then,
$$\Delta T = \frac{k}{1000} = \frac{K}{10} = K_f \text{ or } K_{1000}$$

where, K_f is known as **molal depression constant or cryoscopic constant** and may be defined as the **depression in freezing point produced by dissolving 1 mole of a solute in 1000 g of the solvent.**

Equation (4) then becomes,

$$\Delta T = \frac{1000 K_f w_1}{w_2 m_1} \quad \dots (6)$$

Cryoscopic Constants of Solvents

Solvent	K _f	Solvent	K _f
Water	1.86°	Benzene	1.86°
Acetic acid	3.9°	Formic acid	2.8°
Camphor	40°	Naphthalene	6.8°

Relation between k , latent heat of fusion (L_f) and freezing point of the solvent (T).

van't Hoff deduced thermodynamically, that,
$$k = \frac{RT^2}{L_f}$$

where all the letters have their usual significance. (Here L_f represents latent heat of fusion per gram of solvent).

EXPERIMENT No. 1

Object : To find the molecular weight of the given solute in water by depression in freezing point method.

Apparatus : Beckmann thermometer, Beckmann freezing point apparatus, two stirrers—one small and one large, one pipette, ice and NaCl mixture and one ordinary thermometer.

Theory : The molecular weight of a solute is determined from the formula :

$$m_1 = \frac{1000 K_f w_1}{w_2 \Delta T} \quad \dots (1)$$

where all the letters have their usual significance.

Construction of Beckmann Apparatus : The Beckmann apparatus consists of an inner tube *A* having a side tube *T* to introduce the solute. The inner tube is fitted in an outer tube *B*, which acts as an air jacket and ensures slower and uniform cooling of the liquid. The whole apparatus is placed in a glass jar containing the freezing mixture. A stirrer S_1 and Beckmann thermometer T_1 are dipped through two holes in a cork in the inner tube *A*. Another stirrer S_2 is introduced in the outer vessel. The whole apparatus is shown in fig. (2).

Construction and Setting of the Beckmann Thermometer : Beckmann thermometer as shown in fig. (3), is especially constructed for measuring out the small difference of temperatures at any point of the ordinary thermometer scale but not the actual freezing points. It is provided with an open scale of only $5^\circ\text{--}6^\circ$, graduated in 0.01° . It consists of a large bulb connected with an undulated glass tubing at the top closed at the upper end, with the help of a fine capillary glass tube of uniform bore which runs over the porcelain scale.

Let us assume that the zero of the thermometer is set at 25°C and that it is desired to make a new setting such that 0°C should fall on the upper part of the scale.

To begin with, the thermometer does not contain enough mercury and if the bulb were immersed in ice water, the mercury column would disappear into the bulb. To add more mercury to the thermometer, tilt it to transfer the mercury from the reservoir to the space above the fine capillary inseal. Now, if the thermometer is held in an upright position, the mercury can be frequently caused to run down from the space, and join the main column by a quick jerk or sharp tap. If this does not occur readily, the bulb of the thermometer should be held in warm water until the main column rises to join the mercury at the top. On cooling, it will draw this mercury down with it.

Next, the bulb of the thermometer should be placed in a beaker containing ice. The excess mercury in the above space can then be returned to the reservoir by inverting the thermometer and giving it a sharp tap. This operation must be carried out quickly, before

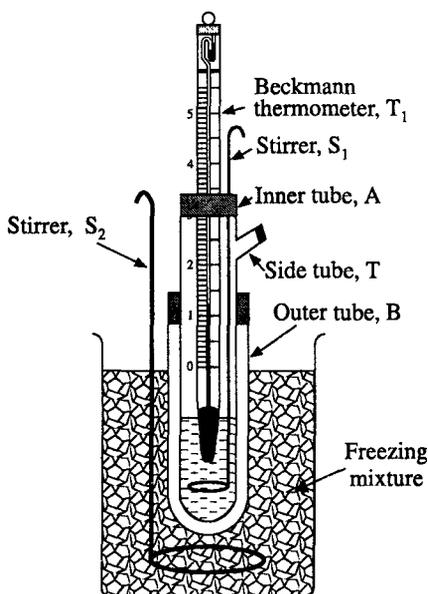


Fig. 2 : Beckmann apparatus

1. Differential Thermometers : These thermometers are used to measure small differences in temperature with relatively high precision. If the difference in temperature is less than 0.1°C , it is necessary to use either a multiple function thermocouple or some special device. For ordinary purposes, mercury-in-glass thermometers of the Beckmann or Philadelphia differential type are satisfactory.

These thermometers are provided with usually large bulbs, with capillary stems graduated to 0.01°C , and with reservoir at the upper end of the capillary which permits the amount of mercury in the bulbs (and thereby setting the thermometers) to be changed at lower portion. The zero of this type of thermometer may be set to any temperature from -10 to $+120^\circ\text{C}$. Their range is about 5°C . With the aid of a small magnifying glass, a "meniscus reader", these may be read with a precision of 0.001°C .

The thermometer should be tapped with a pencil before each reading, as the mercury column has a tendency to stick.

the mercury in the bulb has become appreciably warmer. On returning the thermometer to the ice bath it will probably be found out that due to safety bulb, there is now too much mercury in the thermometer. This excess should be removed cautiously by heating the bulb with warm water or even with the palm of the hand and thereby forcing the excess, drop by drop out of the capillary inseal. In some thermometers, each drop forced out, lowers the scale reading by 1°C .

If it is desired to set a thermometer to a temperature above that of the initial setting, the procedure will be similar.

For setting the Beckmann thermometer, its bulb is placed in a beaker containing ice and then it is seen whether the mercury level is stationary on the thermometer scale or not. If it is, then the thermometer is said to be set. If not, and the mercury level is much below, it means that there is less mercury in the bulb and in such cases, mercury is to be added from the upper reservoir. The mercury thread is then broken near the top by giving a sharp tapping when the temperature of the bath is slightly higher than the freezing point of the pure solvent.

If mercury level is above the scale, it means that too much mercury has been added in the bulb and it must be transferred to the reservoir. This can be achieved by placing the thermometer in slightly hot water and expelling the mercury until its amount is so adjusted (as above) that the mercury level stays on the scale.

Procedure : The Beckmann thermometer is first set as described above. The whole apparatus is fitted as shown in fig. (2). Then 20 ml of water is taken in the inner tube and the Beckmann thermometer is immersed in such a way that its bulb dips in the liquid.

The liquid is stirred gently with the stirrer S_1 and allowed to super-cool a little below its freezing point. It is then stirred vigorously, when crystallisation of ice starts. As the freezing starts, the mercury thread of the thermometer begins to rise till it becomes stationary at a particular level. This temperature is noted. It is the freezing point of the pure solvent.

The inner tube is removed and warmed to melt the solid solvent. A definite weight of the solute is then added through the side tube. When a homogeneous solution is obtained, freezing point of the solution is taken and noted in the same manner as that of the pure solvent.

Observations : Weight of the solvent = w_2 g
F. pt. of the pure solvent = T°

S.N.	Amount of solute in g (w_1)	F. pt. of the solution (T_1°)	Depression in f. pt. ($\Delta T = T - T_1$)	Molecular weight
1.
2.
3.
4.

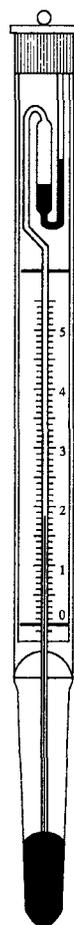


Fig. 3 : Beckmann thermometer

Calculations : The molecular weight (m) of the solute is calculated by the formula given by equation (1).

Result : The molecular weight of the given substance =

Precautions : (i) The temperature of the freezing mixture should be only 5° below the freezing point of the pure solvent.

(ii) The reading of the freezing point must be noted as soon as crystallisation starts, *i.e.*, when the level of mercury becomes stationary on shooting.

(iii) The stirring should be uniform at the rate of about 10 per minute. Rapid stirring should be avoided as it would produce heat due to friction.

(vi) The solvent must be pure and should not form mixed crystals with the solute.

(v) Super-cooling should be avoided, either by seeding effect or by constant stirring of the solution.

EXPERIMENT No. 2

Object : To find out the concentration (0-5%) of the given solution of urea in water.

Apparatus : Same as in experiment 1.

Theory : As concentration and depression in freezing point are directly proportional to each other, a curve between concentration and depression in freezing point will be a straight line. The concentration of the unknown solution can be determined by any point on this line.

Procedure : The freezing point of water is taken as described in expt. 1. A number of solutions of different concentrations of urea are prepared, say from 1 to 5%. The freezing point of each solution is then determined as usual. The freezing point of unknown solution is also determined.

Observations : Freezing point of pure water = T°

S.N.	Concentration of solution	F. pt. of the solution (T_1°)	Depression in f. pt. ($\Delta T = T - T_1^\circ$)
1	1%
2.	2%
3.	3%
4.	4%
5.	5%
6.	Unknown

Calculations : A curve is plotted between depression in freezing point (ΔT) and concentration, which is a straight line as shown (fig. 4). That point on the concentration axis is found which corresponds to the depression in the freezing point for the unknown solution.

Result : The concentration of the unknown solution = ...%

Precautions : Same as in experiment 1.

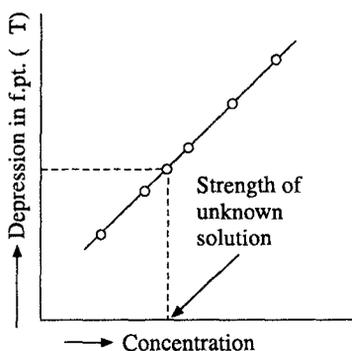


Fig. 4.

EXPERIMENT No. 3

Object : To find the molecular weight of sulphur, α -naphthol or biphenyl by freezing point method using naphthalene as solvent.

Apparatus : Boiling tube carrying $0.1 \times 100^\circ$ thermometer, wire stirrer, air jacket tube, water bath, weighing tube etc.

Theory : The freezing point of naphthalene is 80.3°C and its molal depression constant is 6.8° . A number of substances dissolve in naphthalene giving solutions, from which pure naphthalene separates out at its freezing point. Freezing point can be measured on $1/10$ th degree thermometer by the method of cooling curves. The molecular weight can then be calculated by the relation,

$$\Delta T = \frac{1000K_f w_1}{m_1 w_2}$$

The experiment can be conducted by keeping weight of naphthalene (solvent) constant and by increasing the weight of the solute, w_1 (say sulphur). The corresponding values of ΔT are determined. A graph is plotted with ΔT values on Y-axis and w_1 values on the X-axis. This should give a straight line passing through the origin. The slope of this line will be given by,

$$\text{Slope} = \frac{1000K_f}{m_1 w_2}$$

Thus, the value of m_1 , the molecular weight of solute can be calculated, provided the values of slope, K_f and w_2 are known.

Procedure : Weigh accurately about 10 g of naphthalene powder in a clean boiling tube. Place a thermometer ($\frac{1}{10}$ th $\times 100^\circ$) and a wire loop stirrer in it. Melt

the naphthalene powder in a water bath heated to its boiling point. Wipe the boiling tube dry and keep it in an air jacket. Stir gently and regularly. Take temperature readings every half minute between 85°C and 65°C. The freezing point of pure naphthalene can be calculated from temperature-time graph.

Weigh accurately about 1 g of well powdered solute (say sulphur) in a weighing tube. Introduce it into the boiling tube containing naphthalene in steps of about 0.2 g. Weigh accurately by difference. After each addition, remelt naphthalene and stir to dissolve the solute completely. The freezing point of the mixture or solution is obtained by cooling curve method, as for pure naphthalene.

Observations and Calculations : Prepare a table of ΔT and w_1 values. Plot a curve between ΔT and w_1 and determine the slope of the straight line. The molecular weight (m_1) of the solute can be determined as follows :

$$m_1 = \frac{1000 \times K_f}{\text{Slope} \times w_2}$$

Result : The molecular weight of the given solute =

Precautions : Do not try to pull the thermometer out when naphthalene has frozen completely. It should be lifted out white freezing is incomplete or by remelting naphthalene.

EXPERIMENT No. 4

Object : To find out the degree of dissociation of calcium nitrate (or KCl) in 1 M, 0.5M and 0.25M solutions in water. Also find its van't Hoff factor.

Apparatus : Same as in experiment 1.

Theory : We have already deduced that,

$$\Delta T \propto \Delta p \propto \frac{1}{\text{Mol. wt.}} \left(\text{From } \Delta T = \frac{1000w_1}{w_2m_1} \right)$$

But we know that

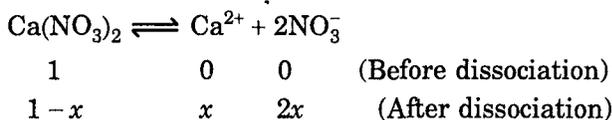
$\Delta p \propto$ osmotic pressure \propto concentration \propto number of particles.

As a result of dissociation, the total number of particles increases; hence the depression of freezing point will also increase. Therefore, the molecular weights of those substances which dissociate, will be lower than their normal molecular weights.

$$\therefore \text{Number of molecules} \propto \frac{1}{\text{Mol. wt.}}$$

$$\therefore \frac{\text{No. of molecules before dissociation}}{\text{No. of molecules after dissociation}} = \frac{\text{Experimental mol. wt.}}{\text{Normal mol. wt.}}$$

Calcium nitrate dissociates as follows,



If we start with 1 mole of $\text{Ca(NO}_3)_2$ and if x be the degree of dissociation (which is defined as the fraction of the total substance ionised or dissociated), then the amounts of the various substances after dissociation shell be as shown above.

Number of molecules before dissociation = 1

Number of molecules after dissociation = $1 - x + x + 2x = 1 + 2x$

$$\therefore \frac{1}{1 + 2x} = \frac{\text{Experimental mol. wt.}}{\text{Normal mol. wt.}} = \frac{1}{i}$$

(where, i = van't Hoff factor)

The normal molecular weight of $\text{Ca}(\text{NO}_3)_2$ can be calculated from its formula, viz., $40 + 2(14 + 48) = 164$. The experimental molecular weight can be determined from the experiment itself.

Procedure : The procedure is the same as described in experiment 1.

Observations : Tables are the same as in experiment 1.

Calculations : Let the molecular weight of $\text{Ca}(\text{NO}_3)_2$ be calculated by means of equation (5) (page 86) as m_1 . If x is the degree of dissociation then

$$\frac{1}{1 + 2x} = \frac{m_1}{164}$$

Since the value of m_1 is known (determined experimentally), the value of x can be calculated easily. The van't Hoff factor (i) is given by,

$$i = \frac{\text{Normal mol. wt.}}{\text{Experimental mol. wt.}} = \frac{164}{m_1}$$

Thus, we can calculate the value of i .

Result : (i) The degree of dissociation of $\text{Ca}(\text{NO}_3)_2 = \dots\%$

(ii) van't Hoff factor = ...

EXPERIMENT No. 5

Object : To find out the pH of a weak acid, say 0.1 N oxalic acid (or malonic acid) solution near 0°C.

Apparatus : Same as in experiment 1.

Theory : pH of a solution is defined as the logarithm of the reciprocal of the hydrogen ion concentration $[\text{H}^+]$, in a given solution, i.e.,

$$\text{pH} = \log \frac{1}{[\text{H}^+]}$$

The hydrogen ion concentration, i.e., $[\text{H}^+]$ is given by the product of the degree of dissociation and concentration. So, our aim will be to determine the degree of dissociation of oxalic acid.

Procedure : Prepare 0.1N oxalic acid solution in distilled water. Determine the freezing points of distilled water and 0.1N oxalic acid solution.

Observations : Same as in experiment 4.

Calculations : Suppose x is the degree of dissociation of 0.1N oxalic acid. The value of x can be calculated as in experiment 4. We then have, $[\text{H}^+] = x \times 0.1$.

$$\text{Therefore, pH} = \log \frac{1}{[\text{H}^+]} = \log \frac{1}{0.1x}$$

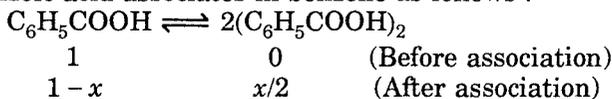
Result : The pH of 0.1N oxalic acid =

Object : To find out the apparent molecular weight and degree of association of benzoic acid in benzene.

EXPERIMENT No. 6

Apparatus : Same as described in experiment 1.

Theory : Association is a phenomenon of combination of two or more than two molecules of a substance to form an additive molecule known as **associated molecule**. Benzoic acid associates in benzene as follows :



If x is the degree of association of benzoic acid, then number of molecules before and after association will be 1 and $\left(1 - \frac{x}{2}\right)$, respectively. As the number of molecules is reduced, the molecular weight of benzoic acid (or those substances which associate) will be higher than its normal molecular weight.

As discussed in experiment 4, we have,

$$\frac{\text{Experimental mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{Number of molecules before association}}{\text{Number of molecules after association}}$$

$$\therefore \frac{\text{Experimental molecular weight}}{\text{Normal molecular weight}} = \frac{1}{1 - \frac{x}{2}}$$

The normal molecular weight of $\text{C}_6\text{H}_5\text{COOH}$ is 122, while its experimental molecular weight can be determined by means of the experiment. Value of x , the degree of association, can then be calculated.

Procedure : As the solvent in this case is benzene which freezes at about 4.5°C , hence the Beckmann thermometer should be set at this temperature. A thermometer which is set for water cannot be used in this case. For doing this, an ordinary and Beckmann thermometer are dipped in a small beaker containing ice and liquid water. The temperature of water is maintained between 4°C and 5°C . At this temperature, the thread of mercury in the Beckmann thermometer is broken and it is ascertained whether the mercury stands on the scale or not at temperature between 4° and 5° . When this is achieved, the thermometer is said to be set for solvent benzene.

The remaining procedure is exactly the same as in experiment 1 or 4.

Observations : Same as in experiment 1 or 4.

Calculations : The experimental molecular weight (m_1) of benzoic acid is calculated as in experiment 1. Its normal molecular weight is 122. Then from the formula, we can calculate the degree of association, x .

$$\frac{1}{1 - \frac{x}{2}} = \frac{m_1}{122}$$

Result : (i) The degree of association of benzoic acid = ...%.

(ii) Apparent (or experimental) molecular weight
of benzoic acid =

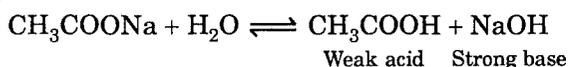
EXPERIMENT No. 7

Object : To find out the degree of hydrolysis of the given substance, say CH_3COONa , near 0°C in $0.5M$ solution.

Apparatus : Same as in experiment 1.

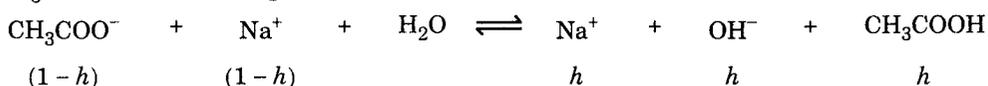
Theory : Hydrolysis of a salt is defined as the decomposition of the salt by means of water to give free acid and free base and thereby produce acidity or

alkalinity in the solution depending on the relative strength of the acid or base generated. For example, the hydrolysis of CH_3COONa will give an alkaline solution as follows :



The degree of hydrolysis (h) of a salt is defined as, 'the fraction of the total salt hydrolysed' (h is generally expressed in percentage).

All the colligative properties, such as depression in freezing point, depend upon the number of solute particles in them. They are considerably affected due to hydrolysis, as the number of solute particles in solution changes. Due to hydrolysis, H^+ and OH^- ions are produced in the solution, thus the number of solute particles increases and the depression in freezing point is affected. If the concentration of CH_3COONa is 1 mole per litre, then we have,



Number of particles after hydrolysis

$$= (1-h) + (1-h) + 3h = h + 2$$

Number of particles before hydrolysis = 2

$$\frac{\text{Observed } \Delta T}{\text{Calculated } \Delta T} = \frac{h + 2}{2} \quad \dots (1)$$

Knowing the values on the left hand side, we can calculate degree of hydrolysis, h .

Procedure : Same as in preceding experiments. Prepare 0.5M solution of sodium acetate.

Observations : The observed depression in freezing point can be directly found by experiments as described before.

Calculations : The calculated depression in freezing point can be obtained from the formula, $\Delta T = \frac{1000K_f w_1}{w_2 m_1}$

The value of m_1 in this case can be taken equal to 82. The values of w_1 and w_2 are already known for the experiment. Hence, we can determine the calculated depression in freezing point (ΔT_0). From weight data, find the molality of the solution and calculate ΔT_e . If no hydrolysis were to occur and the dissociation were complete, then from equation (1) we can calculate h , degree of hydrolysis, from the formula,

$$h = 2 \left[\frac{\Delta T_0}{\Delta T_e} - 1 \right]$$

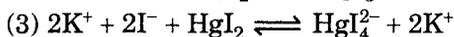
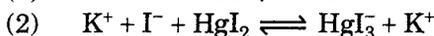
Result : The degree of hydrolysis of $\text{CH}_3\text{COONa} = \dots\%$.

EXPERIMENT No. 8

Object : To study the formation of complex ions in solution of mercuric iodide in potassium iodide solution.

Apparatus : Same as in experiment 1.

Theory : A molar solution of KI in water freezes at -10°C . When small quantities of HgI_2 are added to it, HgI_2 dissolves and the freezing point of the solution rises indicating a reduction in the molality of the solution. This occurs only to a limited value when further addition of HgI_2 fails to dissolve. The ionisation occurs according to the following equations :

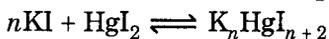


Potassium ions remain constant and hence the molality due to them will also remain constant. If added HgI_2 were to form only HgI_3^- ions (vide equation 2), this should not make any change in the freezing point, as there is no change in the number of moles of ions in the solution on addition of HgI_2 [Fig. 5(a)].

If, on the contrary, added HgI_2 were to form only HgI_4^{2-} ions, there will be a change in the number of moles from four on the left side of equation (3) to three on the right side. This reduces the molality of ions in the solution and so the freezing point rises. Maximum rise will correspond to addition of 0.5 mole of HgI_2 for one mole of

KI in solution. Further increase in the freezing point over the freezing point of the KI solution will be linearly related to moles or grams of HgI_2 added [Fig. 5(b)]. If both HgI_3^- and HgI_4^{2-} ions are formed, a curved line will be obtained [Fig. 5(c)].

Let n moles of KI react with 1 mole of HgI_2 to form a complex as follows :



If w_1 g of KI requires w_2 g of HgI_2 for the complete conversion of the former into complex, the number of moles (n) of KI reacting with 1 mole of HgI_2 can be given by,

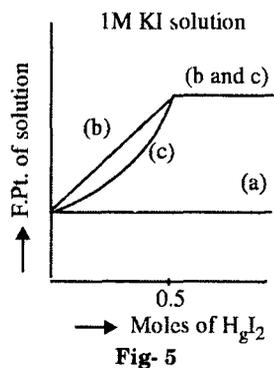
$$n = \frac{254.4}{166} \times \frac{w_1}{w_2} = 1.53 \times \frac{w_1}{w_2} \quad \dots (1)$$

Procedure : Dissolve accurately about 0.5 g of KI in 30 ml distilled water and determine its freezing point. The freezing point of water can be determined as usual. Now, add 0.2 g of HgI_2^* in KI solution and dissolve it. The freezing point of this solution is then determined. Further additions of 0.2 g of HgI_2 (in parts) are made and the freezing points of the solutions measured as usual.

Observations and Calculations : The freezing points of water, pure KI solution and solutions of KI and HgI_2 are noted down.

A curve is then plotted between the depression in freezing point values (Y-axis) and the amount of HgI_2 added (X-axis). The curve will give of two lines and the point of intersection corresponds to the amount of HgI_2 required just sufficient to form the complex with 0.5 g KI, taken initially. The value of n is then calculated from equation (1).

Result : The complex formed has the formula



EXPERIMENT No. 9

Object : To find out the molecular weight of a given substance by Rast's camphor method.

Apparatus : Ordinary thermometer, capillary tube, melting point apparatus etc.

Theory : This method is used to determine the molecular weight of those solutes which are soluble in camphor. In this method, advantage is taken of the fact that molal depression constant of camphor is very high, viz., 40° . As the depression in freezing point is large it can, therefore, be determined by an ordinary thermometer.

Procedure : A small quantity of camphor is put in a capillary tube and its melting point is determined in the usual way as done in the case of organic compounds. Then a solution is prepared by dissolving a small amount of the given solute in about 10–12 times the weight of camphor and melted on a flame. The melt is allowed to cool. Thus, it is solidified. The melting point of this solid mass is then determined as that of camphor. Thus, the depression in freezing point can be calculated. The melting point is measured by heating the capillary tube in a bath containing liquid paraffin.

Observations :

Freezing point of camphor $= T_1^\circ$

Freezing point of solid mass
(solute + camphor) $= T_2^\circ$

Weight of solute dissolved in camphor $= w_1\text{g}$

Weight of camphor $= w_2\text{g}$

Calculations : The depression in freezing point, $\Delta T = T_1 - T_2$. The molecular weight (m_1) of the solute is given by,

$$m_1 = \frac{1000K_f w_1}{w_2 \Delta T}$$

Thus, the value of m_1 can be easily calculated.

Result : The molecular weight of the given substance =

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 10

Object : To determine the relative strength of acids.

The strength of an acid is given by the number of H^+ ions which it can give in solution. State at which an acid gives the largest number of H^+ ions in solution at equivalent dilution is called the strength of the acid.

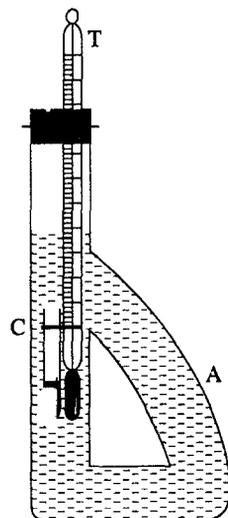


Fig. 6 : Rast's method

A special type of tube, known as Thiele's tube (fig. 6) can also be used. The tube is filled with liquid paraffin upto its bent portion. The lower portion of Thiele's tube is gently heated and that temperature is noted at which the solid just starts melting

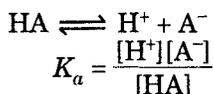
The concentration of H^+ ions depends upon the degree of dissociation (α) of the acid. Hence, the degree of dissociation of the acids at the same dilution is determined. Acid having a higher degree of dissociation will be stronger, i.e.,

$$\frac{\alpha_1}{\alpha_2} = \frac{[H^+]_1}{[H^+]_2}$$

EXPERIMENT No. 11

Object : To determine the dissociation constant of acetic acid in aqueous solution near $0^\circ C$.

Theory : If the dissociation constant of a weak acid (HA) is K_a , then,



or,

Since both H^+ and A^- ions are produced in equal concentration, therefore,

$$[H^+] = [A^-]$$

$$K_a = \frac{[H^+]^2}{[HA]}$$

Hence,

If the original concentration of the weak acid is C , then the concentration of the undissociated acid at equilibrium is very nearly the same as the original concentration of the acid. Therefore,

$$K_a = \frac{[H^+]^2}{C}$$

The value of $[H^+]$ can be determined as in experiment 5.

Alternatively, if α is the degree of dissociation of the acid at dilution of V litre, the dissociation constant is given by,

$$K_a = \frac{\alpha^2}{(1-\alpha)V} = \frac{\alpha^2 C}{(1-\alpha)} \quad \dots(1)$$

where C (mole/dm³) is the concentration of the acid.

Procedure : Prepare 0.4, 0.2 and 0.1M solutions of acetic acid and determine the degree of dissociation (α) at each dilution by measuring the depression in freezing point of these solutions (Refer experiment 4). The value of K_a can be evaluated by using equation (1).

EXPERIMENT No. 12

Object : To determine the latent heat of fusion of ice per gram (L_f).

As discussed before, van't Hoff gave the formula,

$$K_f = \frac{RT^2}{1000 L_f}$$

The value of K_f can be experimentally determined as already discussed. The value of T can be substituted equal to $0 + 273 = 273$ K. The value of L_f can then be calculated easily.

EXPERIMENT No. 13

Object : To determine van't Hoff factor and find the apparent degree of association of benzoic acid and acetic acid in 1 M and 0.5 M solutions of benzene, near the freezing point of the liquid.

Refer to experiments 4 and 6.

EXPERIMENT No. 14

Object : To analyse cryoscopically a given mixture of urea and glucose or determine the percentage composition of binary mixture of non-electrolytes.

Theory : If w gram of a mixture of urea and glucose is dissolved in W gram of water and ΔT is depression in freezing point, then,

$$\Delta T = K_f m_{total}$$

where

$$m_{total} = \text{molality of the mixture.}$$

If symbols u and g represent urea and glucose, then,

$$\begin{aligned} \Delta T &= K_f(m_u + m_g) \\ &= K_f \left(\frac{w_u \times 1000}{M_u \cdot W} + \frac{w_g \times 1000}{M_g \cdot W} \right) \\ &= \frac{1000K_f}{W} \left(\frac{w_u}{M_u} + \frac{w_g}{M_g} \right) \\ &= \frac{1000K_f}{W} \left[\frac{w_u}{M_u} + \frac{(1 - w_u)}{M_g} \right] \end{aligned}$$

M_u and M_g are the molecular weights of urea and glucose. Knowing all the values, we can calculate w_u , from which w_g can also be calculated, as $w_g = 1 - w_u$.

Procedure : Take about 25-40 g of water accurately weighed in the freezing point tube and determine its freezing point. Add an accurately weighed amount (0.2 to 0.4g) of the mixture to the solvent. Dissolve it and determine the freezing point of the solution. Make several additions. Then the composition of the mixture is calculated as described above.

Object : To determine K_f value of a given solvent. A solute of known molecular weight is provided.

EXPERIMENT No. 15

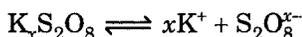
Proceed as in experiment 1. Plot a curve between ΔT values and $\frac{1000w_1}{w_2 m_1}$ values of different solutions. The slope of the straight line graph gives the value of K_f , as

$$\Delta T = \frac{1000K_f w_1}{w_2 m_1}$$

Object : To verify the formula of the complex salts like $K_2S_2O_8$, $K_4Fe(CN)_6$ cryoscopically.

EXPERIMENT No. 16

Theory : Suppose the formula of the complex salt $K_2S_2O_8$ is $K_xS_2O_8$, which ionises as,



If the dissociation is complete, the number of particles in the solution would be $x + 1$, whereas it is unity, if no dissociation occurs. Let ΔT_1 be the normal depression of freezing point calculated on the assumption that no dissociation occurs. Let ΔT_2 be the observed depression of freezing point of the solution containing a known amount of the complex salt in a known amount of water (solvent). Then,

$$\frac{\Delta T_2}{\Delta T_1} = x + 1 \quad \dots (1)$$

But ΔT_1 can be calculated from the formula,

$$\Delta T_1 = \frac{1000K_f w_1}{w_2 m_1}$$

where all the terms have their usual significance.

The molecular weight (m_1) of the complex salt would be,

$$x \times 39 + 2 \times 32 + 8 \times 16 = (39x + 192)$$

$$\therefore \Delta T_2 = \frac{1000K_f w_1}{w_2 (39x + 192)}$$

Substituting the values of ΔT_1 and ΔT_2 in equation (1), x can be calculated. Therefore, the formula of the complex salt can be verified.

EXPERIMENT No. 17

Object : To determine the mean activity coefficient of an electrolyte (NaCl) in dilute solution by cryoscopic measurements.

Theory : The evaluation of activity coefficient from freezing point determination is generally used for electrolytes. This method is capable of giving accurate results even when other methods are not applicable.

An equation has been derived thermodynamically giving a relation between activity and concentration. It is given by,

$$d \log a_2 = \frac{d\theta}{\lambda c} + \alpha \cdot \frac{\theta d\theta}{c} \quad \dots (1)$$

where, a = activity of the solute, c = concentration of the solute in the solution, θ = lowering of freezing point of the solution from that of the pure solvent, $d\theta$ = small change in the lowering of freezing point, λ = molal freezing point depression constant or cryoscopic constant, which is defined as the depression of freezing point of a solvent when 1 mole of a solute is dissolved in 1000 g of the solvent, α = constant, whose value is found to be 0.00057.

For dilute solution, the second term on the right hand side of (1) can be neglected. So, equation (1) reduces to,

$$d \log a_2 = \frac{d\theta}{\lambda c} \quad \dots (2)$$

For a uni-univalent electrolyte, we know that mean activity (a_{\pm}) is given by,

$$a_{\pm} = \sqrt{k a_2} \quad \text{or} \quad a_{\pm}^2 = k a_2$$

On taking logarithms, $2 \log a_{\pm} = \log k + \log a_2$

On differentiation, $2d \log a_{\pm} = d \log a_2 \quad \dots (3)$

Combining equations (2) and (3), we get,

$$d \log a_{\pm} = \frac{d\theta}{2 \lambda c} \quad \dots (4)$$

Equation (4) holds good for an electrolyte which dissociates into two ions. For an electrolyte, which, in general, dissociates into ν ions, the integer 2 can be replaced by ν in equation (4). So, equation (4) can be modified as,

$$d \log a_{\pm} = \frac{d\theta}{\nu \lambda c} \quad \dots (5)$$

A function ' j ' is defined as,

$$j = 1 - \frac{d\theta}{\nu \lambda c} \quad \dots (6)$$

Differentiating equation (6) and considering ν and λ as constants we get,

$$dj = \frac{\theta dc}{\nu \lambda c^2} - \frac{d\theta}{\nu \lambda c}$$

or
$$dj = \frac{\theta}{\nu \lambda c} \cdot \frac{dc}{c} - \frac{d\theta}{\nu \lambda c} = (1-j) \frac{dc}{c} - \frac{d\theta}{\nu \lambda c}$$

or
$$\frac{d\theta}{\nu \lambda c} = (1-j) \frac{dc}{c} - dj = (1-j) d \log c - dj$$

Substituting the value of $\frac{d\theta}{\nu \lambda c}$ in equation (5), we get,

$$d \log a_{\pm} = (1-j) d \log c - dj = d \log c - jd \log c - dj$$

or
$$d \log a_{\pm} - d \log c = -jd \log c - dj$$

or
$$d \log \frac{a_{\pm}}{c} = -jd \log c - dj$$

or
$$d \log f_{\pm} = -jd \log c - dj \quad \dots (7)$$

Integrating equation (7), we get,

$$\begin{aligned} \log f_{\pm} &= - \int_{c=0}^{c=c} j d \log c - j \\ &= - \int_{c=0}^{c=c} \frac{j}{c} dc - j \quad \dots (8) \end{aligned}$$

If depression in freezing point (θ) at any molality (m) or concentration (c) is known, then the value of j can be easily evaluated from equation (6). In order to evaluate the integral of equation (8), a graph is plotted between $(-j/c)$ and c as shown in figure (7). The area under the curve between the limits $c = 0$ and $c = c$ will give the value of the integral of equation (8). Once the values of the integral and j are known, the value of f , i.e., activity coefficient can be determined from equation (8).

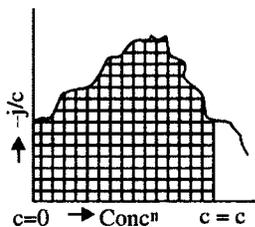


Fig. 7.

The above graphical method is, however, tedious. So, Lewis and Linhardt gave an empirical equation from which the value of activity coefficient can be determined. The equation is,

$$1 - \frac{\theta}{\nu \lambda c} = \beta c^{\alpha}$$

or
$$j = \beta c^{\alpha} \quad \dots (9)$$

where $\alpha, \beta = \text{constants}$, whose values can be determined from freezing point measurements. Taking logarithm of equation (9), we get

$$\log j = \log \beta + \alpha \log c.$$

For two values of j corresponding to two values of c , we can write

$$\log j_1 = \log \beta + \alpha \log c_1 \quad \dots (10)$$

$$\log j_2 = \log \beta + \alpha \log c_2 \quad \dots (11)$$

From equations (10) and (11)

$$\log (j_1/j_2) = \alpha \log (c_1/c_2)$$

$$\text{or} \quad \alpha = \frac{\log (j_1/j_2)}{\log (c_1/c_2)} \quad \dots (12)$$

Substituting the value of α from equation (12) in equation (10) or (11), we can calculate the value of β easily.

Substituting the value of j from equation (9) in (8), we get,

$$\begin{aligned} \log f_{\pm} &= - \int_0^c \frac{\beta c^\alpha}{c} dc - \beta c^\alpha = - \beta \int_0^c c^{\alpha-1} dc - \beta c^\alpha \\ &= - \beta \left[\frac{c^\alpha}{\alpha} \right]_0^c - \beta c^\alpha = - \beta \frac{c^\alpha}{\alpha} - \beta c^\alpha \end{aligned}$$

$$\text{or} \quad \log f_{\pm} = - \frac{\beta (\alpha + 1)}{\alpha} \cdot c^\alpha \quad \dots (13)$$

So, simply by knowing the values of α and β , the value of f_{\pm} can be calculated at any desired concentration (c). This method is applicable only to dilute solutions, as the calculations have been made out on the assumption that the solution is dilute.

Procedure : Prepare 0.005, 0.01 and 0.05 m solutions of NaCl. Determine the depression of freezing points of different solutions. The value of j can be calculated from equation (6), by putting $v = 2$. Then using equations (10) and (11), the values of α and β can be calculated from two values of j at two concentrations (or molalities). Then calculate $\log f_{\pm}$ ($= 2.303 \log f_{\pm}$) and, therefore, f_{\pm} can be calculated by using equation (13) at each concentration (or molality) at the freezing point of water.



6

EBULLIOSCOPY

(Elevation of Boiling Point)

Theory : *The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure.* Since the vapour pressure of a pure solvent is lowered by the addition of a non-volatile solute to it, therefore, we have to provide more heat to the solution in order to bring its vapour pressure equal to that of the atmosphere. In other words, we can easily say that the boiling point of a solvent is increased or elevated by the addition of a non-volatile solute to it. The difference between the boiling point of the solution and that of the solvent is known as the *elevation of boiling point*. It was shown by a number of scientists that the elevation of boiling point is dependent on the concentration of the solute. The theoretical treatment of elevation of boiling point is primarily due to van't Hoff (1885).

The elevation of boiling point is a direct consequence of the lowering of vapour pressure of the solvent by a dissolved solute. To appreciate this, consider a temperature-vapour pressure curve (fig. 1).

The curves AA' , BB' and CC' are the vapour pressure- temperature curves of the pure solvent and dilute solutions 1 and 2, respectively. Since the solutions are dilute, the curves may be taken to be nearly straight lines. T , T_1 and T_2 represent the boiling points of the pure solvent, solutions 1 and 2, respectively.

Consider two similar triangles ABD and ACE from which we have,

$$\frac{AB}{AC} = \frac{AD}{AE}$$

or
$$\frac{T_1 - T}{T_2 - T} = \frac{p - p_1}{p - p_2}$$

where, p , p_1 and p_2 are the respective vapour pressures of the pure solvent, solution 1 and solution 2.

\therefore
$$\frac{\Delta T_1}{\Delta T_2} = \frac{\Delta p_1}{\Delta p_2} \quad \dots (1)$$

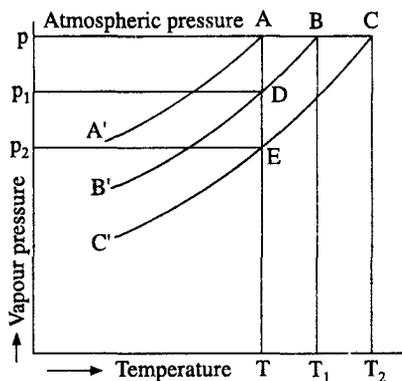


Fig. 1 : Temperature-vapour pressure curve

where, ΔT and Δp terms indicate the elevation of boiling point and lowering of vapour pressure. The subscripts 1 and 2 represent the two dilute solutions 1 and 2. From equation (1), we have,

$$\Delta p \propto \Delta T$$

i.e., lowering of vapour pressure is directly proportional to the elevation of boiling point.

Relation between elevation of boiling point and molecular weight of solute : According to Raoult's law for dilute solutions,

$$\frac{p - p_1}{p} = \frac{n_1}{n_2} = \frac{w_1 m_2}{w_2 m_1} \quad \dots (2)$$

where, n_1 and n_2 are the number of moles of the solute and solvent; w and m terms indicate the weight and molecular weight; subscripts 1 and 2 now represent the solute and solvent, respectively. From equation (2), we have,

$$\Delta p = p \cdot \frac{w_1 m_2}{w_2 m_1} \quad \dots (3)$$

For a given solvent at its boiling point, the terms p and m_2 are constants. Therefore, equation (3) becomes,

$$\Delta p = \text{constant} \cdot \frac{w_1}{w_2 m_1}$$

or
$$\Delta p \propto \frac{w_1}{w_2 m_1}$$

or
$$\Delta T \propto \frac{w_1}{w_2 m_1} \quad (\text{As } \Delta p \propto \Delta T)$$

or
$$\Delta T = k \cdot \frac{w_1}{w_2 m_1} \quad \dots (4)$$

where, k is a constant, known as **elevation of boiling point constant**.

If $\frac{w_1}{m_1} = 1$ and $w_2 = 1\text{g}$, then,

$$k = \Delta T$$

Therefore, elevation of boiling point constant is defined as the '**elevation of boiling point produced when 1 mole of a non-volatile solute is dissolved in 1 g of the solvent**'. But it is not practically possible.

If we take $\frac{w_1}{m_1} = 1$ and $w_2 = 100\text{ g}$, then we have,

$$\Delta T = \frac{k}{100} = K \quad \text{or} \quad K_{100}$$

where K is known as **molecular elevation constant**.

If $\frac{w_1}{m_1} = 1$ and $w_2 = 1000\text{ g}$ then we get,

$$\Delta T = \frac{k}{1000} = K_b \quad \text{or} \quad K_{1000}$$

where, K_b is known as **molal elevation constant** or **ebullioscopic constant** and may be defined as the '*elevation in boiling point produced by dissolving 1 mole of a solute in 1000 g of the solvent*'.

In terms of K and K_b , equation (4) can be written as :

$$\Delta T = \frac{100Kw_1}{w_2m_1} \quad \dots (5)$$

$$\Delta T = \frac{1000K_bw_1}{w_2m_1} \quad \dots (6)$$

Table-1 : Ebullioscopic Constants of Solvents

Solvent	K_b	Solvent	K_b
Water	0.52°	Methyl alcohol	0.80°
Benzene	2.66°	Ethyl alcohol	1.20°
Chloroform	3.85°	Acetone	1.73°
Carbon tetrachloride	5.00°		

Relation between k , latent heat of evaporation per gram (L_e) and boiling point of the solvent (T) : van't Hoff deduced thermodynamically that,

$$k = \frac{RT^2}{L_e} \quad \dots (7)$$

where all the letters have their usual significance.

EXPERIMENT No. 1

Object : *To find the molecular weight of the given solute in water by elevation of boiling point method.*

Apparatus : Beckmann thermometer (or any other accurate thermometer), Landsberger's boiling point apparatus and steam generating flask etc.

Theory : The molecular weight of the solute is given by the formula :

$$m_1 = \frac{1000K_bw_1}{w_2\Delta T} \quad \dots (1)$$

where all letters have their usual significance.

Procedure : First of all, we have to set the Beckmann thermometer (if we are using it). The setting is done on the same lines as explained in the preceding chapter. However, for all practical purposes, we can use any other accurate thermometer. Boiling point apparatus of the Landsberger type as shown in figure (2) is generally used. The rose head (R) ensures uniform distribution of steam through the liquid.

A known quantity, say 20 ml, of water is taken in the graduated inner tube (A). The thermometer (T) is adjusted in such a way that its bulb lies about 1 cm above

the level of water. Now water is boiled in the vessel (*F*) and steam is passed through the delivery tube (*C*). The temperature is noted when it becomes constant. This gives the boiling point of pure water.

Now take out the tube (*A*) and dissolve a weighed quantity (0.5 g) of the given solute in water already present in it. The boiling point of the solution is noted down in the above manner. Now take another set of reading by dissolving 0.5 g more solute and its boiling point is noted.

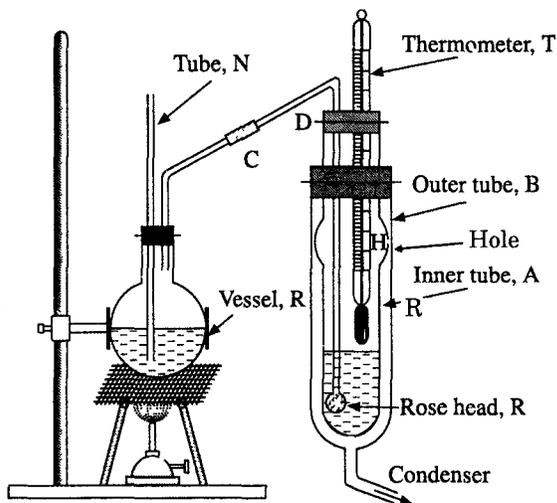


Fig. 2 : Landsberger apparatus

Observations : Weight of the solvent = w_2 g

Boiling point of water = $T^\circ\text{C}$

S.N.	Amount of solute (w_1)	Boiling point of solution (T_1) $^\circ$	Elevation in boiling point $\Delta T = (T_1 - T)^\circ$
1.
2.
3.

Calculations : The molecular weight (m_1) of the solute is calculated according to the formula given by equation (1).

Result : The molecular weight of the solute =

Precautions : (1) The amount of the solute added should be small, as the relation holds good for dilute solutions.

(2) The heating of the liquid should be uniform and for this purpose, one must use the rose-head.

EXPERIMENT No. 2

Object : To find the concentration of the given solution of urea (concentration between 1% and 5%) in water by elevation of boiling point method.

Apparatus : Same as in experiment 1.

Theory : As concentration and elevation in boiling point are directly proportional to each other, hence a curve between concentration of the solute and elevation in boiling point will be a straight line. The concentration of the unknown solution can be determined by any point on the straight line.

Procedure : The boiling point of water is taken as described in experiment 1. A number of solutions

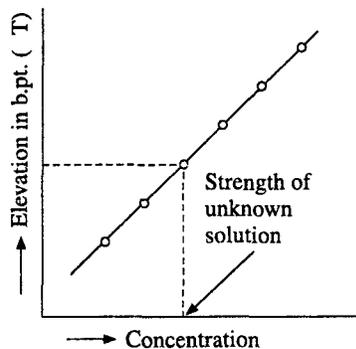


Fig. 3.

of different concentrations of urea are prepared, say from 1% to 5%. The boiling points of these solutions are measured, along with the boiling point of the unknown solution.

Observations : Boiling point of pure water = T°

S.N.	Concentration of the solution	Boiling point of the solution (T_1)	Elevation in boiling point (ΔT)
1.	1%
2.	2%
3.	3%
4.	4%
5.	5%
6.	Unknown

Calculations : A curve is plotted between the elevation in boiling point (ΔT) and concentration (in percentage) of the solute. (fig. 3). That point on the concentration axis is found which corresponds to the elevation in boiling point of the unknown solution.

Result : The concentration of the unknown solution = ...%.

EXPERIMENT No. 3

Object : To find out the degree of dissociation of an electrolyte, say sodium chloride and also to find its van't Hoff factor.

Apparatus : Same as in experiment 1.

Theory : We have already deduced that,

$$\Delta T \propto \Delta p \propto \frac{1}{\text{Mol. wt.}} \left(\text{As } \Delta T = \frac{kw_1}{w_2m_1} \right)$$

But we know that $\Delta p \propto \text{O. P.} \propto \text{concentration} \propto \text{number of molecules}$. As a result of dissociation, the total number of molecules increases, hence the elevation of boiling point also increases. We have,

$$\frac{\text{Number of molecules before dissociation}}{\text{Number of molecules after dissociation}} = \frac{\text{Experimental mol. wt.}}{\text{Normal mol. wt.}}$$

In case of NaCl, we have the following equilibrium :



The degree of dissociation is x and number of molecules before dissociation is unity. From the above relation, we have,

$$\frac{1}{1+x} = \frac{\text{Experimental molecular weight}}{\text{Normal molecular weight}} = \frac{1}{i} \quad \dots (1)$$

where, i = van't Hoff factor.

The normal molecular weight of NaCl can be calculated from its formula, viz., $23 + 35.5 = 58.5$. The experimental molecular weight can be determined from the experiment.

Procedure : Same as described in experiment 1.

Observations : Same as made in experiment 1.

Calculations : Suppose the molecular weight as determined by experiment comes out to be m_1 . Then from equation (1), we have,

$$\frac{1}{1+x} = \frac{m_1}{58.5}$$

Knowing the value of m_1 , we can calculate the degree of dissociation (x) of the electrolyte. The van't Hoff factor (i) is calculated as :

$$i = \frac{\text{Normal molecular weight}}{\text{Experimental molecular weight}} = \frac{58.5}{m_1}$$

Results : (i) The degree of dissociation of sodium chloride = ...%

(ii) van't Hoff factor =

EXPERIMENT No. 4

Object : To find the ebullioscopic constant of water by taking an unknown substance.

Apparatus : Same as in preceding experiments.

Theory : The ebullioscopic constant (K_b) is given by,

$$K_b = \frac{\Delta T w_2 m_1}{w_1 \cdot 1000} \quad \dots (1)$$

where all the letters have their usual significance. If we prepare a solution of a substance of known concentration and find the elevation of boiling point, we can calculate the ebullioscopic constant.

Procedure : Same as in experiment 1.

Observations : Same as in experiment 1.

Calculations : On substituting the various values in equation (1), we can easily calculate the ebullioscopic constant.

Result : The ebullioscopic constant of water =

Alternate Method : An alternate method of determining the ebullioscopic constant of water is based on the fact that if a curve is plotted between elevation of boiling point (ΔT) and

number of moles of solute $\left(\frac{w_1}{m_1}\right)$, it will be a straight line with a slope equal to $\frac{1000K_b}{w_2}$. Knowing the value of w_2 ,

we can calculate the value of ebullioscopic constant.

For this, a number of solutions containing 0.01, 0.02, 0.03, 0.04 and 0.05 mole of the solute in 25 ml of water are prepared. The elevation in boiling point for each solution is determined as usual. A graph is then plotted

as shown in figure (4). The slope is equal to $\frac{1000K_b}{w_2}$,

from which we can calculate K_b , as $w_2 = 25$ g. Mathematically,

$$\tan \theta = \frac{1000K_b}{w_2}$$

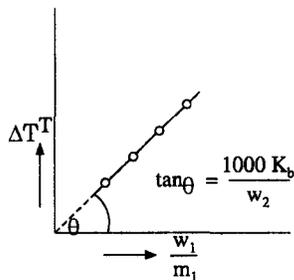


Fig. 4.

EXPERIMENT No. 5

Object : To find the molecular weight of a solute by Cottrell's method.

Apparatus : An accurate thermometer or Beckmann thermometer, Cottrell apparatus etc.

Theory : When a non-volatile solute is dissolved in a solvent, the boiling point of the solvent rises and the molecular weight of the solute is given by the relation,

$$m_1 = \frac{1000K_b w_1}{w_2 \Delta T} \quad [\text{cf. equation (5)}] \quad \dots (1)$$

Procedure : The Cottrell apparatus (fig. 5) consists of boiling tube A which is graduated and contains the liquid under study. The boiling tube is connected by means of a side tube and ground joint *i* with a suitable condenser *w*. A ground glass stopper *s*, open at both ends, fits into the neck *n* of the boiling tube. The bottom of this stopper is connected by a glass cylinder *t*, which serves as a jacket to the thermometer *T* and prevents liquid falling from the condenser on to the thermometer bulb. Inside the jacket *t*, a three armed tube *s*, made of 2–3 mm tubing, is loosely supported. Another glass tube *a* is connected to the joint of the tube *s*. This system of tube *B*, which may be termed the pump, rests lightly on the bottom of the boiling tube, and is prevented from shutting off a small space at the bottom by small glass beads, which are fixed at several points round the rim of the funnel. A thermometer is supported by a rubber stopper *r* in the neck of the glass stopper *s*, and its bulb lies inside the three upper arms of the pump. An inverted funnel *f* is placed in the boiling tube which is attached to the glass tube. It collects the bubbles rising from a few fragments of a porous pot in the liquid. When the liquid begins to boil, the inverted funnel pumps liquid and vapour as stream over the bulb of the thermometer *T* (If Beckmann thermometer is used it must be pre-set). The bulb of the thermometer is placed about 1 cm above the liquid. In this way, the bulb is covered with a thin layer of boiling liquid. This process reduces the super-heating to a minimum and ensures that the temperature reading is exactly that of the boiling liquid.

First a known quantity of the pure solvent is taken in the tube A. It is heated and the constant temperature, *i.e.*, boiling point of the solvent is noted. We should take readings till two concordant readings of the boiling point of the solvent are obtained. If the boiling point is not constant, then it is advisable to re-distill the liquid. After determining the boiling point of the solvent, the gas burner is turned off. A known amount of the solute is dissolved in it. The boiling point of the solution

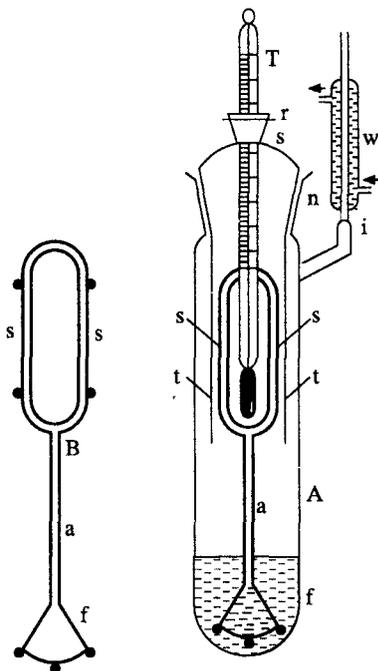


Fig. 5.

can now be taken as in the case of solvent. Make further additions of the solute so that the elevation in the boiling point can be measured at different concentrations.

Observations : Weight of solvent taken = ... g

Boiling point (T) of the solvent =

Weight of solute dissolved	Boiling point of the solution (T_1)°	Elevation in boiling point ($T_1 - T$)°
...
...
...

Calculations : All the values are substituted in equation (1), from which the molecular weight, m_1 of the solute can be calculated.

Result : The molecular weight of the solute = ...

Precautions : (i) If the boiling point of the solvent does not become constant, then it is advisable to re-distill the solvent.

(ii) The liquid should be pumped vigorously over the thermometer bulb. If it is not, the level of the liquid or the rate of heating should be changed.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 6

Object : *To determine the latent heat of evaporation.*

From equation (7) given in the theory, we can calculate the value of latent heat of evaporation per gram of solvent (L_e) provided the values of boiling point (T_1) of the liquid and molal elevation constant (K_b) are known. The value of K_b can be experimentally determined for a given solvent from equation (1) (cf. experiment 4).

EXPERIMENT No. 7

Object : *To determine the pH of an acid, say oxalic acid (or malonic acid).*

We take an acidic solution of known concentration (C) and determine its degree of dissociation (α) [cf. experiment 3]. The logarithm of the reciprocal of hydrogen ion concentration will give the value of pH of the solution.

EXPERIMENT No. 8

Object : *To study the association of organic acids and hydroxy compounds in benzene and other solvents.*

Proceed as in experiment no. 3.

The resistance which a liquid exerts against the displacement of its own molecules is known as viscosity. In other words, we can say that viscosity is a property of the liquid which retards its flow. For example, glycerine does not flow as freely as benzene or alcohol. Thus, glycerine is said to have more viscosity than benzene or alcohol.

The coefficient of viscosity is defined as, **'the force required per unit area to maintain unit difference of velocity between two parallel layers of liquid one centimeter apart.'** If two layers dx cm apart have a difference of velocity dv cm sec⁻¹, then the force F , acting per cm² will be given by

$$F = \eta \frac{dv}{dx}$$

where, η = coefficient of viscosity and is expressed in dyne/cm².

Fluidity : The reciprocal of the coefficient of viscosity is known as **fluidity** and is represented by the symbol ϕ , so that,

$$\phi = \frac{1}{\eta}$$

Units and Dimensions of η : According to the definition of viscosity, its dimensions will be $\frac{\text{dyne}}{\text{cm}^2 \times \frac{\text{cm/sec}}{\text{cm}}}$, i.e., dyne sec cm⁻² or dyne sec per cm².

In CGS system, the unit for coefficient of viscosity is **poise**. It is a larger unit and in experimental work, smaller units like **centipoise** (10⁻² poise), **millipoise** (10⁻³ poise) and **micropoise** (10⁻⁶ poise) are used.

Factors Affecting Viscosity of Liquids : (1) Increase in temperature results in a decrease of viscosity about 2% per degree. The effect of temperature on viscosity of a liquid can be represented by Andrade's equation,

$$\eta = Ae^{E/RT}$$

or
$$\log_e \eta = \frac{E}{RT} + \log_e A$$

or
$$\log_{10} \eta = \frac{E}{2.303RT} + \log_{10} A$$

where, A is a constant for a given liquid and E is the energy to be given to one mole of a liquid to allow its molecules to overcome forces resulting in the flow of liquid.

(2) The presence of solutes, lyophilic colloids and other suspended impurities tends to increase the viscosity of liquids.

(3) Polarity also affects viscosity, *e.g.*, polar compounds are more viscous than non-polar ones. Hydrogen bonding in a molecule also increases viscosity.

(4) Branched chain compounds possess greater viscosity than the straight chain ones.

(5) Generally, increase in molecular weight increases the viscosity of the liquid.

Rheochor : Newton Friend gave a new constant, known as rheochor, which he found to be both additive and constitutive. It is given by,

$$\text{Rheochor} = \frac{M}{d} \cdot \eta^{1/8}$$

Molecular Viscosity : *The product of viscosity and molecular surface is known as molecular viscosity.* Thus,

Molecular viscosity = Molecular surface \times η

$$= \left(\frac{M}{d} \right)^{2/3} \times \eta$$

where, M and d are the molecular weight and density of the liquid.

Measurement of Viscosity : The viscosity of a liquid is usually measured by observing the rate of flow of the liquid through some type of capillary tube. The flow of the liquid must remain steady and should be parallel to the axis of the tube. Besides these, the rate of flow should not exceed a certain value, which depends upon the radius of the tube as well as the viscosity of the liquid. Poiseuille derived a law for determining the coefficient of viscosity which is based on the viscous flow of liquids through capillary tubes. According to him,

$$\eta = \frac{\pi p r^4 t}{8 V l} \quad \dots (1)$$

where, p is the pressure difference maintained between the ends of the tube, r is the radius of the tube, t is the time of flow of the liquid, V is the volume of the liquid flowing across the whole cross-section of the capillary tube, l is the length of the tube and η is the coefficient of viscosity.

Poiseuille's expression holds good when the pressure p , *i.e.*, driving force is just sufficient to drive the liquid through the tube, *i.e.*, on leaving the tube, the velocity of the liquid must be zero. As this condition is not fulfilled, hence a correction factor for the kinetic energy of the liquid must be introduced. In actual practice, however, the conditions are so chosen that the correction factor becomes so small that it can be neglected. The value of absolute viscosity can be directly measured by means of Poiseuille's expression, *i.e.*, by determining the rate of flow of the liquid through a capillary tube of uniform bore and of known dimensions. This procedure is, however, tedious, hence simpler methods are used wherein we compare the viscosities of the two liquids. If the coefficient of viscosity of one liquid is known, then that of other can be calculated.

Principle : The pressure p , at any instant driving a liquid of coefficient of viscosity η , through the capillary tube depends upon the difference of the height h , in the levels of liquid in the two limbs, the density d , and the gravitational force g , *i.e.*, $p \propto h d g$. From equation (1), we have,

$$\begin{aligned} \eta &\propto pt \\ \therefore \eta &\propto h d g t \end{aligned} \quad \dots (2)$$

If η_1 and η_2 be the viscosities of the two liquids under study and d_1, d_2 be their respective densities and t_1, t_2 be the respective time of flow through the same volume, then,

$$\eta_1 \propto h g d_1 t_1 \quad \text{and} \quad \eta_2 \propto h g d_2 t_2$$

Since the apparatus is the same, therefore,

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \dots (3)$$

Thus, by determining the densities and the time of flow of two liquids, the coefficient of viscosity of one of them can be easily calculated, provided the coefficient of viscosity of the other liquid is known.

Ostwald's Viscometer : The apparatus generally used for determination of viscosity of liquids is known as Ostwald's viscometer (Fig. 1-a) (designed by Ostwald). The viscometer (fig. 1) consists of a capillary tube connected at its upper part with a bulb A and at its lower part with a wider U-tube provided with a bulb B. Marks x and y are etched on the capillary tube above and below the bulb A.

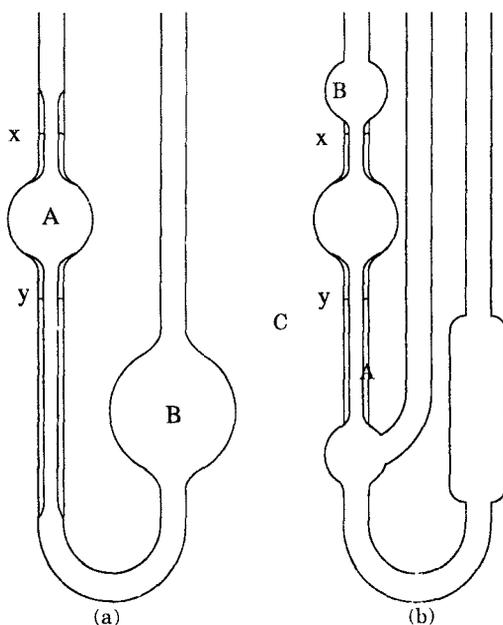


Fig. 1 : Ostwald viscometers

The **suspended level type viscometer** or **Ubbelohde viscometer** (fig. 1-b) has the advantage of being less affected by incorrect alignment, and does not require a fixed volume of test liquid. So, the solution can be diluted in situ. A known volume of the solution, say 20-25 cm³ is introduced into the bulb A, keeping the side arm B closed, the solution is forced through the capillary tube C until the meniscus stands above the mark x. On opening B, while keeping the capillary limb closed, the solution below falls back and the column of the solution xC is held

suspended. In using this, the liquid is sucked into the top bulbs by closing the middle tube with a finger tip. When the tip is removed, air enters and the liquid below the capillary tube recedes into the bend. The liquid flows down from the bulb against atmospheric pressure and the time of flow of the meniscus from mark x to y is determined.

Cleaning of Viscometer : Before using, the viscometer should be thoroughly cleaned so that there are no obstructions in the capillary tube. It must necessarily be free from any greasy material. The viscometer is cleaned by first keeping it filled with a solution of chromic acid (prepared by the reaction between potassium dichromate and conc. sulphuric acid) for a few hours. It is then washed with distilled water and finally dried with alcohol.

Density and its Measurement : Density of a liquid is the mass per unit volume. When we use the term density at a given temperature, it means the relative density at that temperature with respect to the density of water. For all practical purposes, the density of water is taken to be unity at all temperatures.

The density of liquid is conveniently measured by means of a pyknometer [fig. 2] or specific gravity bottle [fig. 3]. Pyknometer consists of a U-tube having a bulb A and two capillary ends. On one arm there is a constriction while the other arm is drawn to a point. In some cases, the two ends are fitted with caps. The specific gravity or density bottle is a round bottomed type glass vessel. It is fitted with a glass stopper containing a fine capillary.

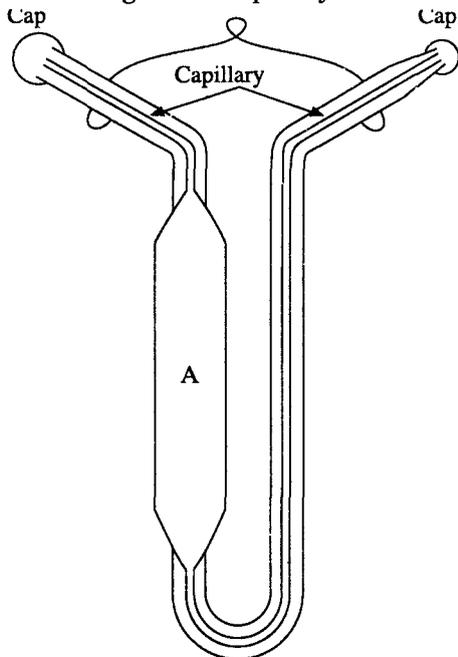


Fig. 2 : Pyknometer

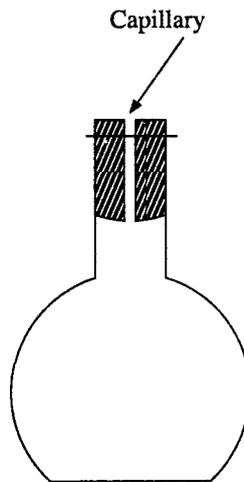


Fig. 3 : Density bottle

The pyknometer or specific gravity bottle is first washed with chromic acid solution and then with distilled water and finally dried with alcohol. The apparatus is then weighed [pyknometer is, however, weighed by suspending it from the beam of the balance with a hook of wire, as shown in fig. 2]. The pyknometer or specific gravity bottle is then filled with distilled water. [Pyknometer is filled by attaching a rubber tube at one end and placing the other end in beaker containing distilled

water and sucking gently. *The presence of air bubbles should be strictly avoided*]. The pycnometer or specific gravity bottle is then again weighed. It is then emptied of water and washed with alcohol and dried. The pycnometer or specific gravity bottle is then filled with the experimental liquid, as before and weighed again.

If the weights of liquid and water be W_1 and W_2 then,

$$\frac{d_1}{d_2} = \frac{W_1}{W_2}$$

or

$$d_1 = \frac{W_1}{W_2} \cdot d_2$$

where, d_2 is the density of water [taken to be unity] and d_1 density of the experimental liquid.

EXPERIMENT No. 1

Object : *To find the relative and absolute viscosity of the given liquid at room temperature.*

Apparatus : Ostwald's viscometer, pycnometer, thermostat, stop watch, thermometer etc.

Theory : The coefficient of viscosity of the given liquid can be calculated according to the following equation,

$$\eta_1 = \frac{d_1 t_1}{d_2 t_2} \cdot \eta_2$$

where all letters have their usual significance.

Procedure : The viscometer is first thoroughly cleaned and dried, as explained above. A definite quantity of water is introduced into the bulb (fig. 1-a) and sucked up through the capillary into the smaller bulb A. Now bring water to touch the mark x and hold it there by placing your finger at the top of the narrow limb. Remove your finger and start the stop watch. Stop it as soon as water touches the mark y . Repeat this process 3-4 times and take the mean value of time. Before noting the time, the viscometer is kept in a thermostat for 10-15 minutes, so that the contents acquire the room temperature.

Now dry the viscometer and fill it with experimental liquid and keep this also in the thermostat for 10-15 minutes, so that the liquid attains the room temperature. Note the time of flow of the liquid between the same marks x and y . Repeat the process 3-4 times and take the mean value of time.

Next, wash and dry the pycnometer and then first weigh it empty. Then fill it with water and finally with the experimental liquid and weigh it both times. Note the room temperature by recording the temperature of water in the thermostat.

Observations : Room temperature = $t^\circ\text{C}$
 Weight of empty pycnometer = W_1 g
 Weight of pycnometer + water = W_2 g
 Weight of pycnometer + liquid = W_3 g

Water					Liquid				
Time of flow in second				Mean value	Time of flow in second				Mean value
...	t_2 sec. (say)	t_1 sec. (say)
...
...

Calculations : Weight of water = $(W_2 - W_1)$ g

Weight of liquid = $(W_3 - W_1)$ g

Density of liquid $(d_1) = \frac{\text{Wt. of liquid}}{\text{Wt. of water}} \times \text{Density of water } (d_2)$

$$= \frac{W_3 - W_1}{W_2 - W_1} \times d_2 = \frac{W_3 - W_1}{W_2 - W_1} \quad (\text{As } d_2 = 1)$$

The relative viscosity of the liquid is given by,

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

The absolute viscosity of the liquid is given by,

$$\eta_1 = \frac{d_1 t_1}{d_2 t_2} \times \eta_2$$

After noting the coefficient of viscosity (η_2) of water at $t^\circ\text{C}$ from the tables, we can easily calculate the value of coefficient of viscosity of the liquid, η_1 .

Result : The coefficient of viscosity of the given liquid at ... $^\circ\text{C}$ = ... poise.

Precautions : [i] The viscometer should be held vertical while performing the experiment.

[ii] The temperature should be maintained constant, as the viscosity is greatly influenced by temperature.

[iii] Same volume of water and the liquid should be taken in the viscometer.

[iv] The time of flow between the marks x and y in the viscometer should be about 2–3 minutes.

EXPERIMENT No. 2

Object : To find the concentration of the given mixture, consisting of two liquids A and B, by viscosity measurement.

Apparatus : Same as in experiment 1.

Theory : By plotting the values of viscosity of solutions against their concentrations, we get a curve from which the concentration of the unknown solution is determined. Curves of various forms are obtained and usually viscosity curves of simple solutions are sagged, *i.e.*, fall below the straight line connecting the viscosities of their components.

Procedure : Prepare a number of solutions by mixing the two liquids A and B in different proportions. The solutions are made up with 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, of A, by volume. The time of flow for each solution is noted by means of Ostwald's viscometer as described in the preceding experiment. The time of flow for the unknown solution is also measured as usual.

The density of each solution as well as the unknown solution is also determined, if we are to calculate the absolute viscosity of the liquid.

Observations : Room temperature = $t^{\circ}\text{C}$

Percentage of components		Time of flow in sec.	Percentage of components		Time of flow in sec.
A	B		A	B	
90%	10%	40%	60%
80%	20%	30%	70%
70%	30%	20%	80%
60%	40%	10%	90%
50%	50%	Unknown solution	---

Calculations : A curve is plotted between the concentration of one component, say A and time of flow in second. We see that a straight line is obtained [fig. 4]. The composition of the unknown solution is calculated by locating and marking the point on the straight line corresponding to its measured time of flow. A perpendicular is drawn from that point on the concentration axis, from which the composition of the unknown solution can be read directly.

Result : The composition of the given mixture is ...% A and ...% B.

Precautions : Same as in preceding experiment.

[**Note :** A curve can also be plotted between viscosity and concentration. In such a case the density of each solution will have to be measured.]

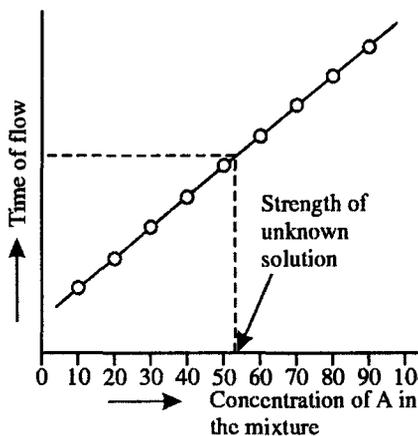


Fig. 4.

EXPERIMENT No. 3

Object : To find the temperature coefficient for given liquid.

Apparatus : Same as in experiment 1.

Theory : The viscosity of a liquid usually decreases with temperature. The temperature coefficient $\left(\frac{d\eta}{dt}\right)$ can be obtained by determining the absolute viscosity of the liquid compared with that of water at regular intervals of 5° , ranging from room temperature to a temperature say 60°C . The values of viscosity are plotted against temperature and the temperature coefficient can then be calculated from the graph for a range of 5° .

Procedure : First clean and dry the viscometer as usual. Then determine the time of flow of water at room temperature, say $t^\circ\text{C}$. Similarly, the time of flow of water is determined at temperatures (for range of 5°C) upto 60°C by keeping the filled viscometer in the thermostat or a beaker. For this purpose, the viscometer is to be clamped vertically in the thermostat in such a way that it can be viewed easily and the mark x is well below the water surface of the thermostat [fig. 5]. The temperature of the thermostat can be regulated and changed at will.

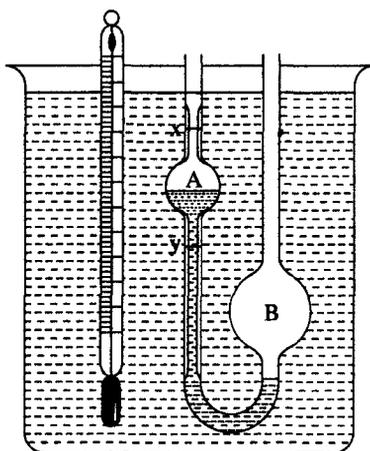


Fig. 5.

Next, the time of flow of the liquid at room temperature is determined. Similarly, the time of flow of liquid is also determined at different temperatures for a range of 5°C upto 60°C . This is done by filling the viscometer with the liquid and then keeping it in the thermostat at the same values of temperature, as in the case of water.

The density of water is determined with the help of a pycnometer at room temperature. The density of the liquid is determined at different temperatures.

- Observations :** Room temperature = $t^\circ\text{C}$
- Weight of empty pycnometer = W_1 g
- Weight of pycnometer + water = W_2 g
- Weight of pycnometer + liquid at $t^\circ\text{C}$ = W_3 g
- Weight of pycnometer + liquid at $(t + 5)^\circ\text{C}$ = W_4 g
-
-

Temperature ($^\circ\text{C}$)	Time of flow of liquid (sec)	Time of flow of water (sec)
t°
$(t + 5^\circ)$
.....

Calculations : Density of liquid at $t^\circ\text{C} = \frac{W_3 - W_1}{W_2 - W_1} \times 1$

Similarly, we can calculate the density of the liquid at different temperatures, taking the density of water to be unity.

The viscosity of liquid $[\eta_1]$ at $t^\circ\text{C}$ is given by,

$$\eta_1 = \frac{d_1 t_1}{d_2 t_2} \cdot \eta_2, \text{ where all letters have their usual significance.}$$

The viscosity of the liquid is similarly determined at different temperatures, with the help of the above expression. The viscosity of water at different temperatures can be taken from the standard table.

A graph is plotted between absolute viscosities as ordinate and temperatures as abscissa. From this graph, we can calculate the value of temperature coefficient between any range of temperatures as follows :

Temperature coefficient

$$= \frac{\text{Viscosity at one temp. } [t_1^\circ\text{C}] - \text{Viscosity at another temp. } [t_2^\circ\text{C}]}{t_1 - t_2}$$

Result : The temperature coefficient for the given liquid = ...

Precautions : Same as in experiment 1. Besides these precautions, we must ensure ourselves that the liquid has attained the temperature for which we are to consider the values.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 4

Object : To determine the influence of temperature on viscosity.

For this purpose, a graph is plotted between $\log_{10} \eta$ and reciprocal of absolute temperature, which is a straight line for non-associated liquids, e.g., heptane, benzene, carbon tetrachloride etc. For non-associated liquids, e.g., methyl alcohol, ethyl alcohol, toluene, nitrobenzene, the curve deviates from straight line behaviour.

EXPERIMENT No. 5

Object : To calculate the molecular weight of a high polymer by means of viscosity measurements.

According to Mark-Houwink equation,

$$[\eta] = KM^x \quad \dots(1)$$

or,

$$\log [\eta] = \log K + x \log M \quad \dots(2)$$

where, M is the molecular weight of high polymer and K is a constant for the given solvent-polymer system at a definite temperature and is of the order of 10^{-4} , x is also a constant and is known as *shape factor* and is usually of the order of 0.65.

The value of $[\eta]$ is known as **intrinsic viscosity** which is obtained as the intercept of the curve between $\frac{\eta_{sp}}{c}$ and c , where c is the concentration of the high polymer in grams per 100 ml of the solution. The term η_{sp} is known as **specific viscosity** and can be calculated by means of the expression :

$$\eta_{sp} = \frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}}$$

The values of the factor x for flexible randomly coiled linear chain molecules vary from 0.5 to 0.8. For rigid rod like molecules, the value of x may rise to even 2. The values of K and x for some polymer-solvent systems are given in the

following table. For obtaining the values of K and x experimentally for any polymer-solvent system, a graph is plotted between $\log [\eta]$ and $\log M$ values.

Table-1. K and x values for some polymer-solvent systems

Polymer	Solvent	$K \times 10^5$	x	$M \times 10^{-5}$
Polypropylene	Benzene	27	0.71	60-300
Polystyrene	Benzene	122.7	0.73	2-8
Polyvinyl acetate	Methanol	101	0.50	40-300
Polyvinyl alcohol	Water	20	0.76	6-20
Polyethylene glycol	Water	156	0.50	0.2-8
Polymethyl methacrylate	Acetone	7.5	0.70	~15.0
Polyvinyl acetate	Acetone	21.4	0.68	40-300
Polyvinyl acetate	Chloroform	20.3	0.72	40-300

In measuring viscosities of polymer solutions, the apparatus should be thoroughly cleaned. The solutions should be filtered free of suspended impurities and immediately after use, the apparatus, e.g., viscometer, pipette etc should be emptied, washed, cleaned and dried before being kept.

The concentrations can be changed by dilution with solvent.

Procedure : Prepare a solution containing about 0.5 g (but accurately weighed) polystyrene in 25 g of toluene. Take a suitable volume of the solution in viscometer at 25°C and determine the time of flow 2-3 times.

Withdraw the solution from the viscometer and by means of a graduated pipette mix equal volumes of this solution and the solvent and determine the time of flow of the same volume of the resulting solution (1%). The viscometer must first be rinsed with this solution before filling it. Similarly, prepare 0.50% and 0.25% solutions by serial dilutions and find the time of flow for each dilution. Finally determine the time of flow of the same volume of pure solvent. Determine the densities of pure solvent and the solutions.

Observations :

- (i) Time of flow of the solvent = ..., ..., ..., Mean = t_0
- (ii) Density of pure solvent = d_0
- (iii) For solutions.

Concentration	Flow Time				Density (d)	η/η_0	$\eta_{sp} = \frac{\eta}{\eta_0} - 1$	η_{sp}/c
	(i)	(ii)	(iii)	Mean (t sec)				
2%								
1%								
0.5%								
0.25%								

Calculations : We know that,

$$\frac{\eta}{\eta_0} = \frac{dt}{d_0 t_0}$$

where t and t_0 are the flow time of the solution and the pure solvent, respectively and d and d_0 are their respective densities. If the densities of the solution and the solvent are very close (in case of dilute solutions), then the above equation becomes,

$$\frac{\eta}{\eta_0} = \frac{t}{t_0}$$

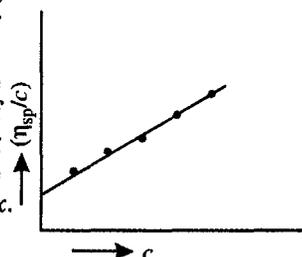
Therefore,
$$\frac{\eta_{sp}}{c} = \left(\frac{t}{t_0} - 1 \right) / c$$

or,
$$\frac{\eta_{sp}}{c} = \left(\frac{td}{t_0 d_0} - 1 \right) / c \quad (\text{when densities differ appreciably})$$

Then calculate and tabulate the values of η/η_0 , η_{sp} and η_{sp}/c . Plot a graph between η_{sp}/c (y-axis) and the concentration (x-axis) and from the intercept of the straight line (when $c = 0$), calculate the intrinsic viscosity.

Then using equation (1), calculate the molecular weight of the polymer, taking known values of K and x . Alternately, values of the constants K and x can be determined by working with samples of the polymer of known molecular weights in the same solvent and using equation (2). A plot of $\log [\eta]$ and $\log M$ (abscissa) will be a straight line with intercepts equal to $\log K$ and slope x . Therefore, K and x can be calculated.

We can find the molecular weights of polymers like polystyrene, polymethyl methacrylate in toluene (solvent).



EXPERIMENT No. 6

To determine by viscosity method, whether the following pairs of liquids form molecular compounds or not :

- (a) Water and ethyl alcohol (b) Methyl alcohol and ethylidene chloride
(c) Nitric acid and chloroform. (d) Benzene and ethyl alcohol.

Theory : A curve is plotted between $\frac{\log \eta^E}{x_1 \cdot x_2}$ (y-axis) and $(x_1 - x_2)$ (x-axis). The formation of a compound between two liquids and its composition is indicated by a maximum point on the above curve. The term η^E is the excess viscosity of a mixture and is given by,

$$\log \eta^E = \log \eta_{mix} - x_1 \log \eta_1 - x_2 \log \eta_2,$$

where x_1, x_2 = mole fractions of the liquids 1 and 2 and η_1, η_2 = viscosities of the liquids 1 and 2.

EXPERIMENT No. 7

Object : *To study the variation of viscosity with composition of the mixture of water and ethanol.*

Proceed as in experiment no. 2.

EXPERIMENT No. 8

Object : *To determine the viscosity of different mixtures of benzene and nitrobenzene and also test the validity of Kendall's equation.*

Kendall's equation is represented as,

$$\log \phi_{mix} = x_1 \log \phi_1 + x_2 \log \phi_2$$

where, ϕ and x represent the fluidity and mole fraction and subscripts 1 and 2 represent the two liquids 1 and 2. Mixtures of similar liquids, *e.g.*, benzene and toluene obey the above equation. If the two liquids, *e.g.*, phenol and amine form complexes in the mixture, the observed fluidities are less than the calculated values, *i.e.*, viscosity increases rapidly on mixing. Mixtures of two dissimilar liquids, *e.g.*, alcohol and benzene have lower viscosities than the calculated values.



SURFACE TENSION

The surface of a liquid remains in a state of tension because the molecules which are present in it are being constantly subjected to a force pulling them downwards. This downward pull is the result of a force of attraction which the molecules, present in the bulk of the solution, exercise on the molecules present on the surface. The surface molecules are also pulled sideways by the other surrounding molecules, but since the sideway forces are equal and opposite in magnitude they cancel each other, resulting in no sideway pull. The tension at the surface, is known as *surface tension* and can be defined as; '***the force acting on a surface at right angles to any line of unit length***'.

The surface tension is represented by the Greek symbol γ and its unit is **dyne cm^{-1}** . Due to this tension on the surface, the liquids try to occupy the least area and that is why the drops of liquids are spherical. This is because in a sphere the surface area is minimum for a given volume. The rise of a liquid in a capillary is also due to surface tension.

There are a number of methods for determining surface tension of liquids. Two of them are :

- (1) **Drop fall method.**
- (2) **Capillary rise method.**

[I] DROP FALL METHOD

(1) **Drop Number Method :** This is the method which is generally used to determine the surface tension of liquids in laboratory. The method is based on the principle that the weight (W) of a liquid falling from a capillary tube held vertical, is approximately proportional to the surface tension of the liquid. Hence, if the surface tension of two liquids be γ_1 and γ_2 and W_1 and W_2 be the mean weights of their drops falling from the same capillary tube, then,

$$\frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2}$$

(The drop falls out when its weight becomes equal to $2\pi r\gamma$, where r = radius of the tube.)

The apparatus used in these determinations consists of a bulb A fused with a capillary tube B and is called **stalagmometer** or **drop pipette** (fig. 1). It is more convenient to count the drops formed by a given volume of a liquid than to

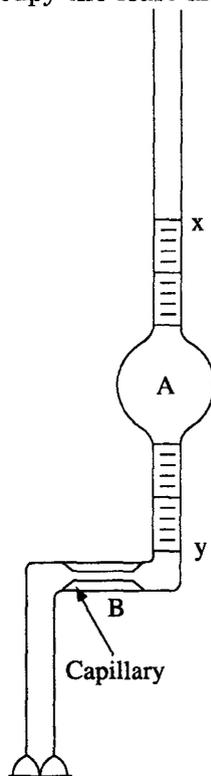


Fig. 1 :
Stalagmometer

find the weight of the drops. Let the number of drops of two liquids be n_1 and n_2 for the same volume V of the liquids, *i.e.*, from x to y , then,

$$W_1 = \frac{V}{n_1} d_1 \text{ and } W_2 = \frac{V}{n_2} d_2$$

where, d_1 and d_2 are the respective densities of the liquids. Hence,

$$\frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2} = \frac{Vd_1/n_1}{Vd_2/n_2} = \frac{n_2d_1}{n_1d_2} \quad \dots (1)$$

If the surface tension of one of the liquids is known then surface tension of the other can be easily calculated from equation (1). The densities of the liquids can be measured by means of a pycnometer or specific gravity bottle [explained in the preceding chapter]. All the measurements are to be carried out at the same temperature.

Stalagmometer : This is an instrument [fig. 1] used to determine the surface tension of a liquid. It was designed by Traube and consists of a pipette with a capillary outflow tube, the end of which is flattened out. This is done to give a larger dropping surface. The surface is carefully ground flat and polished. There are two marks, one just above the bulb A, while the other is just below it [x and y]. In order to measure the fraction of a drop with an accuracy of 0.05 of a drop, we can calibrate for a short distance above and below the upper and lower marks. The calibration can be done by first determining the number of scale divisions which correspond to one drop.

Precautions while using stalagmometer : Before using, the stalagmometer is first carefully washed with a solution of chromic acid and then with distilled water. Finally, it is washed with alcohol and dried. It must be borne in mind that the tip of lower end should not come in contact with hand, desk or some other thing, as it may be contaminated with a trace of grease. Slight traces of grease will alter the size of the drops, hence their number. The stalagmometer should be held vertical and should not be shaken, because on shaking the drops may fall out even before attaining their maximum size.

It must also be kept in mind that the rate of flow of liquid through the tip should not be fast, it should be about 12–18 drops per minute. If the rate of flow is fast, then it can be decreased by attaching a piece of rubber tubing with a screw pinch cock to the open end and adjusting the pressure (fig. 2) so that only 12–18 drops fall out per minute. Once this adjustment of pressure is made, it should be kept unchanged during the whole experiment.

(2) Drop Weight Method : This method depends on the equilibrium between the weight of a drop, which is just about to fall from the end of a vertical tube and an upward force due to surface tension acting around the periphery of the drop. In case the drops fall off from the capillary end under its own weight, free from kinetic force of flow and vibrations, the size

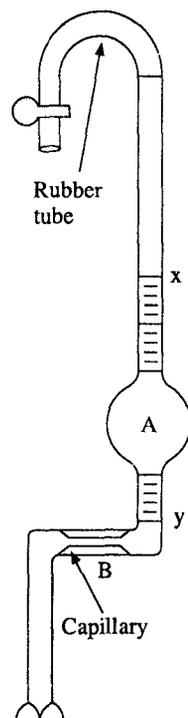


Fig. 2 :
Stalagmometer with
rubber tubing

of the drop will depend on the surface tension of the liquid and the external radius of the jet of the capillary. The force supporting the drop is given by $2\pi r \gamma$, where γ is the external radius of the jet. The drop falls off when its weight becomes equal to this force, *i.e.*,

$$2\pi r \gamma = W = mg = vdg$$

where m is the mass of the drop, d is the density of the liquid and v is the volume of the drop.

In fact, only a portion of the drop falls. According to Harkins and Brown, the fraction of the ideal drop which falls is a function of $r/v^{1/3}$. The actual weight of the drop which falls will be given by,

$$mg = 2\pi r \gamma f(r/v^{1/3})$$

or

$$\gamma = \frac{mg}{2\pi r f(r/v^{1/3})} = \frac{F mg}{r} \quad \dots (1)$$

where F is a correction factor depending on $(r/v^{1/3})$. It is thus possible to determine the surface tension of a liquid by determining the mass of a drop of the liquid, its volume (v) from a rough measurement of density ($v = \frac{m}{d}$) and the outer radius of the jet. The value of correction factor, F corresponding to a particular value of $v/r^{1/3}$ can be seen from the following table.

Table-1.

$\frac{v}{r^{1/3}}$	F	$\frac{v}{r^{1/3}}$	F	$\frac{v}{r^{1/3}}$	F
5000	0.172	3.433	0.25874	0.048	0.2617
250	0.198	2.995	0.36065	0.980	0.2602
58.1	0.215	2.637	0.26124	0.912	0.2585
24.7	0.2256	2.3414	0.2635	0.865	0.2570
17.6	0.2305	2.093	0.26452	0.816	0.2550
13.28	0.2352	1.884	0.26522	0.692	0.2499
10.29	0.2396	1.7062	0.26562	0.570	0.2430
8.19	0.2441	1.5545	0.26566	0.512	0.2441
6.662	0.2479	1.4235	0.26544	0.455	0.2491
6.522	0.25135	1.3095	0.26495	0.396	0.2512
4.653	0.25419	1.211	0.26407		
3.975	0.25661	1.124	0.2632		

[II] CAPILLARY RISE METHOD

It is observed that when a capillary tube is dipped in a liquid that wets its surface, the liquid rises in the capillary tube. The height for a given capillary tube varies with the surface tension and density of the liquid.

Suppose a liquid of density d rises in a capillary tube of radius r , to a height h (fig. 3). If γ be the surface tension, then the total force (F) due to surface tension, raising the liquid column upward is given by,

$$\begin{aligned} F &= \text{Inside circumference of the capillary} \times \text{Surface tension} \\ &= 2\pi r \gamma \text{ dyne} \end{aligned}$$

$$\begin{aligned} \text{Force of gravity pulling the liquid downward} \\ &= \text{Weight of the liquid column of height } h \\ &= vhdg = \pi r^2 \cdot hdg \end{aligned}$$

where $d = \text{density of the liquid.}$

At equilibrium,

$$2\pi r\gamma = \pi r^2 hdg$$

$$\text{or } \gamma = \frac{rhdg}{2} \text{ dyne cm}^{-1} \quad \dots (2)$$

In case of liquids where wetting is not perfect, *i.e.*, the angle of contact (θ) between glass and liquid is not zero, then,

$$\gamma = \frac{rhdg}{2 \cos \theta} \text{ dyne cm}^{-1}$$

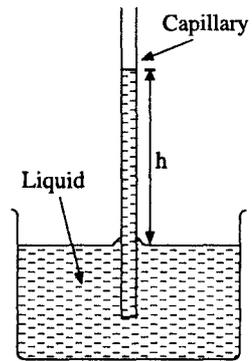


Fig. 3.

Thus, from equation (2) we can calculate the surface tension of any liquid. The value of r , *i.e.*, radius of the capillary is measured by travelling microscope; h , the height through which the liquid rises is measured by a cathetometer; and d , the density of the liquid by pyknometer.

Parachor : Mcleod (1923) found the relation between surface tension and temperature and suggested the following equation,

$$\frac{\gamma^{1/4}}{(D-d)} = C$$

where, D is the density of the liquid, d is the density of the saturated vapours of the liquid and C is a constant. The expression holds good for a wide range of temperature.

Sugden modified the above equation by multiplying both sides by the molecular weight (M) of the liquid, *i.e.*,

$$\frac{M\gamma^{1/4}}{D-d} = C.M = [P] \quad \dots (3)$$

where, $[P]$ is the parachor of the substance. At ordinary temperature, the value of d is very small as compared to D , hence from equation (3), we get,

$$\frac{M\gamma^{1/4}}{D} = [P]$$

If $\gamma = 1$, then $[P] = \frac{M}{D} = \text{molecular volume.}$ Therefore, parachor is defined as,

'the molecular volume at a temperature when the surface tension of the liquid is unity'.

Parachor has been found to be an additive¹ and constitutive² property, and can thus be used for deciding the chemical constitution or structure of substances.

1. **Additive property** : Such a property of a molecule is defined as the property which is the sum of the corresponding properties of the atoms constituting the molecule, *e.g.*, molecular weight is an additive property, because the weight of a molecule is obtained by adding the masses of the constituent atoms.
2. **Constitutive property** : Such a property of a molecule is defined as the property which depends upon the constitution of the molecule, *i.e.*, on the arrangement of atoms within the molecule. Optical activity is a constitutive property.

EXPERIMENT No. 1

Object : To find the surface tension of a given liquid by drop number method, at room temperature.

Apparatus : Stalagmometer, thermometer, pycnometer, balance, thermostat, beaker etc.

Theory : The surface tension (γ_2) of the given liquid can be calculated according to the following expression,

$$\gamma_2 = \frac{n_1 d_2}{n_2 d_1} \cdot \gamma_1 \quad \dots (1)$$

where all letters have their usual significance.

(For details see the preceding pages)

Procedure : First, the stalagmometer is washed with a solution of chromic acid, then with distilled water and finally with alcohol and then dried. Attach a small piece of a clean rubber tube to the upper end of the stalagmometer. The rubber tubing with a screw pinch cock on it is used to regulate the flow of liquid, by limiting the influx of air.

Fill the stalagmometer with water by dipping it in a beaker containing water and sucking till the water rises above the mark x (fig. 2). Now bring the level of water to the mark x . Open the pinch cock and adjust it so that the rate of flow of drops is about 12–18 drops per minute. When this is adjusted, refill the stalagmometer with distilled water as above without changing the pressure. Then start counting the drops when the meniscus passes the upper mark x and stop when it just crosses the lower mark y . Repeat the process 3–4 times.

A correction can be applied to the total number of drops counted, if the passage of the meniscus past the two marks x and y does not coincide with the falling of a drop.

Remove the rubber tubing from the stalagmometer and rinse it with the liquid. Now fill the liquid and count the number of drops for the flow of the liquid from mark x to y . Repeat the process 3–4 times.

A pycnometer is also washed and weighed empty. It is again weighed after filling it with water and the given liquid (*Details are given in the preceding chapter*).

The liquid can be kept in a constant temperature bath or thermostat for 15 minutes, so that it attains the room temperature.

Observations : Room temperature = $t^\circ\text{C}$
 Weight of empty pycnometer = W_1 g
 Weight of pycnometer + water = W_2 g
 Weight of pycnometer + liquid = W_3 g

Liquid	Number of drops	Surface tension
Water Mean value of $n_1 = \dots$	γ_1
Liquid Mean value of $n_2 = \dots$	γ_2

Calculations :

$$\frac{\text{Density of liquid } (d_2)}{\text{Density of water } (d_1)} = \frac{\text{Weight of liquid}}{\text{Weight of water}} = \frac{W_3 - W_1}{W_2 - W_1}$$

The surface tension of the liquid can be calculated by equation (1), after seeing the value of γ_1 from the table.

Result : The surface tension of the liquid at $t^\circ\text{C} = \dots$ dyne/cm.

Precautions : (1) The stalagmometer should be held vertical.

(2) The stalagmometer should be absolutely clean from any greasy matter. Great care must be taken to ensure that the tip of the stalagmometer does not come in contact with hands or the working table.

(3) The rate of flow of the liquid should be about 12–18 drops per minute.

(4) The drops should be allowed to fall off from the stalagmometer tip under their own weight and should not be pushed away by the kinetic flow.

EXPERIMENT No. 2

Object : To determine the surface tension of nitrobenzene at 30°C by drop weight method.

Apparatus : Drop weight surface tension apparatus, travelling microscope, thermostat, weighing bottle, pure nitrobenzene.

A simple drop weight apparatus is shown in figure (4). It consists of a U-shaped capillary B, the lower end of which is ground flat and polished. The capillary B is connected to a large side tube A, in which the liquid is placed. By means of a cork, B is fitted in to a protecting vessel V and the cork also carries a glass tube, T which acts as an air vent and C is a small weighing bottle.

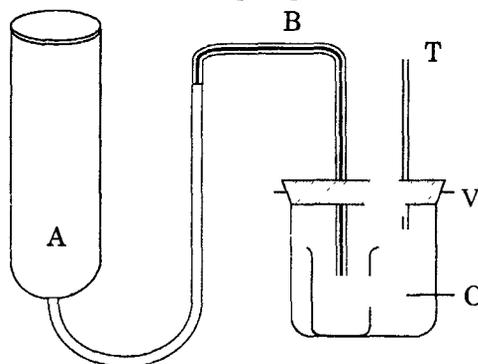


Fig. 4 : Drop weight apparatus

Procedure : Thoroughly clean and dry the glasswares and assemble the apparatus as shown in figure (4). Weigh accurately a dried weighing bottle C and place it under the tip of the capillary B in the protecting vessel, V. Immerse the whole apparatus in a thermostat set at a temperature of 30°C .

Add the test liquid (nitrobenzene) through the side tube A and the capillary and carefully adjust the level in the side tube so that the rate of formation of a drop is per 4-5 min. For this purpose, 1 cm head of liquid is quite sufficient. Now

carefully introduce extra liquid in the side tube or apply a slight pressure so that subsequent drops break away after 35-40 seconds. Note that the drops must fall only under the influence of gravity. Collect 25-30 drops and weigh the collected liquid. (In case more volatile liquid is used, the bottle containing the liquid should be cooled in ice cold water before weighing).

The external radius of the jet of the capillary is determined by means of a travelling microscope. The density of the liquid is determined by means of a pycnometer or density bottle at the required temperature.

Observations : Weight of empty weighing bottle = W_1 g

Weight of weighing bottle + Liquid = W_2 g

Number of drops = ...

Radius of the jet of the capillary = ...

The density of the experimental liquid is tabulated as given in experiment 1.

Calculations : From the weight of known number of drops calculate the weight of one drop. This weight is divided by the density of the liquid used, calculate the volume (v) of one drop. Then calculate $v/r^{1/3}$ and find the corresponding value of F from table-1. Thereafter, the surface tension of the liquid is calculated from equation (1).

Result : The surface tension of nitrobenzene at 30°C

= ... dyne/cm.

EXPERIMENT No. 3

Object : To find the composition of the given mixture of two components A and B.

Apparatus : Same as in experiment 1.

Theory : A number of solutions of A and B are prepared and the number of drops in each case is determined as usual. A graph is then plotted between the number of drops (or surface tension) and the concentration of one liquid, say A. The surface tension or the number of drops of the unknown mixture is also determined, whose concentration can then be determined from the graph.

Procedure : Prepare a number of mixtures containing 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, and 10%, A. Fill the stalagmometer (after washing and drying it, as already explained) with each solution in turn and then count the number of drops for each solution. The number of drops of the unknown mixture is also similarly counted.

Observations : Room temperature = $t^\circ\text{C}$.

Composition of mixture		Number of drops	Composition of mixture		Number of drops
A	B		A	B	
90%	10%	...	40%	60%	...
80%	20%	...	30%	70%	...
70%	30%	...	20%	80%	...
60%	40%	...	10%	90%	...
50%	50%	...	Unknown mixture		...

Calculations : A graph (fig. 5) is plotted between concentration of A (X-axis) and number of drops (Y-axis). The point corresponding to the number of drops of the unknown mixture is found. From that point a perpendicular is drawn on the concentration axis and the value gives the required concentration.

Result : The composition of the given mixture = ... A%;
...%B.

Precautions : Same as in experiment no. 1.

Note : A curve between surface tension and concentration can also be plotted, for which density of each solution has to be measured.

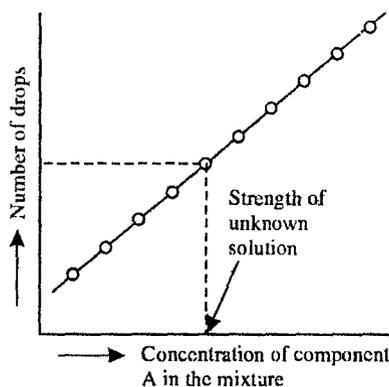


Fig. 5 : Graph between number of drops and concentration

EXPERIMENT No. 4

Object : To find the surface tension of given liquid by single capillary rise method.

Apparatus : Capillary tube, beaker, pyknometer, weight box, cathetometer, microscope etc.

Theory : When a capillary tube of a uniform bore is immersed in a liquid, then the liquid rises to a certain height. The surface tension of the liquid can be calculated by the expression,

$$\gamma = \frac{rhdg}{2}$$

where all letters have their usual significance. (For details see earlier pages).

Procedure : First the capillary tube is washed and dried. It is then dipped in experimental liquid, which is taken in a beaker. The liquid rises in the tube and after sometime it rises to a maximum height. Then, by means of a cathetometer, the reading of the liquid level in the beaker is taken. The cathetometer is then fixed at the meniscus of the liquid in the capillary. The density of the liquid is also taken by means of a pyknometer, as usual. The radius of the capillary tube is measured by means of a microscope.

Observations : Room temperature = $t^{\circ}\text{C}$
 Weight of empty pyknometer = W_1 g
 Weight of pyknometer + water = W_2 g
 Weight of pyknometer + liquid = W_3 g
 Initial reading of cathetometer = h_1 cm
 Final reading of cathetometer = h_2 cm
 Diameter of the capillary = R cm

Calculations : Density of the liquid = $\frac{W_3 - W_1}{W_2 - W_1} \times 1$

Rise of liquid in the capillary = $(h_2 - h_1) = h$ cm

Radius of the capillary = $\frac{R}{2} = r$ cm

The surface tension of the given liquid is calculated according to the formula,

$$\gamma = \frac{rhdg}{2} \text{ dyne cm}^{-1}$$

Result : The surface tension of the liquid at $t^\circ\text{C}$
= dyne cm^{-1} .

Precautions : (i) The bore of the capillary should be uniform.

(ii) The capillary should be absolutely clean.

(iii) The diameter of the capillary should be about 0.2 – 0.5 mm.

EXPERIMENT No. 5

Object : To find surface tension of given liquid by double capillary rise method or differential capillary rise method.

Apparatus : Double capillary or two capillaries of different diameters, pyknometer, cathetometer, beaker etc.

Theory : In single capillary rise method, it is difficult to determine the level of the flat surface of the liquid, provided it is not present in large quantity. If the liquid is present in small quantity, then it becomes difficult to find its surface tension accurately. This difficulty can, however, be removed by using a double capillary.

If two capillary tubes of radii r_1 and r_2 are dipped into the same level in a liquid of density d , the surface tension of liquid can be calculated by measuring the difference in height (Δh), to which the liquid rises in the two tubes. The surface tension is then given by,

$$\gamma = \frac{g}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)} \cdot d \cdot \Delta h$$

For the same pair of capillary tubes, r_1 and r_2 are constant, therefore,

$$\gamma = \text{constant} \cdot d \cdot \Delta h$$

Description of double capillary : Double capillary consists of two capillary tubes of uniform bores of 2 mm and 0.5 mm, respectively. These tubes are then joined together to form a U-tube, with a small hole at the lowest point [fig. (6)].

Procedure : First the double capillary is washed and dried. It is then immersed and clamped vertically in a beaker containing a known liquid, say benzene (BDH quality, *i.e.*, whose surface tension at room temperature is known). The liquid rises in the two capillary tubes and the height upto which the liquid rises is measured for both the tubes by means of a cathetometer upto an accuracy of 0.002 cm.

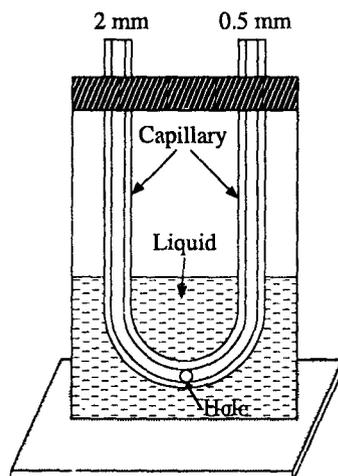


Fig. 6 : Double Capillary

The double capillary is again washed with water and then with the experimental liquid, whose surface tension is to be determined. It is then dipped into a beaker containing the experimental liquid and the rise of the liquid in the two capillary tubes is measured as before.

The density of the liquid is measured by means of a pyknometer as usual.

Observations : Room temperature	= $t^{\circ}\text{C}$
Weight of empty pyknometer	= W_1 g
Weight of pyknometer + benzene	= W_2 g
Weight of pyknometer + water	= W_3 g
Weight of pyknometer + liquid	= W_4 g

Table for Δh (by cathetometer)

S.N.	Standard liquid (benzene)			Unknown liquid		
	Reading of one tube (h_1)	Reading of second tube (h_2)	Δh_b = $h_2 - h_1$	Reading of one tube (h_1)	Reading of second tube (h_2)	Δh = $h_2 - h_1$
1.
2.
3.

Surface tension of benzene at $t^{\circ}\text{C} = \gamma_b$ dyne/cm

Calculations : Density of the liquid, $d = \frac{W_4 - W_1}{W_3 - W_1} \times 1$

Density of benzene, $d_b = \frac{W_2 - W_1}{W_3 - W_1} \times 1$

The value of constant $\left[\frac{g}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)} \right]$ for the double capillary is given by

$\frac{\gamma_b}{d_b \cdot \Delta h_b}$, which can now be calculated. Say its value is K_1 . The surface tension of the given liquid is then calculated according to the formula,

$$\gamma = K_1 d \cdot \Delta h$$

Since all the values are known, the value of γ can be easily calculated.

Result : Surface tension of the given liquid at $t^{\circ}\text{C}$

$$= \dots \text{ dyne cm}^{-1}.$$

Precautions : (i) The constant for the double capillary should be accurately determined by taking a liquid which is absolutely pure.

EXPERIMENT No. 6

Object : To determine the surface tension of toluene at a series of temperatures by double capillary rise method and then calculate the critical temperature of the liquid.

Apparatus : Same as in preceding experiment.

Theory : Far from the critical temperature, the change of surface tension of normal (non-associated) liquids with temperature is given by the following empirical equation,

$$\gamma = \gamma_0 \left(1 - \frac{t}{t_c} \right)^n$$

where t_c is the critical temperature and γ_0 and n are constants.

On taking logarithm and differentiating γ with respect to temperature, we get

$$t = t_c + \frac{n \gamma}{(d\gamma/dt)}$$

If values of $\frac{\gamma}{(d\gamma/dt)}$ (abscissa) are plotted against temperature, t (ordinate), a straight line is obtained, whose intercept on the ordinate will be equal to t_c .

Procedure : Determine the surface tension of toluene at a series of temperatures, say 20, 25, 30, 35, 40, 45, 50°C.

Observations : Same as in preceding experiments.

Calculations : Divide the difference of surface tension at 20 and 30°C by the temperature increment, i.e., 10°. This gives $d\gamma/dt$ at the mean temperature of 25°C. Similarly, calculate $d\gamma/dt$ at 30, 35, 40 and 45°C.

Plot $\frac{\gamma}{d\gamma/dt}$ (abscissa) versus temperature (ordinate). The intercept of the straight line so obtained on the ordinate gives the value of the critical temperature. The slope of this straight line will give the value of the constant, n .

EXPERIMENT No. 7

Object : To find the surface tension of methyl alcohol, ethyl alcohol and *n*-hexane at room temperature and then calculate the atomic parachors of carbon, hydrogen and oxygen.

Apparatus : Stalagmometer, pycnometer, three liquids, beakers etc.

Theory : As explained before, the parachor, $[P]$ of a liquid of molecular weight M and density D is given by.

$$[P] = \frac{M\gamma^{1/4}}{D}$$

where, γ = surface tension.

First, the surface tension and density of each liquid is determined by means of a stalagmometer and pycnometer as usual. Thus, the value of parachor of each liquid can be calculated. Atomic parachors of carbon, hydrogen and oxygen can be found as follows :

$$(a) \quad [P_{\text{EtOH}}] - [P_{\text{MeOH}}] = [P_{\text{CH}_2}]$$

$$(b) \quad [P_{\text{hexane}}] - 6[P_{\text{CH}_2}] = 2[P_{\text{H}}]$$

$$(c) \quad [P_{\text{CH}_2}] - 2[P_{\text{H}}] = [P_{\text{C}}]$$

$$(d) \quad [P_{\text{MeOH}}] - 4[P_{\text{H}}] - [P_{\text{C}}] = [P_{\text{O}}]$$

Procedure : First the stalagmometer is washed and dried, as explained before. It is then filled with water and clamped vertically.

The number of drops is counted between two marks x and y [cf. fig. (2)].

Similarly, the stalagmometer is washed with every liquid in turn and the number of drops are counted, as usual. The densities of each liquid are also measured by pycnometer, as usual. The room temperature is also noted.

Observations : Room temperature = $t^\circ\text{C}$

Weight of empty pycnometer = W_1 g

Weight of pycnometer + water = W_2 g

Weight of pycnometer + CH_3OH = W_3 g

Weight of pycnometer + $\text{C}_2\text{H}_5\text{OH}$ = W_4 g

Weight of pycnometer + n -hexane = W_5 g

Liquid	Number of drops	Average number of drops	Liquid	Number of drops	Average number of drops
Water	...	n_w	$\text{C}_2\text{H}_5\text{OH}$...	n_e
CH_3OH	...	n_m	n -Hexane	...	n_h

Let the molecular weights of CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and n -hexane be M_1 , M_2 and M_3 , respectively.

Calculations : Density of methyl alcohol = $\frac{W_3 - W_1}{W_2 - W_1}$

Density of ethyl alcohol = $\frac{W_4 - W_1}{W_2 - W_1}$

Density of n -hexane = $\frac{W_5 - W_1}{W_2 - W_1}$

(Density of water is taken to be unity).

The surface tension of each liquid is calculated according to experiment no. 5. Once the values of surface tension are known, the parachor values can be calculated, as all the factors, viz., molecular weight, density and surface tension are known in the expression,

$$[P] = \frac{M\gamma^{1/4}}{D}$$

The atomic parachors of C, H and O can then be calculated, as explained in the theory of this experiment.

Result : The parachor values of methyl alcohol, ethyl alcohol and n -hexane are ..., ..., and ..., respectively, while the atomic parachors of C, H and O are ..., ..., and ..., respectively.

Precautions : Same as described in experiment 5.

EXPERIMENT No. 8

Object : To find out the parachor of a solid (say *p*-dichlorobenzene) in a given solvent (say benzene) by double capillary rise method, assuming the mixture law to hold good.

(Note : The parachor of a solid can also be determined with the help of a stalagmometer or a single capillary).

Apparatus : Double capillary, beaker, cathetometer, pyknometer, measuring flask etc.

Theory : The parachor of a solid is determined by dissolving the solid in a suitable solvent, so as to get a solution of known concentration. If $[P_m]$ be the parachor of the solution, then according to mixture law, $[P_m]$ is related to parachors $[P_1]$ and $[P_2]$ of the solute and solvent, respectively, by the equation,

$$[P_m] = x[P_1] + (1 - x)[P_2] \quad \dots (1)$$

where, x is the mole fraction of the solute in the solution.

The parachor of the solvent is calculated as,

$$[P_2] = \frac{M_2 \gamma_2^{1/4}}{D_2} \quad \dots (2)$$

where all letters have their usual significance.

The parachor of the mixture is given by,

$$[P_m] = \frac{\gamma_m^{1/4}}{D_m} [xM_1 + (1 - x)M_2] \quad \dots (3)$$

All the values in equations (2) and (3) are known, hence we can calculate the values of $[P_2]$ and $[P_m]$. On substituting these values in equation (1), we can calculate the parachor of the solid, $[P_1]$.

The mole fraction (x) of solute is given by,

$$x = \frac{n_1}{n_1 + n_2} = \frac{W_1/M_1}{W_1/M_1 + W_2/M_2}$$

where, n_1 and n_2 are the number of moles of solute and solvent, respectively, W_1 is the weight (in g) of solute of molecular weight M_1 dissolved in W_2 g of solvent of molecular weight M_2 .

Procedure : First a solution of known concentration of solute is prepared in the solvent (benzene), *i.e.*, by dissolving 10 g of the solid in 100 g of the solvent in a measuring flask.

Double capillary is first washed and dried and then dipped into a beaker containing benzene. The height of benzene in the two capillary tubes is determined by means of a cathetometer, as explained in experiment 4.

Then the double capillary is dipped into a beaker containing the solution and the height of the solution in the two capillary tubes is determined as explained above.

The density of the mixture or solution and the solvent (benzene) is determined as usual by means of pyknometer. Note the room temperature by means of a thermometer.

Observations : Room temperature = $t^{\circ}\text{C}$
 Weight of empty pyknometer = W_1 g
 Weight of pyknometer + water = W_2 g
 Weight of pyknometer + benzene = W_3 g
 Weight of pyknometer + mixture = W_4 g
 Weight of empty weighing tube = W_5 g
 Weight of weighing tube + solid = W_6 g
 Capacity of the measuring flask = 100 ml (say)
 Molecular weights of solid and solvent are, say M_1 and M_2 .

Liquid (benzene)			Mixture (solution)		
Reading of one tube, h_1	Reading of other tube, h_2	$\Delta h = (h_2 - h_1)$	Reading of one tube, h_1	Reading of other tube, h_2	$\Delta h = (h_2 - h_1)$
...
...

Calculations : Density of benzene, $D_2 = \frac{W_3 - W_1}{W_2 - W_1}$

Density of mixture, $D_m = \frac{W_4 - W_1}{W_2 - W_1}$

(Density of water is taken to be unity).

The surface tensions of benzene and mixture are now calculated as explained in preceding experiments. Let their values be γ_2 and γ_m , respectively. The parachor values of benzene [P_2] and mixture [P_m] are calculated as follows :

$$[P_2] = \frac{M_2 \gamma_2^{1/4}}{D_2}$$

and

$$[P_m] = \frac{\gamma_m^{1/4}}{D_m} [xM_1 + (1-x)M_2]$$

The value of x , i.e., mole fraction of solute is calculated as follows :

$$x = \frac{(W_6 - W_5)/M_1}{(W_6 - W_5)/M_1 + 100/M_2}$$

if $(W_6 - W_5)$ g of solid is dissolved in 100 g of benzene.

The value of [P_1], i.e., parachor of solid can then be easily calculated by the formula :

$$[P_m] = x[P_1] + (1-x)[P_2]$$

Result : The parachor of the given solid = ...

Precautions : Same as in preceding experiments.

EXPERIMENT No. 9

Object : To find out the molecular surface energy and the association factor of ethyl alcohol.

Apparatus : Stalagmometer, pyknometer, beaker, etc.

Theory : If a liquid suspended in another liquid of the same density with which it neither mixes nor reacts, is withdrawn under the action of gravity, it assumes a spherical shape. Molecular surface of the liquid is the surface of the sphere, taken up by one mole of liquid. It has been found that molecular surfaces are proportional to $V^{2/3}$, where V is the molecular volume. The molecular surface energy of the liquid is then given by $\gamma.V^{2/3}$, where, γ = surface tension of the liquid. If v be the specific volume and M the molecular weight of the liquid, then $V = vM$.

Therefore, molecular surface energy $= \gamma.V^{2/3} = \gamma(Mv)^{2/3}$.

The molecular surface energy is a linear function of temperature and varies with temperature according to the relation,

$$\gamma(Mv)^{2/3} = K(T_c - t - 6),$$

where, T_c and t are the critical temperature and observation temperature, respectively.

At two different temperatures t_1 and t_2 we have,

$$\gamma_1(Mv_1)^{2/3} = K(T_c - t_1 - 6)$$

$$\gamma_2(Mv_2)^{2/3} = K(T_c - t_2 - 6)$$

or

$$K = \frac{\gamma_1(Mv_1)^{2/3} - \gamma_2(Mv_2)^{2/3}}{t_2 - t_1}$$

or

$$K = \frac{\gamma_1 \left(\frac{M}{d_1} \right)^{2/3} - \gamma_2 \left(\frac{M}{d_2} \right)^{2/3}}{t_2 - t_1} \quad \dots (1)$$

where, d_1 and d_2 are densities of the liquid at temperatures t_1° and t_2° , respectively.

Equation (1) is known as **Ramsay-Shield equation**. The value of K^* for most of the non-associated liquids is approximately equal to 2.12. But for associated liquids, the value of K is much lower than 2.12. If, however, the molecular weight is multiplied by a factor α , where α is greater than one, then a value of 2.12 is obtained for K . The factor α is known as **association factor** and depicts the number of times the mean molecular weight of a liquid is greater than the normal molecular weight. Thus, for associated liquids, we have,

$$\frac{\gamma_1 \left(\alpha \cdot \frac{M}{d_1} \right)^{2/3} - \gamma_2 \left(\alpha \cdot \frac{M}{d_2} \right)^{2/3}}{t_2 - t_1} = 2.12 \quad \dots (2)$$

From equation (1), we have,

$$\frac{\gamma_1 \left(\frac{M}{d_1} \right)^{2/3} - \gamma_2 \left(\frac{M}{d_2} \right)^{2/3}}{t_2 - t_1} = K \quad \dots (3)$$

Therefore, dividing equation (2) by (3), we get,

$$\alpha = \left(\frac{2.12}{K} \right)^{3/2} \quad \dots (4)$$

*K also gives the value of rate of change of molecular surface energy with temperature.

Thus, the degree of association of a liquid may be calculated from equation (4).

Procedure : The surface tension of ethyl alcohol is determined at two different temperatures, say at room temperature and at 50°C, by stalagmometer method, as usual. Then densities of ethyl alcohol are determined at the same two temperatures by means of a pycnometer.

Observations : Same sets of observations are taken as described in experiment 1. In this case, observations are noted at two temperatures, *i.e.*, at room temperature and at 50°C.

Calculations : The molecular surface energy at both the temperatures can be calculated by the formula, $\gamma \left(\frac{M}{d} \right)^{2/3}$, as we know all the unknown factors.

Similarly, the value of K is calculated by means of equation (3). Once the value of K is known, the value of association factor α , can be calculated by equation (4).

[**Note :** The surface tension and density of ethyl alcohol at two temperatures are calculated, as explained in preceding experiments.]

Result : The molecular surface energy = ...

Association factor = ...

Precautions : Same as described in preceding experiments.

OTHER METHODS FOR DETERMINING SURFACE TENSION

[I] du Nouy's Tensiometric or Torsion Balance Method

This method is very rapid as well as convenient. It is used more widely than any other method for determining the surface tension of a liquid specially in industrial laboratories. This method involves the measurement of the force required to raise a ring of platinum wire from the surface of the liquid with an angle of contact of 0°. The required force is determined by measuring the torsion of the wire of the torsion balance which is calibrated to measure to give the value of surface tension directly.

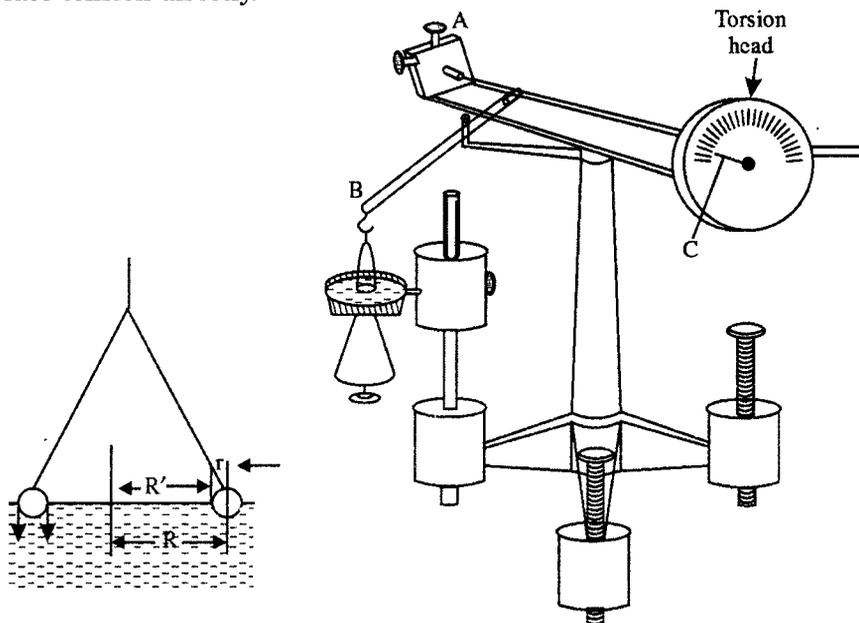


Fig. 7 : du Nouy's torsion balance

Suppose R' and r are the radii of the circular ring and the wire, respectively. When the ring is raised out of the liquid, it holds up a hollow cylinder of liquid with vertical walls of radii R' and $R' + 2r$ [see figure (7)]. The total force, F which is equal to the weight of the liquid (mg) suspended is given by,

$$F = mg = 2\pi \gamma R' + 2\pi \gamma (R' + 2r)$$

$$= 4\pi \gamma (R' + r) = 4\pi \gamma R$$

or
$$\gamma = F/4\pi R = mg/4\pi R \quad \dots (1)$$

where $R = R' + r =$ mean radius of the ring.

Let γ_1 and γ_2 be the surface tensions of the experimental liquid and the standard liquid and m_1 and m_2 be the respective weight forces to keep the beam in horizontal position, then

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1 g / 4\pi R}{m_2 g / 4\pi R} = \frac{m_1}{m_2} \quad \dots (2)$$

EXPERIMENT No. 10

Object : *To study the change of surface tension of a mixture of ethanol and water with composition by torsion balance method.*

Apparatus : Torsion balance, platinum ring, absolute ethanol etc.

Theory : As explained above.

Procedure : (A) **Calibration of the instrument**

Thoroughly clean the platinum wire with hot acid cleaning mixture, rinse with distilled water and heat it to red hot in a luminous flame. Avoid touching of the ring, hang it from the hook on the beam, B . Turn the knob till the pointer comes at zero of the scale and adjust the torsion of the wire with the help of a back screw A , so that the beam lies in a horizontal position. Now place a small weighed piece of paper on the ring and twist the wire until the beam is again horizontal. Record the reading of the pointer on the scale. Now put 50, 100, 200, 500 mg weights turn by turn and note the torsion angles (pointer readings on the scale) to bring the beam again in the horizontal position. Finally, plot a graph between the weights on the ring, including that of the piece of paper and the torsion angles. If the torsion of the wire is proportional to the torsion angles we will get a straight line. So, the force weight working on the beam can be read from this calibration curve simply by measuring the torsion angle.

(B) Method : Now remove the piece of paper and the weights from the ring and set the beam in horizontal position with the pointer resting at zero reading on the scale. Put a small amount of experimental liquid in a cleaned watch glass or shallow dish and place it on the platform meant for the purpose. Raise the platform slowly with the help of a lift screw till the liquid just touches the ring. The ring will be pulled down by surface tension force and the beam will tilt down. The knob is turned to twist the torsion wire to bring the beam in horizontal position and simultaneously lower the platform until the ring is torn from the surface. Note the position of the pointer on the scale when the ring jumps out of the liquid. The procedure is repeated several times till concordant readings are obtained.

Similarly, the torsion angles for pure water, absolute ethanol and 0.1, 0.05, 0.01, 0.005 and 0.001M aqueous ethanol solutions are determined by the above procedure. The temperature of the experiment is also noted.

Observations : Temperature of the experiment = ... °C

Radius of the ring = ... cm

Weight of the piece of paper = ... g

(1) For calibration of the instrument

S. No.	Weight on the ring (mg)	Torsion head reading (b)	Weight force (gram) (a)	Torsion angle per g ($b/a = y$)
1.	Paper	... deg		
2.	Paper + 50	... deg		
3.	Paper + 100	... deg		
4.	Paper + 200	... deg		
5.	Paper + 500	... deg		
				Mean = ...

Torsion angle per gram weight from the slope of the straight line, $y = \dots$

(2) For surface tension of the liquid

S. No.	Liquid	Torsion head reading, x (degree)	Weight force $m = x/y$ (g)	Surface tension $\gamma = \frac{mg}{4\pi R}$
	Water	...		
		...		
		...		
	Ethanol	...		
		...		
		...		

Calculations : From the pointer reading and the calibration curve calculate the weight force, F . Then calculate the surface tension of each liquid mixture by means of equation (1) or (2) (on page 140) and plot their values against concentration of ethanol.

Result : The change of surface tension of the mixture with concentration is studied as above.

Precautions : (i) The ring should be cleaned afresh before use for every new liquid.

(ii) The ring should remain flat and circular.

(iii) Laboratory air should be free from vapours of surface active substances.

[II] Jaeger's Maximum Bubble Pressure Method

Procedure and Theory : We know that to have a stream of air bubbles formed through a jet tube dipping in a liquid, we need to blow with some pressure. The minimum pressure required to form a continuous stream of air bubbles depends on several factors, *viz.*, the depth to which the jet end of the tube dips below the liquid surface, size of the opening of the jet and the surface tension of the liquid.

In case the radius of the jet opening is small, the air bubbles blown slowly out of it are *spheriecal* in shape. The formation of bubbles starts with a flat surface. At this stage, the excess pressure (Δp) of air inside the jet over the atmospheric

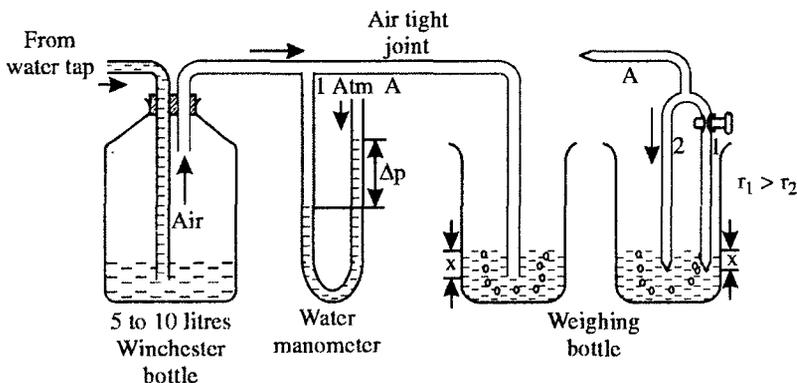


Fig. 8 : Jaeger's Method

pressure just equals the hydrostatic pressure of the liquid column of height h , where h is the depth below the liquid surface upto which the jet dips. As the excess pressure (Δp) increases, the flat air-liquid interface starts assuming a spherical shape and its radius begins to decrease from infinity value for the flat surface. The minimum radius of the air-liquid interface at the jet will equal the radius of the jet opening. The excess pressure (Δp), radius of curvature of the interface (R), surface tension (γ) of the liquid are related to each other by the following expression

$$\Delta p = \frac{2\gamma}{R} + hdg \quad \dots (1)$$

where d = density of the liquid

h = depth of jet opening below the liquid surface

g = acceleration due to gravity.

From equation (1), it is clear that smaller the value of R , greater will be the value of Δp and for a minimum value of R , the excess pressure of air inside the curved interface will have the maximum pressure. If the pressure of the air inside is further increased, the hemisphere of interface expands to assume a spherical shape. The radius R begins to increase, the need of excess pressure to maintain the interface becomes less and the air pressure built up inside tends to become less which causes the escape of air bubbles from the jet. Therefore, when the air bubbles begin to form a stream, radius of curvature of the interface, R just exceeds the radius of the hemispherical interface of the opening of the jet, r . So we can write,

$$\Delta p = \frac{2\gamma}{r} + hdg \quad \dots (2)$$

If we dip two jets of opening radii r_1 and r_2 in a liquid A to the same depth h , we can write from equation (2),

$$(\Delta p_A)_1 = \frac{2\gamma_A}{r_1} + hd_A g$$

$$(\Delta p_A)_2 = \frac{2\gamma_A}{r_2} + hd_A g$$

$$\therefore (\Delta p_A)_1 - (\Delta p_A)_2 = 2\gamma_A \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad \dots (3)$$

Similarly, for another liquid B, we have

$$(\Delta p_B)_1 - (\Delta p_B)_2 = 2\gamma_B \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad \dots (4)$$

Dividing equation (3) by (4), we get

$$\frac{\gamma_A}{\gamma_B} = \frac{(\Delta p_A)_1 - (\Delta p_A)_2}{(\Delta p_B)_1 - (\Delta p_B)_2} \quad \dots (5)$$

If γ_A is known, a measurement of $(\Delta p_A)_1$ and $(\Delta p_A)_2$ can give the value of the apparatus constant, $\left(\frac{1}{r_1} - \frac{1}{r_2} \right)$. In this way, the need for the measurement of h (which should be the same for both the jet tubes) and the densities of the liquids d_A and d_B disappears.

Sugden further modified the double jet method by getting the bubble formation at the jets by reducing the pressure on the surface of the liquid by using a suction pump instead of having the bubble formation by pushing out the air under pressure. In this method, the bubbles will be formed at the smaller jet only when the stop cock on the larger jet tube is closed.

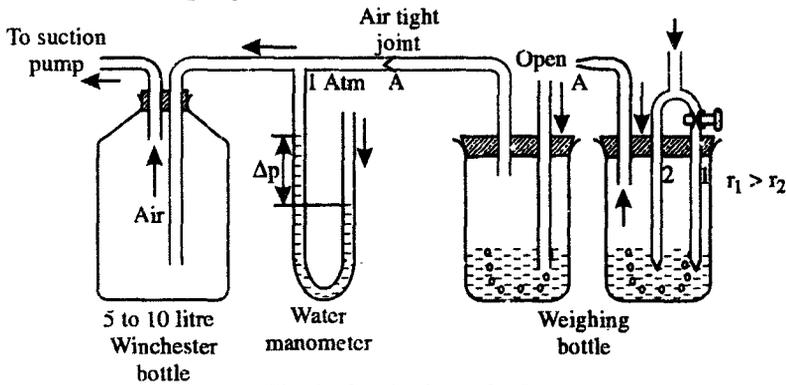


Fig. 9 : Sugden's method

Observations : Temperature, $t = \dots$ °C.

Surface tension of liquid A, $\gamma_A = \dots$ dyne/cm (From standard table)

S. No.	Liquid A		Liquid B	
	Δp_1 (cm)	Δp_2 (cm)	Δp_1 (cm)	Δp_2 (cm)
1.
2.
3.
Mean (cm)	

Calculations : The value of γ_B can be calculated from either equation (2) or (5).

Result : The surface tension of the unknown liquid = ... dyne/cm.

[III] Wettable Blade Method

For measuring surface tension of pure liquids and solutions, wettable blade method is used which is an equilibrium or static method. The wettable blade is a sand blasted thin platinum plate about 2 cm × 2 cm in size. It can be suspended from a torsion balance (like du Nouy's balance) or a torsion balance using a wire. When it is made just to touch the surface of a liquid, the liquid wets the blade and tends to spread over it. The blade is pulled into the liquid because of surface tension force. An external force is then applied to the suspension wire from the torsion balance or by putting weights on the weight pan of the balance till the blade is brought to its original position of touching the liquid surface. When this equilibrium is attained we can say,

$$\gamma = \frac{\text{External force}}{\text{Contact length}}$$

An advantage of this method is that no correction factor has to be applied.

Procedure : First clean the blade. Suspend the blade and adjust the balance to counterpoise the weight of the blade. Raise the sample till the plate just touches the bottom edge of the blade. The blade is immediately pulled into the liquid. Adjust the balance to bring the original position of the blade. Measure the thickness (t) and breadth (b) of the blade. The contact length is then $(2t + 2b)$.

Precautions : The blade should be clean. For this purpose, the blade is flamed. It may be dipped in concentrated HNO_3 before flaming. The process may be repeated, if necessary.

EXPERIMENT No. 11

Object : To find the surface excess or molar surface area by using Gibb's adsorption equation.

Apparatus : Same as used in wettable blade method.

Theory and Procedure : Gibb's adsorption equation is given by,

$$\Gamma = -\frac{c}{RT} \cdot \frac{d\gamma}{dc} = -\frac{1}{RT} \cdot \frac{d\gamma}{d \ln c}$$

where Γ = surface excess, c = concentration in moles per litre, γ = surface tension.

Surface tension is measured at a series of different concentrations. A graph is then plotted between γ (ordinate) and $\log c$ (abscissa). From the slope of the graph $[d\gamma/d \log c]$ is obtained at each concentration and Γ can be calculated. Since Γ has the dimensions of mole per square centimetre, $1/\Gamma$ is the area per mole of solute or molar surface area. The function $\ln c$ can be easily replaced by $2.303 \log c$.

EXPERIMENT No. 12

Object : To determine the critical micelle concentration of a soap by surface tension measurement.

Theory : Addition of soaps and other surface active agents lowers the surface tension of water to an appreciable extent. If the solution is not too dilute, the surface tension of the mixture varies directly with logarithm of concentration of the added substance. However, in case of soap and other substances undergoing association, the curve shows a break which corresponds to critical micelle concentration.

Procedure : Prepare a 0.2 M solution (stock solution) of potassium laurate (soap) of molecular weight 238.4 in distilled water. Then, by successive dilution of the stock solution, prepare 0.1, 0.05, 0.025, 0.02, 0.01, 0.001 M solutions of potassium laurate.

Determine the surface tension of each of the above solutions by drop fall method.

Calculations : Now plot a curve between surface tension (ordinate) and logarithm of the concentration of potassium laurate (abscissa). A break in the curve so obtained gives the critical micelle concentration of the soap.

Result : The critical micelle concentration of soap. =

EXPERIMENT No. 13

Object : To study the variation of surface tension of solutions of *n*-propyl alcohol with concentration and also determine the limiting cross-sectional area of alcohol molecule.

Theory : *n*-Propyl alcohol is a surface active substance, *i.e.*, it lowers the surface tension of water. The concentration of the solute (alcohol) will, therefore, be greater on the surface than in the bulk of the solution. The surface excess concentration is given by Gibb's adsorption isotherm.

$$\Gamma = - \frac{c}{RT} \cdot \frac{d\gamma}{dc} = \frac{1}{2.303 RT} \cdot \frac{d\gamma}{d \log c} \quad \dots (1)$$

where Γ is the surface excess concentration per unit area of the surface in a solution of concentration, c (mol dm^{-3}) and surface tension γ .

Procedure : Prepare 500 cm^3 2M aqueous solution (stock solution) of alcohol (60 g/500 cm^3 of solution). Prepare 1.75, 1.50, 1.25, 1.00, 0.75, 0.50, 0.25 and 0.120 M solutions (dilute respectively 87.5, 75, 62.5, 50, 37.5, 25, 12.5 and 6.0 cm^3 of the stock solution to 100 cm^3) by quantitatively diluting the stock solution.

Determine the surface tension of pure alcohol and each of the solutions by the differential capillary rise method. Also determine the densities of the solutions and alcohol using density bottle or pycnometer. For very dilute solutions the density of water may be taken as unity.

Calculations : (i) Plot values of surface tension, γ (ordinate) against $\log c$ (abscissa). Draw the tangents to these curves at different concentrations and determine the values of $d\gamma/dc$ and $d\gamma/d \log c$ at these concentrations by measuring their slopes.

(ii) Calculate the surface excess concentration, Γ , at each concentration using equation (1) ($R = 8.314 \times 10^7$ erg degree $^{-1}$ mol $^{-1}$).

(iii) Plot the values of Γ (ordinate) against c (abscissa) and determine the limiting value of Γ_{max} at higher concentrations. This limiting value gives the number of moles of alcohol per cm^2 of surface. The area of the surface occupied by

1 mole of the solute (alcohol) will be $1/\Gamma_{\max} N \text{ cm}^2$ or $10^{16}/\Gamma_{\max} N \text{ \AA}^2$ where N is Avogadro's number. This gives the limiting cross-sectional area of the alcohol molecule.

Result : The limiting cross-sectional area of alcohol molecule =

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 14

Object : To show that surface activity of alcohol increases with chain length.

The aqueous solutions of many substances, even when very dilute, have surface free energy very much less than that of pure water. Substances producing such an effect are known as *surface active or capillary active substances*.

Prepare 0.2 M solution of each alcohol by dissolving in proportions 2.3 ml of ethyl; 3.6 ml of *n*-butyl; 4.4 ml of amyl in 200 ml of distilled water. Find out the molecular surface energy for each alcohol, which is found to decrease as we move from ethyl to amyl alcohol.

On the same lines, we can find the variation of surface energy of an alcohol with concentration. Plot the necessary curve. The experiments should proceed from the more dilute to the concentrated solutions.

EXPERIMENT No. 15

Object : To determine the interfacial tension between benzene and water at room temperature and test the validity of Antonoff's rule.

Theory : Interfacial tension is determined by estimating the drop weight of the heavier liquid when the dropping tip is dipped in the lighter liquid, say benzene in this case. It is convenient to estimate the weight of the drop from observations on its volume than from direct weighing.

Procedure : We take a 10 ml graduated tube, at the upper end of which a valve is arranged, to control the flow of liquid. The valve is so adjusted that a drop is formed in not less than 20 sec. The dropping tip dips below benzene contained in a beaker. After setting the dropping rate, watch the water level falling in the tube, so as to be ready to read the level just as the drop falls. Read the level again just after 5–10 drops have fallen. Note the temperature of benzene in order to find its density from the tables.

$$\begin{aligned} \text{Volume of water for 10 drops in benzene} &= V \text{ ml} \\ \therefore \text{Volume of one drop} &= \frac{V}{10} \text{ ml} = \frac{V}{10} \text{ g} \end{aligned}$$

$$\text{Density of benzene at } t^\circ\text{C} = d_1$$

$$\text{Weight of } \frac{V}{10} \text{ ml benzene} = m_1$$

$$\text{Weight of water drop in benzene} = \left(\frac{V}{10} - m_1 \right) \text{ g}$$

$$\text{Suppose the drop weight (i.e., weight of one drop) for water in air} = m_2 \text{ g}$$

$$\therefore \text{Interfacial tension between benzene and water}$$

$$\gamma_{bw} = \frac{\left(\frac{V}{10} - m_1\right)}{m_2} \cdot \gamma$$

where, γ = surface tension of water at $t^\circ\text{C}$.

[**Note :** Validity of Antonoff's rule

Show that, $\gamma_{bw} \approx \gamma_b - \gamma_w$

Similarly, we can find the interfacial tension of benzene-water in the presence of an alcohol, say amyl alcohol].

EXPERIMENT No. 16

Object : *To compare the cleansing powers of two samples of detergents supplied to you.*

Cleansing power of soaps and detergents can be determined by the reduction in surface tension of water caused by them. Greater the reduction, more will be the cleansing capacity of detergent. For comparing the cleansing power of detergents, we make solutions of equal weight of these detergents in a fixed volume of water.

The weighed quantity of the detergent is added to pre-heated pre-measured volume of water in a beaker. Solution is then made by gentle stirring by a rod and it is then cooled. The solution is allowed to stand for a while for insoluble impurities to settle down. It may be filtered hot, if necessary. The solution is filled in the stalagmometer by very gentle suction and foam formation is carefully avoided.

As soaps form gels in water at room temperature even at low concentration of about 5%, these will then not flow from capillary tubes. So, to avoid this, the measurements should be made at temperature of 40°C or above or concentrations may be made in the range of 0.1 to 0.5%.

The solution should be free from suspended particles which will clog the capillary tubes. The solution is allowed to stand for a short time so that insoluble impurities may settle down. It may be filtered hot, if necessary.

As the concentrations of solutions are low, their density will almost be the same as that of water. Thus,

$$\frac{\gamma_1}{\gamma_2} = \frac{d_1 n_2}{d_2 n_1}$$

So, the surface tension may be compared in terms of number of drops for a fixed volume. Larger the number of drops, smaller will be the surface tension of the solution and better will be the cleansing action of the soap in solution.



9

VAPOUR PRESSURE OF LIQUIDS

When a liquid is in equilibrium with its vapour at a particular temperature, the vapour exerts certain pressure, which is known as the **vapour pressure** of the liquid at that specified temperature.

The vapour pressure of a liquid increases with temperature and the temperature at which its value becomes equal to atmospheric pressure is known as the **boiling point of the liquid**. The relation between vapour pressure (p) and temperature (T) is expressed by the following equation :

$$\log p = A - \frac{B}{T} \quad \dots (1)$$

where, A and B are constants for the given liquid. Therefore, if values of $\log p$ (ordinate) are plotted against $1/T$ (abscissa), a straight line is obtained with a slope equal to $-B$ and intercept on the ordinate will be A .

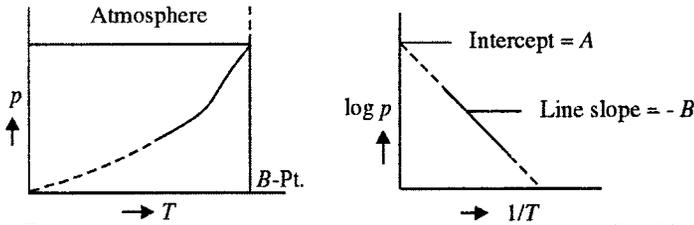


Fig 1 : Effect of temperature on vapour pressure of a liquid

The boiling point and pressure are related through Clausius-Clapeyron equation, given by,

$$\frac{d \log p}{dT} = \frac{\Delta H_v}{RT^2} \quad \dots (2)$$

where, ΔH_v is the latent heat of vaporisation per mole at absolute temperature T and p is the vapour pressure of the liquid at temperature T . Integrating equation (2), we get,

$$\int_{p_1}^{p_2} d \log p = \int_{T_1}^{T_2} \frac{\Delta H_v}{RT^2} dT$$

On solving within the given limits, we get,

$$\log_{10} \frac{p_2}{p_1} = \frac{2.303 \Delta H_v}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots (3)$$

where, p_1 and p_2 are the vapour pressure at temperature T_1 and T_2 . The value of R may be put equal to 1.987 calories or 8.314 joule.

Measurement of Vapour Pressure : Two methods are generally used for determining the vapour pressure of liquids.

(1) *Static method* : This method consists in evaporating a liquid in Torrcillian vacuum over a mercury column at a specified temperature. The maximum depression of mercury column thus produced by the saturated vapour is noted, which equals the vapour pressure of the liquid evaporated.

(2) *Dynamic method* : This method consists in progressively reducing the pressure over the surface of the liquid, till it begins to boil at the desired temperature. The external pressure thus applied equals the vapour pressure of the liquid.

EXPERIMENT No. 1

Object : *To determine the vapour pressure of a pure liquid, say benzene, at a series of temperatures and also to determine the heat of vaporisation of the liquid.*

Apparatus : Ordinary distillation apparatus, vacuum pump, manometer etc.

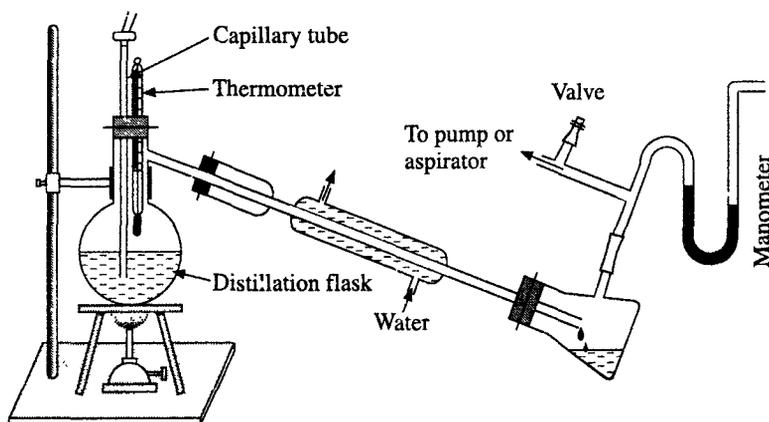


Fig. 2 : Distillation apparatus

Theory : Vapour pressure of volatile liquids over a range of temperatures can be determined by means of an ordinary distillation unit. A vacuum pump used is for evacuating unit. For detailed account see fig. (2).

Procedure : The apparatus is as shown in figure (2). Take about 200 ml of the liquid in a distillation flask and fit it with a thermometer and a fine capillary which dips in the liquid. (*Capillary is used to avoid bumping*). Now, keep the valve closed and evacuate the system as far as possible till the boiling of the liquid starts. Stop evacuating and allow some air to enter the system by opening the valve a little. Now close the valve again.

Heat the liquid very slowly, till the liquid begins to boil and distils over at a rate of 1 drop/second. Note the steady temperature readings as well as manometer readings. Now, slightly raise the pressure by opening the valve a little. Heat the liquid further so that it just boils and distils over. Note the temperature and manometer reading. Similarly, the boiling points of the liquid are noted at a series of different pressures. Finally, note the barometric pressure also.

Observations : Note the pressure and boiling points of the liquid in a tabular form.

Calculations : The difference between the barometric pressure and the pressure difference on the manometer gives the vapour pressure (p) of the liquid at the equilibrium temperature. Plot $\log p$ (Y -axis) against $1/T$ (X -axis) and calculate the mean latent heat of vaporisation (ΔH_v) over a range of temperatures T_1 and T_2 using equation (3).

Result : The heat of vaporisation at ... °C is ... mm.

Precautions : (i) Open the valve very slowly.

(ii) Note the temperature reading only when it becomes constant.

EXPERIMENT No. 2

Object : To determine the vapour pressure of water at different temperatures using Smith and Menzies apparatus.

Apparatus : Smith and Menzies apparatus etc.

Description of the apparatus : Smith and Menzies method is useful when only a small quantity of a liquid is available. The apparatus is as shown in figure (3). It consists of a bulb tube B of the shape shown, which is partly filled with the

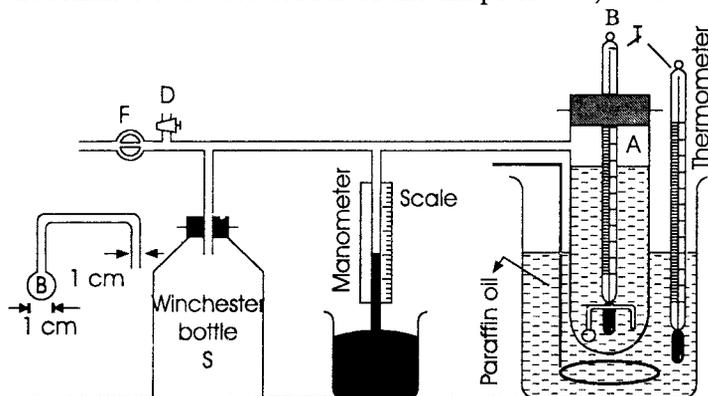


Fig. 3 : Smith and Menzies apparatus

liquid under examination by alternate heating and cooling. The bulb B is attached to a thermometer T by means of a thread. It is then placed in a hard glass boiling tube A , which is filled with high boiling point paraffin oil. The tube A is placed in a larger vessel of a suitable liquid (water, glycerine etc.) having a stirrer and a thermometer. The pressure on the surface of the liquid in A is adjusted by connecting the tube A to an exhaust pump, manometer and a pressure stabilizer (a large Winchester bottle, S).

Procedure : Fill the bulb B to $2/3$ rd with water and connect it to a thermometer T by means of a thread. Fill the tube A with paraffin oil and the outer bath with water. Test the apparatus for leakage, if any. Then admit some air through valve D . Raise the temperature of the bath to 30°C . Stir the bath liquid well, so that it attains a steady temperature. Wait till the temperature in tube A becomes constant. Now reduce the pressure in the apparatus by opening the stopcock F and connect it to the exhaust pump. As the pressure falls, at first air bubbles

and later bubbles of vapour come from the bulb *B* due to the boiling of the liquid under reduced pressure. Now close the stop cock *F* and allow the liquid to boil in the bulb tube for a short duration, so that air bubbles are completely removed from the bulb. Now open the stop cock *D* so that air enters the apparatus slowly till the bubbles just cease to come from the bulb *B*. Now close the stop cock *D* and note the temperature on thermometer *T* and manometer reading. The vapour pressure of the liquid at this recorded temperature is given by barometric pressure–manometer reading.

Now measure the vapour pressure of water from 10°C to 85°C by raising the temperature of the bath in steps.

Observations : Barometer reading = P mm Hg

Temperature ($T^{\circ}\text{C}$)	25°	35°	45°	55°	65°	75°	85°
Manometer reading (p mm)							
Vapour pressure ($P - p$ mm Hg)							

Calculations : The values of $\log p$ (ordinate) are plotted against $1/T$ (abscissa). A straight line will be obtained given by the expression,

$$\log p = A - B/T$$

Extrapolate the curve and find the temperature at which $p = 760$ mm. and compare this value with the known standard boiling point of water.

Result : The vapour pressures of water at different temperatures are ...

EXPERIMENT No. 3

Object : To determine the vapour pressure of benzene at different temperatures by Ramsay–Young apparatus. Also determine latent heat of vaporisation.

Apparatus : Ramsay–Young apparatus etc.

Description of the apparatus : It is shown in figure (4). It consists of a boiling tube with fairly strong walls, provided with a side tube. This tube is fitted with a rubber cork having two holes for inserting a thermometer *T* and a dropping funnel. The thermometer is covered with a thin pad of cotton wool tied on it with

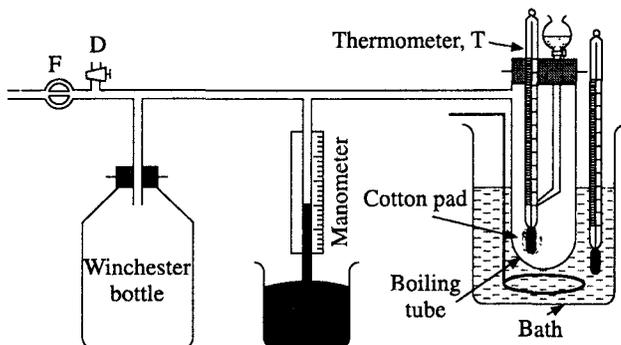


Fig. 4 : Ramsay–Young apparatus

a thread. The stem of dropping funnel is bent in such a way that it just touches the cotton pad or wool. The boiling tube is then placed in a bath containing water,

glycerine etc. Another stirrer and thermometer are dipped in the outer bath as shown. The side tube is connected to a vacuum pump and in the vacuum line a manometer and Winchester bottle are inserted. The Winchester bottle minimises the air leak and by its bulk increases the stability of pressure. Stop cock *D* connected to the side tube before the vacuum line, allows air to enter the apparatus slowly. Another stop cock *F* is connected to a vacuum pump.

To ascertain whether the apparatus is air tight, turn the stop cock *F* so that the apparatus is connected to the vacuum pump and can be exhausted. After opening the pump for a short time, close the stop cock *F*. If there is no movement of mercury in the manometer, the apparatus is taken to be air tight.

Procedure : When the apparatus is air tight, fill the bath with water (or any other suitable liquid) and then take the experimental liquid in the dropping funnel. Adjust the pressure in the apparatus to some low value such as 20–30 mm Hg by operating the vacuum pump. The height of Hg in the manometer should stand at 20–30 mm. Now allow a few drops of the experimental liquid out of the dropping funnel on to the cotton pad or wool surrounding the thermometer *T*. As the liquid evaporates, the temperature falls and eventually reaches a steady value, say T_1° . The vapour pressure of the liquid at T_1° , will thus be equal to the pressure of air in the apparatus. Note the thermometer and manometer readings. Thus,

Vapour pressure at $T_1^\circ = (\text{Barometer reading, } P - \text{Manometer reading, } p_1)$.

Now, some air is allowed to enter the apparatus slowly by opening the stop cock *D*, so that air pressure inside the apparatus reaches a somewhat higher value, say 50 mm Hg. This change causes the reading of thermometer *T* to change. More drops of the liquid are then allowed to fall out of the dropping funnel, so that they fall on the cotton pad or wool. The new temperature T_2° thus obtained is again noted. The new readings of thermometer and manometer are also noted. Thus,

Vapour pressure at $T_2^\circ = (\text{Barometer reading, } P - \text{Manometer reading, } p_2)$.

Similarly, temperature for other values of vapour pressure in steps of 80 mm to 70 mm can also be noted.

Observation : Barometric pressure = P mm Hg

Temperature (T K)
Manometer reading (p mm Hg)
Vapour pressure ($P - p$ mm Hg)

Calculations : Same as described in experiment 2. The latent heat of vapourisation is calculated from equation

$$\log_{10} \frac{p_2}{p_1} = \frac{2.303 \Delta H_v}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Plot a graph of logarithms of vapour pressure ($\log p$) against the reciprocals of the Kelvin scale temperature, T . A straight line will be obtained represented by the equation,

$$\log p = A - \frac{B}{T}$$

Result : The vapour pressures of the liquid at different temperatures are shown in the above table.

EXPERIMENT No. 4

Object : To study the variation of vapour pressure of a liquid (benzene) using an isoteniscope.

Apparatus : Isoteniscope, filter pump or vacuum pump, manometer, glass sided thermostat,

Theory : An isoteniscope consists of a bulb A, about 2 cm in diameter connected to a small U-tube with limbs about 3-4 cm long. It is connected to an evacuating device and a manometer, M, through a joint valve C. A large Winchester bottle D, is also connected [fig. (5)], which acts as a buffer to stabilise the pressure. The isoteniscope is put in a bath, preferably in a thermostat.

Procedure : Fill 2/3 of the bulb A and the U-tube with the experimental liquid and assemble the apparatus as shown in figure (5). For testing the apparatus for any leakage, evacuate it by connecting through tap, T to the vacuum pump. After operating the pump for a while turn off the tap. If the manometer reading does not change with time, it means that the apparatus is air tight.

Put the isoteniscope in an ice bath at nearly 0°C. Evacuate the system so that the liquid in the bulb, A starts boiling and all the air is displaced from the isoteniscope. Turn off the tap. When the isoteniscope acquires a constant temperature of the bath, open the tap (T) slowly to allow the air to enter the system so that the liquid levels in U-tube are the same. Make final adjustments of the pressure very carefully. Record the manometer readings and the temperature of the bath. Ensure the total removal of the air by repeating the evacuation process

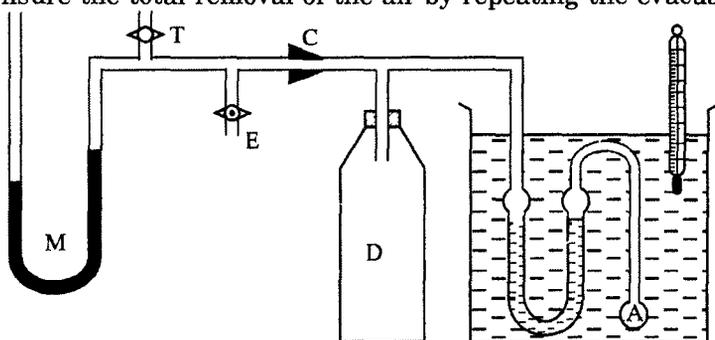


Fig. 5 : Isoteniscope

and allowing the air to enter while keeping the temperature of the bath constant. If all the air has been removed, then concordant readings of the manometer with liquid levels in U-tube at the same heights should be recorded.

Raise the temperature of the bath and when the liquid has acquired the new temperature, admit air again carefully by opening the tap a little till the liquid levels in the U-tube remain constant. Note the pressure difference of manometer and the temperature of the bath. Make further recordings at every 5°C upto the boiling point of the liquid (~ 80°C for benzene). Finally record the barometric pressure.

Calculations & Result : Same as in preceding experiments.

1. SOLUTIONS OF SOLIDS IN LIQUIDS

When a small amount of sodium chloride is placed in a beaker filled with water at constant temperature and stirred or left to itself, it will slowly disappear; more rapidly if it is stirred than when left alone. If we add further quantities of sodium chloride, it will also disappear. Thus, sodium chloride is said to have dissolved and to have formed a **solution**.

An indefinite quantity of sodium chloride will not dissolve in water at a particular temperature, *i.e.*, after a certain amount has dissolved in water, further addition will remain undissolved. When this state is reached, water is said to be **saturated** and the solution is known as **saturated solution**. Saturated solution is thus seen to be in equilibrium at the temperature at which it is saturated, with the undissolved substance. On increasing the temperature, more sodium chloride will dissolve until the solution becomes saturated at the higher temperature.

While dealing with solutions, one comes across with two terms, *viz.*,

(i) *The substance which is dissolved* which, in the above example, is sodium chloride. This substance is known as **solute**.

(ii) *The substance in which the solute dissolves* which, in the above example, is water. This is known as **solvent**.

The solubility is dependent on the nature of both solute and solvent and can be defined as, '***the number of grams of the substance which will dissolve in 100 grams of the solvent at a particular temperature***'. Sometimes, solubility is also defined as, '***the number of grams of the solute contained in 100 grams of the saturated solution at a particular temperature***'.

The solubility of a solute depends upon temperature and pressure. The dependence of solubility on pressure is so small that the pressure is almost always ignored while making solubility measurements. The solubility of most substances increases with an increase of temperature, but the dependence of solubility on temperature is not the same for any two substances or solvents. In case of some substances, the solubility increases rapidly with temperature, while in some other case it increases but slowly. For example, at 0°C, 115 gram of silver nitrate will dissolve in 100 gram of water, while at 100°C, 910 grams dissolve in 100 gm water.

The change in solubility with changing temperature is usually expressed by means of a **solubility curve**, which is obtained by plotting the solubilities as ordinate against temperature as abscissa, and drawing a curve through the points. Several solubility curves for a number of substances are shown in fig. (1).

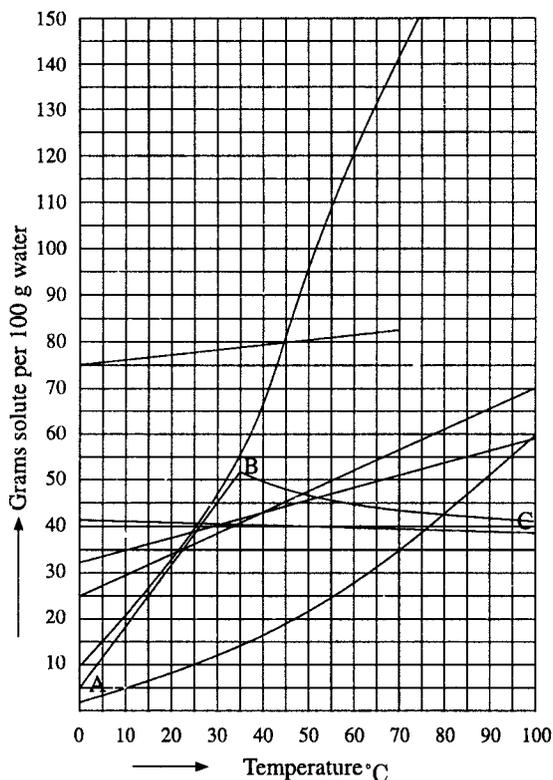


Fig. 1 : Solubility curves

The solubility of some substances decreases as the temperature is increased, *e.g.*, at 0°C , 1.539 gram of lithium carbonate dissolves in 100 grams of water, whilst at 100°C , only 0.728 grams of the salt dissolves in the same quantity of water. In case of some substances, the solubility first decreases with increasing temperature but then increases after a certain temperature, *e.g.*, the solubility of sodium sulphate increases upto 32.4°C and then decreases beyond 32.4°C .

Ordinarily, when a saturated solution of a solid substance is cooled, some of the substance separates generally in the form of crystals, because the solubility decreases as the temperature decreases. It sometimes happens that on cooling a saturated solution very carefully and in the absence of any undissolved solute, there is no separation of the dissolved substance. When this occurs, the cold solution is said to be **super-saturated**, *i.e.*, it contains more dissolved substance than the quantity which corresponds with the solubility. Such a solution is, however, unstable and if the smallest crystal of the solute is added to it, there is an immediate separation of the solute.

The solubility of a substance in liquid is often affected by the presence of a second solute, *e.g.*, presence of hydrochloric acid reduces the solubility of sodium chloride and barium chloride in water; alcohol reduces the solubility of substances in water.

Determination of Solubility : For the determination of solubility of any solute, it is important to prepare a saturated solution at the desired temperature.

Preparation of saturated solution : A saturated solution can be prepared by either of the following two methods :

(a) In the first method, the solute is first brought in contact with the solvent at a particular temperature and the solute is added till no more of it dissolves. It is, however, a time consuming method.

(b) The second method is based on the fact, that usually solubility of a substance increases with temperature. For example, if we are required to prepare a saturated solution at 25°C, then the solvent is heated to a higher temperature, say 35–40°C and the substance is dissolved in it which is in excess. The amount present in the solution at a higher temperature is more than sufficient to saturate it at a higher temperature. The solution is cooled and the solid begins to crystallise out. At 25°C, the supernatant liquid is taken and is assumed to be saturated with the solid. This method is usually employed in actual practice.

(1) Evaporation method for determining solubility :

This method is generally used for those substances which do not decompose at a temperature 10–20°C higher than the boiling point of the solvent. In this method, a suitable solvent at the required temperature is weighed in a silica or porcelain dish and the solution is evaporated to dryness first on a wire gauge and then on a water bath and finally in an oven to a constant weight. In this way, the amount of the solid present in a definite quantity of the saturated solution and so in a known quantity of the solvent can be determined. Now the solubility can be calculated.

(2) Gravimetric method for determining solubility :

It is usually followed in the case of salts which are stable at temperatures 10 to 15°C higher than the boiling point of the solvent and for those substances which react with suitable reagents in solution to form sparingly soluble product. This method consists in evaporating a weighed amount of the solution. A saturated solution is prepared at a particular temperature and weighed. It is then heated till whole of the solvent is evaporated. The residue is again weighed. From this, we can calculate the number of grams of solute present in 100 grams of the solvent.

(3) Volumetric method for determining solubility :

It is generally applied to determine the solubility of organic acids and bases. A saturated solution of the acid is first prepared at a desired temperature. A definite volume of the saturated solution is then titrated against a standard solution of an alkali, from which we can calculate the solubility of the solute.

EXPERIMENT No. 1

Object : To determine the solubility of a given salt at room temperature and also to draw its solubility curve.

Apparatus : Thermostat, beakers, stirrer, thermometer etc.

Theory : The solubility of salt is determined by preparing its saturated solution at a number of temperatures and then a curve is plotted taking the solubility as ordinate and temperature as abscissa.

Procedure : Suppose the solubility of KCl is to be determined. Take about 50 ml of distilled water in a beaker and add to it some amount of the given salt (KCl)

and stir the contents. Now heat the solution to about 85–90° and go on adding further amount of the salt. **Please note that the salt should be in excess at 85–90°C.** Now cool the solution and as the temperature falls to say 80°C, pipette out about 4–5 ml of the supernatant liquid quickly and transfer it to a previously weighed beaker or watch glass. Then again pipette out about 4–5 ml of the supernatant liquid, when the temperature falls to 70°C and again transfer it to a previously weighed another beaker or watch glass. Repeat the above process at temperatures 60°, 50°, 40°, 30°C and room temperature (*The solution should be cooled in a larger beaker containing water*).

Now weigh each beaker or watch glass. Dry the solution in an electric oven at 120°C or on a water bath, till whole of water evaporates. When only dry residue of the solid is left behind, weigh all the beakers or watch glasses again.

S. N.	Temperature (°C)	Weight of watch glass (g)	Weight of watch glass + solution (g)	Weight of watch glass + residue (g)	Weight of residue (g)	Weight of water (g)
1.	80°	a_1	b_1	c_1	$c_1 - a_1$	$b_1 - c_1$
2.	70°	a_2	b_2	c_2	$c_2 - a_2$	$b_2 - c_2$
3.	60°	a_3	b_3	c_3	$c_3 - a_3$	$b_3 - c_3$
4.	50°	a_4	b_4	c_4	$c_4 - a_4$	$b_4 - c_4$
5.	40°	a_5	b_5	c_5	$c_5 - a_5$	$b_5 - c_5$
6.	30°	a_6	b_6	c_6	$c_6 - a_6$	$b_6 - c_6$
7.	Room temperature	a_7	b_7	c_7	$c_7 - a_7$	$b_7 - c_7$

Calculations : Solubility of the given salt in 100 g of water at:

$$80^\circ\text{C} = \frac{c_1 - a_1}{b_1 - c_1} \times 100$$

$$70^\circ\text{C} = \frac{c_2 - a_2}{b_2 - c_2} \times 100$$

.....
.....

$$30^\circ\text{C} = \frac{c_6 - a_6}{b_6 - c_6} \times 100$$

A curve is plotted with solubility as ordinate and temperature as abscissa and on joining the points, we get the solubility curve.

Result : Solubility of the given salt at room temperature = ...%.

Precautions : (i) While pipetting out, only the supernatant liquid should be taken out.

(ii) To ensure complete evaporation of the solvent repeated weighing and drying is done till the weight is constant.

(iii) While pipetting hot solutions, usually small crystals separate on the surface of the liquid, which get into the pipette. To avoid this, use a pipette the tip of which is tied a piece of dry filter paper.

(iv) The pipette should be warmed by sucking hot water repeatedly at that temperature at which the measurement is to be made, otherwise the solute will deposit at the cold wall of the pipette as soon as it comes in contact with the pipette.

EXPERIMENT No. 2

Object : To find the heat of solution of a substance, say oxalic acid by solubility method.

Apparatus : Same as in preceding experiment.

Theory : The method of measuring the heat of solution by solubility method is based on the application of van't Hoff equation (1) to solubility of a solute at two different temperatures.

$$\frac{d \log S}{dT} = \frac{\Delta H}{RT^2} \quad \dots (1)$$

where, S is the solubility of the solute in 1000 gram of solvent, ΔH is the heat of solution and T is the absolute temperature.

Assuming ΔH to be independent of temperature, we can write,

$$\int_{S_1}^{S_2} d \log S = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT$$

or
$$\log_e S_2 - \log_e S_1 = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or
$$\log_{10} S_2 - \log_{10} S_1 = \frac{\Delta H}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad \dots (2)$$

Hence, by determining the solubilities S_1 and S_2 at two different temperatures T_1 and T_2 , we can calculate the heat of solution, ΔH from equation (2).

Procedure : The solubilities of oxalic acid are determined at two different temperatures, say 30° and 45°C, exactly on the same lines as described in experiment no. 1.

Observations : Same sets of observations are taken as in experiment no. 1.

Calculations : The solubilities of oxalic acid in gram per 100 gram of water at 30°C and 45°C are calculated on the same lines as described in experiment no. 1.

Suppose on calculation the two solubilities are s_1 and s_2 at two temperatures $T_1^\circ\text{C}$ and $T_2^\circ\text{C}$ [30°C and 45°C in this case]. Then these values are converted into solubilities in mole per 1000 gram of water as follows :

$$S_1 \text{ (mole per 1000 gram of water)} = \frac{s_1 \times 1000}{m_1 \times 100}, \text{ at } T_1^\circ\text{C}$$

$$S_2 \text{ (mole per 1000 gram of water)} = \frac{s_2 \times 1000}{m_1 \times 100}, \text{ at } T_2^\circ\text{C}$$

(m_1 is the molecular weight of the solute which is equal to 126.0 in this case).

Knowing the values of S_1 and S_2 at two different temperatures ($T_1 + 273$) K and ($T_2 + 273$) K, we can calculate the heat of solution (ΔH) of oxalic acid from equation (2).

Result : The heat of solution of oxalic acid = ... cal. per mole.

Precautions : Same as in preceding experiment.

EXPERIMENT No. 3

Object : To determine the solubility of an organic acid, say benzoic acid at 40°C and at a temperature lower than the room temperature. Also obtain the heat of solution of benzoic acid.

Apparatus : Pipette, beakers, burette, conical flasks, thermometer etc.

Theory : A saturated solution of the acid is first prepared slightly above 40°, *i.e.*, at 50–60°C. The solution is then cooled to 40°C and a definite volume of it is titrated against a standard solution of an alkali, say sodium hydroxide.

A saturated solution is also prepared at room temperature and its temperature is lowered by surrounding the beaker containing the solution with ice. When the temperature falls to the desired value, a known volume of the solution is pipetted out and titrated against a standard solution of alkali.

Procedure : Take about 25 ml distilled water in a beaker and heat it to about 55–60°C. Prepare a saturated solution of benzoic acid at this temperature by continuous stirring of the solution. Allow the solution to cool gradually. As soon as the temperature falls to 40°C, pipette out 10 ml of the solution in a conical flask. Now titrate this solution against $N/50$ NaOH, using phenolphthalein as an indicator.

For measuring the solubility at a temperature lower than the room temperature (say at 10°C), prepare a saturated solution of benzoic acid at room temperature in about 50 ml of distilled water. To lower the temperature, the beaker containing the solution is surrounded with ice pieces contained in a bigger beaker. When the required temperature is reached, *i.e.*, 10°C, pipette out about 25 ml of the supernatant liquid in a clean beaker (the tip of the pipette should be tied with a filter paper). Then take 10 ml of this solution in a conical flask and titrate it against $N/50$ NaOH, using phenolphthalein as an indicator. Repeat titration for concordance. At temperatures below room temperature the pipette need not be washed and dried between titrations.

Observations :

S.No.	Temperature (°C)	Volume of $\frac{N}{50}$ NaOH required by 10 ml of the solution (ml)	Normality of the solution
1.	40°	v_1	$\frac{Nv_1}{50 \times 10}$
2.	10°	v_2	$\frac{Nv_2}{50 \times 10}$

Calculations : (i) *Solubility at 40°C,*

From normality equation, we have,

$$N_1 V_2 = N_2 V_2$$

Solution Alkali

or
$$N_1 \times 10 = \frac{N}{50} \times v_1$$

or
$$N_1 = \frac{N \times v_1}{50 \times 10}$$

Amount of benzoic acid per 100 gram of water, *i.e.*, solubility at 40°C.

$$= \frac{v_1 \times 122 \times 100}{50 \times 10 \times 1000} \text{ g (Eq. wt. of benzoic acid = 122)}$$

(ii) *Solubility at 10°C.*

Similarly, we can calculate the amount of benzoic acid per 100 grams of water, *i.e.*, solubility at 10°C

$$= \frac{v_2 \times 122 \times 100}{50 \times 10 \times 1000}$$

Calculate the heat of solution ΔH by using equation (2) [cf. experiment 2]

Result : The solubility of benzoic acid at 40°C is ...%, while at 10°C it is ...%.
Heat of solution of benzoic acid = ... cal/mole.

Precautions : Same as in preceding experiment.

EXPERIMENT No. 4

Object : *To determine the solubility product of Ca(OH)₂ at room temperature.*

Apparatus and Chemicals : Cork fitted conical flasks (250 ml), 100 ml graduated flasks, Pipettes of 50 ml and 25 ml capacity, graduated cylinder, filtration sets, titration set, dry filter paper rounds, 200 ml of 0.1M NaOH solution (free from carbonate), 10 g pure Ca(OH)₂, standard 0.05M HCl, phenolphthalein (indicator).

Theory : The solubility product can be determined from solubility measurement. Solutions of NaOH of 0.1M, 0.05M and 0.025M concentration can be saturated with, for example, Ca(OH)₂ and solubility of Ca(OH)₂ can be determined by titrating the filtered solution with 0.05M HCl solution.

Procedure : First, standardise the NaOH solution by titrating it against standard 0.05M HCl solution. Place 100 ml of pure water and 0.1M NaOH solution separately in two conical flasks. Prepare 0.05M and 0.025M NaOH solutions by measuring 50 ml and 25 ml of 0.1M NaOH solution into each of the graduated flasks (100 ml) and make the solutions upto the mark with CO₂ free distilled water. Transfer the solutions to the remaining conical flasks.

Add about 2 g of Ca(OH)₂ into each conical flask. Cork and shake the flasks. Shake them for about an hour. Allow to stand and filter each solution through a dry filter paper. Protect against absorption of CO₂ from air. Reject the first few millilitres of solution (nearly 5 ml) and collect the remaining filtrate. Titrate 20 ml

portion from each solution against 0.05M HCl solution, using phenolphthalein as an indicator.

Observations and Calculations : From the titration values, obtain the following for each flask :

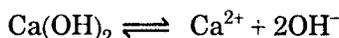
(a) Initial concentration of OH^- ions due to NaOH alone.

(b) Total concentration of OH^- ions after saturation with $\text{Ca}(\text{OH})_2$. From this, excess concentration of OH^- ions due to dissolved $\text{Ca}(\text{OH})_2$ is calculated.

(c) Concentration of Ca^{2+} ions from excess concentration of OH^- ions over that due to NaOH.

Concentration of Ca^{2+} ions = $\frac{1}{2}$ [Excess concentration of OH^- ions]

$\text{Ca}(\text{OH})_2$ ionises as follows :



$\therefore K_s$ for $\text{Ca}(\text{OH})_2 = [\text{Ca}^{2+}] [\text{OH}^-]^2$

= [Conc. of Ca^{2+} ions] [Total conc. of OH^- ions]²

All concentrations should be in mole per litre of solution.

Experimental temperature = ... °C.

Flask No.	[NaOH] = a	[OH ⁻] = b	Excess [OH ⁻] = (b - a)	[Ca ²⁺] = $\frac{1}{2}(b - a)$	Solubility of $\text{Ca}(\text{OH})_2$ = $\frac{1}{2}(b - a)$	Solubility product, $[\text{Ca}^{2+}] [\text{OH}^-]^2$ = $\frac{1}{2}(b - a) \times b^2$
1	—					
2	0.025					
3	0.05					
4	0.1					

Result : The solubility product of $\text{Ca}(\text{OH})_2 = \dots$

EXPERIMENT No. 5

Object : To study the variation of the solubility of AgBrO_3 in KBrO_3 solution and to determine the solubility product of AgBrO_3 .

Apparatus and Chemicals : Five glass stoppered bottles or conical flasks, pipettes, titration set, 250 ml 0.1M KBrO_3 solution, 250 ml 0.1M KNO_3 solution, standard 0.002M KCNS solution, ferric alum (indicator) solution, solid AgBrO_3 .

Theory : The solubility product of AgBrO_3 is given by,

$$K_s = [\text{Ag}^+] [\text{BrO}_3^-]$$

In presence of common ion BrO_3^- , the concentration of BrO_3^- ion is increased. Since solubility product is constant at a given temperature, the concentration of Ag^+ ions and so the solubility of AgBrO_3 will be lowered in presence of KBrO_3 .

The solubility of sparingly soluble salts is a function of ionic strength. So, increase in ionic strength of inert salt causes the solubility to increase. It is thus necessary that total ionic strength must be kept constant while changing the concentration of the common ion.

Procedure : Take 50, 40, 30, 20, 10 ml of 0.1M KBrO_3 solution in five glass stoppered bottles (numbered 1 to 5) and add to them 0, 10, 20, 30, 40 ml of 0.1M KNO_3 solution, respectively. To each bottle add 50 ml water. This gives the same ionic strength (0.05 in each bottle (Ionic strength $= \frac{1}{2} \sum c_i z_i^2$, where c_i and z_i are the ionic concentration and valency of the ion, respectively).

Add AgBrO_3 in excess to each bottle, stopper tightly and shake vigorously for several hours (preferably for 1-2 days). Filter each solution through a dry filter paper, rejecting the first 5–10 ml of the filtrate. Titrate 20 ml of each sample of filtrate with standard KCNS solution (standardise KCNS solution with standard AgNO_3 solution) using ferric alum as an indicator. Determine the concentration of Ag^+ in each solution.

Observations : Room temperature = ... °C

Bottle no.	Initial conc. of BrO_3^- due to KBrO_3 $= a \text{ mol L}^{-1}$	Conc. of Ag^+ due to AgBrO_3 $= b \text{ mol L}^{-1}$	Conc. of BrO_3^- due to AgBrO_3 $= b \text{ mol L}^{-1}$	Total conc. of BrO_3^- due to $\text{KBrO}_3 + \text{AgBrO}_3$ $= (a + b) \text{ mol L}^{-1}$	Solubility of AgBrO_3 $= b \text{ mol L}^{-1}$	Solubility product of AgBrO_3 $= b \times (a + b)$
1						
2						
3						
4						
5						

Calculations : From the titre value, calculate the concentration of Ag^+ ions and thus that of BrO_3^- due to dissolution of AgBrO_3 . This concentration is added to the initial concentration of BrO_3^- to give the total concentration of BrO_3^- ions in the solution saturated with AgBrO_3 . The values of $[\text{Ag}^+]$ are plotted as ordinate against $\frac{1}{[\text{BrO}_3^-]}$ (abscissa). The slope of the straight line so obtained gives the solubility product of AgBrO_3 .

Result : The solubility product of $\text{AgBrO}_3 = \dots$

EXPERIMENT No. 6

Object : To study the effect of ionic strength on the solubility of CaSO_4 and so determine its thermodynamic solubility product and mean ionic activity.

Apparatus and Chemicals : Eight glass stoppered bottles, titration set, Calcium sulphate dihydrate, 300 ml 1M KNO_3 solution, standard 0.02M EDTA solution (obtained by dissolving 3.21 g of disodium ethylene diamine tetra-acetic acid in 500 ml of solution), Eriochrome black T or calcon (indicator).

Theory : The thermodynamic solubility product (K_t) of CaSO_4 is given by,

$$K_t = a_{\text{Ca}^{2+}} \cdot a_{\text{SO}_4^{2-}} = [\text{Ca}^{2+}] [\text{SO}_4^{2-}] \cdot f_{\text{Ca}^{2+}} \cdot f_{\text{SO}_4^{2-}}$$

$$\text{or} \quad K_t = K_s \cdot f_{\text{Ca}^{2+}} \cdot f_{\text{SO}_4^{2-}} = K_s \cdot f_{\pm}^2 \quad \dots (1)$$

where K_s is the classical solubility product given by,

$$K_s = [\text{Ca}^{2+}] [\text{SO}_4^{2-}] = [\text{Ca}^{2+}]^2 \quad \dots (2)$$

where a represents activity term, f is activity coefficient and f_{\pm} is the mean activity coefficient of CaSO_4 . It is clear from equation (2) that K_s can be calculated at a particular ionic strength by determining the solubility of CaSO_4 .

According to Debye-Huckel equation,

$$\log f_{\pm} = -\frac{Az_+z_- \sqrt{\mu}}{1 + B \sqrt{\mu}} \quad \dots (3)$$

where μ is the ionic strength of the solution. For CaSO_4 , $z_+ = z_- = 2$ and the constants A and B have the values 0.51 and 1.25, respectively at 25°C . Therefore, equation (3) becomes.

$$\log f_{\pm} = -\frac{2.04 \sqrt{\mu}}{1 + 1.25 \sqrt{\mu}} \quad \dots (4)$$

Taking logarithm of equation (1),

$$\log K_t = \log K_s + 2 \log f_{\pm}$$

$$\text{or} \quad pK_t = pK_s - 2 \log f_{\pm} \quad \dots (5)$$

where $pK_t = -\log K_t$, $pK_s = -\log K_s$

Combining equations (4) and (5), we get

$$pK_s = pK_t - \frac{4.08 \sqrt{\mu}}{1 + 1.25 \sqrt{\mu}} \quad \dots (6)$$

Therefore, if pK_s values (ordinate) are plotted against $\frac{\sqrt{\mu}}{1 + 1.25 \sqrt{\mu}}$ values (abscissa), a straight line is obtained with a slope of -4.08 and intercept pK_t .

Procedure : Take by means of a burette 0, 10, 20, 30, 40, 50, 60, 70 ml of 1M KNO_3 solution and 100, 90, 80, 70, 60, 50, 40, 30 ml of water in stoppered bottles numbered from 1 to 8. This gives a series of KNO_3 solutions of ionic strength 0 to 0.70.

Add excess of CaSO_4 to each bottle, stopper tightly and shake vigorously for about 3-4 hours to attain equilibrium. Filter the contents of each bottle through a dry filter paper and collect the filtrate in dry beakers after rejecting the first 5-10 ml of the solution.

Now take 10 ml of the filtrate in a conical flask, add to it about 100 ml of water, about 0.5 ml of 5% NaOH solution and two drops of calcon (indicator). Titrate the pink solution with EDTA solution (taken in a burette) till the colour changes to blue (However, in case of Eriochrome black-T as indicator, the colour will change from pink to orange). Thus, determine the concentration of Ca^{2+} ions in each solution.

Observations : Room temperature = ...°C.

Bottle no.	Conc. of KNO_3 = $a \text{ mol L}^{-1}$	Conc. of Ca^{2+} = $b \text{ mol L}^{-1}$	$K_S = [\text{Ca}^{2+}]^2$ = b^2	Total ionic strength, $\mu = a + 4b$	$\frac{\sqrt{\mu}}{1 + 1.25 \sqrt{\mu}}$
1	0				
2	0.1				
3	0.2				
4	0.3				
5	0.4				
6	0.5				
7	0.6				
8	0.7				

Calculations : Calculate $[\text{Ca}^{2+}]$ from titre readings and so $K_S [= (\text{Ca}^{2+})^2]$ in each solution. Calculate the total ionic strength, $\mu = \frac{1}{2} \sum c_i z_i^2$ of KNO_3 and CaSO_4 in each solution. The total ionic strength is the concentration of KNO_3 (mol L^{-1}) plus four times the concentration of CaSO_4 . Then a curve is plotted between pK_S (ordinate) against $\frac{\sqrt{\mu}}{1 + 1.25 \sqrt{\mu}}$ (abscissa). The intercept of the straight line so obtained on the ordinate axis is pK_t , from which the value of K_t can be calculated. The mean ionic activity coefficient f_{\pm} in each solution can be calculated by using equation (1).

Result :

EXPERIMENT No. 7

Object : To study the variation of solubility of potassium hydrogen tartrate with ionic strength using a salt having a common ion and there from to determine the mean ionic activity coefficients.

Apparatus and Chemicals : Six glass stoppered bottles, thermostat, potassium hydrogen tartrate, potassium chloride, standard 0.001M NaOH solution, phenolphthalein solution (indicator).

Theory : The thermodynamic solubility product (K_t) for the uni-univalent potassium hydrogen tartrate is given by

$$K_t = a_+ \cdot a_- = (C_+ f_+) \cdot (C_- f_-) = (C_{\pm} f_{\pm})^2$$

$$\therefore f_{\pm} = \frac{\sqrt{K_t}}{C_{\pm}} \quad \dots (1)$$

where f_{\pm} and C_{\pm} are the mean ionic activity coefficient and mean ionic concentration of the salt.

Taking logarithm of equation (1),

$$\log f_{\pm} = \frac{1}{2} \log K_t - \log C_{\pm}$$

or
$$\log C_{\pm} = \frac{1}{2} \log K_t - \log f_{\pm}$$

or
$$\log C_{\pm} = \frac{1}{2} \log K_t + \frac{0.51 \sqrt{\mu}}{1 + 1.25 \sqrt{\mu}}$$

$$\left[\because \log f_{\pm} = -\frac{Az_+z_-\sqrt{\mu}}{1+B\sqrt{\mu}} \quad \text{where } A \text{ and } B \text{ are constants and} \right.$$

for water at 25°C their respective values are 0.51 and 1.25].

The plot of $\log C_{\pm}$ (ordinate) against $\frac{0.51 \sqrt{\mu}}{1 + 1.25 \sqrt{\mu}}$ (abscissa) is linear. The intercept at $\mu = 0$ (or $f_{\pm} = 1$) is $\log \sqrt{K_t}$ ($\frac{1}{2} \log K_t$). Therefore, by evaluating K_t , we can calculate mean f_{\pm} at any mean ionic concentration by using equation (1).

If the solubility of potassium hydrogen tartrate is C_1 mol L⁻¹ in a solution of potassium chloride of concentration C_1 mol L⁻¹, then mean ionic concentration C_{\pm} of potassium hydrogen tartrate will be $\sqrt{C_2(C_1 + C_2)}$.

Procedure : Prepare 100 ml each of 0.0025, 0.05, 0.1, 0.2 and 0.3M solutions of potassium chloride and put these solutions in dried stoppered bottles. In one of the bottles take water only. Now add excess of potassium hydrogen tartrate in each bottle and shake them vigorously in a thermostat at 25°C for 2-3 days. Filter each solution through a small dry filter paper and collect the filtrate in separate flasks after rejecting the first 5-10 ml of the solution.

Titrate 10 ml of the filtrate of each of the solution with standard 0.1M NaOH solution using phenolphthalein solution as an indicator. Now, calculate the concentration C_2 of potassium hydrogen tartrate in each solution.

Observations : Same as in experiment 6.

Calculations : Plot C_{\pm} , i.e., $\log \sqrt{C_2(C_1 + C_2)}$ (ordinate) against $\frac{0.51 \sqrt{\mu}}{1 + 1.25 \sqrt{\mu}}$ (abscissa) and extrapolate the straight line to $\mu = 0$. The intercept on ordinate gives the value of $\log \sqrt{K_t}$. Then, calculate K_t and f_{\pm} at each ionic strength by using equation (1). The total ionic strength (μ) in each solution is taken to be $(C_1 + C_2)$.

Result :

SOLUTIONS OF GASES IN LIQUIDS

The solubility of a gas in liquid can be expressed in two ways, viz., solubility and absorption coefficient.

(a) Solubility : The solubility of a gas in a liquid at a given temperature and pressure is the volume of the gas in millilitres which just saturates 1 ml of the liquid, the gas volume being measured at the same temperature and pressure at which the solubility is determined.

(b) **Absorption coefficient** : It is defined as the volume of the gas in millilitres which just saturates 1 ml of the liquid by the gas absorbed, the gas volume being measured at N.T.P.

EXPERIMENT No. 8

Object : To determine the solubility of oxygen in water at room temperature.

Apparatus : Gas solubility apparatus, mercury, water and oxygen gas.

Description of the apparatus : The apparatus used for determining the solubility of a sparingly soluble gas in a liquid is shown in figure (2). It consists of a burette *B* connected to another tube *A*. The burette and the tube both are filled at one end of the burette which is connected on one end *E* with the gas supply and on the other with a rubber tube which, in turn, is connected to a gas absorption vessel, *D*, through another three way stop cock, *C*₂. A two way stop cock *C*₃ is fitted at the other end of the vessel, *D*. Inner volume of *D* is pre-determined by weighing the amount of water required to fill it completely.

Procedure : The apparatus is set up as described above. The absorption vessel, *D* is filled with air-free water and is placed in a thermostat at room temperature. The tube *A* is raised so that the burette *B* is completely filled with mercury. Pure oxygen is admitted through *C*₁ and allowed to escape through side tube *F* to sweep the air from the connecting tube. (A connecting tube with a very narrow bore can be used whose volume can be neglected). When all air of the connecting tube has been swept out, the stop cock *C*₁ is so turned as to fill the burette *B* with oxygen. The volume of the gas is measured at atmospheric pressure by levelling the mercury in *A* and *B*. The stop cock *C*₁ is then turned so as to connect the burette with the absorption vessel, *D*. Now first open the stop cock *C*₃ and then *F* and collect 20-25 ml water in a weighed flask. The weight of water so collected is determined. As the total volume of absorption vessel *D* is known, the volume of water left in it and also the air space can be calculated.

Continue the flow of oxygen from the burette *A* to the absorption vessel and shake it each time by taking it out of the thermostat till no more oxygen dissolves in water in absorption vessel, *i.e.*, till the mercury level in *B* remains constant. Level the mercury in *A* and *B* and note the volume of oxygen in the burette at atmospheric pressure.

Observations : Room temperature = ... °C

Volume of absorption vessel, *D* = *V*₁ ml

Volume of water run out = *V*₂ ml

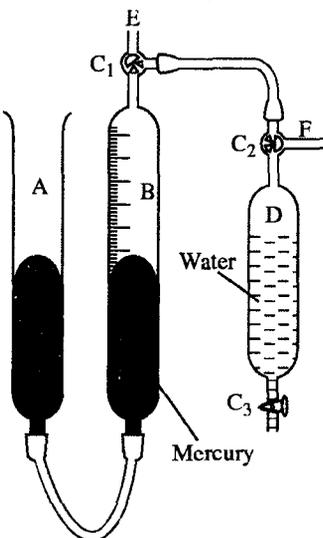


Fig. 2 : Apparatus for measuring the solubility of a sparingly soluble gas

Volume of gas taken in the burette = V_3 ml

Volume of gas left in the burette = V_4 ml

Calculations : Volume of water used as solvent = $(V_1 - V_2)$ ml

∴ Volume of gas dissolved in $(V_1 - V_2)$ ml of water to get a saturated solution
= (Initial volume of gas in B) – (Final volume of gas in B) – (Volume of water run out from D)

$$= (V_4 - V_3 - V_2) \text{ ml}$$

This volume has been measured at room temperature and atmospheric pressure. To calculate the solubility of oxygen, this volume must be changed to N.T.P. by assuming the water vapour pressure at the experimental temperature. The barometric pressure is assumed to remain constant during the experiment.

∴ Solubility of oxygen at room temperature = $\frac{(V_4 - V_3 - V_2)}{(V_1 - V_2)}$

Result : The solubility of oxygen at room temperature = ...

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 9

Object : *To study the influence of the addition of various substances on the solubility of solutes.*

When an electrolyte is added to saturated solution of a solute, the equilibrium between the solute and the solution is disturbed and some of the solid separates out. In other words, the solubility decreases. The decrease in solubility can be determined by adding various electrolytes in the same amounts, and titrating the clear solution against an alkali or can be determined by gravimetric method.

Make a saturated solution of sodium chloride at room temperature. Now filter the solution through a filter paper. Collect 20 ml of the solution in each of the three dry test tubes. To them add 10 ml of conc. HCl, 10 ml conc. HNO₃ and 10 ml of alcohol. Determine the solubilities in each case as usual and tabulate the results as explained in experiment 1.

EXPERIMENT No. 10

Object : *To study the effect of concentration of an electrolyte such as KCl, NaCl, Na₂SO₄, K₂SO₄ on the solubility of an organic acid (benzoic acid or salicylic acid) at room temperature.*

Theory : On addition of an electrolyte to a saturated solution of a weak acid, some of the dissolved substance gets separated, i.e., the solubility of the substance decreases with the addition of an electrolyte.

Procedure : In a beaker prepare about 400 cm³ nearly saturated solution of the acid (say benzoic acid) at a temperature about 10°C above the room temperature. Allow the solution to cool down to room temperature with constant

stirring. Filter the solution and collect the filtrate in a dry beaker, rejecting first 5-10 cm³ of the solution.

By means of a 25 cm³ pipette, transfer 50 cm³ of the saturated solution in each of the five properly labelled dry conical flasks. Add 1, 2, 3, 4 and 5 g of KCl in different flasks, stir the contents and allow them to stand for nearly 15 minutes.

Filter these solutions separately in dried beakers, rejecting first 10 cm³ of the filtrate in each case.

Determine the solubility of the acid without the addition of KCl, by titrating 10 cm³ of the saturated solution with 0.05 M NaOH in the usual way. Repeat the determination by taking another 10 cm³ of the solution.

Similarly, determine the solubility of the acid in presence of different concentrations of KCl by titrating 10 cm³ of the solution with 0.05M NaOH from each flask.

Observations : Room temperature =

Amount of KCl added to 50 cm ³ of solution	Conc. of KCl solution %	Wt of empty tube	Wt of tube + solution	Wt of solution	Vol. of 0.05 M NaOH used with 10 cm ³ solution	Wt of the acid	Solubility

Calculations : Calculate the solubility of the acid per 100 g of the solvent as mentioned before. Plot a graph between the solubility (ordinate) and the concentration (abscissa) of KCl added.

Similarly, the effect of other electrolytes can be studied.

EXPERIMENT No. 11

Object : *To study the variation of solubility of Ca(OH)₂ in NaOH solution and also to determine its solubility product.*

Apparatus and Chemicals : Four 250 cm³ glass stoppered conical flasks (or bottles), two 100 cm³ measuring flasks, graduated cylinder, 250 cm³ 0.1 M NaOH solution (free from carbonate), standard 500 cm³ 0.05 M HCl, about 10 g pure Ca(OH)₂, phenolphthalein indicator.

Theory : In the presence of excess of common ion, *i.e.*, OH⁻ to Ca(OH)₂, the activity (or concentration) of the common ion is large. In order to maintain the constant value of solubility product, the activity or concentration of Ca²⁺ should decrease, *i.e.*, the solubility of Ca(OH)₂ will be decreased. The classical solubility product of Ca(OH)₂ is given by,

$$K_c = C_{Ca^{2+}} \times C_{OH^-}^2 \quad \dots (1)$$

where $C_{Ca^{2+}}$ and C_{OH^-} are the concentrations (moles/dm³) of Ca²⁺ and OH⁻, respectively in the solution saturated with Ca(OH)₂.

Procedure : Place 50 cm^3 and 25 cm^3 of $0.1M$ NaOH solution separately in two 100 cm^3 measuring flasks and make the solution upto the mark with CO_2 -free distilled water so as to get 0.05 and $0.025 M$ NaOH solutions. By means of a measuring cylinder, take nearly 100 cm^3 each of pure water, 0.1 , 0.05 and $0.025M$ NaOH solutions in four stoppered conical flasks.

Add nearly 2 g of Ca(OH)_2 into each of the flasks, stopper tightly and shake the flasks vigorously at least for one hour (it is better to keep the flasks overnight). Filter the contents of each flask through a dry filter paper and collect the filtrate in a dry beaker rejecting the first $5\text{-}10 \text{ cm}^3$.

Titrate 20 cm^3 aliquot of each of the solutions with standard $0.05M$ HCl using phenolphthalein as an indicator and determine the concentration of OH^- in each solution.

Observations : Temperature of the experiment (room temp.) =

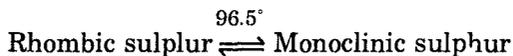
Bottle no.	Initial conc. of OH^- due to NaOH (a mol dm^{-3})	Total conc. of OH^- due to NaOH and Ca(OH)_2 (b mol dm^{-3})	Conc. of OH^- due to Ca(OH)_2 ($b - a$) mol dm^{-3}	Conc. of Ca^{2+} $\frac{1}{2}(b - a)$ mol dm^{-3}	Solubility of Ca(OH)_2 $\frac{1}{2}(b - a)$ mol dm^{-3}	Solubility product $\frac{1}{2}(b - a) \times b^2$
1						
2						
3						
4						

Calculations : Concentration of OH^- obtained by titration is the total concentration due to NaOH and Ca(OH)_2 . Subtracting the initial concentration of OH^- due to NaOH from that obtained by titration, we get the concentration of OH^- due to dissolved Ca(OH)_2 . Half of this difference gives the concentration of Ca^{2+} and hence the solubility of Ca(OH)_2 can be calculated.



TRANSITION TEMPERATURE

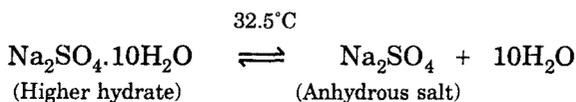
Pure substances undergo physical changes at certain definite temperatures, which are characteristic of the substance and the change in question. For example, there are boiling points and freezing points at which a liquid begins to boil or freeze. In addition to boiling point and melting point, there are other equally definite temperatures at which definite physical changes take place. For example, many substances are capable of existing in two or more crystalline forms such as rhombic sulphur and monoclinic sulphur. Rhombic sulphur changes to monoclinic form at 96.5°C and the two are in equilibrium at this temperature. This temperature is thus known as *transition temperature* or *transition point*.



At ordinary temperatures, the stable form of sulphur is rhombic and also at all temperatures upto 96.5°. At 96.5°, rhombic form changes into monoclinic form, and this form of sulphur is stable at all temperatures beyond 96.5° upto the melting point. At 96.5° and at no other temperature, both rhombic and monoclinic sulphur may exist together, at the stable equilibrium. Similarly, in the case of mercuric iodide, the vermilion coloured variety, which crystallises in tetragonal crystals, is the stable form at all temperatures upto 127°C, and above 127°C, the stable form is coloured yellow and crystallises in rhombic crystals. Both forms may co-exist in stable equilibrium at the transition temperature, 127°C.

Not only are transition temperatures found in the case of polymorphous substances but they are also found in the case of all hydrated and double salts. Thus, a definite hydrate is stable only between definite temperature limits; above the higher limit, the anhydrous salt or the lower hydrate is stable, while below the lower limit the higher hydrate is stable. In such cases, the temperature at which one hydrate changes into another constitutes the transition temperature.

Sodium sulphate (decahydrate), *i.e.*, Glauber's salt, is stable at ordinary temperature, but at 32.5°C, it changes into anhydrous salt, which is stable above 32.5°C. Thus, the equilibrium is represented as :



Transition temperatures may be determined from observations on a given physical property of the substance. At transition temperature, the two forms or two hydrates of a substance, in equilibrium at the transition point differ from one

another and so the methods used for the determination of the transition temperature are based on the above facts. Some of the methods which we will discuss are as follows :

- (i) *Dilatometric method.*
- (ii) *Solubility method.*
- (iii) *Thermometric method.*

EXPERIMENT No. 1

Object : *To find out the transition temperature of Glauber's salt by dilatometric method.*

Apparatus and Chemicals : Dilatometer with capillary tube, thermometer, a millimeter scale, 600 ml beaker, kerosene oil or xylene, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

Theory : Many substances change in volume when one form is converted into another. Therefore, if the temperature at which a decided change in volume occurs is noted, it will form the nucleus of the determination of the transition temperature. In other words, if the temperature, at which there is an abrupt change in volume is observed, it will give the value of the transition temperature. This variation in temperature is determined by means of a *dilatometer*.

Procedure : A dilatometer consists of an elongated tube *A* of about 30–40 ml capacity [fig. (1)]. A long capillary tube *B* about 0.5 mm in diameter is sealed to the bulb, and the other end of the bulb *C* is left open. The bulb is filled with the substance under investigation and the open end *C* sealed off. **Before starting the experiment, the dilatometer must be washed and dried.**

The vessel is evacuated and the spaces between the particles of the substance filled with a liquid (*in this case kerosene oil or petrol*) in which the substance is insoluble or very slightly soluble. The later fact is advisable as under these conditions, the change at the transition temperature is accelerated. The liquid must be filled such that it just enters the capillary tube. The dilatometer, when filled as described above, acts like a large thermometer. An opal glass scale, graduated in mm is fastened to the back of the capillary.

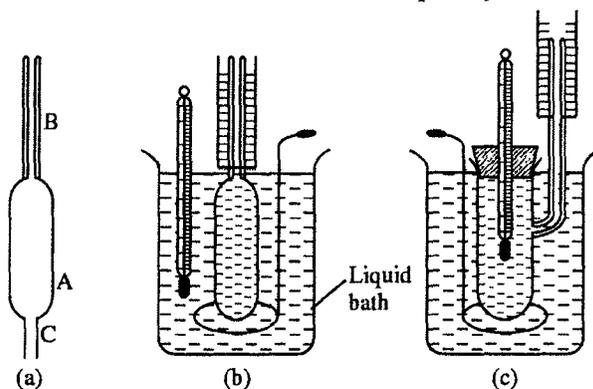


Fig. 1 : Dilatometer

- (a) Before filling (b) When set up for making measurements
(c) An alternate set up

The bulb is immersed in a liquid bath, the temperature of which may be changed 10° below and above the transition point. After the bulb and contents have been taken on the temperature constant bath, the height of the liquid in the capillary is noted. The temperature of the bath is also noted.

The temperature of the bath is slowly increased by one degree and the height of the liquid in the capillary as well as the temperature are again noted. This operation is repeated degree by degree until the change has taken place and about $7-8^\circ$ higher than the change.

So long as the conversion of one form ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) to the other (Na_2SO_4) has not taken place, the liquid will rise regularly in the capillary for equal increments of temperature. But at the point the change starts, a very much larger rise will be observed in the capillary, if the original substance is denser than the substance into which it is changing. In the reverse case, a decreasing rise will be observed. After the change is complete, the amount of rise for equal increments of temperature will again be regular, but it is not necessary that it will be the same as it was before the change. The rise during the change, in addition to a thermal expansion of the substance, is due to the change in volume of the substance.

When sufficient readings have been taken, the temperature of the bath is decreased slowly and the height in the capillary as well as the temperature of the bath are again noted.

In this particular case, the bath is first heated to 37°C , degree by degree and then cooled. It will be observed that at about 33°C , the meniscus of the liquid in the capillary will rise more for one degree increase of temperature than at any other temperature.

Alternate set ups for the dilatometer are shown in figure 1(c) and figure (2).

Observations :

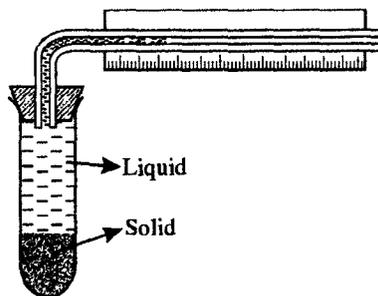


Fig. 2 : An improvised dilatometer

Temperature ($^\circ\text{C}$)	Reading of the liquid meniscus in the capillary on heating (cm)	Reading of the liquid meniscus in the capillary on cooling (cm)	Mean reading (cm)
27			
28			
29			
30			
31			
32			
33			
34			
35			
36			
37			

Calculations : The height of the liquid is plotted as ordinate against the temperature as abscissa. The curves are drawn for rising and falling temperatures (fig. 3). The two curves *ABCDE* and *ABFDE* are obtained which should theoretically coincide with one another. This is, however, never observed in actual practice. The reason is that a time lag occurs in the change, *i.e.*, the change does not take place instantaneously at the transition point, but at a temperature slightly above the transition temperature in the heating portion of the curve and slightly below the transition temperature in the cooling portion of the curve. The mean of the two temperatures corresponding to points *C* and *F* gives the transition temperature.

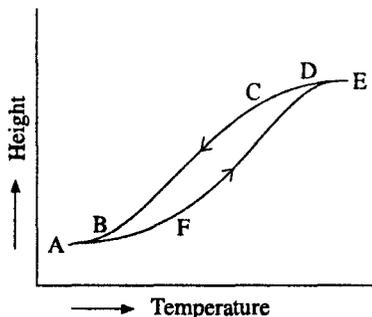


Fig. 3 : Heating and cooling curves

Result : The transition temperature of Glauber's salt is ...°C.

Precautions : (i) Near the transition point, heating and cooling should be done very slowly as this will bring the points *C* and *F* more closer.

(ii) The bulb should be filled to about 3/4 of its volume, with the salt.

(iii) While filling the dilatometer, care must be taken that no air bubbles remain in the interstices of the salt powder.

(iv) The liquid in the capillary should stand at the lower part of the scale.

EXPERIMENT No. 2

Object : To find the transition temperature of Glauber's salt (sodium sulphate) by solubility method.

Apparatus : Porcelain dish, pipette (10 ml), water bath or thermostat, thermometer, beakers, stoppered bottle etc.

Theory : At the transition point, two substances which are in equilibrium with one another and change into one another on changing the temperature, have the same solubility. Hence, if the solubility of the two substances is determined at a number of temperatures and temperature-solubility curves are drawn, it is found that the curves cut, when produced. The temperature at which the two curves intersect is the temperature of equal solubility, *i.e.*, the transition temperature.

Procedure : Take about 150 ml of distilled water and 100 gram of powdered Glauber's salt in a 250 ml stoppered bottle. Cover the stopper and shake in a thermostat at room temperature for about 30 minutes. Allow the solid to settle down. Pipette 10 ml of the solution in a stoppered weighing bottle and weigh it. Now transfer the solution to a porcelain dish, taking care to wash all the solution from the bottle to the dish and then evaporate the solution to dryness. Place the dish in an oven at 120°C and when the residue is completely dried, weight of anhydrous salt is taken.

Shake the bottle of solution for 10–15 minutes more and repeat the above process by withdrawing 10 ml of the saturated solution.

Now raise the temperature of the thermostat to say 28°C and determine the solubility as before, add more water or $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, if need be. Similarly, find the solubility at different temperatures say 30°, 32°, 34°, 36°, 40°, and 45°C by suitably adjusting the thermostat.

A convenient device to maintain constant temperature for short periods is to use a wide mouth thermos flask containing water at the desired temperature. Arrangement can then be made to keep the beaker almost wholly immersed in water.

An alternate and easier method of determining solubility at various temperatures is to prepare a saturated solution of Glauber's salt at a temperature of about 10–15°C higher than its transition temperature. Then the temperature is slowly decreased by cooling and then 10 ml of the solution is pipetted out at the desired temperature and solubility determined as usual.

Observations :

Temperature (°C)	Weight of empty porcelain dish, W_1 g	Weight of porcelain dish + 10 ml solution, W_2 g	Weight of porcelain dish + residue, W_3 g	Weight of residue, $(W_3 - W_1)$ g	Weight of solvent, i.e., water, $(W_2 - W_3)$ g	Solubility = $\frac{(W_3 - W_1)}{(W_2 - W_3)} \times 100$ g per 100 g
...
...

Calculations : Plot the solubilities as ordinate against temperature as abscissa and draw a curve [fig. (4)]. It will be observed that the curve breaks at about 32°C.

To find the exact transition point, produce the curve made by joining the points below the break and also that made by joining the points above the break. The point of intersection will give the transition temperature.

Result : The transition temperature of Glauber's salt is ...°C.

Precautions : (i) Saturated solutions must be prepared at the desired temperatures.

(ii) The residue must be completely dry.

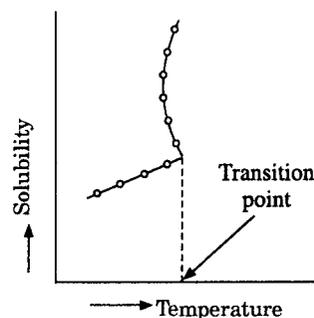


Fig. 4.

EXPERIMENT No. 3

Object : To find the transition temperature of Glauber's salt by thermometric method.

Apparatus : A thin glass boiling tube, beaker, thermometer graduated to 0.1°C, stirrer etc.

Theory : When a solid is heated, its temperature rises regularly until the melting point is reached. At this point, the temperature remains steady till whole of solid is converted into liquid. When the conversion is complete, the temperature

will again rise in a regular manner. The heat added to the substance while it is melting, is used up as latent heat to effect the melting. Similar principle is used in determining the transition point by thermometric method.

If a substance is heated slowly, its temperature rises regularly till its transition point is reached. At this point, the temperature stops rising till the conversion is complete. After the change, the temperature again commences to rise regularly. On the other hand, if a substance has been heated above its transition point and is cooled slowly, its temperature will fall at a definite rate till the transition point is reached. The temperature stops falling at the transition point, till whole of the substance has been converted into another form. After the change is complete, the temperature again falls regularly.

By plotting the rate of heating or cooling, *i.e.*, the number of degrees per minute by which the temperature falls or rises, as ordinate against temperature as abscissa, a cooling or heating curve is obtained. The point where the curve breaks will determine the transition point.

Procedure : Take about 50 g of Glauber's salt in a thin walled glass tube A, insert a stirrer S_1 made of silver wire and a thermometer T_1 (graduated to 0.1°C) into the salt [fig. (5)]. Support the tube A in a large beaker B full of water, provided with a glass stirrer S_2 and a thermometer T_2 .

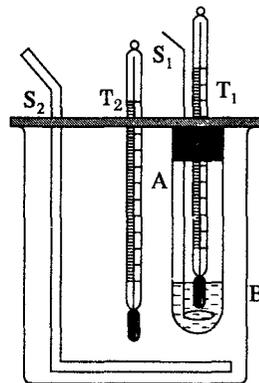


Fig. 5.

Raise the temperature of water in the beaker B to 28°C and keep it there for about 30 minutes. Raise the temperature of the beaker slowly and continuously to about 38°C , at the rate of 1° in about ten minutes. Note the temperature of the salt every two minutes and record the time as well as the temperature.

Now cool the beaker slowly and read the temperature of the salt every two minutes and record the time as well as temperature till it reaches the room temperature.

It will be noticed that at about 32°C , the rate of heating and cooling of the salt will be slower than at other temperatures.

Observations :

Time (minutes)
Temperature ($^\circ\text{C}$)

Calculations : Plot the temperature as abscissa and the number of minutes, counted from the time at which the heating or cooling starts, as ordinate. Draw a heating and cooling curve [fig. (6)] by joining the points. It will be of the same nature as described in preceding experiment. Find out the transition temperature by taking the mean of the temperatures at points A and A'.

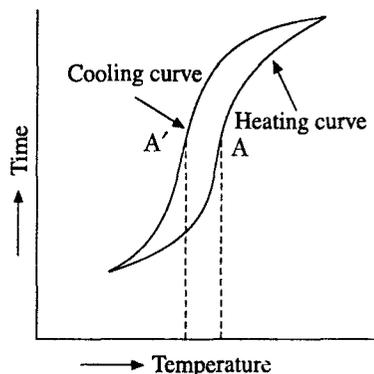


Fig. 6.

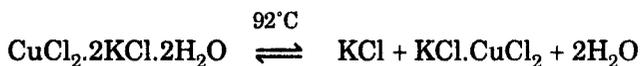
Result : The transition temperature of Glauber's salt is ...°C.

Precautions : Heating and cooling should be slow near the transition temperature.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 4

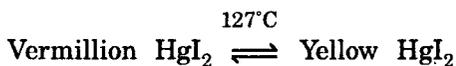
Object : *To determine the transition temperature of double chloride of copper and potassium.*



Heating in this case is commenced at 85°C and is continued to 95°C.

EXPERIMENT No. 5

Object : *To determine the transition temperature of mercuric iodide.*



EXPERIMENT No. 6

Object : *To determine the transition temperature of sulphur system.*

The transition temperature of sulphur (96.5°C) can be obtained by determining the solubility curves of rhombic and monoclinic sulphur in nitrobenzene between 80°C and 110°C.



12

PARTITION COEFFICIENT

When a substance which is soluble in each of the two immiscible or partially miscible liquids is shaken with a mixture of the two solvents, it distributes itself in a perfectly definite form between them. If a solution of a substance in a given solvent is shaken with a second solvent immiscible with the first solvent and in which the solute is soluble, then the solute can be extracted in parts from the first solvent and passed into the second solvent.

If the solute has the same molecular weight in both the solvents, then it is found that after shaking, the ratio of concentration of the solute in the two solvents is constant. The concentration can be expressed in g/litre or g equivalent/litre. If C_A and C_B be the concentrations of a solute in two solvents A and B, then it has been found that,

$$\frac{C_A}{C_B} = K$$

where, K is a constant known as **partition coefficient** or **distribution coefficient** which is *independent of the actual concentration of the solutions*.

EXPERIMENT No. 1

Object : To find the partition coefficient of iodine between carbon tetrachloride and water.

Apparatus : Reagent bottles, burette, pipette, conical flask, separating funnel etc.

Theory : Since iodine exists in the same molecular state in both the solvents, as explained above, the partition coefficient K , will be given by,

$$K = \frac{\text{Concentration of I}_2 \text{ in CCl}_4 \text{ layer}}{\text{Concentration of I}_2 \text{ in H}_2\text{O layer}}$$

Procedure : First of all prepare a saturated solution of iodine in carbon tetrachloride (about 5%) and filter. Now, take three reagent bottles and label them with numbers 1, 2 and 3. Now add the following things in these bottles as specified below:

Bottle 1 : 40 ml saturated solution of iodine in CCl_4 + 0 ml of pure CCl_4 + 150 ml of distilled water.

Bottle 2 : 30 ml saturated solution of iodine in CCl_4 + 10 ml pure CCl_4 + 150 ml distilled water.

Bottle 3 : 25 ml saturated solution of iodine in CCl_4 + 15 ml pure CCl_4 + 150 ml distilled water.

Now stopper each bottle and shake well for 20–30 minutes. The results of this experiment depend on how much the shaking is done. **More the shaking, better are the results.** Allow the mixture to separate into two layers. Now separate both carbon tetrachloride and water layers of each reagent bottle, by means of a separating funnel [fig. (1)] and place them in separate numbered vessels.

Now pipette 25 ml of the aqueous layer of bottle no. 1 into a conical flask. Add 4–5 drops of starch solution. Now titrate it against N/100 sodium thiosulphate solution. Repeat the process till you get two concordant readings. Similarly, titrate

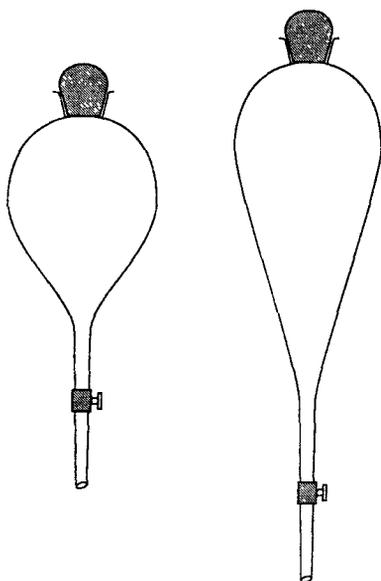


Fig. 1 : Separating funnels

25 ml of each aqueous layer of the other two bottles numbered 2 and 3 against N/100 sodium thiosulphate solution.

Similarly, first take about 25 ml of water in a conical flask and pipette out 5 ml of the carbon tetrachloride layer of bottle no. 1 into it and add about 4-5 drops of starch solution. The addition of water helps in the titration by gradually extracting iodine into water layer where the reaction with sodium thiosulphate takes place. By covering the carbon tetrachloride layer with water layer, loss of iodine as vapour from the exposed solution is also prevented. Now titrate it against N/10 sodium thiosulphate solution. Repeat the process till you get two concordant readings. Similarly, titrate 5 ml of the carbon tetrachloride layer of the other two bottles numbered 2 and 3 against N/10 sodium thiosulphate solution.

Observations : Room temperature = $t^{\circ}\text{C}$.

Bottle number	Titration with aqueous layer				Titration with CCl_4 layer			
	Volume taken (ml)	Initial reading of burette (ml)	Final reading of burette (ml)	N/100 Hypo used (ml)	Volume taken (ml)	Initial reading of burette (ml)	Final reading of burette (ml)	N/10 Hypo used (ml)
1	25			V_2	5			V_3
	25			(say)	5			(say)
	25				5			
2	25			V_2'	5			V_3'
	25			(say)	5			(say)
	25				5			
3	25			V_2''	5			V_3''
	25			(say)	5			(say)
	25				5			

Calculations :

(i) *Bottle 1. (a) For water layer :*

$$N_1 \times 25 = \frac{N}{100} \times V_2$$

$$\therefore N_1 = \frac{N \times V_2}{25 \times 100}$$

\therefore Concentration (C_1) of I_2 in water layer

$$= \frac{127 \times V_2}{25 \times 100} \text{ g equiv/litre}$$

(b) *For CCl_4 layer :*

$$N_1 \times 5 = \frac{N}{10} \times V_3$$

$$\therefore N_1 = \frac{N \times V_3}{5 \times 10}$$

Concentration (C_2) of I_2 in CCl_4 layer

$$= \frac{127 \times V_3}{5 \times 10} \text{ g equiv/litre.}$$

$$\therefore \text{Partition coefficient, } K = \frac{C_2}{C_1}$$

Similarly, we can find and calculate the partition coefficient of iodine between carbon tetrachloride and water for bottles no. 2 and 3. We will see that for all the

three bottles the values of K comes out to be nearly constant. Take the mean of all the three values.

Result : The partition coefficient of iodine between carbon tetrachloride and water is

Precautions : (i) The solute should be thoroughly mixed with the immiscible solvents. The mixing should be continuously done for at least 30–45 minutes.

(ii) It is important to avoid the contamination of the aqueous layer by CCl_4 layer, since iodine is so much concentrated in the non-aqueous layer that even a drop of the CCl_4 solution would produce an appreciable error in the result.

EXPERIMENT No. 2

Object : To find the partition coefficient of benzoic acid between water and benzene.

Apparatus : Same as in preceding experiment.

Theory : If the solute has the same molecular weight in both the immiscible solvents, A and B *i.e.*, it is in the same molecular state, then its partition coefficient K , between the two layers will be given by,

$$K = \frac{C_A}{C_B}$$

where, C_A and C_B are the respective concentrations of the solute in the two solvents.

Suppose in one solvent, say in solvent A , the solute has the normal molecular weight, while in the second solvent B , it is associated as follows :



In such a case, the ratio $\frac{C_A}{C_B}$ will not be constant. The value of partition coefficient can now be calculated as follows :

Let C_1 be the concentration of the solute X in phase I (first solvent A) and let C_2 be its concentration in phase II (second solvent B) [fig. (2)]. Applying the law of mass action to the equilibrium $(XY) \rightleftharpoons n(XY)_n$; we get,

$$K_c = \frac{[X]^n}{[(X)_n]}$$

$$\therefore [X] = [K_c \times (X)_n]^{1/n} = \text{constant} \times [(X)_n]^{1/n} \quad \dots (2)$$

If in solvent B the solute exists largely as associated molecules, which is generally true except at large dilutions, the concentration of the associated molecule $[(X)_n]$, may be taken as equal to C_2 , the total concentration; *i.e.*,

$$[(X)_n] = C_2$$

From equation (2), we have,

$$[X] = \text{constant} \times \sqrt[n]{C_2}$$

As the distribution law is valid only when concentrations of similar molecular species in the two solvents are taken into consideration, therefore,

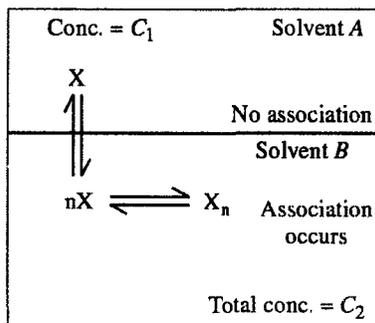


Fig. 2.

$$\frac{C_A}{C_B} = \frac{C_A}{[X]} = \text{constant or } \frac{C_1}{n\sqrt{C_2}} = \text{constant} = K \text{ (partition coefficient)}$$

[Note : In case of benzoic acid, which generally exists as dimer in aprotic solvents, the value of $n = 2$].

Procedure : Dissolve about 15 g of benzoic acid in about 200 ml benzene. Now take three reagent bottles and make the following mixtures in each of them.

Bottle number	Volume of benzoic acid solution in C_6H_6 (ml)	Volume of pure C_6H_6 (ml)	Volume of distilled water (ml)
1	50	0	50
2	40	10	50
3	30	20	50

Stopper the bottles properly and shake all the bottles for about 20–30 minutes. Now allow the mixture to separate into two layers the lower layer will be the aqueous layer, while the upper layer will be the benzene layer. Now separate each layer of each bottle by means of a separating funnel.

Now take 10 ml of the benzene layer by means of a pipette in a conical flask and add a few drops of phenolphthalein. Titrate it against N/10 NaOH solution. Repeat the process till you get two concordant readings. Similarly, titrate the benzene layer of each bottle by pipetting out 10 ml of the solution and titrating it against N/10 NaOH solution.

Pipette out 10 ml of the aqueous layer from the first bottle and titrate it against N/100 NaOH solution, using phenolphthalein as an indicator. Repeat the process for the other bottles also.

Observations : Room temperature = $t^\circ C$

Bottle number	Titration with aqueous layer				Titration with benzene layer			
	Volume taken (ml)	Initial burette reading (ml)	Final burette reading (ml)	Volume of N/100 alkali used (ml)	Volume taken (ml)	Initial burette reading (ml)	Final burette reading (ml)	Volume of N/10 alkali used (ml)
1	10			V_2 (say)	10			V_3 (say)
	10				10			
2	10			10		
	10				10			
3	10			10		
	10				10			

Calculations :

Bottle 1. (a) For water layer : $N_1V_1 = N_2V_2$

or
$$N_1 \times 10 = \frac{N}{100} \times V_2$$

$$\therefore N_1 = \frac{N \times V_2}{100 \times 10}$$

$$\therefore \text{Concentration } (C_1) \text{ of benzoic acid in water layer} = \frac{122V_2}{100 \times 10}$$

$$\text{(b) For benzene layer : } N_1V_1 = N_3V_3$$

$$\text{or } N_1 \times 10 = \frac{N}{10} \times V_3$$

$$\therefore N_1 = \frac{N \times V_3}{10 \times 10}$$

$$\therefore \text{Concentration } (C_2) \text{ of benzoic acid in benzene layer}$$

$$= \frac{122 \times V_3}{10 \times 10}$$

Similarly, the values of C_1 and C_2 for the remaining bottles 2 and 3 can be calculated. Then for each bottle, the value of partition coefficient K , is calculated as follows, which comes out to be constant.

$$K = \frac{C_1}{(C_2)^{1/2}}$$

The mean of all the values of K is taken as the partition coefficient.

Result : The partition coefficient of benzoic acid

between water and benzene =

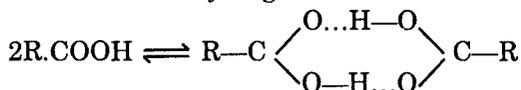
Precautions : Same as in preceding experiment.

EXPERIMENT No. 3

Object : To find the dimerisation constant of benzoic acid in benzene medium.

Apparatus : Same as in preceding experiment.

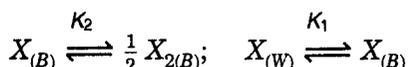
Theory : Organic monocarboxylic acids tend to dimerise in non-polar solvents, say benzene on account of hydrogen bond formation.



$$\text{or } \text{Acid} \xrightleftharpoons{K_2} \frac{1}{2} (\text{Acid})_2$$

K_2 is the dimerisation constant of the acid.

The partition of a monocarboxylic acid (X) between water and benzene may be represented as.



The subscripts W and B represent water and benzene layer, respectively. The equilibrium constants, K_1 and K_2 for the above equilibrium are given by :

$$K_1 = \frac{[X_{(B)}]}{[X_{(W)}]} \quad (K_1 = \text{partition coefficient})$$

$$K_2 = \frac{[X_{2(B)}]^{1/2}}{[X_{(B)}]} \quad (K_2 = \text{dimerisation constant})$$

If C_W and C_B represent the total concentration in water and benzene layers; then according to principle of mass balance, we have,

$$C_W = [X_{(W)}] \quad \dots (1)$$

$$C_B = [X_{(B)}] + 2[X_{2(B)}] \quad \dots (2)$$

Dividing equation (2) by (1), we get,

$$\begin{aligned} \frac{C_B}{C_W} &= \frac{[X_{(B)}] + 2[X_{2(B)}]}{[X_{(W)}]} \\ &= \frac{[X_{(B)}]}{[X_{(W)}]} + \frac{2[X_{2(B)}]}{[X_{(W)}]} = K_1 + \frac{2K_2^2 [X_{(B)}]^2}{[X_{(W)}]} \\ &= K_1 + 2K_2^2 \cdot \frac{[X_{(B)}]^2}{[X_{(W)}]} \cdot \frac{[X_{(W)}]}{[X_{(W)}]} = K_1 + 2K_2^2 K_1^2 [X_{(W)}] \\ &= K_1 + 2K_2^2 \cdot K_1^2 \cdot C_W \end{aligned}$$

Therefore, a plot of $\frac{C_B}{C_W}$ (ordinate) against C_W (abscissa) should be a straight line with a slope equal to $2K_2^2 K_1^2$ and intercept K_1 . Thus, from the slope and intercept, we can calculate the values of K_1 and K_2 .

Procedure: Exactly the same as in experiment 2. For a good curve, take 5–6 bottles, if possible, instead of three bottles taken in experiment 2.

Observations: Exactly the same observations as made in experiment 2.

Calculations: Calculate the values of C_1 and C_2 for each bottle, exactly on the same lines as done in experiment 2. In this case, C_1 and C_2 values will correspond to C_W and C_B . Now

calculate the values of $\frac{C_B}{C_W}$ for each bottle. Plot a curve

with $\frac{C_B}{C_W}$ values as ordinate against C_W values as abscissa. The curve will be a straight line [fig. (3)] and the slope of the straight line on abscissa and intercept on the ordinate will be given by $2K_2^2 K_1^2$ and K_1 , respectively.

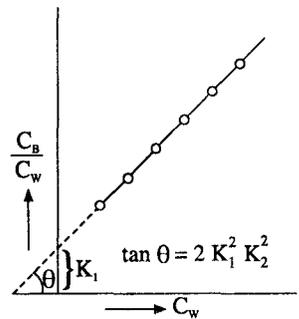


Fig. 3.

$$\therefore (1) \quad 2K_1^2 K_2^2 = \dots$$

and $(2) \quad K_1 = \dots$

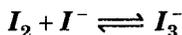
From these two equations, we can calculate the value of dimerisation constant, K_2 of benzoic acid.

Result : The dimerisation constant of benzoic acid in benzene is ...

Precautions : Same as in preceding experiment.

EXPERIMENT No. 4

Object : To find the equilibrium constant for the tri-iodide formation



Apparatus : Same as in preceding experiment.

Theory : When iodine is distributed between carbon tetrachloride and water, the simple distribution law is obeyed, according to which,

$$K = \frac{\text{Concentration of iodine in } CCl_4 \text{ layer}}{\text{Concentration of iodine in water layer}}$$

However, the above equation is not applicable, if iodine is distributed between an organic solvent, say carbon tetrachloride and an aqueous solution of potassium iodide, because in the aqueous layer, the complex KI_3 or the complex ion I_3^- is formed due to the reaction: $(KI + I_2 \rightleftharpoons KI_3)$. The distribution law can be applied provided the concentration of free iodine in the aqueous layer is taken into account.

If iodine is distributed between CCl_4 and an aqueous solution of KI , then the total concentration of iodine in the aqueous layer is given by the sum of the concentration of free iodine in the aqueous layer and the concentration of iodine present as KI_3 or I_3^- . The total concentration of iodine in the aqueous layer can be determined by titration with standard sodium thiosulphate solution. The concentration of iodine in the CCl_4 layer can also be determined by titration with standard sodium thiosulphate solution. Thus, the concentration of free iodine in the aqueous layer can be determined by dividing the concentration of iodine in CCl_4 layer by the partition coefficient. Now, we can calculate the values of I_3^- and I^- ions, provided the initial concentration of KI is known. Once the value of C_{I_2} , C_{I^-} and $C_{I_3^-}$ are known, we can calculate the equilibrium constant according to the expression,

$$K = \frac{C_{I_3^-}}{C_{I_2} \times C_{I^-}} \quad \text{or} \quad \frac{C_{KI_3}}{C_{I_2} \times C_{KI}} \quad \dots (1)$$

Let K_1 be the partition coefficient of iodine between organic and water layer. Suppose C_1 mole/litre and C_2 mole/litre is the concentration of iodine in organic layer and aqueous KI layer, respectively.

$$\therefore [\text{Free } I_2] \text{ in aqueous layer} = \frac{C_1}{K_1} \text{ mole/litre}$$

$$\therefore [I_3^-] = \text{Total iodine concentration in aqueous layer} - \text{free iodine concentration,} \\ \text{i.e., [free } I_2]$$

$$= \left(C_2 - \frac{C_1}{K_1} \right) \text{ mole/litre.}$$

Let the initial concentration of I^- be C_3 mole/litre. As one mole of I_3^- is formed out of one mole of I^- , therefore, concentration of free KI at equilibrium will be given by,

$$[\text{Free KI}] = \left[C_3 - \left(C_2 - \frac{C_1}{K_1} \right) \right] \text{mole/litre}$$

Thus, according to equation (1), we get,

$$K = \frac{\left(C_2 - \frac{C_1}{K_1} \right)}{\frac{C_1}{K_1} \times \left[C_3 - \left(C_2 - \frac{C_1}{K_1} \right) \right]}$$

Procedure : Take 3 stoppered reagent bottles and make the following solutions.

Bottle 1. 40 ml saturated I_2 solution in CCl_4 + 10 ml of pure CCl_4 + 200 ml water.

Bottle 2. 30 ml saturated I_2 solution in CCl_4 + 20 ml of pure CCl_4 + 200 ml water.

Bottle 3. 20 ml saturated I_2 solution in CCl_4 + 30 ml of pure CCl_4 + 200 ml water.

Shake the solutions well for about 20–30 minutes. Allow the two layers to separate clearly. Now from bottle 1, pipette out 5 ml of the CCl_4 solution into a conical flask containing 10 ml $N/10$ KI solution and 1 ml of starch solution. Now titrate it with $N/10$ $Na_2S_2O_3$ solution. Similarly, pipette out 50 ml of the aqueous layer into a conical flask containing 10 ml of $N/10$ KI solution and 1 ml of starch solution. Now titrate it against $N/100$ $Na_2S_2O_3$ solution. Repeat the procedure for the remaining bottles numbered 2 and 3.

Important : *It is advisable to avoid contamination of the aqueous layer by the CCl_4 layer as iodine is so much concentrated in the CCl_4 layer, that even a drop of the CCl_4 solution may produce an appreciable error in the estimation.*

Now carry out similar experiment with $M/10$, $M/15$, $M/20$ KI solution in place of water, by taking another set of three bottles.

Bottle 4. 40 ml of saturated solution of I_2 in CCl_4 + 10 ml of pure CCl_4 + 200 ml of $N/10$ KI solution.

Bottle 5. 30 ml of saturated solution of I_2 in CCl_4 + 20 ml of pure CCl_4 + 200 ml of $N/15$ KI solution.

Bottle 6. 20 ml of saturated solution of I_2 in CCl_4 + 50 ml of pure CCl_4 + 200 ml of $N/20$ KI solution.

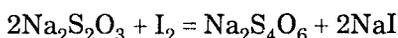
Observations :

Bottle number	Volume of $N/10$ $Na_2S_2O_3$ for 5 ml of organic layer (ml)	Volume of $N/100$ $Na_2S_2O_3$ for 50 ml of aqueous layer (ml)	Concentration of I_2 in organic layer C' (Normality)	Concentration of I_2 in aqueous layer C'' (Normality)	$K_1 = \frac{C'}{C''}$
1	Mean
2	$K_1 = \dots$
3

Bottle number	Volume of N/100 Na ₂ S ₂ O ₃ for 50 ml aqueous layer (ml)	Volume of N/10 Na ₂ S ₂ O ₂ for 5 ml organic layer (ml)
4
5
6

Calculations : Suppose the strength of Na₂S₂O₃ solution

$$= x \text{ N/10}$$



i.e., 1 mole of Na₂S₂O₃ \equiv $\frac{1}{2}$ mole of I₂

\therefore 1000 ml N—Na₂S₂O₃ \equiv 0.5 mole of I₂

\therefore 1 ml N—Na₂S₂O₃ \equiv 0.5×10^{-3} mole of I₂

\therefore 1 ml N/10—Na₂S₂O₃ \equiv 0.5×10^{-4} mole of I₂

\therefore 1 ml x N/10—Na₂S₂O₃ \equiv $x \times 0.5 \times 10^{-4}$ mole of I₂

V_1 ml x N/10—Na₂S₂O₃ \equiv $x \times V_1 \times 0.5 \times 10^{-4}$ mole of I₂

Similarly, 1 ml x .N/100—Na₂S₂O₃ \equiv $x \times 0.5 \times 10^{-5}$ mole of I₂

V_2 ml x .N/100—Na₂S₂O₃ \equiv $x \times V_2 \times 0.5 \times 10^{-5}$ mole of I₂

As 5 ml of organic layer is pipetted out for titration, therefore,

5 ml contains, $\times V_1 \times 0.5 \times 10^{-4}$ mole of I₂/litre

\therefore 1000 ml contains, $\frac{x \times V_1 \times 0.5 \times 10^{-4}}{5} \times 1000$ mole of I₂/litre

$$C_1 = 0.01 x V_1 \text{ mole/litre}$$

Similarly, 50 ml of aqueous layer is pipetted out for titration,

\therefore 50 ml contains, $x \times V_2 \times 0.5 \times 10^{-5}$ mole of I₂/litre

\therefore 1000 ml contains, $\frac{x \times V_2 \times 0.5 \times 10^{-5}}{50} \times 1000$ mole of I₂/litre

$$C_2 = x \times V_2 \times 10^{-4} \text{ mole/litre.}$$

Bottle number	Conc. of total I ₂ in aqueous layer (mole/lit) C ₂	Conc. of I ₂ in organic layer (mole/lit) C ₁	Conc. of free I ₂ in aqueous layer C ₁ /K ₁	Conc. of KI ₃ formed [C ₂ - (C ₁ /K ₁)] (mole/lit)	Conc. of KI initially, C ₃ (mole/lit.)	Conc. of KI in equilibrium C ₃ - [C ₂ - (C ₁ /K ₁)] (mole/lit)	K (mole ⁻¹ lit.)
4
5
6

∴ Mean value of equilibrium constant = ...

Result : The equilibrium constant for the tri-iodide formation $I_2 + I^- \rightleftharpoons I_3^-$ is ... mole⁻¹ lit.

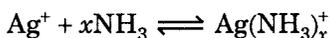
Precautions : Same as in preceding experiments.

EXPERIMENT No. 5

Object : *To study the complex formation and to find the formula of the silver ammine complex by partition method.*

Apparatus : Burette, pipettes, beakers, conical flasks etc.

Theory : A complex compound is formed when an ammonia solution is added in excess to a solution containing silver ions, *i.e.*,



The equilibrium constant is thus given by,

$$K = \frac{[Ag(NH_3)_x^+]}{[Ag^+][NH_3]^x} \quad \dots (1)$$

We can thus find the formula of the complex, provided we know the value of x . The value of x cannot be determined directly by simple titration, because the equilibrium shifts from left to the right side as ammonia is gradually removed during titration. Thus, the concentration of free ammonia and complexed ammonia cannot be determined by the above method. However, the theory of determining x is given below :

According to solubility product principle, a precipitate is obtained when the ionic product exceeds the solubility product of the substance. Similarly, when a solution of KCl is added to AgNO₃ solution, AgCl will be precipitated when the ionic product $[Ag^+][Cl^-]$ exceeds the solubility product, K_s of AgCl. We know that,

$$K_s = [Ag^+][Cl^-] \quad \dots (2)$$

If ammonia is added to the system containing silver nitrate, a stable complex is formed between Ag⁺ and ammonia, which results in fall of concentration of Ag⁺ ions. Therefore, relatively large concentration of chloride ions is to be added to ammonical silver nitrate in order to precipitate AgCl. Thus, when precipitation occurs, the concentration of free silver ions in the solution is inversely proportional to the concentration of chloride ions added, *i.e.*,

$$[Ag^+] = \frac{K_s}{[Cl^-]} \quad \text{[From equation (2)]} \quad \dots (3)$$

When AgCl is precipitated from ammonical silver nitrate, we have from equations (2) and (3),

$$K = \frac{[Ag(NH_3)_x^+][Cl^-]}{K_s[NH_3]^x} \quad \dots (4)$$

If we add a large excess of ammonia, the concentration of the complex ions, Ag(NH₃) _{x} ⁺ is constant for the given set of experiments. Thus, from equation (4), we have,

$$K = \text{constant} \times \frac{[\text{Cl}^-]}{[\text{NH}_3]^x} \quad \dots (5)$$

If V_1 and V_2 be the volumes of KCl and ammonia added, then equation (5) can be written as,

$$K = \text{constant} \times \frac{V_1}{V_2^x}$$

or
$$\frac{V_1}{V_2^x} = \text{constant}$$

or
$$\log V_1 = x \log V_2 + \log (\text{constant}).$$

On plotting $\log V_1$ as ordinate against $\log V_2$ as abscissa we get a straight line, whose slope is equal to x .

Procedure : Prepare 250 ml of 2M ammonia solution and 200 ml of M/200 potassium chloride solution. *The former solution can be prepared by titrating a concentrated solution of ammonia against hydrochloric acid and then diluting it accordingly to get 2M solution.* Prepare the following mixtures containing ammonia solution, M/100 AgNO₃ solution and distilled water.

Mixture number	AgNO ₃ solution (ml)	Ammonia solution (ml)	Distilled water (ml)
1	25	15	60
2	25	20	55
⋮	⋮	⋮	⋮
6	25	40	35

Now titrate each mixture with standard M/200 KCl solution, until permanent cloudiness just occurs. Note the titrant volume. Say it is T_1 ml.

Repeat the above series of experiments, but make the total volume to $(100 - T_1)$ ml instead of 100 ml. Again titrate each mixture solution with standard KCl solution, until a permanent cloudiness just occurs. Let the second titrant volume be T_2 ml.

Calculations :

Mixture number	Volume of NH ₃ (V_2 ml)	$\log V_2$	T_1 (ml)	$T_2 = V_1$	$\log V_1$
1					
2					
⋮					
6					

Now plot $\log V_1$ as ordinate against $\log V_2$ as abscissa and find out the slope. Therefore, slope = x .

Result : The formula of the silver ammine complex is

Precautions : The solution of ammonia should be kept well stoppered, otherwise its concentration may change.

EXPERIMENT No. 6

Object : *To find the formula of complex cuprammonium ion or study the complex formation between copper sulphate and ammonia solution.*

Apparatus : Same as in preceding experiments.

Theory : An intense blue colour is obtained due to the complex formation, when a solution of cupric salt is mixed with ammonia solution, *i.e.*,



If we know the value of x , we can find out the formula of the cuprammonium complex ion. Ammonia will be consumed in the formation of the complex, while some of it will remain in free state. We can, however, calculate the value of x , if we know the concentration of ammonia in the free state as well as in complex state.

We take any one immiscible solvent in which one of the compounds, say free ammonia, is soluble, but not others. We can then find the concentration of this component in the solvent without disturbing the equilibrium (1), with the help of its partition coefficients between the two immiscible solvents.

In the present case an aqueous solution of known concentration of copper sulphate in ammonia is mixed with an immiscible solvent, say chloroform. The total ammonia, both free and complex, is determined by titration of the aqueous layer. The concentration of ammonia in the chloroform layer is also determined by titration. We can now calculate the concentration of free ammonia in the aqueous layer, by the value of partition coefficient of ammonia between water and chloroform. Thus, we have,

$$\text{Partition coefficient, } K = \frac{[\text{NH}_3] \text{ in aqueous layer}}{[\text{NH}_3] \text{ in chloroform layer}}$$

\therefore Concentration of complexed NH_3

$$= \text{Total concentration of ammonia [both as } \text{NH}_3 \text{ and } \text{Cu}(\text{NH}_3)_x^{2+}] - \text{Concentration of free ammonia.}$$

From the initial copper sulphate solution, we can calculate the value of x .

Procedure : The actual procedure consists of two steps :

(1) Determination of partition coefficient of ammonia between water and chloroform.

Prepare at least three mixtures of ammonia, chloroform and distilled water as follows :

Mixture number	Volume of 1.2N NH_4OH (ml)	Volume of chloroform (ml)	Distilled water (ml)
1	40	40	20
2	50	40	10
3	60	40	0

Shake the bottles well for about 20–25 minutes and separate the water and chloroform layers in each bottle. Now from bottle number 1, pipette out 10 ml of the aqueous layer (top layer) and titrate it with $N/2$ HCl solution. (Exact $N/2$ HCl solution is prepared, as described earlier), using methyl orange as an indicator. Now take 20 ml of the chloroform layer (lower layer) of the first vessel and titrate it against $N/20$ HCl solution, using the same indicator. Repeat the above process for the aqueous and chloroform layers of each mixture contained in bottles number 2 and 3.

(2) Determination of the formula of cuprammonium ion.

Take 40 ml of 1.2 N solution of ammonia in a reagent bottle and add 5 ml of $M/2$ CuSO_4 solution. Shake the contents till all the precipitate dissolves. Add 5 ml of ammonia solution, so that the total volume of the mixture becomes 50 ml. Now add 50 ml of chloroform. Shake the contents for 20–25 minutes and allow the two layers to separate out.

Now pipette out 10 ml of the upper aqueous layer in a conical flask. Add some distilled water to it and titrate it against $N/2$ HCl using methyl orange as an indicator. The blue colour initially masks the colour of the methyl orange but fades out before the end point is reached.

Take whole of the chloroform layer in a big conical flask and titrate it against $N/20$ HCl solution, using the same indicator.

The above procedure is repeated with a lower concentration of ammonia. In the next experiment, take 35 ml of ammonia solution in a reagent bottle and add 5 ml of $M/2$ CuSO_4 solution. Now add 10 ml distilled water to make the volume 50 ml. Add 50 ml of fresh chloroform so that the total volume become 100 ml. Now shake the contents and titrate each layer as described above.

A third series of solutions can be made by mixing 25 ml ammonia, 5 ml CuSO_4 , 20 ml distilled water and 50 ml chloroform. The process as described above is, however, repeated.

Observations : (1) Table for partition coefficient

S.N.	Bottle number	Volume of $N/2$ HCl used for 10 ml of aqueous layer	Volume of $N/20$ HCl used for 25 ml of chloroform layer

(2) Table for the value of x

S.N.	Bottle number	Volume of $N/2$ HCl used for 10 ml of aqueous layer (V_1 ml)	Volume of $N/20$ HCl used for 50 ml of chloroform layer (V_2 ml)

Calculations : (1) Table for calculating partition coefficient of ammonia between H_2O and $CHCl_3$

Bottle number	Concentration C_1 of NH_3 in aqueous layer (in normality)	Concentration C_2 of NH_3 in chloroform layer (in normality)	Partition coefficient $K = C_1/C_2$
1
2
3

(2) Table for calculating the value of x

Bottle number	Concentration of NH_3 (free + complexed) = $\frac{V_1}{20}$ mole/litre (x_1)	Concentration of NH_3 in chloroform layer = $\frac{V_1}{1000}$ mole/litre	Concentration of free NH_3 in aqueous layer = $\frac{K.V_2}{1000}$ mole/litre (x_2)
1
2
3

The concentration of copper sulphate is $1/20$ g mole per litre, as its $M/2$ solution has been diluted ten times.

Bottle number	Concentration of combined NH_3 = $(x_1 - x_2)$ mole/litre	Concentration of cupric ions, $[Cu^{2+}]$ (g ion/litre)	Value of x = $\frac{[Total NH_3]}{[Cu^{2+}]}$ = $20 \times (x_1 - x_2)$
1	1/20
2	1/20
3	1/20

Result : The formula of cuprammonium complex ion is ...

Precautions : (i) The bottles should be tightly corked so that no evaporation of ammonia takes place.

(ii) No water layer should enter the chloroform layer while separating and titrating the later layer.

(iii) A cork should also be fitted on the stem of the funnel to rest on top of the unstoppered bottle, so as to reduce the loss of ammonia by evaporation.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 7

Object : To determine the partition coefficient of succinic acid between water and ether.

For this experiment prepare 4-5% succinic acid solution (stock solution). Take 50, 40 and 30 ml of the stock solution in three glass stoppered bottles labelled as 1, 2 and 3 and add 0, 10 and 20 ml of water, respectively to make the total volume of 50 ml in each bottle. Now add 50 ml of ether to each bottle, cork them and shake vigorously for 25-30 minutes. *After final shaking swirl the bottles so that any drops of liquid adhering to the sides of the bottle settle down.* When the two layers have separated completely the upper layer will be of ether and the lower of water.

Pipette out 10 ml of ether layer from bottle no. 1 in a conical flask containing about 20 ml of distilled water. Titrate this solution with $\frac{N}{20}$ NaOH solution using phenolphthalein (indicator) solution. Record at least 3 readings for the ether layer for each bottle.

Now record three titre values for the aqueous layer, from each bottle using 10 ml of solution each time and titrating it against $\frac{N}{10}$ NaOH solution, using phenolphthalein solution as an indicator. Record the observations and tabulate the results as given in experiment no. 2

If the values of $C_{\text{water}}/C_{\text{ether}}$ for all the three bottles are the same, it can be said that distribution law has been verified.

EXPERIMENT No. 8

Object : *To determine the molecular weight of succinic acid in benzene by determining its partition coefficient with water.*

Suppose n moles of succinic acid associate in benzene, then according to partition law,

$$K = \frac{\text{Concentration of moles of acid in benzene layer, } (C_1)^{1/n}}{\text{Concentration in moles of acid in aqueous layer, } (C_2)}$$

where K = partition coefficient.

On taking logarithms, we get,

$$\log K = \frac{1}{n} \log C_1 - \log C_2 \quad \text{or} \quad \log C_2 = \frac{1}{n} \log C_1 - \log K$$

On plotting $\log C_2$ as ordinate against $\log C_1$ as abscissa, we get a straight line whose slope will be equal to $1/n$ and intercept will be equal to $-\log K$.

The molecular weight of the acid in benzene will be n times its normal molecular weight.

EXPERIMENT No. 9

Object : *To study the partition of salicylic acid or picric acid between water and benzene and between water and chloroform.*

Proceed as in experiment no. 2.

EXPERIMENT No. 10

Object : *To find the dimerisation constant of phthalic acid in a suitable solvent of your choice.*

Proceed as explained in experiment no. 3.

EXPERIMENT No. 11

Object : *To find the partition coefficient of acetic acid between water and cyclohexane or butanol.*

Apparatus and Chemicals : Three burettes, four 100 ml bottles or separating funnels, 2M acetic acid (116 ml of glacial acetic acid per litre of solution), titration set, 0.5 and 0.1M NaOH solutions, solvent residue bottles, phenolphthalein solution (indicator).

Procedure : Prepare the following solutions :

2M acetic acid (ml)	Organic solvent (ml)	Water (ml)
50	25	0
35	25	15
25	25	25
10	25	40

Shake each mixture for 5-10 minutes and allow to stand till layers separate completely. Separate the layers and titrate 10 ml portions of the layers. Use 0.1M NaOH solution for titrating organic layer and 0.5 M NaOH solution for titrating water layer.

Plot a graph between C_{org} and C_{water} and between C_{org} and C_{water}^2 and tabulate the results. The results can be compared for cyclohexane and butanol.

EXPERIMENT No. 12

Object : *To find the molecular state of benzoic acid in benzene and water.*

Proceed as explained in experiment no. 2. The molecular state of benzoic acid in benzene is found to be dimeric, as values of $\sqrt{C_{\text{benzene}}}/C_{\text{water}}$ remain constant for different bottles.



Graham classified the matter into two types, *viz.*, **crystalloids** and **colloids** on the basis of their diffusion across an animal membrane or a parchment paper. The dissolved particles of crystalloids passed easily through the membrane, whilst the dissolved particles of colloids did not pass through it. As the terms indicate, a colloid is a substance which does not crystallise and this is the meaning applied to these terms by Graham. Hence, it follows that crystalloids and colloids are different kinds of matter. But modern work has shown that crystalloids and colloids are not different kinds of matter but rather different states of matter.

The properties of colloidal solutions are markedly different from those of true solutions. A true solution is a homogeneous mixture of a solute and solvent, *i.e.*, every part of a true solution has the same composition. In true solutions, the solute exists generally as simple molecules, which are invisible under all circumstances and the size of the particles in a true solution varies and is generally less than 10^{-7} cm in diameter. On the contrary, a colloidal solution is heterogeneous in character. The colloidal particles vary in size from 10^{-5} to 10^{-7} cm in diameter and can be seen under the influence of an ultramicroscope.

Thus, we can conclude that a colloidal system is a heterogeneous system of two phases. The substance which is distributed in a medium, *i.e.*, substance which is subdivided into smaller parts is known as **dispersed phase** and the medium in which the particles are distributed is known as **dispersion medium**. For example, in a colloidal solution of ferric hydroxide in water, the former is the dispersed phase and the latter is the dispersion medium. The degree to which the reduction of the size of the dispersed phase has been carried out is known as **dispersity** of the system. There are two types of colloids.

(i) **Lyophilic or hydrophilic colloids** : Such colloids form colloidal solution by bringing them in contact with water, *e.g.*, starch, gum, arabic etc. (lyo = solvent, hydro = water, philic = loving).

(ii) **Lyophobic colloids** : Such colloids cannot form a colloidal solution by simply bringing them in contact with water, but special methods have to be devised, *e.g.*, sols of metal sulphides, metal hydroxides and metals etc. (phobic = hating).

Purification of Colloidal Solutions : The colloidal solutions obtained by any method may contain some impurities, both in the dissolved as well as suspended state. The latter can be easily removed by simple filtration method. The suspended impurities can, however, be removed by a process known as **dialysis**. This process consists in supporting a parchment membrane *a*, which is stretched along a shallow glass bell jar *b* in a large vessel *C* of water [fig. (1)]. The vessel is known

as **dialyser**. The impure solution is poured into the dialyser, when the crystalloid molecules pass into the water. The solution is kept for 24 hours to carry out dialysis. The water in *C* must be changed repeatedly and eventually the colloidal solution becomes free from crystalloids. A better form of dialyser [fig. (2)] can be made from a tube of parchment paper, which is soaked in water and placed in a wide cylinder of distilled water. The colloidal solution is poured into the tube, when the separation occurs. There should be an outlet and an inlet for water, to perform the process of dialysis more quickly.

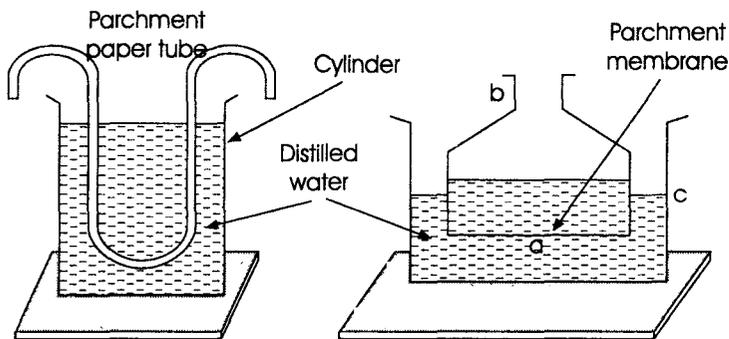


Fig. 1 : Dialyser

Fig. 2 : Dialysis

Precipitation of Colloids and Schulze-Hardy Law : We see that when an electrolyte is added to a sol, precipitation occurs. The precipitation value of an electrolyte is defined as, '*the minimum concentration of the electrolyte, expressed in millimoles of the electrolyte per litre of the colloidal solution, necessary to bring about precipitation or coagulation of the sol, when the electrolyte is added to the sol*'.

The precipitation, coagulation or flocculation value of an electrolyte depends upon the nature of the colloid, its method of preparation, concentration of sol and the nature and valency of the active ion (ion which is responsible to bring about precipitation).

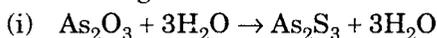
In the coagulation of a positively or negatively charged sol, the active ions will be anions or cations, respectively of an electrolyte. The addition of an electrolyte will cause the charge on the colloidal particles to neutralise. Once the colloidal particles are robbed off their charge, they come together and coagulate. On this basis, Schulze and Hardy gave a law according to which, '*higher the valency of the active ion, greater will be its coagulating power*.' In other words, we can say that higher the valency, the lower is the precipitation value.

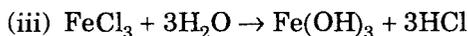
EXPERIMENT No. 1

Object : To prepare colloidal solution of arsenic sulphide, antimony sulphide, ferric hydroxide, sulphur, silver and gold.

Apparatus : Dialyser, vessel, beakers, parchment paper etc.

Theory : The colloidal solution of the substances, can be prepared according to the following reactions :





Procedure : (i) **As₂S₃ sol :** Weigh about 100 g of pure As₂O₃ and boil it for 10-15 minutes in 200 ml of distilled water till it completely dissolves. Now cool the solution to room temperature. If whole of As₂O₃ has not dissolved, filter it to get a clear solution. Now pass H₂S gas slowly into As₂O₃ solution, taken in a beaker. **The H₂S gas is previously washed by bubbling through water.** The H₂S gas is passed till the opalescent liquid becomes yellow turbid. Now the excess of H₂S is removed by bubbling a stream of CO₂ or H₂ gas through the beaker. Filter the sol through a fluted filter paper and collect the filtered sol in another beaker. Now dialyse this sol by means of a parchment paper (as described earlier), for 24 hours. This will give almost pure As₂S₃ sol.

(ii) **Sb₂S₃ sol. :** Prepare 0.5% solution of tartar emetic in distilled water and place it in a beaker or a dropping funnel. Place 200 ml of water in a flask and pass a not too fast stream of H₂S, which is washed by bubbling it through water.

Allow the tartar emetic solution to fall drop-by-drop into the H₂S solution in which H₂S is passing. Under these conditions, Sb₂S₃ will not precipitate but will remain in the colloidal form as a deep orange coloured solution. Now remove the excess of H₂S gas, by passing either CO₂ or H₂ gas through the sol. After doing this, the sol is filtered and the filtrate is dialysed, as already explained.

(iii) **Fe(OH)₃ sol :** Prepare fresh saturated solution of ferric chloride (30%). Take about 500 ml of distilled water in a beaker and boil it. To this boiling water, add drop-by-drop 10 ml saturated solution of ferric chloride with constant stirring. With the fall of each drop, ferric chloride is hydrolysed to form a deep red sol of ferric hydroxide. The sol thus obtained is dialysed as explained above.

(iv) **Sulphur sol :** Add 20 ml of 0.1M sodium thiosulphate to 100 ml of water. Then add drop-by-drop and with constant stirring 1 ml of 2M HCl. The yellow coloured sulphur sol is formed slowly. Dialyse the sulphur sol to remove NaCl formed during the reaction.

(v) **Silver sol :** Take 500 ml of 0.05N silver nitrate solution. Add 5 to 10 ml of 1% tannic acid solution and heat to 70-80°C. Now add 10 ml of 1% sodium carbonate solution drop-by-drop and with constant stirring. Silver carbonate thus formed is immediately reduced by tannic acid to give a tea coloured silver sol. The impure silver sol is then dialysed to remove the electrolytic impurities.

(vi) **Gold sol : (a) Blue gold sol :** Add 1 ml of 1% chloroauric acid (HAuCl₄) solution to 200 ml water. Add drop-by-drop and with constant stirring 1% hydrazine solution. A blue coloured gold sol is formed immediately. The sol is dialysed to get it in pure form.

(b) **Red gold sol :** Add 1 ml of 1% chloroauric acid to 200 ml water and then make it alkaline with 2M NH₄OH. Then add drop-by-drop and with constant stirring fresh and dilute tannin solution, till an intense red colour is formed. Increase the temperature of mixture to boiling point and add 1 ml more of 1% chloroauric acid and a little more tannin solution. The sol is dialysed to get pure sol.

Precautions : (i) While preparing the sol of As_2S_3 and Sb_2S_3 , excess of H_2S should be completely removed.

(ii) During dialysis, water should be continuously changed after every hour to obtain good results.

EXPERIMENT No. 2

Object : To find the precipitation values of arsenious sulphide sol by using monovalent, bivalent and trivalent cations. Also test the validity of Schulze-Hardy law and Freundlich's adsorption isotherm.

Apparatus : A number of boiling test tubes etc.

Theory : As already discussed, the precipitation value is the minimum concentration of the electrolyte, expressed in millimole of the electrolyte per litre of the sol, necessary to bring about its precipitation. According to Schulze-Hardy law, the precipitation value should decrease with increasing valency of the active ions.

It is supposed that ions of opposite charge get adsorbed on colloidal particles and thus bring down the zeta potential below a critical value. As zeta potential is responsible for the stability of sols, hence its decrease below a critical value will cause coagulation. Hence, electrically equivalent ions of different valencies should be adsorbed, *i.e.*, the quantity of univalent, bivalent and trivalent ions adsorbed should be in the ratio 3.0, 1.5 and 1.5, respectively.

Freundlich's adsorption isotherm can be written as,

$$P = kC^{1/n}$$

where the above mentioned numbers 3.0, 1.5, 1.0 should be proportional to P . C is the precipitation value, n is an integer whose value varies from zero to unity. Therefore, on taking logarithm, we get,

$$\log P = \log k + \frac{1}{n} \log C$$

Thus, a plot of $\log P$ and $\log C$ should be a straight line, if Freundlich's adsorption isotherm is valid.

Procedure : Take 10 cleaned and dried test tubes. Number them from 1 to 10 and arrange them in a test tube stand. Now take two burettes and fill one of them with distilled water and the other with 0.2M NaCl solution.

How to observe the coagulation stage

Sometimes, it becomes very difficult to decide whether coagulation has occurred or not. We can face this situation by examining the solution in the test tube from the top downwards and to compare with the tube in which no electrolyte has been put. The change to a deeper colour is taken as incipient or beginning of coagulation. It may be easier to recognise this situation by seeing vertically down a tube.

Having found the approximate salt concentration required to precipitate a sol, a more accurate value can be measured by repeating the above experiment with smaller change in the concentration range between values where precipitation (or coagulation) has and has not occurred.

Now prepare the following solutions :

Test tube number	Amount of distilled water (ml)	Amount of 0.2M NaCl solution (ml)	Observations
1	9	1	In this table, note against each test tube whether the solution remains clear or turbid after adding As_2S_3 sol.
2	8	2	
3	7	3	
4	6	4	
5	5	5	
6	4	6	
7	3	7	
8	2	8	
9	1	9	
10	0	10	

In each of the above ten test tubes, add 10 ml of freshly prepared pure sol of As_2O_3 . Stopper the test tubes by a rubber cork and shake the contents by inverting the test tubes. After an hour, invert the tubes again. Now allow them to stand for about 2 hours. Now note in which test tube the solution becomes turbid. Record this observation in the above table. Suppose the solution remains clear upto the fifth test tube, but becomes turbid in each of the next test tubes. This means that precipitation occurs between 5 and 6 ml of 0.2M NaCl. In the next set, prepare the following solutions.

Test tube number	Amount of distilled water (ml)	Amount of 0.2M NaCl solution (ml)	Observations
11	5.0	5.0	Note the same observations as made in the previous table.
12	4.9	5.1	
13	4.8	5.2	
14	4.7	5.3	
15	4.6	5.4	
16	4.5	5.5	
17	4.4	5.6	
18	4.3	5.7	
19	4.2	5.8	
20	4.1	5.9	
21	4.0	6.0	

Add 10 ml of pure As_2S_3 sol in each of the above test tubes and keep them for about 2 hours. Note in which test tube the precipitation occurs, *i.e.*, solution becomes turbid. The test tube in which turbidity occurs will give the precipitation

value for NaCl. Prepare 0.005M barium chloride and 0.0005M potash alum solutions. Find out the precipitation values for these electrolytes, as done in the case of sodium chloride.

Dilute the original sol two times. Repeat the procedure and find out the precipitation value for As_2S_3 sol, having half of the previous concentration.

Calculations : The concentration of NaCl in each test tube from number 1 to 10 can be calculated as follows :

1 ml of 0.2M stock NaCl solution contains 0.2 millimole (1 millimole \equiv 0.001 mole). This amount is then diluted to 20 ml (10 ml distilled water and solution + 10 ml sol). Therefore, 100 ml of such solution would contain $\frac{0.2}{20} \times 1000 = 10$ millimole.

Similarly, the concentration of NaCl solution in other test tubes from 2 to 10 will be 20, 30, 40, 50, 60, 70, 80, 90 and 100 millimole per litre. Similarly, the concentration of NaCl solution in test tubes 11 to 21 can be calculated. The concentration in millimole per litre can thus be found from the second set of test tubes, which will give the precipitation value of NaCl.

Similarly, we can calculate and find out the precipitation value of BaCl_2 and potash alum.

Since in the three electrolytes, the active ions are Na^+ , Ba^{2+} and Al^{3+} ions, respectively, we observe that the precipitation value decreases in the order Na^+ , Ba^{2+} , Al^{3+} , which proves Schulze-Hardy law.

For proving the validity of Freundlich adsorption isotherm, proceed and calculate as follows :

Experiment 1				Experiment 2			
Electrolyte	Precipitation value (C)	log C	log P	Electrolyte	Precipitation value (C)	log C	log P
NaCl (Na^+)	log 3.0	NaCl (Na^+)	log 3.0
BaCl_2 (Ba^{2+})	log 1.5	BaCl_2 (Ba^{2+})	log 1.5
Alum (Al^{3+})	log 1.0	Alum (Al^{3+})	log 1.0

We observe that the values of C are the same in both the experiments (In experiment 2, the solution concentration is half of that in experiment 1), which also proves Schulze-Hardy law.

A plot of log P as ordinate against log C as abscissa is a straight line in both the experiments, which proves the validity of Freundlich adsorption isotherm.

Result : The precipitation value for As_2S_3 sol of Na^+ , Ba^{2+} and Al^{3+} ions is ... , ... and ... , respectively.

Precautions : (i) The turbidity in each test tube should be observed very carefully.

EXPERIMENT No. 3

Object : To investigate the nature of charge on particles in a given colloidal solution and determine their electrophoretic velocity and zeta potential.

Apparatus : Burton's cataphoretic apparatus, D.C. supply, cathetometer, voltmeter, conductance bridge, colloidal solution of As_2S_3 or $Fe(OH)_3$, 0.1N KCl solution.

Theory : When a potential is applied to a sol, its particles migrate towards the oppositely charged electrodes. The direction of movement thus depends upon the nature of charge on sol particles.

Electrophoretic mobility of a sol particle is defined as *its migration velocity under a potential gradient of 1 volt/cm*. Potential gradient (P.G) is given by,

$$\text{P.G.} = \frac{\text{Applied voltage (volt)}}{\text{Distance between two electrodes (cm.)}}$$

If, on applying a voltage of V volt between two electrodes l cm apart, the boundary of a sol moves a distance d cm in t sec, then,

$$\text{Potential gradient} = \frac{V}{l} \text{ volt/cm.}$$

$$\text{Migration velocity, } u = \frac{d}{t} \text{ cm/sec.}$$

$$\begin{aligned} \therefore \text{Electrophoretic mobility} &= \frac{\text{Migration velocity}}{\text{Potential gradient}} \\ &= \frac{d/t}{V/l} = \frac{dl}{tV} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1} \end{aligned}$$

Moreover, an electrical double layer is formed at the interface between the dispersed phase and dispersion medium. The magnitude of the potential between these layers, known as **zeta potential** (ξ) is given by the relation,

$$\xi = \frac{4\pi\eta u}{E.D.}$$

where, η is the viscosity of the dispersion medium, u is the migration velocity of colloidal particles, E is the potential gradient and D is the dielectric constant of the medium.

Procedure : Thoroughly clean the U-tube and grease well all the taps so that they do not leak. Keep the taps in the side arms open and by means of a long funnel fill the lower part of the U-tube by the sol (say As_2S_3), so that some of the sol enters the side arms. Turn off all the taps and remove any sol from the parts of the side arms above the taps.

Now carefully fill the top portion of the U-tube with water (dispersion medium) and insert two platinum foil electrodes in the dispersion medium. Note the positions of the electrodes. Open the taps in the side arms and care should be taken

that the sol and dispersion medium do not mix so that sharp boundaries are formed.

Now focus the telescope of the cathetometer on one of the boundaries and note its initial reading. Now join the electrodes with D.C. supply or rectifier with A.C. at a potential difference of 100-150 volt. Allow the current to pass for about 15-20 minutes. Note the exact potential applied and the time of its passage. Record the direction of migration of the boundary and also note its final position by means of cathetometer.

Now remove the sol and the dispersion medium from the U-tube and after washing it thoroughly, fill it with 0.1N KCl solution. Insert the electrodes in the limbs and put them exactly at the same position as in the case of sol. Measure the resistance of the solution column between the electrodes by means of a conductance bridge. Lower or raise the electrodes by an exactly known distance (say 1 cm) and determine the resistance of the new solution column.

The viscosity of the sol can be measured by using Ostwald's viscometer or as an approximation its viscosity can be taken to be equal to that of the dispersion medium, which may be seen from the standard table.

Observations : Potential applied = V volt (say)

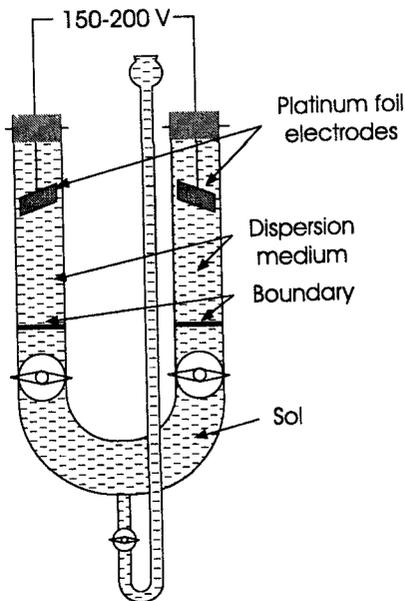


Fig. 3 : Electrophoretic apparatus

S.N.	Initial position of boundary	Final position of boundary	Distance travelled	Time of passage of current
1	x cm	t sec
2	(say)	(say)

Viscosity of the dispersion medium = η

Resistance of 0.1N KCl solution column between the electrodes at the same position = R_1 ohm

Resistance of the new solution column = R_2 ohm

Distance through which one electrode is moved = l cm

Calculations : As the sol particles migrate towards the anode, therefore, the particles carry a negative charge.

Distance between the foils of the two electrodes

$$= \frac{l \times R_1}{R_1 - R_2} = L \text{ cm}$$

\therefore Potential gradient

$$= \frac{V}{L} = E \text{ volt cm}^{-1}$$

Migration velocity, $u = \frac{x}{t}$ cm/sec

\therefore Electrophoretic mobility $= \frac{x/t}{E} = \frac{x}{t \cdot E}$

Zeta potential, $\xi = \frac{4\pi\eta \cdot u}{D \cdot E} = \frac{4\pi\eta \cdot x/t}{D \cdot E}$

[The value of dielectric constant (D) is seen from the table].

Result : (i) The charge on sol particles = ...

(ii) Electrophoretic mobility = $\text{cm}^2 \text{sec}^{-1} \text{volt}^{-1}$

(iii) Zeta potential = ...

Precautions : (i) The boundary should be very sharp.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 4

Object : To find the precipitation values of a number of active ions for a ferric hydroxide sol.

The active ions in this case, will be anions as ferric hydroxide sol is positively charged. Take three electrolytes containing Cl^- , SO_4^{2-} , PO_4^{3-} ions and proceed as usual.

EXPERIMENT No. 5

Object : To find the effect of electrolytes on the viscosity of a gelatin gel.

Prepare a gelatin gel (5%) and determine its viscosity by means of an Ostwald's viscometer. Then take 4-5 solutions of gelatin gel and add to them different electrolytes of same concentration, say KCl , NaCl , KNO_3 , BaCl_2 etc. Determine the viscosities of each gel as usual. Compute the results.

EXPERIMENT No. 6

Object : To find the effect of concentration of an electrolyte on the viscosity of a gelatin gel.

Prepare a 5% gelatin gel and determine its viscosity as usual. Now determine the viscosities of gelatin gel after adding a fixed quantity of 1%, 2%, 3%, 4%, 5% solutions of an electrolyte, say NaCl . Plot a curve between viscosity and concentration.

EXPERIMENT No. 7

Object : To study the effect of gelatin solution on the precipitation values of NaCl and BaCl_2 for silver sol.

Silver sol is negatively charged and so the precipitating ions will be Na^+ and Ba^{2+} . The sol of silver prepared by reduction of AgNO_3 by tannic acid may be

used without dialysis. Prepare 0.5% gelatin solution by digesting 1 g of gelatin powder in 200 ml of water at 80°C to 50°C. Cool the solution. Solutions of gelatin of concentration higher than 1% will set to give gels on cooling.

Now take five cleaned, steamed and labelled test tubes. Put 1, 2, 3, 4 and 5 ml of gelatin solution and 4, 3, 2, 1 and 0 ml of water in numbered test tubes (1 to 5). To each test tube add 5 ml of silver sol drop-by-drop with continuous shaking. Add to these solutions 2M NaCl and then repeat the experiment with BaCl₂ solution (as done in the case of NaCl). Record the volumes of electrolyte required for coagulation in each case.

EXPERIMENT No. 8

Object : *To study the protective action of a hydrophilic colloid (such as starch, gelatin) on the precipitation of lyophobic sols.*

Take 10 test tubes and take 10 ml of As₂S₃ sol in each of them. Now add 0, 1, ...8, 9, ml of 0.1% starch solution to test tubes numbering 1, 2, ...9, 10. Add 1 ml of 10% NaCl solution to each test tube. Mix the contents of each tube thoroughly and allow them to stand for 24 hours. At the end of the given time, ascertain in which test tube the precipitation is just prevented. Calculate the number of milligrams of starch in that test tube. The various test tubes contain 0, 1, 2 ... 8, 9, milligrams of starch.

EXPERIMENT No. 9

Object : *To study mutual coagulation of As₂S₃ sol and Fe(OH)₃ sol and to determine the optimum ratio for precipitation.*

When two sols of opposite charges are mixed, mutual coagulation occurs. When two sols are mixed within certain narrow limits, the ratio of concentration is known as the **optimum ratio**. The excess of one or the other prevents the coagulation completely or brings about incomplete precipitation.

By means of graduated pipettes take 1, 2, 3, ...8, 9 ml of As₂S₃ sol in 9 test tubes and add 9, 8 ... 2, 1 ml of Fe(OH)₃ in the respective tubes. Mix the sols in each test tube thoroughly and allow the test tubes to stand for 3-4 hours. Now ascertain in which test tube complete precipitation has occurred and thus determine the optimum ratio. In this case, the optimum proportions will be about 9 ml of As₂S₃ sol and 1 ml of Fe(OH)₃ sol.

Now repeat the experiment with quantities of As₂S₃ and Fe(OH)₃ sol as 9.3 ml and 0.7 ml ; 9.2 ml and 0.8 ml ; 9.1 ml and 0.9 ml ; 9.0 ml and 1.0 ml; 8.9 ml and 1.1 ml ; 8.8 ml and 1.2 ml ; 8.7 ml and 1.3 ml in different test tubes and determine the optimum ratio.



The phenomenon of adsorption, also known as surface phenomenon has been known in one form or the other since 1773, when Scheele discovered the uptake of gases by charcoal. Lowitz (1785) found that charcoal can take up colouring matter from solutions as well. The term adsorption was first used by Kayser (1881) at the suggestion of du Bois Reymond. *The phenomenon of higher concentration of any molecular species at the surface of a solid than in the bulk of a solid or liquid is known as adsorption.* As a result of adsorption, there is a decrease of residual surface forces and, therefore, that of surface energy.

The solid which takes up gas, vapour or solute from a solution is known as adsorbent, the gas or solid which is held to the surface of the solid is called adsorbate. Since colloids have very small dimension, they have very high surface area per unit mass, hence they are good adsorbents. Other adsorbents are silica gel, charcoal, clay etc.

Adsorption should be clearly distinguished from absorption. In absorption, the substance is not only retained on the surface, but passes through the surface to become uniformly distributed throughout the body of a solid or liquid. On the contrary, in adsorption the substance is retained only on the surface, and does not pass through the surface of solid or liquid. It is hence clear that during adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, whereas in absorption the increase in concentration is uniform throughout the body of the absorbing substance.

The amount of a gas adsorbed by a solid depends on various factors, *viz.*, temperature and pressure of the gas, area of adsorbent and the nature of the adsorbent and the adsorbate gas.

EXPERIMENT No. 1

Object : *To study the adsorption of acetic acid on charcoal and to prove the validity of Freundlich's adsorption isotherm and Langmuir's adsorption isotherm.*

Apparatus : Burette, pipette, reagent bottles etc.

Theory : We know that the amount adsorbed is dependent on pressure and temperature. Hence, we can say that the amount (a) adsorbed is a function of pressure (P) and temperature (T). *i.e.*,

$$a = f(P, T)$$

A plot of P and a , keeping temperature constant is known as adsorption isotherm.

Freundlich adsorption isotherm : Freundlich (1909) proposed an empirical equation to represent, in general, the adsorption relationship and is classically known as Freundlich adsorption isotherm. According to it,

$$\frac{x}{m} = kc^{1/n} \quad \dots (1)$$

where, x is the amount of solute adsorbed, m is the amount of adsorbing material, c is the equilibrium concentration of adsorbate in the solution, k is a constant depending upon the nature of both adsorbent and adsorbate, while n is another constant which is dependent on the nature of the adsorbate. The value of $1/n$ is generally less than unity. On taking logarithms of equation (1), we get,

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \quad \dots (2)$$

If the values of $\log x/m$ are plotted as ordinate against $\log c$ as abscissa, we get a straight line, with a slope, $1/n$ and intercept on the ordinate $\log k$.

Langmuir adsorption isotherm : Langmuir (1918) gave a relation between the amount adsorbed and the concentration for a unimolecular layer, which is known as Langmuir adsorption isotherm. According to it,

$$\frac{x}{m} = \frac{k_1 k_2 c}{1 + k_1 c} \quad \dots (3)$$

where, k_1 and k_2 are constants.

Equation (3) can also be written as

$$\frac{c}{x/m} = \frac{1}{k_1 k_2} + \frac{c}{k_2} \quad \dots (4)$$

Thus, if the values of $\frac{c}{x/m}$ are plotted as ordinate against c as abscissa, we get a straight line with a slope equal to $1/k_2$ and intercept on the ordinate equal to $1/k_1 k_2$.

Procedure : Prepare $N/2$ acetic acid and $N/10$ NaOH solution by dilution method. Take six stoppered reagent bottles, clean and dry them. Now prepare the following solutions in each bottle.

Bottle	N/2 acetic acid (ml)	Distilled water (ml)	Amount of charcoal (g)
1	50	0	1.0
2	40	10	1.0
3	30	20	1.0
4	25	25	1.0
5	20	30	1.0
6	10	40	1.0

Now stopper each bottle and shake all the bottles thoroughly well, one after the other. The shaking should be done for at least one hour. Then allow them to stand. Filter each solution through a filter paper and collect the filtrate in numbered beakers. Reject the first 5 ml of each filtrate. Now pipette out 10 ml of

each filtered solution in a conical flask and titrate it with $N/10$ NaOH solution, using phenolphthalein as an indicator. Repeat the titration with each solution till you get two concordant readings for each solution.

In the end or beginning, titrate the stock solution of acetic acid (10 ml) also by means of $N/10$ NaOH solution.

Observation : 10 ml of stock acetic acid solution $\equiv x$ ml of $N/10$ NaOH.

Bottle No.	Initial concn. (c_0) of acid before adsorption	Equilibrium concn. (c_e) of acid after adsorption	Amount of acid ($c_0 - c_e$) adsorbed (ml of NaOH)
1	x
2	$(4/5)x$
3	$(3/5)x$
4	$(1/2)x$
5	$(2/5)x$
6	$(1/5)x$

Calculations : $x = c_0 - c_e$ and $m = 1$ g in each case.

We can calculate x/m for each bottle and then find the value of $\log x/m$. The logarithm of c_e terms is also noted in each case.

Then a graph is plotted with $\log x/m$ as ordinate and $\log c_e$ as abscissa. We observe that it will be a straight line. The slope of this line will thus be equal to $1/n$. This proves the validity of Freundlich adsorption isotherm.

To prove the validity of Langmuir adsorption isotherm, the values of $\frac{c_e}{x/m}$ are plotted as ordinate against c_e as abscissa. If the adsorption isotherm is obeyed, the curve will be a straight line.

Result : The validity of Freundlich and Langmuir adsorption isotherms for the adsorption of acetic acid on charcoal has been tested.

Precautions : (i) For filtration, small filter papers should be used so that error due to any adsorption of the acid by the filter paper is minimised.

(ii) The first 5 ml of filtrate of each bottle should be thrown away.

EXPERIMENT No. 2

Object : To determine the surface area of the given powdered catalyst sample by means of B.E.T. adsorption isotherm.

Apparatus : Adsorption apparatus with complete accessories, burette, pipette etc.

Theory : The determination of surface area of a catalyst is of great importance in industries, where catalysts play an important role in the manufacture of a number of articles. A number of methods are available to determine the surface area of catalyst, but the gas adsorption method of Brauner, Emmett and Teller (B.E.T.) is widely used as it is simple and easy to set up.

Brauner, Emmett and Teller showed how to extend the Langmuir's approach to the multi-molecular layer adsorption and gave an equation which has come to

be known as B.E.T. equation. The equation has been derived by them mathematically and is given by,

$$\frac{p}{v(p_0 - p)} = \frac{1}{cv_m} + \frac{(c - 1)p}{cv_m p_0} \quad \dots (1)$$

where, p_0 is the saturation pressure of the gas, v is the volume of the gas adsorbed at N.T.P. and at pressure p of the system, v_m is the volume of the gas adsorbed at N.T.P. when the adsorbent's surface is completely covered with a unimolecular layer of the adsorbate and c is a constant.

From equation (1), it is clear that if we plot $\frac{p}{v(p_0 - p)}$ term (ordinate) against $\frac{p}{p_0}$ term (abscissa), we get a straight line. The slope and intercept of the straight line are given by :

$$\text{Slope} = \frac{c - 1}{cv_m} \quad \dots (2)$$

$$\text{Intercept} = \frac{1}{cv_m} \quad \dots (3)$$

From equations (2) and (3), we have

$$v_m = \frac{1}{(\text{slope} + \text{intercept})} \quad \dots (4)$$

If we know the cross-section of the gas molecule, *i.e.*, the area of the surface covered by each adsorbed molecule, we can easily calculate the surface area of the adsorbent (catalyst) as follows :

Since 22,400 ml of a gas at N.T.P. occupies N mole ($N =$ Avogadro number), hence v_m ml of the gas at N.T.P. will occupy $\frac{N.v_m}{22400}$ molecules. If x be the weight of the adsorbent and A be the cross-section of each adsorbed molecule, then,

$$\text{Surface area per gram of the adsorbent} = \frac{N.v_m \cdot A}{22400 x} (\text{meter})^2$$

In B.E.T. method, nitrogen gas is commonly used and the value of A for nitrogen at the liquid nitrogen temperature is $16.2 A^2$ or $\frac{16.2}{10^{20}}$ (meter)².

Procedure : Before explaining the actual process of performing the experiment, one must understand the construction and principle of the apparatus [fig. (1)].

A calibrated burette B (capacity 50 ml) is connected to a mercury reservoir R_1 . A mercury manometer M is connected to the burette through a three way stopcock S_1 , which is also connected to the gas reservoir. The manometer is connected to a mercury reservoir R_2 through another stopcock S_2 . The mercury reservoirs can be moved upwards or downwards as desired. By adjusting these reservoirs, we can adjust the levels of mercury in the burette and manometer. The manometer is connected to a vacuum line through a stopcock S_3 . The closed limb of the manometer is connected to a catalyst tube C through the stopcock S_4 . A three

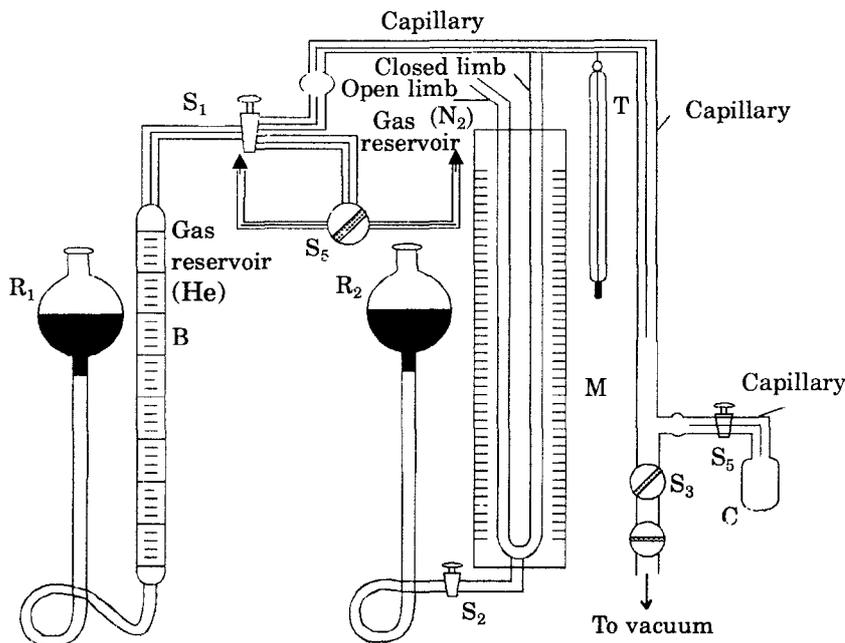


Fig. 1 : B.E.T. apparatus

way stopcock S_5 connects the apparatus with the two gas reservoirs. A thermometer T is also hung through the apparatus to note the room temperature. All the stopcocks and ground glass joints of the apparatus are lubricated with high vacuum grease for operation under high vacuum.

The procedure involves the addition of a known quantity of a gas to a previously evacuated apparatus containing the adsorbent. The volume of the gas adsorbed at equilibrium is also determined. Close stopcocks S_2 and S_5 . Open stopcock S_4 and connect the burette B with manometer through S_1 . Through S_3 , evacuate the whole apparatus for a couple of hours. Now close S_3 . Make the mercury levels in R_1 and B the same, by adjusting reservoir R_1 . Open S_1 so as to connect the burette B with the gas reservoirs and connect the apparatus with the helium gas reservoir through S_5 . Collect some volume, say 30 ml of the gas in B . Now close S_5 . Now introduce slowly and carefully by means of S_1 , 5 ml of helium gas into the other parts of the apparatus. Again make the mercury levels in R_1 and B the same and note the exact volume of the gas transferred to the apparatus. Now, let the state of equilibrium reach and then note down the readings of both limbs of manometer M , *i.e.*, open scale reading (O.S.R.) and closed scale reading (C.S.R.). The pressure of the gas is given by [Atmospheric pressure - (C.S.R. - O.S.R.)]

Now, again introduce further amount of helium gas through S_1 . Again note the C.S.R. and O.S.R., after proceeding as explained above.

Since helium gas is inert, it does not get adsorbed on the catalyst surface. Hence, measurement of volume of the gas at different pressures gives a curve,

known as **calibration curve**. The above explained procedure may be repeated for any other gas which gets adsorbed on the catalyst.

Suppose at a particular pressure p_1 cm, the adsorbate gas has a volume v_1 ml. From the calibration curve, we can read the volume say v_2 ml corresponding to the same pressure p_1 cm. Since some amount of the gas has been adsorbed, we will have $v_1 > v_2$. The value $(v_1 - v_2)$ ml will give us the volume of the gas adsorbed at pressure p_1 cm. Similarly, we can calculate the volume of the gas adsorbed at other pressures. These volumes can be converted to N.T.P. values, which will give the value of v of equation (1).

For surface area measurement, we generally use nitrogen gas. For finding out the surface area at liquid air temperature, the sample carrying tube C is placed in a thermos flask containing liquid air. At liquid air temperature, the value of p_0 for nitrogen is 80 cm.

Before starting the adsorption experiment, the whole helium gas is to be removed by evacuation, which is done by stopcock S_3 . Close it and connect the gas reservoir through S_1 . Through S_3 introduce a certain volume say 30 ml of N_2 gas to B. Now close S_5 . The catalyst tube C is then placed in a thermos flask containing liquid air. Now through S_1 introduce about 5 ml of N_2 gas to other parts of the apparatus. Note the volume of the gas transferred, after bringing the mercury level in R_1 and B the same and waiting for 10—15 minutes. The manometer readings, *i.e.*, C.S.R. and O.S.R. are also noted. Now again transfer 5 ml of N_2 gas and repeat the procedure and note the volume of the gas transferred and the corresponding pressure through the manometer M . Take at least six readings. Also note the atmospheric pressure from a barometer

- Observations : Room temperature = $t^\circ\text{C}$ (say)
- Atmospheric pressure = P cm (say)
- Weight of sample of catalyst taken = W g (say)
- Value of p_0 for N_2 at liquid air temperature = 80 cm

(i) For calibration curve of helium gas

Volume of He (ml)	Open scale reading (O.S.R.) (cm)	Closed scale reading (C.S.R.) (cm)	$p = P - (\text{C.S.R.} - \text{O.S.R.})$ (cm)
...			
...			
...			
...			

(ii) Table for adsorbable nitrogen gas

Volume of N_2 gas (v_1 ml)	O.S.R. (cm)	C.S.R. (cm)	$p = P - (\text{C.S.R.} - \text{O.S.R.})$ (cm)	Volume of v_2 from calibration curve (ml)	$v_3 = v_1 - v_2$ (ml)	v_3 when converted to N.T.P. = v (ml)
...						
...						
...						

Calculations : First a calibration curve is drawn for helium gas, *i.e.*, a curve between p of helium gas and volume of helium gas. The value of v_2 (cf table ii) is seen from this calibration curve corresponding to the same pressure as observed for nitrogen gas. Now the following values are also calculated likewise :

Volume of p (cm) (from table ii)	$P_0 - p$	$\frac{p}{v(P_0 - p)}$	$\frac{p}{P_0}$
...			
...			
...			

Now plot the values of $\frac{p}{v(P_0 - p)}$ as ordinate against p/P_0 as abscissa. We get a straight line, the slope and intercept of which can be easily calculated. From it the value of v_m can be determined, as

$$v_m = \frac{1}{\text{slope} + \text{intercept}}$$

After knowing the value of v_m , we can find out the surface area of the catalyst, according to the expression :

$$\text{Surface area} = \frac{N \times v_m \times A}{22400 \times W} \text{ metre}^2 \text{ per g}$$

($N = 6.023 \times 10^{23}$ and A for nitrogen = $16.2/10^{20}$)

Result : The surface area of the given catalyst is ... meter² per gram.

Precautions : (i) The whole apparatus should be completely evacuated before filling either helium or nitrogen gas.

(iii) There should be no leakage anywhere in the assembly.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 3

Object : To study the adsorption of iodine from alcoholic solution on charcoal.

Prepare 250 ml of nearly 0.5 M solution of iodine in ethanol (Dissolve 32 g of iodine in ethanol and make the solution 250 ml in a volumetric flask). Add an accurately weighed amount, about 1.0 g of active powdered charcoal in six different well cleaned and dried stoppered and labelled reagent bottles.

Now add 50, 40, 30, 20, 15, 10 ml of iodine solution in ethanol by burette and 0, 10, 20, 30, 35, 40 ml of pure ethanol in the respective six bottles. Shake the bottles well and keep them in a thermostat till they attain constant temperature. Continue shaking the bottles intermittently. Prepare 500 ml of 0.2M sodium thiosulphate solution and titrate 10 ml of iodine solution with it using starch solution as an indicator. Then determine the exact concentration of the stock solution of iodine.

Now filter the contents of each bottle by means of filter papers and collect the filtrate in properly cleaned, dried and labelled flasks. (Reject the first 5-10 ml portion of the filtrate from each bottle). Now titrate 5 ml each from bottles no. 1 and 2, 10 ml from bottles 3 and 4 and 20 ml from bottles no. 5 and 6 with standard hypo solution using starch solution (freshly prepared) as an indicator. Now calculate the equilibrium concentration in each bottle.

Calculate the amount of iodine adsorbed by charcoal as in experiment 1 and tabulate the observations and results. Also, test the validity of Freundlich and Langmuir's adsorption isotherms as explained in experiment 1.

EXPERIMENT No. 4

Object : *To study the adsorption of oxalic acid on charcoal and test the validity of Langmuir and Freundlich adsorption isotherm.*

Proceed as in experiment no. 1. Take 2 g of animal charcoal and titrate the filtrate either by a standard solution (N/10) of NaOH or KMnO_4 .

EXPERIMENT No. 5

Object : *To study the effect of temperature on adsorption.*

Perform the experiment at different temperatures and then plot a curve between temperature and amount of the substance adsorbed.

EXPERIMENT No. 6

Object : *To study the adsorption of certain dyes such as methyl violet, picric acid or malachite green on charcoal.*

The initial and final concentration of the dye in solution can be obtained by measuring the optical density of the solution at λ_{max} spectrophotometrically or colorimetrically. The difference between initial and final optical density will be a measure of the dye adsorbed by charcoal.



PHASE EQUILIBRIUM

LIQUID-LIQUID EQUILIBRIA (Partially Miscible Liquids)

EXPERIMENT No. 1

Object : To draw the mutual solubility curve of two immiscible liquids and to find out the critical solution temperature of phenol-water system.

Apparatus : Boiling tube and an outer jacket, beaker, thermometer, stirrer etc.

Theory : When two partially miscible liquids are mixed and shaken together, we get two solutions of different composition. For example, on shaking phenol and water, we get two layers; the upper layer is a solution of water in phenol and the lower layer is a solution of phenol in water. At a fixed temperature, the composition of each solution is fixed and both the solutions are in equilibrium. (Two solutions of different composition existing in equilibrium with one another are known as *conjugate solutions*.) Above a particular temperature, such solutions are completely miscible in all proportions. This temperature is known as *critical solution temperature* or *consolute temperature*. As in this particular case, the mutual solubility increases with temperature, hence it is also known as upper consolute temperature.

Mutual Solubility Curve : If we have two liquids A and B and we mix them, we get a mixture of composition c_1 . At any temperature t_1° or below t_1° , the two layers are completely miscible. Thus, the point corresponding to temperature t_1° and composition c_1 is known as the *miscibility point*. If we take another mixture of A and B of composition c_2 , we can find out the temperature, say t_2° above which the two layers become completely miscible. Similarly, we can find out corresponding temperatures for a number of mixtures of A and B. If now a curve is plotted with temperature as ordinate against concentration as abscissa, we get a mutual solubility curve of the shape as shown in figure (1). It is found that above

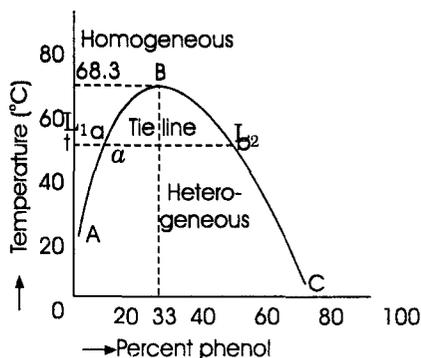


Fig. 1 : Miscibility Curve

B, the two liquids will become miscible in all proportions and hence it is known as **critical solution temperature**.

Procedure : The apparatus consists of an inner boiling tube *A* fitted into an outer tube *B* by means of a rubber cork. The inner tube is fitted with a cork containing two holes, one for the stirrer *S* and another for thermometer *T*. The stirrer should move freely without touching the thermometer. The whole apparatus [fig. (2)] is then placed in a big beaker containing water, the temperature of which can be raised slowly by means of a low flame burner.

Exactly eight gram of phenol weighed out in a weighing tube is transferred into the inner tube *A*. Now 7 ml of water is added to it by means of a graduated pipette. The mixture is stirred by means of stirrer *S*. Water in the outer beaker is heated gradually and the mixture is stirred continuously. At a certain temperature, the mixture becomes clear and this temperature is noted by means of thermometer *T*. Now take out the inner tube along with the jacket from the beaker

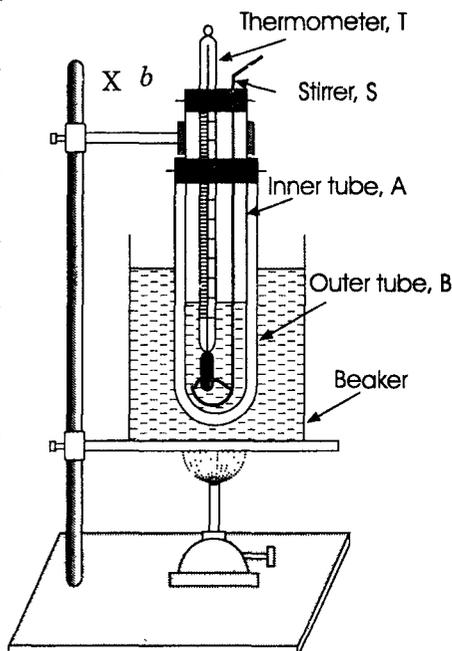


Fig. 2 : Apparatus for determining C.S.T.

and allow the solution to cool down slowly. Note the temperature at which the mixture again becomes heterogeneous, *i.e.*, opalescent. Again heat the solution in the beaker and then cool it down and find out the temperatures. The temperature at which opalescence disappears and appears should not differ by 0.1°C.

Now add 2 ml of distilled water more to the inner boiling tube *A* and again find out as explained above, the temperature at which the opalescence disappears and re-appears. The temperatures are noted after adding 2 ml more of distilled water each time.

Observations are made and we see that the temperature of complete miscibility rises, reaches a maximum value and then decreases. The experiment is performed till the complete miscibility has fallen below 60°C.

Observations : Weight of phenol = 8.00 g

Density of water = 1 g/ml

S.N.	Weight of water (W g)	Percentage by weight of phenol $= \frac{8}{8 + W} \times 100$	Miscibility temperature		
			Opalescence disappears (°C)	Opalescence re-appears (°C)	Mean value (°C)
1	7 g
2	9 g
...

Calculations : A curve is plotted with miscibility temperature as ordinate against concentration of phenol (percentage by weight) as abscissa. The curve will

be the mutual solubility curve of phenol-water system [fig. (1)]. The maxima of the solubility curve will give the critical solution temperature.

Result : The critical solution temperature of phenol-water system is ...°C.

Precautions : (i) The temperature of the solution should be increased or decreased slowly.

(iii) The mixture of phenol and water should be continuously stirred.

EXPERIMENT No. 2

Object : To plot a graph for the miscibility temperature of a mixture of 5 ml of 80% phenol and 5 ml of water in presence of 0.0 to 1.0% NaCl in aqueous layer in steps of 0.2% and to find the amount of NaCl in the given solution of unknown percentage.

Apparatus : As described in experiment no. 1.

Theory : Critical solution temperatures are very sensitive to the presence of small amounts of impurities soluble in one or both the components. On this basis, we can detect and estimate the amount of water in alcohols (Crismer's test). It is a general rule that if the impurity is soluble in one of the components, its presence in the system raises the upper critical solution temperature and decreases the lower critical solution temperature. If the impurity is soluble in both the components, then its presence decreases the upper critical solution temperature and raises the lower critical solution temperature.

The change in the critical solution temperature is found to be linearly proportional to the percentage of impurity. The miscibility temperature of a mixture of fixed amount of components is also changed in the same way as the critical solution temperature for the system. This change can also be used for determining the percentage of impurity.

Procedure : Measure exactly 5 ml of 80% phenol solution in each of 7 test tubes. Prepare stock solution of 1% NaCl (100 ml). Prepare 10 ml of 0.2, 0.4, 0.6, 0.8% NaCl solution by mixing 2, 4, 6 and 8 ml of 1% NaCl solution with 8, 6, 4 and 2 ml of distilled water. Take 5 ml of pure water and 0.0, 0.2, 0.4, 0.6, 0.8 and 1% NaCl solution in six of the test tubes each containing 5 ml of phenol solution and 5 ml of the unknown solution to be estimated in the seventh test tube. Now find the miscibility temperature for all the seven mixtures. Plot a graph between the percentage of salt in solution (x -axis) and the miscibility temperature (y -axis). Draw a line through the points and from the graph read the composition for the unknown solution corresponding to miscibility temperature.

Observations : Weight of phenol in each tube = 5 ml of 80% phenol = g
Volume of water added in each test tube = 5 ml

Test tube number	Percentage of NaCl	Miscibility temperature
1	0.0
2	0.2
3	0.4
4	0.6
5	0.8
6	1.0
7	Unknown solution

Result : The amount of salt in the unknown solution =

EXPERIMENT No. 3

Object : *To determine the composition and the amount in the layers obtained by mixing 55 g of phenol and 45 g of water at any given temperature.*

Apparatus : As in preceding experiments.

Theory : The composition of the conjugate layers at a given temperature, say t° will be given by the extremities of the tie line drawn at that temperature. If L_1 and L_2 are the left hand and right hand layers and X is a point on it representing the total composition of the system in the problem (55 g of phenol and 45 g of water), [See fig. (1)], then the relative amount of the two layers can be calculated using the Lever rule, which is given by,

$$\frac{W_1}{W_2} = \frac{XL_2}{XL_1}$$

As $W_1 + W_2 = 100$

$$\therefore \frac{W_1}{100 - W_1} = \frac{XL_2}{XL_1} \quad \dots (1)$$

Thus, the amounts of the two layers W_1 and W_2 can be easily calculated.

Procedure, Observations and Calculations : Proceed exactly in the manner as described in experiment 1. Obtain the mutual solubility curve [fig. (1)]. Draw a tie line at the desired temperature say $t^\circ\text{C}$. Now read the compositions (a, b) of the conjugate layers at this temperature from the ends of the tie line.

Now depict a point corresponding to 55 g of phenol and 45 g of water and measure the distance of X from points L_1 and L_2 . Then calculate the amount of the two liquid layers by means of equation (1).

LIQUID-VAPOUR EQUILIBRIA
(Completely Miscible Liquids)

Theory : According to Raoult's law, in an ideal binary mixture of two miscible liquids, the partial pressure of each component is proportional to its mole fraction. Thus, a curve between partial pressure or total pressure and mole fraction of each component will be linear. The solutions, however, show positive or negative deviations from Raoult's law. In former deviations, the partial pressure of each component or the total vapour pressure will be higher than that calculated from Raoult's law. Similarly, for negative deviations, the partial pressure values will be lower than the ideal values.

In case the deviations are small, the vapour pressure increases regularly with the composition from vapour pressure of less volatile to that of more volatile component. The vapour pressure— composition curve will thus not exhibit any maximum or minimum. The curve, will thus be continuous as shown in figure (3), the boiling point of the mixture lying between those of pure components. Such a mixture on distillation will give the vapour relatively rich in the component of

higher vapour pressure and the boiling point will rise regularly. The distillate will be richer in the more volatile component, leaving behind the less volatile one. Such a binary liquid mixture can be separated by repeated distillation or fractional distillation.

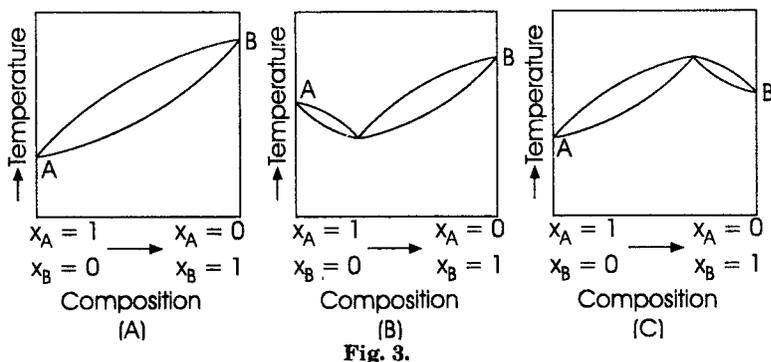


Fig. 3.

If, however, the vapour pressure—composition curve shows a maximum or minimum, the boiling point curve will pass through a maximum or minimum as shown in figure (3) (B) and (C). Fractional distillation of a binary liquid mixture with a maximum will give the pure component present in excess as the distillate and a constant boiling point mixture, known as **azeotrope** as the still. The composition of azeotrope will correspond to the maximum point.

On the contrary, fractional distillation of a binary liquid mixture with a minimum will give the pure component present in excess as the still and a constant boiling point mixture (azeotropic mixture) as the distillate. The composition of the azeotropic mixture will correspond to the minimum point.

Thus, the constituents of binary liquid mixtures having a maximum or minimum cannot be separated by fractional distillation.

EXPERIMENT No. 4

Object : To study the boiling point-composition curve for the binary liquid mixtures of two miscible liquids, e.g.,

- | | |
|----------------------------|-----------------------------|
| (a) A—Benzene (80.2°) | B—Toluene (110.6°) |
| (b) A—Benzene (80.2°) | B—Carbon disulphide (46.3°) |
| (c) A—Benzene (80.2°) | B—Hexane (69.0°) |
| (d) A—Acetone (56.3°) | B—Ether (34.6°) |
| (e) A—Acetone (56.3°) | B—Water (100°) |
| (f) A—Chlorobenzene (152°) | B—Bromobenzene (156.2°) |

Apparatus : A three necked distillation flask fitted with a condenser, Abbe refractometer, thermometer ($\pm 0.1^\circ$), micro-burette, burner etc.

Theory : The liquid mixtures form systems with regularly increasing boiling points. The curves will thus be continuous [See figure (3) B].

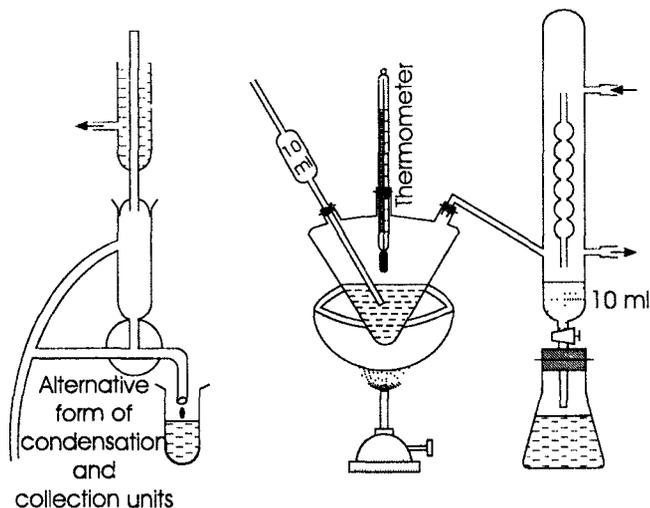


Fig. 4.

Procedure, Observations and Calculations : Prepare binary mixture (1 ml each) of two liquids by mixing known volumes (1 + 9, 2 + 8, ..., 9 + 1). Now measure the refractive index of each mixture as well as of pure liquids with the help of Abbe refractometer. Plot a refractive index (y -axis) against composition (x -axis).

Now take 15-20 ml of one of the liquids in the flask and set the apparatus as shown in figure (4). Heat the flask and reflux the contents for about 10 minutes, so that equilibrium is established. Record the equilibrium temperature as the boiling point of the liquid. Similarly, the boiling point of the other liquid is determined.

Now take 10 ml of liquid A in the flask and 1 ml of liquid B. Heat and reflux the mixture for about 10 minutes. When equilibrium is attained, note the boiling point of the mixture. When distillation starts, reject the first 3-5 ml of distillate. Remove the burner and now collect the distillate in a cooled flask and stopper it immediately. Determine the refractive index of the distillate and residue and from refractive index-composition curve, determine their composition. (The residue from the flask is collected as soon as the flame is put off and it is then cooled immediately).

Repeat the above determination with successive additions of 1.0, 1.5, 2.0, 2.5 ... 4.5, 5 ml of liquid B.

Now plot the compositions (in mole fraction) (x -axis) of the distillate and residue in equilibrium against the boiling point (y -axis) and obtain the vaporus and liquidus curves.

EXPERIMENT No. 5

Object : To study the boiling point-composition curves for the following binary liquid mixtures :

- A-Acetone (56.3°), B-Chloroform (61.2°),
- A-Water (100°), B-HCOOH (99.2°).

Apparatus : As in preceding experiments.

Theory : These liquids form systems with maximum boiling points. From the boiling point-composition curve we can determine the composition and boiling point of the azeotropic mixture. (For details, see theory of liquid-vapour equilibria).

Procedure, Observations and Calculations : Same as in experiment 4.

EXPERIMENT No. 6

Object : To study the boiling point-composition curves for the following systems of binary liquid mixtures :

- | | |
|------------------------------------|--------------------------------|
| (a) A—Benzene (80.2°) | B—Ethanol (78.3°) |
| (b) A—Benzene (80.2°) | B—Methanol (64.7°) |
| (c) A—Benzene (80.2°) | B—Isopropyl alcohol (64.7°) |
| (d) A—Carbon tetrachloride (76.8°) | B—Methanol (64.7°) |
| (e) A—Chloroform (61.2°) | B—Methanol (64.7°) |
| (f) A—Acetone (56.3°) | B—Carbon tetrachloride (76.8°) |

Apparatus : Same as in preceding experiments.

Theory : These liquid mixtures form the systems with minimum boiling points. From the boiling point-composition curves, we can calculate the composition and boiling point of the azeotropic mixture. (For details, see theory of liquid-vapour equilibria).

Procedure, Observations and Calculations : Same as in experiment 4.

EXPERIMENT No. 7

Object : To draw a phase diagram for lead and tin and from it find out the melting points of the two components. Also find the eutectic temperature of the binary system.

Apparatus : Pyrex test tubes (6" × 3/4"), thermometer (graduated to 0.1°C) etc.

Theory : A cooling curve for a substance is a curve between temperature and time of cooling. It is started when the entire mass is liquid and is continued till it is completely solidified. The curve will be continuous, as long as there is no transition or change of phase. At a certain temperature, the liquid begins to solidify and heat is found to be liberated during this phase change of liquid to solid. This method is known as *thermal analysis*. Due to this liberation of heat the cooling curve [fig. (5)] becomes discontinuous. The cooling curve ABCD consists of three parts.

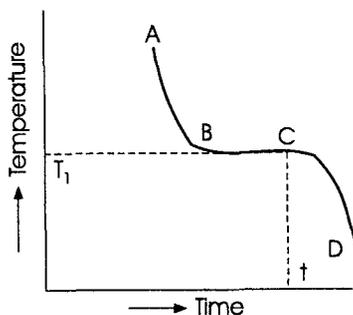


Fig. 5

(i) **AB**, which corresponds to the cooling of the liquid. At temperature T_1 , the liquid begins to solidify.

(ii) **BC**, which corresponds to the separation of the solid. The solid is formed at a rate just sufficient to counterbalance the heat loss by radiation and hence the temperature remains constant. At time t , the liquid is completely converted into solid.

(iii) **CD**, which corresponds to the cooling of the solid phase of the substance.

The above cooling curve is obtained for a pure substance. If a mixture of two components A and B (melting point of A is say higher than that of B) is melted and cooled and if the percentage of A is higher than that of B in the mixture, then it is seen that the melting point of A will be lowered due to the presence of B . At a certain temperature, known as **transition temperature**, solid A will crystallise earlier, leaving the liquid richer in B . After some more cooling, the composition of the liquid will reach a ratio of A to B so as to allow the separation of A and B simultaneously in the crystalline form. Thus, that temperature at which the two solids A and B are in equilibrium with the solution is known as **eutectic temperature** (Greek : eutectic = easy melting).

Figure (6), depicts the cooling curve of a mixture of two components A and B . The first break in the curve occurs at B' where one of the components, say B begins to solidify or crystallise. During this solidification process, heat is liberated and, therefore, the temperature falls more slowly. It is to be noted that the temperature does not remain constant (cf. cooling curve of a pure substance), because the composition of the mixture (amount of A : amount of B) is changing continuously whereby the temperature of solidification correspondingly changes. At a certain temperature T_2 , known as eutectic temperature, the remaining liquid solidifies as a whole, i.e., both the components A and B crystallise out simultaneously.

If we draw cooling curves for a number of mixtures of A and B of known concentration and plot the corresponding transition temperatures as ordinate against concentration as abscissa, we get a phase diagram [fig. (7)], from which we can find the melting points of the two components as well as the eutectic temperature of the system.

Procedure : First prepare the following mixtures of lead and tin by weighing them separately.

Mixture	1	2	3	4	5	6	7
Lead	8 g	7 g	6 g	5 g	4 g	3 g	2 g
Tin	2 g	3 g	4 g	5 g	6 g	7 g	8 g

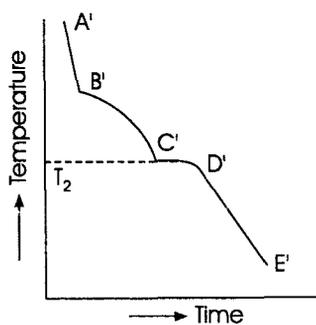


Fig. 6

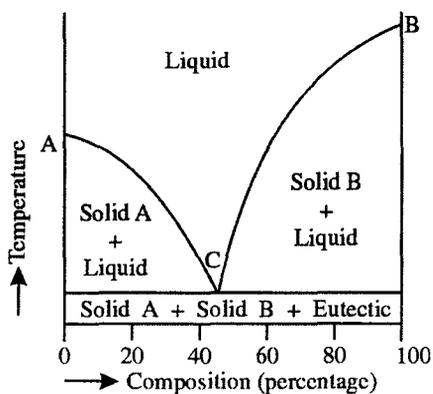


Fig. 7

The apparatus [fig. (8)] consists of a pyrex tube A, fitted in an outer boiling tube B. A thermometer is inserted in the tube A, by enclosing the thermometer in another thin walled glass tube. Glass wool is kept in the outer tube B, to minimise the loss of heat.

Take the first mixture of lead and tin and heat it over bunsen flame till it has completely melted. Pour this molten mixture into the inner tube A, watching the thermometer. If the mercury goes slightly above 350° or 355° , then just pull out the thermometer for a while. Add a little graphite powder over the top of the melt and allow it to cool. Now note the temperature of the melt after every 30 seconds or 1 minute, as the case may be. (If the rate of cooling is slow, observe reading after a minute). Remove the thermometer and pour out the contents of the inner tube. Wash and dry it and repeat the above process for the remaining mixture of lead and tin.

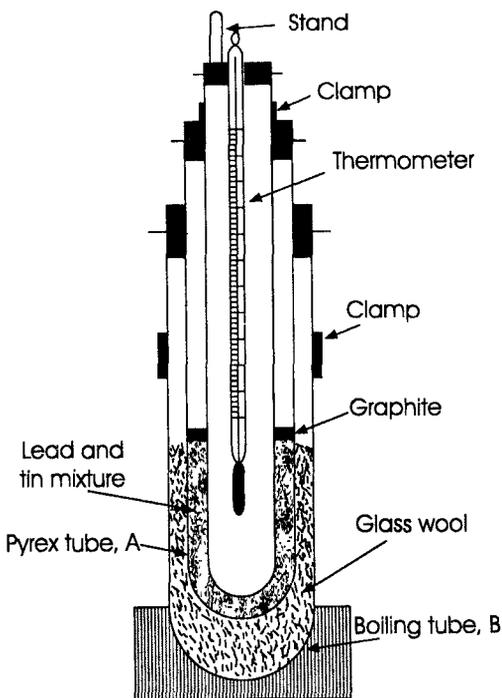


Fig. 8

Observations :

Mixture 1		Mixture 2		Mixture 3		Mixture 4		Mixture 5		Mixture 6		Mixture 7	
Time	Temp												

Calculations : First draw a cooling curve as already described before, for every mixture of lead and tin. Time in seconds or minutes is taken as abscissa while temperature ($^\circ\text{C}$) as ordinate. From the cooling curves, find the transition temperature for each mixture and tabulate the results as follows :

Mixture	Composition Pb : Sn	Transition temperature ($^\circ\text{C}$)
1	80 : 20	...
2	70 : 30	...
3	60 : 40	...
4	50 : 50	...
5	40 : 60	...
6	30 : 70	...
7	20 : 80	...

Now, if we draw a curve with transition temperature as ordinate and percentage composition of lead as abscissa. We get a diagram as shown in figure (7). The two curves AC and BC can be obtained by extrapolating the two curves. Points A , B and C will thus give the melting points of lead, tin and eutectic temperature, respectively. We can also find the eutectic composition (represented by point C).

Result : Melting point of lead = ... °C

Melting point of tin = ... °C

Eutectic temperature of lead—tin system = .. °C

Precautions : (i) Cooling curves should be obtained for as large number of mixtures as possible.

(ii) The temperature of the mixtures should fall slowly.

EXPERIMENT No. 8

Object : *To determine the phase diagram of naphthalene and diphenyl system.*

Apparatus and Chemicals : 11 test tubes, a boiling tube as air jacket, 100°C thermometer, a small ring stirrer, beaker, pure naphthalene and diphenyl.

Procedure : Prepare the following mixtures of the two components by taking weighed amounts in properly labelled test tubes.

Naphthalene (g)	10	9	8	7	6	5	4	3	2	1	0
Diphenyl (g)	0	1	2	3	4	5	6	7	8	9	10

Fit up a thermometer and a ring stirrer in one of the test tubes through a cork fitted in the tube. Place the test tube in hot water contained in a beaker and melt the contents completely. Remove the test tube from the bath, wipe it clean and place it in the large boiling tube which serves as an air jacket. Clamp the boiling tube in a beaker containing crushed ice to ensure uniform cooling. Allow the temperature to fall, stir thoroughly and record the temperature after every 30 seconds. Note the temperature at which crystals begin to separate from the molten mass. Continue to record the temperature until it becomes constant and the whole mass solidifies. Similarly, repeat the determination with other mixtures.

Plot the cooling curve between temperature (ordinate) and time (abscissa) for each of the mixtures and from each curve, determine the maximum temperature of first arrest and the eutectic temperature.

Plot the values of freezing point (ordinate) against composition (abscissa) in mole fraction and obtain the freezing point curve of the system.

EXPERIMENT No. 9

Object : *To determine the freezing point diagram of o-nitrophenol and p-toluidine system.*

Apparatus and Chemicals : Boiling tubes, 0.5°C thermometer (100°C), pure o-nitrophenol and p-toluidine.

Procedure : Take 15 g of *o*-nitrophenol in a boiling tube and fit up a thermometer and a ring stirrer into it through a cork. Melt the compound by immersing the tube in hot water.

Suspend the boiling tube in a wider glass tube (air jacket) clamped in a beaker packed with crushed ice. Record the temperature reading after every 30 seconds while stirring the liquid constantly till the arrest in cooling is reached. The temperature of arrest will be the freezing point of the pure component.

Now add 1 g of *p*-toluidine into the boiling tube, melt the contents and record the temperature after every 30 seconds as before till the final eutectic halt is obtained at nearly 15°C. Make further additions of 1, 2, 3, 4, 5 g of *p*-toluidine and obtain the cooling curves for each mixture.

Similarly, determine the freezing point of *p*-toluidine in the presence of increasing amounts of *o*-nitrophenol.

Calculations : Plot the cooling curve between temperature (ordinate) and time (abscissa) for each of the mixtures, and from each curve determine the maximum temperature of first arrest and the eutectic temperature. Finally, plot these freezing points (ordinate) against composition (mole fraction) of the mixture and construct the phase diagram of the system.

EXPERIMENT No. 10

Object : To construct a phase diagram for a two component system by plotting cooling curves for mixtures of different compositions. Any of the following systems can be studied.

- | | |
|------------------------------|-----------------------------|
| (a) A—Benzoic acid | B—Cinnamic acid |
| (b) A—Naphthalene | B— β -Naphthol |
| (c) A—Naphthalene | B—Benzoic acid |
| (d) A—Naphthalene | B— <i>p</i> -Naphthylamine |
| (e) A—Phenol | B—Salicylic acid |
| (f) A—Acetamide | B— <i>p</i> -Toluidine |
| (g) A— <i>o</i> -Nitrophenol | B—Naphthylamine (55 to 15°) |
| (h) A—Acetamide | B—Salicylic acid |

Procedure : Suppose the two components are benzoic acid (A) and cinnamic acid (B). Prepare the following mixtures of A and B, by weight in grams.

Component	Weight (g)										
A	10	9	8	7	6	5	4	3	2	1	0
B	0	1	2	3	4	5	6	7	8	9	10

Now melt the first mixture in a test tube, kept in a bath of liquid paraffin or glycerine. When the whole mass has melted, remove the tube from the bath and fix it with a thermometer and a stirrer into the boiling tube which serves as an air jacket. Stir the mixture slowly with the stirrer and note the temperature every half minute. Note the temperature at which crystals of the solid are first formed. Allow the temperature to fall and find out that temperature/s at which the solid-liquid system shows temperature halt, before complete solidification. Lowest

temperature halt will be the eutectic temperature. Repeat the above procedure for all the other mixtures of *A* and *B*.

Plot the phase diagram. The diagram may either be of the types shown in figure (9) (a), (b) and (c). Figure (9) (a) corresponds to a simple eutectic system, figure (9) (b) corresponds to a compound formation having an incongruent melting point at *D* and eutectic at *C*, while figure (9) (c) refers to compound formation with a congruent melting point at *D* and eutectic at *C* and *E*.

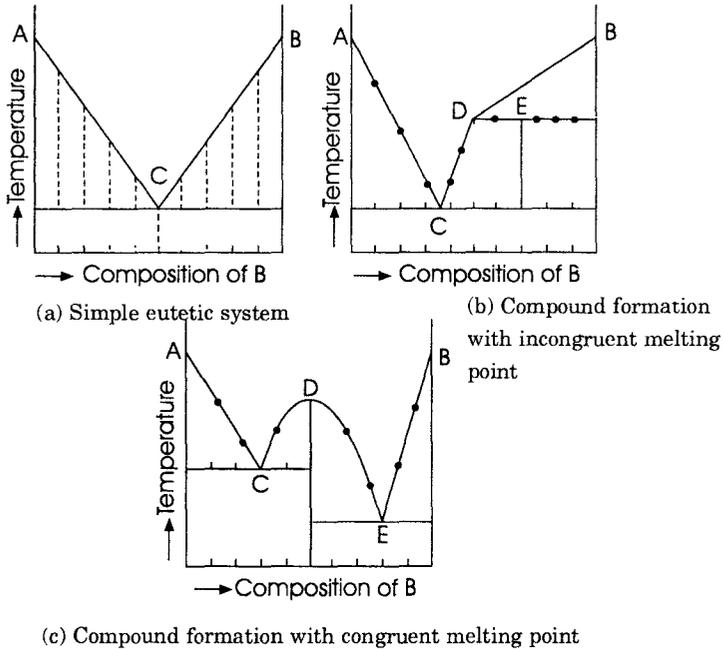


Fig. 9 : Temperature-composition curves

THREE COMPONENT SYSTEMS

For a three component system $C = 3$, so from phase rule equation we have

$$F = C - P + 2$$

$$= 3 - P + 2 = 5 - P$$

If all the three components occur in one phase, $P = 1$, so

$$F = 5 - 1 = 4$$

Of these, temperature, pressure and concentration of two components can be taken as independent variables. So, in order to draw a phase diagram of such a system, two restrictions may be applied for the sake of simplicity.

- (a) The temperature may be taken as constant.
- (b) The condensed form of system may be considered only, *i.e.* system without vapour phase or keeping vapour pressure as constant.

The composition of a three component system is represented on a triangular graph where the two concentrations can be taken as independent variables, while the third and dependent concentration is given by subtracting the weight or mole (or mole fractions) percentages of two components from 100. The corners of the triangular graph depict pure components and sides the binary compositions. Any point within the triangle represents a ternary system. It is a convention that

mutually immiscible components are taken on the base line and the component miscible in both the components is taken as the apex of the triangle, *e.g.*, in ethanol, benzene and water system, water and benzene are taken on the base line, whereas ethanol is taken at the apex (Ethanol is soluble in both water and benzene).

EXPERIMENT No. 11

Object : *To obtain the phase diagram for water-ethanol- benzene system at room temperature.*

Apparatus : Glass stoppered bottles (50 ml), thermostat (or water bath).

Procedure : Take three burettes containing water, benzene and ethanol. Prepare six mixtures by weight composition of benzene and ethanol volumetrically (densities of benzene and ethanol are 0.879 g ml^{-1} and 0.789 g ml^{-1} , respectively) having ethanol 10, 30, 50, 70, 90 and 95% (rest benzene) each about 20 gram. Now add water carefully to each solution from the burette with constant shaking to a point of first appearance of turbidity. Keep the temperature constant. Calculate the mole fraction or percentage of each component in the limiting homogeneous ternary mixtures and plot on a triangular graph. Measure the refractive index of the slightly turbid mixture. Add some more water to form two mutually immiscible phases and allow them to settle down. Then measure refractive index of each phase.

Observations : Temperature = ... °C

Density of benzene = 0.879 g ml^{-1}

Density of ethanol = 0.789 g ml^{-1}

Bottle No.	Weights of components*		
	Benzene	Ethanol	Water
1	18 g (... ml)	2 g (... ml)	a g (... ml)
2	14 g (... ml)	6 g (... ml)	b g (... ml)
3	10 g (... ml)	10 g (... ml)	c g (... ml)
4	6 g (... ml)	14 g (... ml)	d g (... ml)
5	2 g (... ml)	18 g (... ml)	e g (... ml)
6	1 g (... ml)	19 g (... ml)	f g (... ml)

Calculate the percentage by weight for ternary solutions (limiting composition).

Bottle no.	Refractive index			Benzene	Ethanol	Water
	Solution	Phase I	Phase II			
.1
2
3
4
5
6

*The required volumes of benzene and ethanol can be calculated for the specified weights. Weight of water can be calculated from the titre volumes used to get the turbidity point.

The percentages may now be plotted on a triangular graph paper. Mark the areas of complete miscibility and partial miscibility. Also plot on the same graph the refractive index observed for the ternary solutions against the ratio of water : benzene. This serves as a calibration curve for the refractive indices.

For each bottle, the refractive indices (as also the compositions) of two layers obtained by over-titration are fixed on the refractive index calibration curve. Suppose these values are a_1 and b_1 for bottle 1. From a_1 and b_1 on the refractive index curve we draw vertical lines to the miscibility curve. The new values of a_2 and b_2 are joined. Thus the line $a_2 b_2$ gives us the **tie line**.

Similarly, tie lines can be plotted for the remaining bottles. It is seen that these tie lines are neither horizontal nor parallel to $a_1 b_1$. The reason for this is that water and benzene have different miscibilities in ethanol. When a tie line is obtained, the phases in equilibrium for any overall composition c_1 can be read off from the tie line ends.

On the triangular graph, the mutually immiscible or partially miscible liquid pair is taken as the *base* and the third liquid which is completely miscible in the other two solvents is taken as the *apex*. The highest point on the dome curve is known as *plait point* or isothermal critical point of the system.

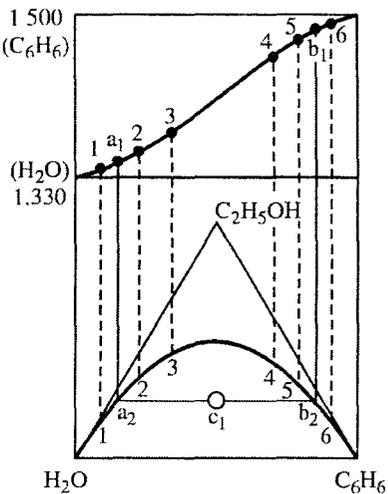


Fig. 10 : Miscibility curve

EXPERIMENT No. 12

Object : To obtain a solubility curve for a ternary system of liquids, say water-acetic acid-chloroform system.

Apparatus : Pipette, burette, stoppered bottles (50 ml), thermostat (or water bath).

Theory : In this experiment, we find the effect of mutual solubility of a pair of partially miscible liquids on adding a third component. When the third component is soluble in only one of the other two component liquids, the mutual solubility of the two liquids is decreased, while if the third component is soluble in both the other two component liquids, the mutual solubility of the latter is increased.

On mixing water and chloroform we get two conjugate solutions of different compositions. When acetic acid is added to them, the mutual solubility of water and chloroform increases and a point is reached at which the mixture becomes homogeneous. The quantity of acetic acid which is to be added to make the two solutions homogeneous will depend upon the relative proportions of water and chloroform in the mixture.

If water is added to a homogeneous mixture of two completely miscible liquids-acetic acid and chloroform, a heterogeneous mixture, *i.e.*, two layers are formed when a certain amount of water, depending upon the concentration of acetic acid and chloroform in the mixture, has been added.

Procedure : Prepare five solutions of acetic acid and chloroform in which the percentage composition by weight of chloroform is 10, 20, 40, 60 and 80%. Since

the densities of acetic acid and chloroform are 1.05 and 1.50 g/ml, hence the five solutions of the above compositions will be as follows :

Bottle 1 : 21.4 ml CH_3COOH + 1.7 ml CHCl_3

Bottle 2 : 19.1 ml CH_3COOH + 3.3 ml CHCl_3

Bottle 3 : 14.3 ml CH_3COOH + 6.7 ml CHCl_3

Bottle 4 : 9.5 ml CH_3COOH + 10.0 ml CHCl_3

Bottle 5 : 4.8 ml CH_3COOH + 13.3 ml CHCl_3

Now distilled water is added in very small quantity in each bottle. After adding water the bottle is well shaken. The addition of water is continued till on shaking, a turbidity is just obtained, which indicates a heterogeneous mixture. (*The final addition of water should be made drop-by-drop. Do not add more water at any one time*). Similarly, the procedure is repeated for the other four bottles.

Observations : Room temperature = $t^\circ\text{C}$.

S.N.	Volume of acetic acid (ml)	Volume of chloro- form (ml)	Volume of water (ml)	Percent by weight of acetic acid	Percent by weight of chloro- form	Percent by weight of water
1	21.4	1.7
2	19.1	3.3
3	14.3	6.7
4	9.5	10.0
5	4.8	13.3
6	—	—	99.0	1.0
7	—	—	8	...	0.8	99.2

Note : We also take mixtures containing 99.0% and 0.8 by weight of chloroform and 1.0% and 99.0% by weight of water, as in the binary system chloroform-water, for weight percentage upto nearly 0.8% of chloroform in water and 1% water in chloroform, the system is homogeneous, but between these two limits, the system becomes heterogeneous. Experimentally, we find out these limits by taking two bottles, one containing water and the other containing chloroform. Then chloroform is added in the former, while water is added in the latter and then we find out the respective values when turbidity just starts.

Calculations : The variation of the miscibility limits with the composition of the three-component mixture is represented by means of a triangular diagram, in which percentages by weight are plotted. (*Such a graph paper can be easily had from the market*). The length of each side of the triangle is 100 and represents the sum of the percentage amounts of the three components. Each apex of the triangle represents pure component.

While plotting the composition of a three-component mixture two points are marked on one side of a triangle representing the percentage amounts of the two components. From these points, lines are drawn parallel to

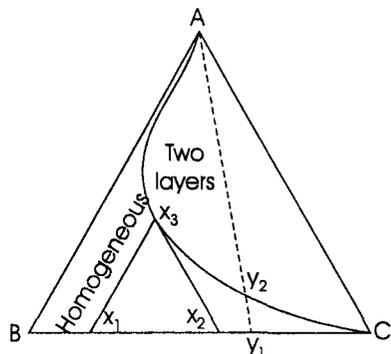


Fig. 11

the other two sides of the triangle. The point of intersection gives the composition of the mixture.

As shown in figure (11), the composition of the point x_1 is 20% chloroform and 45% acetic acid (represented by x_2) and 35% water. If any mixture containing 40% acetic acid and 60% chloroform is taken (represented by y_1) and water is added to it then the composition of the ternary mixture will vary along the line y_1y_2 , when at point y_2 , the solution just becomes turbid.

The curve Ax_3y_2C is obtained from the experimentally determined points. It gives the boundary of composition between homogeneous and heterogeneous mixture. Any point outside and inside the curve will give us a homogeneous and heterogeneous solution, respectively.

Result : The solubility curve for a ternary system is as shown in the diagram.

Precatuions : (i) When turbidity is to appear, water should be added drop-by-drop, especially in the case of the solution richer in chloroform.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 13

Object : To study the mutual solubility and determine the upper and lower consolute temperatures of (a) nicotine-water system (b) glycerol-m-toluidine system.

This experiment is performed on the same line as that for phenol-water type. In this case, however, we will get a closed type of curve [fig. (12)].

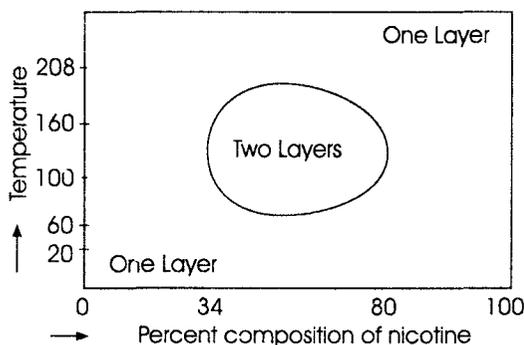


Fig. 12 : Miscibility curve for nicotine-water system

EXPERIMENT No. 14

Object : To study the mutual solubility of triethyl amine-water system and find the critical solution temperature.

In this case, we get a curve just reverse of the phenol-water type. This is because the mutual solubility of triethyl amine and water decreases with increasing temperature. It is found that below 18.5°C , the solution becomes homogeneous, *i.e.*, the two liquids are completely miscible in all proportions below 18.5°C [See figure (13)].

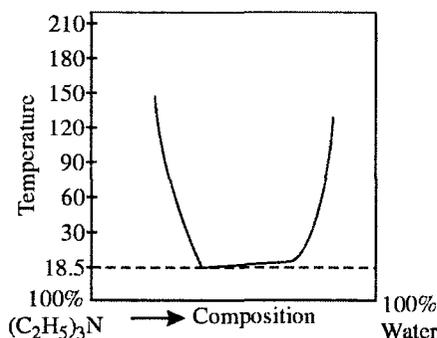


Fig. 13 : Miscibility curve for triethyl amine-water system

EXPERIMENT No. 15

Object : To construct a phase diagrams for : (a) urea (m. pt. 132°C) and phenol (m. pt. 43°C) system, (b) α -Naphthyl amine-phenol system.

Proceed as in experiment no. 10.

EXPERIMENT No. 16

Object : To determine the freezing point curve of picric acid-benzene system.

Proceed as in experiment no. 10.

EXPERIMENT No. 17

Object : To study the influence of impurity on a ternary mixture.

By taking any ternary system, say chloroform-acetic acid-water, we can find out the miscibility curve. To study the effect of impurity, we take 1% or 2% solution of the substance in water, and use it instead of pure water. Then proceed as usual.

EXPERIMENT No. 18

Object : To study the miscibility curve of a ternary system at different temperatures, by taking water-acetic acid-benzene.

Proceed as in experiment no. 11.

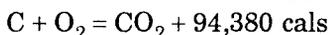
EXPERIMENT No. 19

Object : To construct the phase diagram of three-component system containing ethanol, benzene and water.

Proceed as in experiment no. 12.

THERMOCHEMISTRY

All chemical reactions are accompanied by a thermal change. *i.e.*, there is an evolution or absorption of heat accompanying every chemical reaction. Hence, the equation as generally written does not completely express the reaction. There must be added to it, the amount of heat which is evolved or absorbed during the course of the reaction. Thus, when carbon is heated in an excess of oxygen to form carbon dioxide, it is usual to express the reaction as $C + O_2 = CO_2$. But it does not entirely express what has happened? It is experimentally found that 94,380 cal of heat is evolved. Hence, to express exactly what happens, the equation must be written as,



Therefore, ***thermochemistry is that branch of chemistry which deals with the heat changes accompanying chemical reactions.*** Reactions in which heat is evolved or absorbed are known as ***exothermic*** or ***endothermic reactions***, respectively.

The amount of the heat change in a chemical reaction depends upon the following factors :

(i) *Nature of the reacting substances.*

(ii) *The physical condition of the reacting substances, e.g., solid, liquid, gaseous or in particular allotropic modifications.*

(iii) *The quantities of the substances entering into the reaction.*

When the above conditions of a reaction are definite, the heat evolved or absorbed is also definite. Thermochemical reactions can be classified under the following heads :

(i) *Heat of formation.* (ii) *Heat of solution, dilution, hydration.* (iii) *Heat of neutralisation.* (iv) *Heat of reaction.* (v) *Heat of combustion.*

Heat changes are generally expressed in :

(i) **Calorie**, which is defined as the quantity of heat required to raise the temperature of one g of water from 15° to 16°C. It is written as **cal**.

(ii) **Kilo-calorie**, introduced by Berthelot and is also known as **large calorie**. It is equal to 100 cal and is written as **k.cal** or **Cal**.

(iii) **Centuple calorie**, introduced by Ostwald and is the quantity of heat required to raise the temperature of one gram of water from 0° to 100°C. It is written as **K**.

(iv) **Kilo-joule**, which is used when heat energy has to be compared with or related to other forms of energy. It is equal to 10^{10} erg or 0.2391 cal.

A thermochemical result is expressed by writing the chemical formulae of the reacting substances side-by-side, but separated by commas or colons together with the amount of the heat change which has accompanied the reaction. The chemical symbols are always taken to represent the relative weights in grams which they indicate in the chemical equation. The substances are taken to be present in their normal state. If we write $(K, Cl, 3O) = 18 \text{ Cal}$, it means that 18 k. cal. are evolved when one gram mole of potassium chlorate is formed from its elements. This quantity is thus the heat of formation of potassium chlorate. Similarly, $(NaOH \text{ aq.}, HCl \text{ aq.}) = 13,700 \text{ cal.}$ indicates that when a dilute solution containing one gram mole of sodium hydroxide is exactly neutralised by a dilute solution containing one gram mole of hydrochloric acid, there is an evolution of 13,700 cal. of heat. The symbol aq. is always used to represent a quantity of water, such that the presence of more of it causes no further heat change. A solution is always represented by the symbol aq. written after the formula of the dissolved substance.

A comma is used to separate the formulae of reacting substances when they combine directly, and a colon when they react, but there is no direct combination. Thus, $(N, 3H)$ indicates that nitrogen and hydrogen unite together to form ammonia, while $(NH_3 : 3Cl_2)$ indicates that ammonia and chlorine react to form hydrogen chloride and nitrogen chloride.

CALORIMETERS

For the measurement of heat of various reactions, we can suitably use a thermos flask or another vessel known as a calorimeter. A calorimeter suitable for general experiments with solutions, may be constructed by loosely packing the space between two large boiling tubes or two beakers with cotton wool. The modern vacuum flask has the merit of very good insulation, but the narrowed neck of the ordinary thermos type prevents the use of an efficient stirrer, and if mixing is done by shaking, the water equivalent becomes large and quite indefinite in value. An unsilvered, straight sided Dewar vacuum flask [fig. (1)], avoids this serious disadvantage without serious loss of heat insulation. In addition, its transparency is quite invaluable in experiments on heat of solution etc. The vessel should be closed with a cork or rubber cock, grooved for the stirrer *S*, and carries a short wide tube *t*, through which passes an accurate thermometer *T* (accuracy of $\pm 0.1^\circ$), which is supported externally by a retort clamp. The tube *t* should be stoppered with a plug of cotton wool and serves as inlet for the introduction of liquids or solids into the calorimeter. The stirrer *S* should be quite efficient and may be formed of bent copper or silver wire

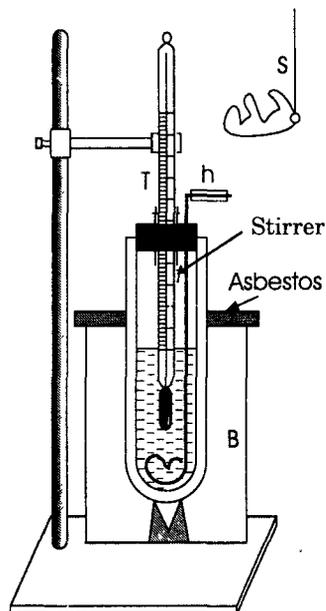


Fig. 1 : Calorimeter

as shown. A sleeve of stout rubber or ebonite tubing h serves as a heat insulating handle. An empty glass beaker B placed as a shield around the calorimeter usually improves the regularity of temperature observations.

Metallic calorimeters are not used as the chemical substances involved may react with them. Stainless steel or gold plated copper calorimeters are normally used in some cases.

EXPERIMENT No. 1

Object : *To find the water equivalent of the calorimeter and also find out the heat of dilution of sulphuric acid.*

Apparatus : Calorimeter, thermometer, stirrer etc.

Theory : During the heat changes, the calorimeter will also take up some of the heat evolved, which should be taken into account by determining the water equivalent or heat capacity of the calorimeter.

The heat capacity or water equivalent of a calorimeter is defined as the number of calories required to heat the calorimeter by 1°C . If M is the mass of the calorimeter and S is its specific heat, then,

$$\text{Water equivalent} = MS.$$

In case of a glass vessel, the water equivalent value is found for such part of the vessel as is actually in contact with the reacting system. In this case, the method of obtaining water equivalent by multiplying the mass and specific heat of the material of the vessel is not practicable. For glass vessels, the water equivalent is found by carrying out an experiment similar to the experiment to be carried out later on in the vessel. As far as possible, equal volumes are used so that the area of the calorimeter in contact with the system does not alter.

If the calorimeter is made of different parts having different specific heat S_1, S_2, S_3, \dots etc. and different mass M_1, M_2, M_3, \dots etc. then,

$$\text{Water equivalent} = M_1S_1 + M_2S_2 + \dots$$

Heat of dilution is the quantity of heat evolved or absorbed when a solution containing one gram mole of a substance in a known quantity of water or other solvent is diluted by further known quantity of that solvent.

Procedure : Take 25 ml of distilled water in the calorimeter and record its temperature estimating it to the nearest 0.1° . Now heat some water in a separate beaker to a temperature about $25\text{-}35^{\circ}$ higher than the room temperature. Now pipette out 24 ml of hot water and add it to another beaker and read its temperature after every half minute for 5 minutes. Add this hot water quickly to the water in the calorimeter. Stir the contents well with a stirrer, and note the temperature after every half minute upto an accuracy of 0.1° . Plot a graph between temperature and time [fig. (2)] and from it find out the temperature of hot water and

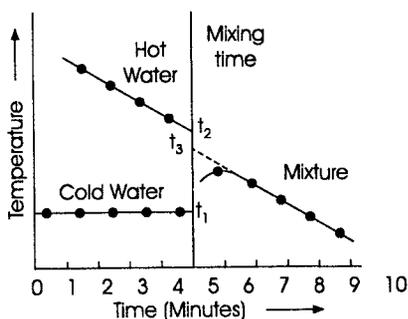


Fig. 2

that of mixture at the time of mixing. On the graph, draw a vertical line for the moment of mixing (when half the water has been poured in) and extrapolate the temperature-time curve of hot water and mixture to this vertical line. The point of intersection will give the desired temperature.

Now in another experiment, take 25 ml of distilled water in the calorimeter and record its temperature to the nearest 0.1° . Now pipette out exactly a known quantity, say 5 ml of sulphuric acid of known strength. Now pour this acid into the calorimeter by holding the tip of the pipette below the water surface and stir the contents of the calorimeter with the pipette itself. Continue stirring and record the temperature-time curve as above. Now record the maximum temperature attained.

Observations : (1) Volume of cold water taken = M_1 ml.

Initial temperature of water = $t_1^\circ\text{C}$

Volume of hot water mixed = M_2 ml

Temperature of hot water = $t_2^\circ\text{C}$

Temperature of the mixed solution = $t_3^\circ\text{C}$

(2) Volume of cold water taken = M_3 ml.

Initial temperature of water = $t_1^\circ\text{C}$

Volume of sulphuric acid = M_4 ml

Highest temperature after addition = $t_4^\circ\text{C}$

Strength of sulphuric acid = x molar.

Calculations :

(1) Heat taken by calorimeter and water

$$= (W + M_1) (t_3 - t_1) \text{ cal}$$

where, W is the water equivalent of calorimeter.

The specific gravity of water is taken as unity.

Heat given out by hot water = $M_2 (t_2 - t_3)$ cal

Heat taken up = Heat given out

$$\therefore (W + M_1) (t_3 - t_1) = M_2 (t_2 - t_3)$$

$$\therefore W = \frac{M_2 (t_2 - t_3) - M_1 (t_3 - t_1)}{(t_3 - t_1)}$$

(2) Heat of dilution of x molar sulphuric acid

$$= (W + M_3 + M_4) (t_4 - t_1) \text{ cal}$$

(The specific gravity of water and aqueous solution of sulphuric acid are both taken to be unity).

Result : (i) Water equivalent of the calorimeter = ...

(ii) Heat of dilution of sulphuric acid = ...

Precautions : (i) The temperatures should be accurately recorded.

(ii) The hot water must be added to cold water and that too immediately.

(iii) The calorimeter should be completely insulated.

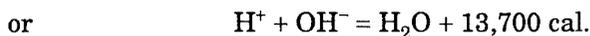
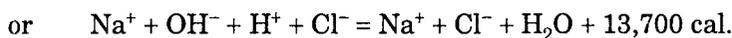
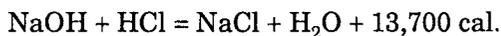
EXPERIMENT No. 2

Object : To find out the heat of neutralisation of sodium hydroxide and hydrochloric acid.

Apparatus : Same as in experiment 1.

Theory : The heat of neutralisation is defined as the *quantity of heat evolved when one gram equivalent of an acid is neutralised by one gram equivalent of a base in dilute solution*. When strong acids in dilute solutions are neutralised by strong bases in solutions of about the same concentration, it is found that the heat evolved is practically a constant quantity for all strong acids and bases, *viz.* 13,700 cal.

If the changes occurring when such solutions react are examined, the reason for this constant quantity becomes clear. Strong acids and strong bases in dilute solution are almost completely ionised, and the same may be said of the salt formed by their union, so that the only change may be said to be the formation of water by the union of hydrogen and hydroxyl ions, as shown by the following equations:



Therefore, heat of neutralisation of strong acids by strong bases represents nothing else but the heat of combination of one gram equivalent of hydrogen ions with one gram equivalent of hydroxyl ions to form water.

Procedure : First determine the water equivalent of calorimeter, as described in experiment no. 1.

To prepare *N*-HCl and *N*-NaOH solutions one proceeds as follows:

(i) Prepare $\frac{N}{2}$ oxalic acid by weighing 7.875g of oxalic acid (A.R.) and dissolve it in water in a 250 ml measuring flask and make the solution upto the mark.

(ii) Prepare NaOH solution of nearly 2*N* strength by dissolving 85 g of caustic soda pellets (from a well sealed or newly opened bottle) per litre of solution.

(iii) Standardise the NaOH solution against oxalic acid and prepare 250 ml of exact *N*-NaOH solution by required dilution (Check by titrating it against standard oxalic acid solution).

(iv) Prepare nearly 2*N*-HCl solution by diluting 50 ml of conc. HCl to 250 ml.

(v) Standardise this HCl solution by titrating it against already standardised *N*-NaOH solution.

(vi) Dilute standardised HCl solution to obtain 250 ml of *N*-HCl solution. Re-check by titrating it against standardised NaOH solution.

Take 100 ml of *N*-HCl in the calorimeter and note the temperature reading after every half minute for 5 minutes. Similarly, take 100 ml of *N*-NaOH in the calorimeter and record its temperature-time curve. Now pour NaOH into calorimeter containing HCl quickly, taking care to avoid splashing. Stir and note the exact time of mixing and note the temperature readings after every half minute for 5 minutes. After the experiment is completed, add a drop

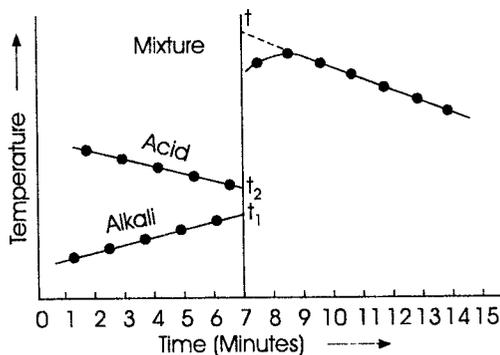


Fig. 3

of phenolphthalein to ascertain whether the acid and base have been completely neutralised or not.

Plot a graph between temperature and time [fig. (3) page 233]. After mixing HCl and NaOH, it will be seen that in the beginning, the temperature rises quickly and starts to fall first irregularly and then in a regular manner. Find out the temperature of the mixture at the time of mixing. From this draw a vertical line at the time of mixing (when half of NaOH has been added in). Also extend the curves through the points when the temperature begins to fall regularly. The point of intersection will give the final temperature after mixing. To obtain the actual temperature of the acid and alkali, at the time of mixing, also plot the temperature readings of each solution against time. The temperature of the solution before mixing can be taken as $\left(\frac{t_1 + t_2}{2}\right)$, as they are mixed in equal volumes.

Observations :

- | | |
|--|------------|
| (1) Volume of cold water taken | = M_1 ml |
| Initial temperature | = t_1 °C |
| Volume of hot water added | = M_2 ml |
| Temperature of hot water | = t_2 °C |
| Final temperature after mixing | = t_3 °C |
| (2) Volume of 1 M HCl | = M_3 ml |
| Volume of 1 M NaOH | = M_4 ml |
| Initial temperature of either HCl or NaOH | = t_4 °C |
| Final temperature after addition of HCl and NaOH | = t_5 °C |

Calculations. (1) Heat taken by calorimeter and water

$$= (W + M_1) (t_3 - t_1) \text{ cal.}$$

where, W is the water equivalent of calorimeter.

$$\text{Heat given out by hot water} = M_2 (t_2 - t_3)$$

$$\text{Heat taken up} = \text{Heat given out}$$

$$\therefore (W + M_1) (t_3 - t_1) = M_2 (t_2 - t_3)$$

$$\therefore W = \frac{M_2 (t_2 - t_3) - M_1 (t_3 - t_1)}{(t_3 - t_1)}$$

$$(2) \text{ Rise of temperature} = (t_5 - t_4)^\circ\text{C}$$

$$\begin{aligned} \text{Heat given out by the solution} &= (M_3 + M_4 + W) (t_5 - t_4) \\ &= Q \text{ cal (say)} \end{aligned}$$

Therefore, Q cal of heat is given out when 0.1 mole of HCl reacts with 0.1 mole of NaOH.

Hence, molar heat of neutralisation

$$= \frac{Q \times 1 \text{ mole}}{0.1} \text{ cal} = 10 \times Q \text{ cal}$$

Result : The heat of neutralisation of hydrochloric acid and sodium hydroxide = ... cal.

Precautions : (i) When the experiment is complete, add a drop of phenolphthalein to the mixture of HCl and NaOH. If a pink colour is seen, then the neutralisation is not complete and the experiment should be repeated.

(ii) The volume and strength of both acid and base should be the same.

(iii) Final temperature should be recorded after thoroughly mixing the contents.

EXPERIMENT No. 3

Object : To determine the heats of neutralization of two acids, e.g., HCl and CH_3COOH and hence their relative strength.

Theory : The strength of an acid or base is the measure of its extent of ionisation, i.e., degree of dissociation at a given concentration. Suppose that the heats of neutralization of HCl and acetic acid against NaOH are x cal and y cal, respectively. If to a mixture containing 1 g equivalent of each acid, 1 g equivalent, of NaOH is added, the two acids will take up NaOH in the ratio of their strengths. Suppose n g equivalents out of 1 gram equiv. of NaOH are neutralized by HCl and the rest $(1 - n)$ by acetic acid. Neutralization of HCl will give nx cal, whereas acetic acid would give $(1 - n)y$ cal. If z is the experimental heat evolved for the mixture, then

$$nx + (1 - n)y = z, \text{ or } n = (z - y)/(x - y)$$

The ratio $n/(1 - n)$ gives the relative strength of HCl and CH_3COOH .

Procedure : Determine the heat of neutralization of HCl and CH_3COOH against NaOH as mentioned in experiment no. 2

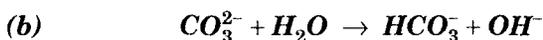
Prepare 0.5 N HCl and 0.5 N CH_3COOH and mix 125 cm^3 of each acid. This gives a mixture (250 cm^3) of the two acids containing 0.25 gram equivalent/1000 cm^3 of each acid.

Add 250 cm^3 of 0.25 N NaOH to this mixture and determine the heat evolved during the reaction. On multiplying this quantity by 16, we get z .

Finally, calculate the ratio $n/(1 - n)$ using the formula given above.

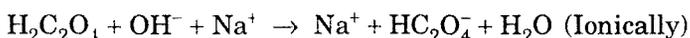
EXPERIMENT No. 4

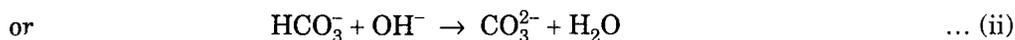
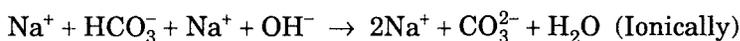
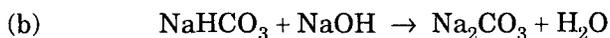
Object : To find the heats of reaction for the reactions :



Apparatus and Chemicals : Same as in experiment 2, 0.5M solutions of $\text{H}_2\text{C}_2\text{O}_4$, NaHCO_3 and NaOH.

Theory : An examination of the reaction equations will show that the reverse reactions can be carried out very easily and their heat of neutralisation can be determined experimentally. These reactions are :





Equations (i) and (ii) are reverse of equations (a) and (b) given in the object of the experiment. The heat of a reverse reaction can be equated with the heat of a direct reaction by changing the sign of ΔH for the reverse reaction.

Procedure : The experiments are carried out by making similar observations as in experiment 2, by mixing 100 ml volumes of 0.5M solutions of NaOH and $\text{H}_2\text{C}_2\text{O}_4$ in one case and NaOH and NaHCO_3 in the other case.

Calculations : Calculate heat of reaction (ΔH) for both reactions as in experiment 2. By reversing the signs of ΔH , we can calculate ΔH for the reactions (a) and (b) which is our object.

Result : The heats of reaction are andcal, respectively.

EXPERIMENT No. 5

Object : *To determine the basicity of a polybasic acid of molecular weight 126. Also obtain the heat of neutralisation for the different stages of neutralisation.*

Apparatus and Chemicals : Apparatus is the same as in experiment 2. Equimolar solutions of the given acid and NaOH.

Theory and Procedure : Take 1000 ml of 1M solution of the acid (obtained by dissolving 126 g in 1000 ml of solution) and add to it 1000 ml of 1M solution of NaOH. The heat evolved will correspond to neutralisation of only 1 mole of H^+ ions. The total available hydrogen ions will be B mole, where B = basicity of the acid. If we add 1000 ml of 1M NaOH solution, only one mole of H^+ ions available from the acid will be neutralised. The heat so evolved will correspond to only one step of neutralisation. If we add further 1000 ml of 1M NaOH solution to the resulting solution, heat is evolved further which is of about the same order as in the first step, though less. This suggests the availability of a second mole of hydrogen ions from one mole of acid. Proceeding stepwise, we shall finally come to a step in which no further heat will be evolved. This should be decided by actual calculation of the heat evolved and not by merely observing the temperature change. When this stage is reached, no more alkali is added after this step. Thus, the basicity of the acid is one less than the steps of addition of NaOH to a stage of no more evolution of heat of neutralisation.

Calculation : For calculating the heat of neutralisation for neutralisation steps separately we should know the water equivalents of the corresponding parts of the thermos flask. This can be obtained by mixing hot water also in equal steps of the same volume as was used for additions of NaOH solution.

In laboratory, experiment is carried out with 100 ml volume steps. Heat evolved is calculated on the basis of temperatures observed before and after each step of reaction in the same way as in experiment 2. At each step of neutralisation, due precaution should be taken to the initial volume of solution.

Result : The basicity of the given acid = ...

EXPERIMENT No. 6

Object : *To find out the heat of neutralisation of acetic acid by sodium hydroxide and from it also calculate the heat of ionisation of acetic acid.*

Apparatus : Same as in preceding experiment.

Theory : The heat of neutralisation of strong acids by strong bases is seen to be about 13,700 cal. But the heat of neutralisation of weak acids by strong bases is less than 13,700 cal. The reason is that the incompletely ionised acid has to become ionised before the hydrogen ion can combine with the hydroxyl ion. The ionisation of the weak acid usually takes place with an absorption of heat and the heat change due to ionisation occurring during the reaction adds algebraically to 13,700 cal.

In the neutralisation of acetic acid by sodium hydroxide, we have the following initial condition, on mixing the two solutions :



Since sodium acetate is completely ionised in the solution, the reaction yields Na^+ , CH_3COO^- ions and H_2O .

In the reaction mixture, the following processes occur :

(i) $(1 - \alpha)$ gram molecules of acetic acid ionise, and if H be the heat of ionisation of acetic acid per gram molecule, then $(1 - \alpha)H$ would be the heat change due to ionisation.

(ii) One gram equivalent of hydrogen ions combine with one gram equivalent of hydroxyl ions, giving a heat evolution of 13,700 cal.

The algebraic sum of the above two quantities is the heat of neutralisation measured, say H_1 ,

$$\therefore H_1 = (1 - \alpha)H + 13,700 \text{ cal.}$$

$$\text{or } H = \frac{H_1 - 13,700}{1 - \alpha} \text{ cal.}$$

Actually, H is a negative quantity, *i.e.*, the ionisation of acetic acid is accompanied by the absorption of heat. Consequently, the value of H_1 will be less than 13,700 cal.

Procedure : Measure the heat of neutralisation of a normal solution of hydrochloric acid by normal solution of sodium hydroxide, as described in experiment 2. Now measure the heat of neutralisation of a normal solution of acetic acid by a normal solution of sodium hydroxide. Draw the temperature-time curve as explained in preceding experiments.

Also, measure the degree of ionisation of a normal solution of acetic acid, by any known method, say conductivity method. The degree of ionisation of acetic acid at the given dilution can be seen from the standard tables also.

Observations :

(1) Volume of cold water taken	= M_1 ml
Initial temperature of cold water	= t_1 °C

Volume of hot water taken	= M_2 ml
Temperature of hot water	= t_2 °C
Final temperature after the addition	= t_3 °C
(2) Volume of 1 M HCl	= M_3 ml
Volume of 1 M NaOH	= M_4 ml
Initial temperature of HCl or NaOH	= t_4 °C
Final temperature on mixing HCl and NaOH	= t_5 °C
(3) Volume of 1 M CH ₃ COOH	= M_5 ml
Volume of 1 M NaOH	= M_6 ml
Initial temperature of CH ₃ COOH or NaOH	= t_6 °C
Final temperature on mixing CH ₃ COOH and NaOH	= t_7 °C

Calculations : (1) As calculated in experiment 1, the water equivalent of the calorimeter is given by,

$$W = \frac{M_2(t_2 - t_3) - M_1(t_3 - t_1)}{(t_3 - t_1)}$$

(2) As calculated in experiment 2, the heat of neutralisation, H_2 of hydrochloric acid by sodium hydroxide is given by $10 \times Q$ cal., i.e.,

$$H_2 = 10 \times Q \text{ cal}$$

where $Q = (M_3 + M_4 + W)(t_5 - t_4)$.

(3) Rise in temperature on mixing acetic acid and sodium hydroxide
= $(t_7 - t_6)$ °C.

Heat given by the solution = $(M_5 + M_6 + W)(t_7 - t_6) = Q_1$ cal

Molar heat of neutralisation, $H_1 = 10 \times Q_1$ cal

The heat of ionisation is thus calculated as,

$$H = \frac{H_1 - H_2}{(1 - \alpha)} \text{ cal}$$

(We can avoid measuring the value of H_2 experimentally and may take it to be equal to 13,700 cal. We have measured H_2 , only to avoid experimental error).

Result : (i) The heat of neutralisation of CH₃COOH by NaOH = ... cal.

(ii) Heat of ionisation of CH₃COOH = - ... cal.

Precautions : Same as in preceding experiments.

EXPERIMENT No. 7

Object : To find out the heat of solution of a given substance.

Apparatus : Same as in preceding experiments.

Theory : The heat of solution is defined as *the quantity of heat evolved or absorbed when one mole of a substance is dissolved in a large excess of solvent or water, so that further dilution does not bring any more heat change.*

It is important that while expressing the heat of solution the exact condition of the solid substance is to be stated, *i.e.*, whether it contains water of crystallisation or not. This is because the heat of solution is often quite different in the two cases.

Procedure : First measure the water equivalent of the calorimeter by the same procedure as described in experiment 1.

Now take about 200 ml of distilled water in the calorimeter. Record its temperature-time curve. Now add a known quantity of the given substance, say KCl and dissolve it in water present in the calorimeter, by means of a stirrer. Record the temperature-time curve as usual. Repeat the above procedure by adding more quantities of the substance and note the final temperature of the solution.

Observations : (1) Volume of cold water taken = M_1 ml

Initial temperature of cold water = $t_1^\circ\text{C}$

Volume of hot water taken = M_2 ml

Temperature of hot water = $t_2^\circ\text{C}$

Final temperature after mixing = $t_3^\circ\text{C}$

(2) Volume of cold water taken = M_3 ml

Initial temperature of cold water = $t_1^\circ\text{C}$

Amount of substance dissolved = W_1 g

Final temperature after mixing the substance = $t_4^\circ\text{C}$

Calculations :

(1) The water equivalent (W) of the calorimeter is calculated as in experiment 1, *i.e.*,

$$W = \frac{M_2(t_2 - t_3) - M_1(t_3 - t_1)}{(t_3 - t_1)}$$

(2) Heat absorbed by solution after adding the substance

$$= (M_3 + W_1)(t_4 - t_1)$$

Heat absorbed by the substance per litre

$$= \frac{(M_3 + W_1)(t_4 - t_1) \times 1000}{M_3} = Q \text{ cal (say)}$$

If M be the molecular weight of the substance, the heat of solution would then be equal to $\frac{Q \times M}{W_1}$ cal per litre.

Result : The heat of solution of the given substance = ... cal.

Precautions : Same as in preceding experiments.

EXPERIMENT No. 8

Object : To determine the integral heat of dilution of sulphuric acid starting with 10 M acid and going down to 5M acid in the order 9M, 8M, 7M, 6M.

Apparatus : Calorimeter, thermometers, beakers, pipettes etc.

Theory : Heat change effects are observed when a given solution is diluted to another give solution. *The heat change accompanying dilution of a solution from one specified concentration to another specified concentration is known as integral heat of dilution.* The integral heat of dilution $\Delta H_{D(m_1 \rightarrow m_2)}$ between two molalities m_1 and m_2 is defined as the heat change taking place when enough solvent is added to a quantity of solution of molality m_1 , containing 1 mole of solute to decrease the molality to the lower value m_2 . Thus, the integral heat of dilution from one concentration to another will be equal to the difference of integral heats of solution of the two concentrations involved.

$$\Delta H_{D(m_1 \rightarrow m_2)} = \Delta H_{I,S}(m_2) - \Delta H_{I,S}(m_1)$$

The integral heat of dilution of an infinitely dilute solution is zero.

Procedure : Determine the water equivalent of calorimeter as in experiment 1. Prepare about 50 ml each of 10M, 9M, 8M, 7M, 6M solutions of H_2SO_4 . Cool all the solutions to room temperature in a water trough. Take 50 ml of distilled water in a dry calorimeter. Prepare its temperature record. Now take 10 ml of the acid solution and keep it in a trough for attaining a constant temperature. Record its steady temperature and transfer acid to water in the calorimeter. Stir and prepare a temperature record of the mixture. Find the temperature of mixture for the moment of mixing. Now calculate the heat evolved for dilution of 10 ml of acid to 50 ml of water. Perform the experiment with other acid solutions also. Also plot a graph between heat of dilution and initial molarity of the acid.

Observations : Water equivalent of calorimeter = W g
 Volume of cold water taken in the calorimeter = 50 ml
 Volume of acid solution added = 10 ml
 Initial molarity of the acid solution = 10 M
 Initial temperature of cold water = $t_1^\circ C$
 Initial temperature of acid solution = $t_2^\circ C$
 Final temperature after dilution = $t_3^\circ C$

Calculations : Consider the density and specific heat of solution as unity.
 Integral heat of dilution, ΔH

$$= (t_3 - t_1)(50 + W) + (t_3 - t_2) \times 10 = a \text{ cal}$$

Moles of acid in 10 ml of 10M acid solution

$$= \frac{10 \times 10}{1000} = 0.1 \text{ mole}$$

$$\therefore \Delta H \text{ per mole of } H_2SO_4 = a \times \frac{1.0}{0.1} = 10a \text{ cal}$$

Similarly, calculate the values of ΔH for other solutions i.e., 9M, 8M, 7M, 6M and 5M solutions.

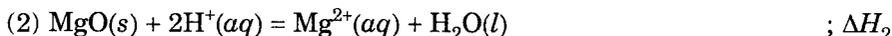
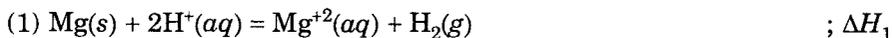
Result : The integral heats of dilution are ...

EXPERIMENT No. 9

Object : To determine the heats of formation of MgO and ZnO calorimetrically.

Apparatus : Same as in preceding experiments.

Theory : The thermochemical equations involved are :



$$\therefore \Delta H_4 = \Delta H_1 - \Delta H_2 + \Delta H_3 \quad \dots (a)$$

The standard value of ΔH_3 at 298K is -68.32 k. cal/mole. Thus, by measuring ΔH_1 and ΔH_2 , we can calculate ΔH_4 , the heat of formation of MgO.

Procedure : Weigh 0.4 g of Mg metal powder. Find out the water equivalent of calorimeter as in experiment no. 1. Now take 200 ml of 0.5M HCl in the calorimeter and prepare its temperature-time record. Add Mg powder to this acid, stir slowly but continuously. Prepare its temperature-time record even after Mg has dissolved. Now calculate the heat of reaction, ΔH_1 .

Now weigh 0.705 g of MgO powder and dissolve it in 200 ml of 0.5M HCl and calculate the heat of reaction, ΔH_2 , as explained above.

Observations and Calculations : The values of ΔH_1 and ΔH_2 are calculated as in preceding experiments, from which ΔH_4 (heat of formation of MgO) is calculated from equation (a).

The heat of formation of ZnO is also calculated in the same manner.

Result : The heats of formation of ZnO and MgO are ... and ... cal, respectively.

EXPERIMENT No. 10

Object : To determine the enthalpy change for the precipitation of one mole of copper or silver by zinc, iron or magnesium powder.

Apparatus and Chemicals : Inert calorimeter, 0.25M copper sulphate, 0.25M silver nitrate, powder form of displacing metal, 0.1° graduated thermometer.

Theory : Same as in experiment 7.

Procedure : Take 50 ml of standard salt solution (0.0125 mole) in the calorimeter and record its temperature for some time till the change in temperature becomes uniform. Weigh about 0.02 mole of displacing metal powder. This should be in excess of the required amount. Dip the metal powder into the solution and stir continuously. Record the temperature after every half minute till the temperature variation becomes uniform. Extrapolate the temperature to the moment of mixing.

Observations : Same as in preceding experiments.

Calculations : Taking the specific heat of solution as $1 \text{ cal ml}^{-1} \text{ K}^{-1}$, the enthalpy change, ΔH is given by,

$$\Delta H = \Delta T \times 50 \times 1 \times \frac{1000}{50} \times \frac{1}{0.25} \text{ cal mole}^{-1}$$

(The enthalpy change for the residual metal has been neglected).

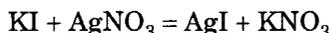
Result : The enthalpy change of precipitation is ... cal mole⁻¹.

EXPERIMENT No. 11

Object : *To find out the heat of precipitation of silver iodide.*

Apparatus : Same as in preceding experiment.

Theory : The heat of precipitation is defined as *the amount of heat evolved or absorbed when one mole of a sparingly soluble salt is precipitated from solution.* The heat of precipitation of silver chloride can be determined by studying the reaction between potassium iodide and silver nitrate, *viz.*,



Procedure : Prepare a solution of 34 g of AgNO_3 in 500 ml of distilled water and also a solution of 33.2 g of potassium iodide in 500 ml of water. (*These solutions contain 1/5 mole of each substance*). Measure 250 ml of potassium iodide solution and add it into the calorimeter. Note the temperature of this solution by means of a thermometer. Now take 250 ml AgNO_3 solution in a separate beaker and measure its temperature after every half minute for 5 minutes. Draw its temperature-time curve.

Add AgNO_3 solution to the KI solution in the calorimeter and stir the contents well. Take a series of temperature readings of the mixture and draw a temperature-time curve.

Determine the water equivalent (W) of the calorimeter, as already described in experiment 1.

Observations :

(1) Volume of cold water taken	= M_1 ml
Initial temperature of cold water	= t_1 °C
Volume of hot water taken	= M_2 ml
Temperature of hot water	= t_2 °C
Final temperature of the mixture	= t_3 °C
(2) Volume of KI solution taken	= M_3 ml
Initial temperature of KI solution	= t_4 °C
Volume of AgNO_3 solution taken	= M_4 ml
Initial temperature of AgNO_3 solution	= t_4 °C
Final temperature after mixing KI and AgNO_3	= t_5 °C
Density of 0.2N KI	= d
Specific heat of KI	= s
Specific heat of solid AgI	= s_1
Weight of silver iodide formed	= W_1 g

Calculations : The heat of reaction, H is given by

$$H = M_3 ds (t_3 - t_4) + W_1 s (t_5 - t_4) + M_4 ds (t_5 - t_4) + W_1 s_1 (t_5 - t_4)$$

The values of d , s and s_1 are 1.0128, 0.966 and 0.0606 for the given experiment. The value of W , the water equivalent of the calorimeter is calculated as explained in experiment 1, viz.,

$$W = \frac{M_2(t_2 - t_3) - M_1(t_3 - t_1)}{(t_3 - t_1)}$$

The amount of silver iodide formed is $\frac{W_1}{M}$ mole (where M = molecular weight of AgI). Therefore, quantity H is $\frac{W_1}{M}$ times the heat of precipitation.

$$\therefore \text{Heat of precipitation} = \frac{W_1}{M} \times H \text{ cal}$$

Result : The heat of precipitation of silver iodide = ... cal

Precautions : Same as in preceding experiments.

EXPERIMENT No. 12

Object : To determine the fuel value of the given fuel by using a bomb calorimeter.

Apparatus and Chemicals : Bomb calorimeter, cylinder of compressed oxygen.

Theory : In a bomb calorimeter, a combustible substance is oxidised to carbon dioxide and water by heating in oxygen at a pressure of 20-25 atmosphere. The reaction is completed under constant volume condition and the measured heat change gives the value of ΔE for the reaction. Though the heat evolved is measured by noting a rise in temperature of the large bulk of water surrounding the calorimeter, the actual rise in temperature is so small that the experimental condition can be taken to be nearly an adiabatic change. Therefore, ΔH value can be calculated from the observed ΔE value according to the following thermodynamic relation,

$$\begin{aligned} \Delta H &= \Delta E + P\Delta V \\ &= \Delta E + \Delta n \cdot RT \end{aligned}$$

where, $\Delta n = (\text{No. of moles of gaseous products}) - (\text{No. of moles of gaseous reactants})$.

Procedure : Construction of a bomb calorimeter. The essential parts of a bomb calorimeter are :

- (i) The bomb
- (ii) Electrical ignition system
- (iii) Calorimeter containing a known weight of water.
- (iv) A precision thermometer usually a Beckmann thermometer or some electrical temperature registering device.
- (v) An insulating wall surrounding the water jacket to make the operation adiabatic.

A bomb calorimeter is as shown in figure (4). The operational details are generally provided by the manufacturer. For each unit standard results are obtained from tables for heat of combustion of benzoic acid, glucose, sucrose, anthracene, naphthalene etc. The value of ΔE for benzoic acid is -6316 cal /mole. One of these reactions can be used for determining the water equivalent of the bomb calorimeter.

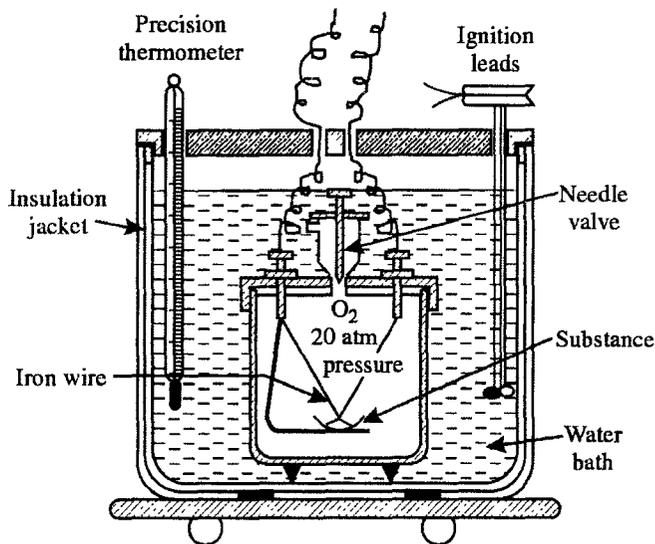


Fig. 4 : Bomb calorimeter.

The weight of fuel sample should be such as to give 6,000–8,000 cal of heat when the calorimeter uses 300–400 ml of water. The substance should not be in a powdered form as it will disperse when oxygen is allowed to flow into the bomb. Samples are used as pellets made in a compression machine. In all experiments, a check is made at the end of the experiment to find whether the combustion is complete or not. There should not be soot anywhere in the bomb, when it is opened after the experiment. In case of incomplete combustion, the experiment is repeated at a higher pressure of oxygen.

The sample pellet is placed in a crucible usually made of fused silica. A special iron wire is used as a fuse between platinum leads. The wire of diameter of nearly 0.004 mm is preweighed carefully. The loop of wire is fixed slightly above the sample in the crucible. The wire is ignited electrically. The burning wire pieces fall on the sample pellet in the crucible and thus ignite the sample pellet. Heat changes due to combustion of iron wire can be computed from the weight of the wire.

Nearly 1 cm^3 of water is added to the bomb to saturate oxygen with water vapours. When crucible, sample pellet and iron wire are properly placed, the bomb is closed and secured properly by a screw cap or a waist nut by using a special wrench.

The atmospheric air present in the bomb is removed from it by flushing it with oxygen. The needle valve in the inlet for oxygen is opened half a turn and the bomb is connected to an oxygen cylinder. The cylinder is opened slowly and oxygen is filled to a pressure of 20–25 atmosphere. The pressure is then released so that this first filling of oxygen is emptied and along with the nitrogen of initial air is also flushed out. Refill the bomb with oxygen to 25 atmosphere pressure and close the needle valve and tighten it. Disconnect the oxygen supply. Place the bomb in the

water calorimeter and watch for any gas bubbles leaking out of the bomb. Dry the outside area of the bomb. Connect the ignition wire terminals to proper posts on the cover. These leads should not be short.

Procedure : Place the bomb in a bucket. The bucket stands on an insulating table made of cork or wood. Fill the bucket with carefully weighed water. Assemble the top of the calorimeter and close it. Start the stirrer in the calorimeter. The temperature is noted after every 30 seconds. When the temperature remains steady for 5 minutes, fire the bomb by turning on the ignition switch and then turning off. Prepare a time-temperature record for nearly 20 minutes till the temperature becomes steady or begins to fall off. From this record of temperature, the maximum temperature reached is noted.

The calorimeter is then disassembled. The pressure of the gas should be released very slowly. Open the bomb and collect the unburnt wire and weigh it. The heat of combustion for iron is given by,

$$\Delta H_{\text{Iron}} = -1600 \text{ calories per g}$$

Calculations : The calorific value (C. V.) of a fuel is given by,

$$\text{C.V.} = \frac{(W + w_1)(t_2 - t_1) - H}{w_2}$$

where, W = Water equivalent of calorimeter

w_1 = Weight of water in calorimeter

w_2 = Weight of fuel used

t_1 = Initial temperature of calorimeter

t_2 = Final temperature of calorimeter

H = Heat evolved due to burning of iron wire

This result will be expressed in calories per gram. It is divided by 1000 to get the C.V. or fuel value in kilo calories per gram. (1 k cal = 4.18 kJ).

Result : The calorific value of the fuel = ... k cal/g.

Errors : The errors in result are observed due to :

- (i) Formation of nitrogen oxide from residual nitrogen in oxygen.
- (ii) The enthalpy needs correction due to change in temperature after the reaction.
- (iii) Loss of heat by radiation.
- (iv) Heat evolved due to combustion of iron wire.
- (v) The ratio $\text{CO}_2 : \text{H}_2\text{O}$ being different for the fuel and the calibrating substance.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 13

Object : To determine the heat of hydration of anhydrous copper sulphate.

Weigh about 15.9 g of anhydrous copper sulphate (obtained by heating $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 150°C for 30 minutes), i.e., 1/10th of a g mole and determine its heat of solution in 360 g of water, as already described. The value obtained will be

the heat of solution of one g mole of anhydrous salt in 200 moles of water. Weigh about 24.9 g of crystallised copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and determine the heat of solution in 360 g of water, which will give the heat of solution of one mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 200 moles of water. If H_1 and H_2 be the heats of solution of the anhydrous salt and pentahydrate, respectively, then

$$H_1 = (\text{CuSO}_4, \text{aq.}) \text{ and } H_2 = (\text{CuSO}_4 \cdot 5\text{H}_2\text{O}, \text{aq.})$$

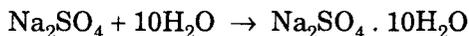
$$H_1 - H_2 = (\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$$

(The specific heat of copper sulphate solution containing one mole in 200 moles of water is 0.9516 over the temperature range $18^\circ\text{C} - 50^\circ\text{C}$).

EXPERIMENT No. 14

Object : *To determine the heat of hydration of sodium carbonate ($\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$).*

The reaction for hydration is



Apparatus and Chemicals : Thermos flask, boiling tube, glass rod, thermometer ($0^\circ - 50^\circ\text{C}$) graduated in 0.1°C , anhydrous sodium sulphate and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

Procedure : The heat of solution of hydrated salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is first determined as in experiment 6. Similarly, determine the heat of solution of anhydrous salt. The water equivalent can be calculated on the basis of known heat of solution of salts like $\text{K}_2\text{Cr}_2\text{O}_7$, KNO_3 or KCl .

Calculation : Heat of hydration of sodium sulphate

= Heat of solution of anhydrous salt

- Heat of solution of hydrated salt

Result : The heat of hydration = ... cal mole⁻¹.

EXPERIMENT No. 15

Object : *To determine the heat of solution at various temperatures.*

Proceed as in experiment 6 by measuring heats of solution at different temperatures. Plot a curve between heat of solution of any substance and temperature.

EXPERIMENT No. 16

Experiment 15 : *To determine the integral heat of solution of a salt at two concentrations and hence the integral heat of dilution.*

The integral heat of dilution between two molalities m_1 and m_2 is defined as the heat effect produced when excess of solvent is added to a solution of molality m_1 containing 1 mole of a solute so that the molality is reduced to m_2 . Thus, the

integral heat of dilution is equal to the difference of integral heat of solution at two concentrations, *i.e.*,

$$\Delta H_D (m_1 \rightarrow m_2) = \Delta H_S (m_2) - \Delta H_S (m_1)$$

So, the integral heat of solution of salt is determined at two concentrations. The difference between the two values gives the integral heat of dilution from one concentration to another.

Proceed as in experiment 7.

EXPERIMENT No. 17

Object : *To determine the heat of neutralisation of acetic acid by ammonium hydroxide.*

Proceed as in experiment 5.

EXPERIMENT No. 18

Object : *To determine the heat of precipitation of BaSO₄.*

Apparatus and Chemicals : Same as in other thermo-chemistry experiments, 500 ml each of 0.4 molar BaCl₂ solution and slightly more than 0.4 molar solution of K₂SO₄ or Na₂SO₄, thermos flask of 100 ml capacity, 250 ml measuring cylinder.

Procedure : First determine the water equivalent of thermos flask for 500 ml of mixtures. Dry the flask and put in it 250 ml of 0.4 M BaCl₂ solution. Rinse a 400 ml beaker with sodium sulphate solution and take 250 ml of sodium sulphate solution in it. A 250 ml measuring cylinder can be used for this experiment. When both the solutions have attained steady temperature, note the temperature of each solution. The solutions are then mixed and the temperature of the mixture is noted. The value of ΔH for precipitation of one mole of BaSO₄ is calculated.

Observations : Water equivalent of thermos flask for 500 ml
of mixture = W g

Temperature of BaCl₂ solution = t_1 °C

Temperature of Na₂SO₄ solution = t_2 °C

Temperature of mixture = t_3 °C

Calculations : Moles of BaSO₄ precipitated

$$= 0.4 \times \frac{250}{1000} = 0.1 \text{ mole}$$

So, heat of precipitation of BaSO₄,

$$\Delta H = (250 + W) (t_3 - t_1) + 250 (t_3 - t_2) = x \text{ cal}$$

or
$$\Delta H = x \times \frac{1}{0.1} = 10x \text{ cal mole}^{-1}$$

Result : The heat of precipitation = ... cal mole⁻¹.

EXPERIMENT No. 19

Object : *To determine the heat of transition of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ by calorimetry.*

Apparatus and Chemicals : Same as in other thermochemistry experiments, Na_2SO_4 (anhydrous), Na_2SO_4 (decahydrate) etc.

Theory : The heat of transition of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ into anhydrous Na_2SO_4 will be equal to the heat of hydration of anhydrous salt with sign reversed. If ΔH_1 and ΔH_2 be the integral heats of solution of anhydrous and hydrated salts, respectively, then heat of transition (ΔH_t) will be given by,

$$\Delta H_t = -(\Delta H_1 - \Delta H_2)$$

Procedure : Grind the hydrated salt in a finely powdered state and determine its integral heat of solution at some specified concentration (ΔH_2), as explained in experiment 6.

Dry some anhydrous salt in an oven and then cool it in a dessicator. Then determine its integral heat of solution at the same concentration (ΔH_1), as explained in experiment 6.

Result : The heat of transition = ... cal mole⁻¹.



REFRACTOMETRY

It is a well known fact that when a beam of light is passed from one medium to another, it suffers refraction, *i.e.*, change of direction. If it passes from a less dense medium to a more dense medium, *i.e.*, from air to water, the beam is refracted towards the normal [fig. (1)]. The angle of incidence (i) is greater than the angle of refraction (r). The refractive index (n) of the second medium with respect to the first is given by the relation,

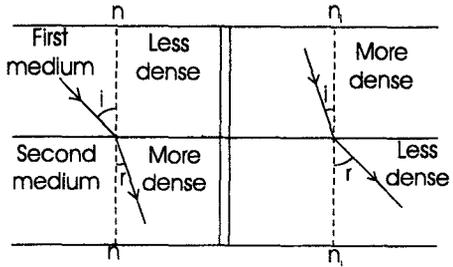


Fig. 1

$$n = \frac{\sin i}{\sin r} \quad (\text{Snell's law of refraction})$$

The value of refractive index is also given by,

$$n = \frac{\text{Velocity of light in vacuum}}{\text{Velocity of light in the medium}}$$

It has been observed that refractive index of a liquid depends on temperature as well as the wavelength of light used. For all practical purposes, the D -line of sodium is used.

Specific Refractivity : Lorenz and Lorentz defined the specific refractivity (or specific refraction) by the equation :

$$R = \frac{1}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$$

where, R is the specific refractivity, d is the density and n is the refractive index of the medium. The value of R is independent of temperature.

Molecular Refractivity : If we multiply the specific refractivity by the molecular weight, M of the medium, we get what is known as molecular refractivity or molecular refraction (R_M).

$$R_M = R \cdot M = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$$

Molecular refractivity is an additive and constitutive property and we have refractivity due to atoms (atomic refractivity) as well as refractivity due to structural factors (structural refractivity)

Determination of Refractive Index : For rapid and accurate measurement of refractive index, a number of instruments known as refractometers are

available. However, for small quantities of liquids, we can easily use Abbe refractometer.

The construction of Abbe refractometer [fig. (2)] consists of two flint glass prisms P_i (lower prism) and P_r (upper prism). The hypotenuse surface of P_r is finely polished, while that of P_i is finely ground. The two prisms are fixed in metal casing at L . The prisms are jacketed so that they can be maintained at constant temperature by circulating water. The prisms are rotated by means of a movable arm M , which carries a reading glass R . In between the two prisms, a thin layer of liquid can be placed.

The position of the border line of total reflection is observed through a fixed telescope T and by turning the movable arm, it is made to coincide with the intersection of the cross-hair in the telescope. The arc A is graduated and directly gives the value of refractive index with an accuracy of 0.001.

Even an ordinary light can be used while working with Abbe refractometer. For this purpose, the telescope is provided with a dispersion compensator C , which consists of two Amici prisms mounted one over the other and can be rotated in opposite direction by turning the milled head H . The optical system of Abbe refractometer is shown in figure (3).

When a drop of liquid is put on the surface of prism P_i and on clamping it with

prism P_r a thin film of liquid spreads between them. Light reflected by mirror G enters the lower prism P_i and passes into the upper prism P_r , which is the refracting prism. The ray of light will be deviated depending upon the angle of incidence. At an angle near 90° to its surface, the rays will be bent the least on entering the prism and rays entering the prism P_r at angles less than 90° will be bent more and they will form the edge of the field [figure (3)]. The line of demarcation between the dark and light fields will be coloured and cannot be seen because when white light is used, it will be refracted to different extents by the prism P_r and liquid. The Amici prism

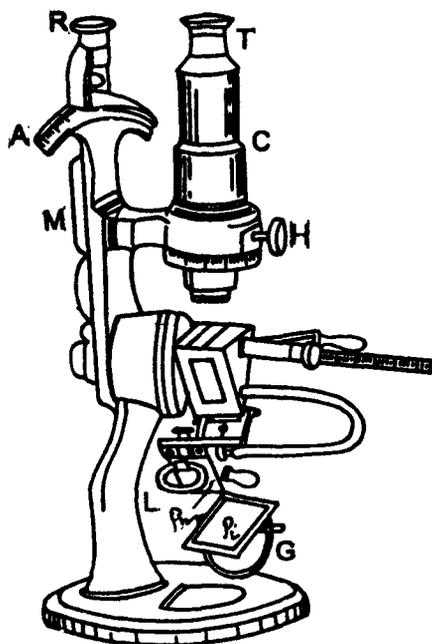


Fig. 2 : Abbe refractometer

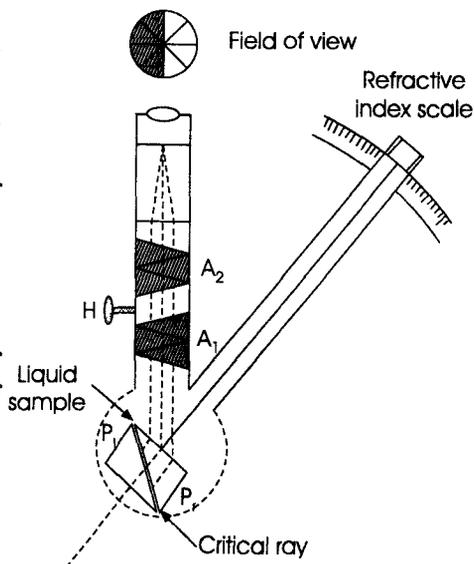


Fig. 3 : Optical system in Abbe refractometer

A_1 corrects for this dispersion. Light of different wavelengths is dispersed by the liquid, prism P_r and by the Amici prism A_1 . As different liquids produce different dispersions, therefore, the second Amici prism A_2 is so adjusted that its dispersion is equal and opposite to that produced by the liquid in prism P_r and A_1 . The Amici prism can be adjusted by turning the milled head H until the compensation is complete, *i.e.*, the colour fringe disappears and a sharp light-dark boundary is observed by the eye piece.

Working of Abbe Refractometer : The refractometer is first placed on working table in such a way that the light from the source is reflected by the mirror G . The mirror is adjusted so as to get the maximum illumination. The prism box is opened by means of the clamp C . The surfaces of the two prisms are cleaned with alcohol or acetone and dried with a soft cotton. **Never scratch the polished upper surface.** Water is then circulated at room temperature through the jacket J surrounding the prism. Water at any temperature can also be circulated from the thermostat.

First the refractometer is tested for its correctness. For it, place one or two drops of distilled water on the lower surface and close the prism box by means of the clamp C . Rotate the mirror G in such a way that it reflects light on the prisms. Move the arm M , till the border line appears in the field. Focus the cross wires of the telescope by sliding the eye up and down. Turn the compensator screw H and adjust the compensator till the coloured lines disappear and the border line coincides exactly with the intersection of the cross wires. Note the reading from the scale. Repeat the process 3 or 4 times and take the mean of all these values. This value should be identical with the standard refractive index of water at room temperature.

The prism box is opened and the polished glass surface is cleaned with either alcohol or acetone and dried. Now 2-3 drops of the experimental liquid are placed on the ground surface of the lower prism. The prism box is closed and refractive index noted, as explained above. If the liquid is volatile, then add it through a groove provided in the prism box. Take three readings and find the mean values of the refractive index.

EXPERIMENT No. 1

Object : *To find out the refractive index of the given liquid and also find its molecular refractivity.*

Apparatus : Abbe refractometer, pycnometer, ordinary light lamp, thermometer etc.

Theory : The molecular refractivity of the liquid is given by,

$$R_M = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2} \quad \dots (1)$$

where all letters have their usual significance.

Procedure : The method consists of two steps. First step consists of determining the refractive index of the liquid by means of Abbe refractometer, as already explained.

Secondly, the density of the liquid is determined by means of a pycnometer, as usual.

Observations : Room temperature = $t^{\circ}\text{C}$

(1) Refractive index of the liquid, $\left. \begin{array}{l} (a) \dots\dots \\ (b) \dots\dots \\ (c) \dots\dots \end{array} \right\} \text{Mean value} = \dots$

(2) Weight of empty pycnometer = $W_1 \text{ g}$

Weight of pycnometer + water = $W_2 \text{ g}$

Weight of pycnometer + liquid = $W_3 \text{ g}$

(3) Molecular weight of the liquid = M (say)

Calculations : The density, d , of the liquid = $\frac{W_3 - W_1}{W_2 - W_1}$

(The density of water is supposed to be unity)

Knowing all the values, we can calculate the value of R_M from equation (1).

Result : The refractive index and molecular refractivity of the liquid are ... and ... , respectively.

Precautions : (i) The polished surface of the prisms of Abbe refractometer should not be scratched.

(ii) Only 2-3 drops of the liquid are sufficient.

EXPERIMENT No. 2

Object : To find out the molecular refractivities of three liquids A, B and C. Also calculate the composition of the liquid C, which is a mixture of two liquids A and B.

Apparatus : Same as in experiment 1.

Theory : The refractive indices of solutions will depend on their composition. The percentage composition of C can be calculated according to the formula;

$$100 (R_M)_C = x (R_M)_A + (100 - x) (R_M)_B$$

where x is the percentage of A in the mixture C.

The value of x can also be determined graphically, *i.e.*, by plotting a curve between concentration of A by weight and molecular refractivities. So, the composition of the solution can be read from the graph by interpolation corresponding to its refractive index.

Procedure : The refractive indices of the three liquids A, B and C are determined by Abbe refractometer, as usual. The densities of each liquid are also determined by pycnometer, as usual. The room temperature is also noted.

Observations : Room temperature = $t^{\circ}\text{C}$

(1) Refractive index measurements	A	B	C

Mean value

(2) Weight of empty pycnometer = $W_1 \text{ g}$

Weight of pyknometer + water = W_2 g

Weight of pyknometer + liquid A = W_3 g

Weight of pyknometer + liquid B = W_4 g

Weight of pyknometer + liquid C = W_5 g

Calculations :

Liquid	Density (d)	Mol. wt. (M)	Molecular refractivity $R_M = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$
A	$\frac{W_3 - W_1}{W_2 - W_1}$
B	$\frac{W_4 - W_1}{W_2 - W_1}$
C	$\frac{W_5 - W_1}{W_2 - W_1}$

Knowing the values of $(R_M)_A$, $(R_M)_B$ and $(R_M)_C$ we can calculate the percentage composition, x of A in the mixture, according to the equation,

$$100 (R_M)_C = x (R_M)_A + (100 - x) (R_M)_B$$

Result : The composition of the mixture is ...% A and ... %B. Molecular refractivities of the liquids A, B and C are ... and ..., respectively.

Precautions : Same as in experiment 1.

Alternative Method : (*Graphical Method*).

A number of mixtures containing A and B are prepared, *i.e.*, by dissolving 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, of A by weight. The refractive index and density of all these solutions are measured by a refractometer and pyknometer, respectively. The molecular refractivities of all these mixtures are then calculated and plotted as ordinate against the percentage composition of A as abscissa. The molecular refractivity of the unknown mixture C is also calculated after determining its refractive index and density. Then we can find out the composition corresponding to the molecular refractivity of the unknown mixture, from the calibration curve.

EXPERIMENT No. 3

Object : To find out the atomic refractivities of carbon, hydrogen and oxygen, by taking methyl acetate, ethyl acetate and *n*-hexane as the experimental liquids.

Apparatus : Same as in preceding experiments.

Theory : Molecular refractivity is an additive and constitutive property and hence the molecular refractivity of a molecule is the sum of refractivities due to atoms constituting the molecule. Therefore,

(i) R_M of ethyl acetate - R_M of methyl acetate

$$= R_M \text{ of } \text{CH}_2 \text{ group.}$$

(ii) R_M of *n*-hexane - $6 \times R_M$ of methyl acetate

$$= 2 \times R_M \text{ of H atom.}$$

(iii) R_M of CH_2 group $- 2 \times R_M$ of H atom $= R_M$ of C atom.

(iv) R_M of methyl acetate $- 3 \times R_M$ of C atom $- 6 \times R_M$ of H atom
 $= 2 \times R_M$ of oxygen atom.

Procedure : The refractive index and density of each liquid, *i.e.*, methyl acetate, ethyl acetate and *n*-hexane are determined as usual by Abbe refractometer and pycnometer, respectively.

Observations :

Liquid	Refractive index (n)	Density (d)	Mol. wt. (M)	Molecular refractivity $R_M = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$
Methyl acetate
Ethyl acetate
<i>n</i> -Hexane

Calculations : After calculating the molecular refractivities of methyl acetate, ethyl acetate and *n*-hexane, we can calculate the atomic refractivities of carbon, hydrogen and oxygen atoms, according to steps (i), (ii), (iii) and (iv), as explained in the theory of this experiment.

Result : The atomic refractivities of C, H and O are ..., ... and ..., respectively,

Precautions : Same as in preceding experiments.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 4

Object : To determine the molecular refractivity of a solid.

Suppose we want to find out the molecular refractivity of a solid, say *p*-dichloro benzene. The solid is first dissolved in benzene. We thus get a solution of known concentration. The molecular refractivities of liquid benzene and the solution are calculated, as usual by using the formula :

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \quad \dots (1)$$

From the mixture law, we have :

$$R_M = xR_1 + (1 - x) R_2 \quad \dots (2)$$

where, R_M is the molecular refractivity of the solution, R_1 and R_2 are the molecular refractivities of the solid and pure liquid and x is the mole fraction of the solid.

The molecular refractivity of the solution is given by,

$$R_M^\circ = \frac{n_m^2 - 1}{n_m^2 + 2} \left[\frac{xM_1 + (1 - x) M_2}{d_m} \right] \quad \dots (3)$$

where, n_m and d_m are the refractive index and density of the solution containing a solid of molecular weight, M_1 dissolved in a solvent of molecular weight, M_2 .

Prepare a solution of the solid substance in the given liquid, the composition in terms of mole fraction of the components being known. Determine the refractive index and density of the mixture and calculate the molecular refractivity of the mixture from equation (3). Also determine the refractive index and density of the liquid say component 2, and calculate the molecular refractivity R_2 .

Now calculate the molecular refractivity R_1 from equation (2) after putting the values of R_2 , R_M and mole fractions (x) and $(1 - x)$ of the respective components. Then calculate the refractive index of the solid from density and molecular weight data by using equation (1).

EXPERIMENT No. 5

Object : *To determine the refractive indices of a series of solutions of KCl and hence determine the composition of the unknown solution of the salt.*

Prepare a number of solutions of KCl in separate beakers containing 2, 4, 6, 8, 10 g of KCl per 100 g of distilled water. Measure the refractive index of each solution and plot a curve between refractive index (ordinate) and concentration (abscissa) of the salt.

EXPERIMENT No. 6

Object : *To study the variation of refractive index with composition of mixtures of carbon tetrachloride and ethyl acetate.*

Procedure : Determine the refractive indices of pure carbon tetrachloride and ethyl acetate by means of Abbe's refractometer.

Prepare a series of solutions of carbon tetrachloride and ethyl acetate by mixing known volumes (1 : 9, 2 : 8, 3 : 7, 4 : 6, etc.) and determine their refractive indices as usual. Determine the densities of pure liquids and one of the mixtures, as usual.

Plot the values of refractive indices (ordinates) and compositions (i) by volume, (ii) by weight and (iii) by mole fraction as abscissa.

Calculate the molar refractivities of pure liquids using the equation $[R] = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho}$. Also calculate the molar refraction for one or more mixtures from the following equation :

$$[R]_{mix} = \frac{n_{mix}^2 - 1}{n_{mix}^2 + 2} \cdot \frac{x_1 M_1 + x_2 M_2}{\rho_{mix}}$$

where n_{mix} and ρ_{mix} are the refractive index and density of the mixture, x_1 and x_2 are the mole fractions of components 1 and 2, respectively and M_1 and M_2 their molecular weights.

Now, calculate the molar refraction of the mixtures from the expression

$$[R]_{mix} = x_1 [R_1] + x_2 [R_2]$$

Compare the value of $[R]_{mix}$ calculated by this formula with that obtained from the former and so test the validity of the latter.

EXPERIMENT No. 7

Object : *To determine the composition of an unknown mixture of two given liquids by refractive index measurements.*

Procedure : First method : Determine the refractive indices of pure liquids and of the mixture as before. Also determine the densities of the liquids and the mixture at the same temperature by using a pycnometer.

Calculate the specific refractivities of pure liquids and of the mixture, and calculate the composition of the mixture using the formula

$$100 r_{mix} = pr_1 + (100 - p) r_2$$

where r_{mix} , r_1 and r_2 are the specific refractivities of the mixture and of the components 1 and 2, respectively; p is the percentage composition of the component 1.

Second method : Prepare different mixtures of known compositions, say 20% , 40%, 60%, 80% by weight, from the given liquids.

Determine the refractive index and the density of each of the mixtures and calculate the specific refractivity. Determine also the refractive index and the density of the given mixture and calculate its specific refractivity.

Now plot the specific refractivities as ordinate against the compositions of the mixtures as abscissa, and read the composition of the unknown mixture on the calibration curve using its specific refractivity.

EXPERIMENT No. 8

Object : *You are provided with two liquids 1 and 2 and their mixtures 3 and 4. By means of a refractometer find the composition of 3 and 4.*

Proceed as explained in experiment 5. Prepare five mixtures of 1 and 2 between the pure liquids and note their refractive indices. Also note the refractive indices of 3 and 4. Draw a graph between compositions and refractive indices. From the graph find the composition of solutions 3 and 4.

EXPERIMENT No. 9

Object : *To determine the molar refractions of ethyl acetate, propyl acetate and butyl acetate and show the constancy of the contribution to the molar refraction made by $-\text{CH}_2$ group.*

Proceed as in experiment no. 3.

EXPERIMENT No. 10

Object : *To determine molar refractivity of ethyl acetate, methyl acetate, ethylene chloride and chloroform and calculate the atomic refractivities of C, H and Cl. The density of each liquid can be measured experimentally or seen from the table.*

Proceed as in experiment nos. 2 and 3.

EXPERIMENT No. 11

Object : To measure refractometrically average polarizability of some of the common solvents.

Theory : The electronic polarisation, P_E of a liquid is given by the relation,

$$P_E = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = R_M \quad \dots (1)$$

where, n is refractive index and is measured for visible light.

Also
$$P_E = \frac{4\pi N\alpha}{3} = R_M \quad \dots (2)$$

where N is Avogadro's number and α is the polarisability of molecules of the liquid or electron polarisability. It is also known as **induced dipole moment of molecule per unit field**. Thus, the value of α can be evaluated from known values of R_M , N and d .

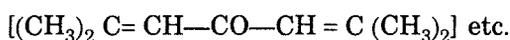
Procedure : Determine the refractive index for the liquid for white light using Abbe's refractometer in the usual way. Also determine the density at the same temperature.

Calculations : Calculate the values of P_E and α from equation (1) and (2).

EXPERIMENT No. 12

Object : To calculate the value of optical exaltation.

When a compound contains two or more double bonds in conjugate positions, then the molecular refractivity is higher than that calculated from the standard values. The difference between the two values is known as *optical exaltation*. We can find optical exaltation in the case of liquids such as hexa-triene ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_3$), phorone



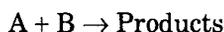
CHEMICAL KINETICS

Chemical kinetics is that branch of chemistry which deals with the study of the rate of chemical reactions and the mechanism by which they occur. In other words, they deal with how fast and through what mechanism a particular reaction occurs.

Reaction Velocity : Reaction velocity is different at different intervals of time and hence it cannot be determined by dividing the amount of the substance transformed by time. It is, however, defined as, '*the rate at which the concentration of a reactant changes with time.*'

Reaction velocity is represented by $-\frac{dc}{dt}$, where dc is the concentration of the reactant left behind after a short interval of time dt . The negative sign implies that the concentration of the reactants left behind decreases with time. It is also represented by $\frac{dx}{dt}$, where dx is the amount of the reactant changed during an interval of time dt .

Velocity Constant : Consider the following reaction :



If a and b be the respective initial concentrations of reactants A and B and x is the amount of each transformed in time t , then according to the law of mass action,

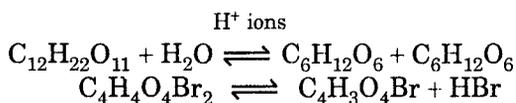
$$\text{Reaction velocity} \propto [A] [B]$$

$$\text{or} \quad \frac{dx}{dt} \propto (a - x) (b - x)$$

$$\text{or} \quad \frac{dx}{dt} = k (a - x) (b - x)$$

where, k is a constant, known as *velocity constant* or *specific reaction rate*.

Molecularity of a Reaction : It is defined as the '*total number of molecules of all the substances taking part in a chemical reaction, as represented by a simple equation.*' For example, molecularity of inversion of cane sugar and decomposition of dibromosuccinic acid will be two and one, respectively.



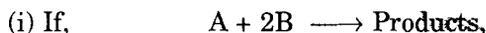
Reactions having molecularity one, two, three, etc. are known as *unimolecular*, *bimolecular* and *trimolecular reactions*, respectively.

Order of Reaction : Reactions are classified not only on the basis of their molecularity but also according to the order of reaction, which is defined as the, 'sum of the powers to which the concentration terms of the reactants must be raised in order to determine the rate of reaction'. For example,



and $\frac{dx}{dt} \propto C_A,$

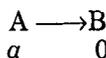
then order of reaction = 1.



and $\frac{dx}{dt} \propto C_A \cdot C_B^2,$

then order of reaction = 1 + 2 = 3.

[I] Zero Order Reactions : A reaction is said to be of zero order if its rate is entirely independent of the concentration of the reactants. Some photochemical reactions and enzymic reactions belong to this category. Consider the following reaction :



(Initially)

For a zero order reaction, the reaction velocity at any time t is given by,

$$\frac{dx}{dt} = k \text{ (constant)}$$

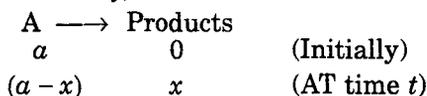
or $dx = k dt$

or $\int_{x_0}^x dx = \int_0^t k dt$

or $x - x_0 = kt$

or $k = \frac{x - x_0}{t}$

[II] First Order Reactions : A first order reaction is that in which the concentration of only one reactant changes with time or in which the rate of reaction is proportional to the first power of concentration of the reactant. The simplest first order reaction is represented by,



Let a mole/litre be the initial amount of the reactant A. Let x mole/litre of it decompose into products, leaving behind $(a - x)$ mole/litre of A. Then for a first order reaction, we have,

$$\frac{dx}{dt} \propto C_A$$

or $\frac{dx}{dt} = k(a - x)$

$$\begin{aligned} \text{or} \quad & \frac{dx}{a-x} = kdt \\ \text{or} \quad & \int \frac{dx}{a-x} = \int k dt \\ \text{or} \quad & -\log_e (a-x) = kt + I_c \quad \dots (1) \end{aligned}$$

where, I_c is an integration constant.

When $t = 0$, $x = 0$, hence, $I_c = -\log_e a$

Therefore, equation (1) becomes,

$$-\log_e (a-x) = kt - \log_e a$$

$$\begin{aligned} \text{or} \quad & kt = \log_e \frac{a}{a-x} \\ \text{or} \quad & k = \frac{1}{t} \log_e \frac{a}{a-x} \quad \dots (2) \end{aligned}$$

$$\text{or} \quad k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} \quad \dots (3)$$

Equations (2) and (3) are known as first order rate equations.

Characteristics of First Order Rate Expressions

(i) The value of velocity constant is independent of the units of concentration chosen.

(ii) The time taken to change the concentration of a reactant to half its initial value is independent of the initial concentration of the reactant.

(iii) The velocity constant has the dimensions of reciprocal time or time^{-1} .

[III] Pseudo Unimolecular Reactions : Reactions which are not unimolecular but obey the first order rate expression are known as pseudo unimolecular reactions. Such reactions involve more than one molecule in the chemical reaction, e.g., inversion of cane sugar, hydrolysis of methyl acetate, hydrolysis of diazo derivatives etc.

[IV] Second Order Reactions : A second order reaction is one in which the reaction velocity is proportional to the product of concentration of two substances or the second power of the concentration of a single substance.

For example : (a) $2A \longrightarrow \text{product}$

$$\frac{dx}{dt} = kC_A^2$$

(b) $A + B \longrightarrow \text{products}$

$$\frac{dx}{dt} = k C_A \cdot C_B$$

Suppose we start with equivalent amounts of both the reactants, say a mole in a certain volume. Let x mole of each be transformed during an interval of time t . The reaction velocity is then given by,

$$\frac{dx}{dt} \propto (a-x)(a-x)$$

$$\text{or} \quad \frac{dx}{dt} = k (a-x)^2$$

$$\begin{aligned} \text{or} \quad & \frac{dx}{(a-x)^2} = k dt \\ \text{or} \quad & \int \frac{dx}{(a-x)^2} = \int k dt \\ & \frac{1}{a-x} = kt + I_c \quad \dots (4) \end{aligned}$$

where, I_c = integration constant.

When $t = 0$, $x = 0$, we have from equation (4),

$$\frac{1}{a} = I_c$$

Therefore, equation (4) becomes,

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$\text{or} \quad k = \frac{1}{t} \left[\frac{1}{a-x} - \frac{1}{a} \right]$$

$$\text{or} \quad k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad \dots (5)$$

The value of k becomes different, when the initial concentrations of the reactants are not equal. Let a and b mole represent the initial concentrations of A and B and let $(a-x)$ and $(b-x)$ be the respective concentrations after an interval of time t , then the reaction velocity will be given by,

$$\frac{dx}{dt} \propto (a-x)(b-x)$$

$$\text{or} \quad \frac{dx}{dt} = k(a-x)(b-x)$$

$$\text{or} \quad \frac{dx}{(a-x)(b-x)} = k dt$$

$$\text{or} \quad \frac{1}{(a-b)} \left[\frac{1}{(b-x)} - \frac{1}{(a-x)} \right] dx = k dt$$

$$\text{or} \quad \frac{1}{(a-b)} \int \left[\frac{1}{(b-x)} - \frac{1}{(a-x)} \right] dx = \int k dt$$

$$\text{or} \quad \frac{1}{(a-b)} \int \left[\frac{dx}{(b-x)} - \frac{dx}{(a-x)} \right] = \int k dt$$

$$\text{or} \quad \frac{1}{(a-b)} \left[-\log(b-x) + \log(a-x) \right] = kt + I_c \quad \dots (6)$$

where I_c = integration constant.

When $t = 0$, $x = 0$, hence from equation (6), we have,

$$\frac{1}{(a-b)} (-\log b + \log a) = I_c$$

$$\text{or} \quad I_c = \frac{1}{(a-b)} \cdot \log \frac{a}{b}$$

Substituting the value of I_c in equation (6), we get,

$$\frac{1}{(a-b)} \log \frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)} \log \frac{a}{b}$$

or
$$kt = \frac{1}{(a-b)} \log \frac{(a-x)}{(b-x)} - \frac{1}{(a-b)} \log \frac{a}{b}$$

or
$$kt = \frac{1}{(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

or
$$k = \frac{1}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad \dots (7)$$

Characteristics of Second Order Rate Expression

(i) The numerical value of velocity constant will change with the change in the units in which concentration is expressed.

(ii) The time required to complete a definite fraction of the reaction is inversely proportional to the concentration of the reactants.

(iii) The unit of velocity constant is $\text{time}^{-1} \times \text{concentration}^{-1}$. If time is expressed in second, then the unit of k will be $(\text{mole/litre})^{-1} \times \text{sec}^{-1}$ or $\text{mol}^{-1} \text{litre sec}^{-1}$.

DRAWING TANGENTS TO CURVES

Suppose we want to draw a tangent to the curve ABC at point B. From B, draw the vertical coordinate line BDE. With any point D chosen as centre and a radius greater than DB, draw arcs intersecting the curve ABC at F and G. Join F and G. Again with D as centre and another radius, draw arcs intersecting the curve ABC at H and J. Join H and J and produce JH and GF to meet at K. Join KB and so KB will be the tangent to the curve at B.

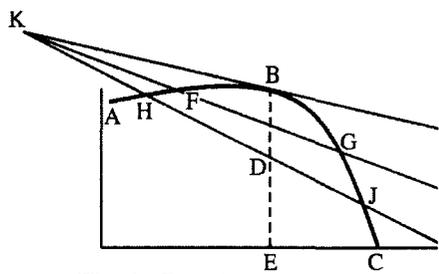


Fig. 1 : Drawing a tangent to a curve

[I] Guggenheim Method— For the Study of First Order Reactions

The fundamental relation due to Wilhelmy correlates the concentration of the reactant with time for which the reaction has been running.

$$C_s = C_0 \cdot e^{-kt}$$

For calculating k from the above equation, we require a precise knowledge of initial and sometimes final and sometimes both these values of a property used to follow the progress of the reaction. In some cases, it may not be possible to know these values. In such a case, the value of k can be calculated as follows :

At any stage of the reaction when time is t ,

$$C_t = (a - x) \quad \text{and} \quad (a - x) = ae^{-kt} \quad \dots (1)$$

At time $t + \Delta t$,

$$a - x' = ae^{-k(t + \Delta t)} \quad \dots (2)$$

Subtracting equation (2) from (1), we get,

$$\begin{aligned} x' - x &= a [e^{-kt} - e^{-k(t + \Delta t)}] \\ &= ae^{-kt} (1 - e^{-k\Delta t}) \end{aligned}$$

$$\text{or} \quad \log (x' - x) = -kt + \log_e \{a(1 - e^{-k\Delta t})\}$$

$$\text{or} \quad \log (x' - x) = \frac{-kt}{2.303} + I \quad \dots (3)$$

where $I = \text{constant}$.

This is the relation when the values of t change, the value of Δt does not change. For calculating the values of $(x' - x)$ for a predicted value of Δt , a graph is plotted between x and t . Then a second graph is plotted between $\log (x' - x)$ and t . The slope of the second graph will be equal to $\frac{-k}{2.303}$. Thus, the value of k can be obtained even when the initial and final values of x are unknown. This method is called *Guggenheim method*.

Before applying the above method, we must be sure that the reaction is of the first order only. Some complex reactions involving reversible and concurrent first order steps give only apparent rate constants by applying this method. For getting accurate results, the time interval (Δt) should be 2 to 3 times the half life period of the reaction. It is generally taken as about half the time of experiment. Inaccuracies creep in for small values of Δt .

For a second order reaction when the initial concentrations of reactants are equal, Roseveare gave an analogous method and the expression given by him is as follows :

$$k = \frac{[(a_2 - a_1) - (a_3 - a_2)]^2}{2(t_2 - t_1)(a_3 - a_1)(a_2 - a_1)(a_3 - a_2)}$$

where a_1, a_2 and a_3 represent the three values of an observed property at three different times t_1, t_2 and t_3 which are separated by a constant time interval. The value of k is expressed in the units in which the factor a is measured.

DETERMINATION OF THE ORDER OF REACTION

(1) Integration Method or Hit and Trial Method

Historically, this was the first method used for determining the order of a reaction. In this method, the initial concentration of all the reactants taking part is determined. The concentration of the reacting substances is then determined at different intervals of time. The different values of a and x are thus determined. These values are then substituted in various order rate expressions and the equation which gives the most constant value of velocity constant for a series of intervals of time will give the order of a reaction. As in this method, equation of every order is tested, hence, it is also known as hit and trial method.

(2) Method of Equifractional Parts

As discussed before, the time taken to complete half the reaction which is of the first order, is independent of initial concentration, but for a second order reaction the time taken is inversely proportional to the initial concentration of reactant, *i.e.*,

$$\text{For a first order reaction; } t_{0.5} = k$$

$$\text{For a second order reaction; } t_{0.5} \propto \frac{1}{a}$$

For a third order reaction ; $t_{0.5} \propto \frac{1}{a^2}$

For n th order reaction ; $t_{0.5} \propto \frac{1}{a^{n-1}}$

Suppose we start with two independent reactions with initial concentrations a_1 and a_2 . Let the time for half the completion of the reaction be t_1 and t_2 , respectively, then

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

or $\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}} \quad \text{or} \quad \frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$

or $\log \frac{t_1}{t_2} = (n-1) \log \left(\frac{a_2}{a_1}\right)$

or $n-1 = \frac{\log t_1 - \log t_2}{\log a_2 - \log a_1}$

or $n = 1 + \frac{\log t_1 - \log t_2}{\log a_2 - \log a_1}$

From this equation n - order of reaction - can be calculated.

(3) Isolation Method

This method was given by Ostwald in 1902. In this method, the concentration of all reactants except one is taken in excess and the order of reaction is then determined by any method with respect to that reactant (which is not taken in excess). Then in another separate experiment, the concentration of any other reactant is not taken in excess, while that of all others is taken in excess. The order of reaction is again determined. The experiment is repeated by isolating each reactant in turn. The total order of reaction will be the sum of the order of all isolated reactions.

Consider the reaction,



The reaction velocity is given as follows ;

$$\frac{dx}{dt} = k \cdot c_A^{n_1} \cdot c_B^{n_2} \cdot c_C^{n_3}.$$

In one experiment, the reactants B and C are taken in excess and the order of reaction determined with respect to A. Suppose it is n_1 . Then in another experiment, reactants A and C are taken in large excess, and the order of reaction with respect to B is determined as above. Let it be n_2 . Similarly, let the order of reaction with respect to C, taking A and B in large excess be n_3 . Then the total order of reaction is given by $n_1 + n_2 + n_3$.

(4) vant's Hoff Differential Method

In this method, the instantaneous rate of reaction is measured as accurately as possible and the logarithm of the rate is plotted against $\log c$. The slope of the curve is equal to the order of the reaction.

For n th order reaction, the reaction velocity is given by,

$$-\frac{dc}{dt} = kc^n$$

where, c is the concentration of the reacting substance.

or
$$\log\left(-\frac{dc}{dt}\right) = \log k + n \log c \quad \dots (8)$$

For practical purposes, $\frac{\Delta c}{\Delta t}$ may be taken as equal to $\frac{dc}{dt}$.

If we start two experiments with two different initial concentrations say c_1 and c_2 , then we have from equation (8).

$$\log\left(-\frac{dc}{dt}\right)_1 = \log k + n \log c_1 \quad \dots (9)$$

$$\log\left(-\frac{dc}{dt}\right)_2 = \log k + n \log c_2 \quad \dots (10)$$

Subtracting equation (10) from (9), we get,

$$\log\left(-\frac{dc}{dt}\right)_1 - \log\left(-\frac{dc}{dt}\right)_2 = n (\log c_1 - \log c_2)$$

or
$$n = \frac{\log\left(-\frac{dc}{dt}\right)_1 - \log\left(-\frac{dc}{dt}\right)_2}{\log c_1 - \log c_2} \quad \dots (11)$$

From equation (11), we can easily calculate n -order of reaction.

(5) Graphical Method

As discussed before, the reaction velocity in a first order reaction varies as one concentration term, while in a second order reaction the reaction velocity is dependent upon two concentration terms and so on. Mathematically,

For a first order reaction : $\frac{dx}{dt} = k(a-x)$.

For a second order reaction : $\frac{dx}{dt} = k(a-x)^2$.

For a third order reaction : $\frac{dx}{dt} = k(a-x)^3$.

In general, for a n th order reaction : $\frac{dx}{dt} = k(a-x)^n$ (12)

Thus, if the curve plotted between dx/dt and $(a-x)$ at different intervals of time is a straight line, the reaction is of the first order. But, if a straight line is obtained by plotting dx/dt and $(a-x)^2$, then the reaction is of the second order. Similarly, if a straight line is obtained by plotting dx/dt and $(a-x)^n$, then the reaction is of the n th order.

The values of dx/dt at different intervals of time can be determined by plotting a curve between x (the amount of the substance decomposed) and time t . The value of dx/dt at a particular time corresponding to a particular value of $(a-x)$ is given by the slope of the curve at that point.

On taking logarithm of equation (12), we get,

$$\log \frac{dx}{dt} = \log k + n \log (a - x)$$

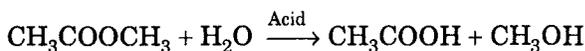
A curve when plotted between $\log dx/dt$ (ordinate) and $\log (a - x)$ (abscissa) will give a straight line. The slope of this straight line will give the value of n , the order of reaction. The intercept which the straight line cuts on the ordinate will give the value of $\log k$.

EXPERIMENT No. 1

Object : *To find the velocity constant of the hydrolysis of methyl acetate catalysed by an acid and also to find the half life period of the reaction.*

Apparatus and Chemicals : Thermostat or water bath, beakers, five 50 ml and two 100 ml conical flasks with corks, burettes, pipettes of 25 ml, 5 ml and 2 ml, 0.5 N HCl, 0.05 N NaOH solution, methyl acetate, stop watch, phenolphthalein (indicator) etc.

Theory : Methyl acetate hydrolyses in presence of an acid which acts as a catalyst to give acetic acid and methyl alcohol.



The reaction velocity is, however, given by,

$$\frac{dx}{dt} = k [\text{CH}_3\text{COOCH}_3] [\text{H}_2\text{O}]$$

Since water is present in large excess, therefore, its concentration remains practically constant throughout the reaction. So,

$$\frac{dx}{dt} = k [\text{CH}_3\text{COOCH}_3]$$

Hence, the rate of reaction is determined by the first power of the concentration of the ester and so the reaction is of the first order. It is, however, a pseudo unimolecular reaction.

As acetic acid is produced during the hydrolysis of methyl acetate, the reaction can be followed by titrating the reaction mixture with standard solution of an alkali.

As the reaction is of the first order, the half life period ($t_{1/2}$) is given by,

$$t_{1/2} = 0.693/k$$

Procedure : Let freshly distilled methyl acetate and $N/2$ hydrochloric acid stand in separate bottles in a thermostat for about half an hour. When they have acquired the temperature of the bath, add 2 ml of methyl acetate with a 2 ml pipette into a conical flask containing 50 ml of $N/2$ HCl. Start the stop watch when half the pipette has been discharged*. Shake the mixture and immediately withdraw 2 ml of the reaction mixture with the help of a 2 ml pipette and transfer it to one of the flasks containing 25 ml ice cold water. This freezes or arrests the equilibrium. Now titrate the solution by adding $N/20$ solution of NaOH from the burette using phenolphthalein as an indicator. The solution should be stirred during titration and the titration should be stopped at the first appearance of light

pink colour. Similarly, again pipette out 2 ml of the reaction mixture after five minutes and repeat the procedure. Repeat the above procedure by withdrawing 2 ml of the reaction mixture after 10, 15, 20, 30, 45 minutes.

For taking infinite reading, *i.e.*, when the hydrolysis of ester is complete, transfer 25 ml of the reaction mixture in a separate conical flask and cork it lightly. Keep this flask in a water bath containing hot water at $60^\circ - 70^\circ\text{C}$ for about half an hour. After this, the flask is cooled to room temperature and then 2 ml of the reaction mixture is titrated as usual. This gives the value of V_∞ .

The amount of NaOH used is equivalent to the total amount of HCl present originally and the amount of acetic acid produced in the reaction. The amount of HCl present originally can be determined by titrating against the same alkali before the start of the reaction. The amount of acetic acid produced after different intervals of time t can be determined by titration.

Observations : (i) Temperature = $t^\circ\text{C}$ (say)

Time (Minutes)	Volume of reaction mixture	Volume of N/20 NaOH required for neutralisation (V_t ml)	($V_\infty - V_t$)
0	2 ml	$= V_0$...
...
...
∞	...	$= V_\infty$...

The amount of acetic acid formed at the end of the reaction is equivalent to the initial amount, a of methyl acetate. Suppose V_0 , V_t and V_∞ are the volumes of N/20 NaOH solution used at zero, t and infinite time, respectively.

The amount of acetic acid produced after time t , *i.e.*, value of x is directly proportional to $V_t - V_0$. The initial concentration of methyl acetate, *i.e.*, value of a is directly proportional to $V_\infty - V_0$. Therefore, amount of ester present at time t , *i.e.*,

$$(a - x) \propto (V_\infty - V_0) - (V_t - V_0) \\ \propto V_\infty - V_t$$

Calculations : The value of k is now calculated, according to the first order rate expression, which is given by,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

or

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

The values of velocity constant can be calculated at different intervals of time t and we see that the values are nearly constant.

*In a first order reaction, the study can be started from any stage of reaction as the initial state. So, it is not necessary to start the stop watch from the beginning. It can be started even after the first titration has been done.

The half life period of the reaction ($t_{1/2}$) is given by,

$$t_{1/2} = \frac{0.693}{k}$$

Substituting the value of k , we can calculate $t_{1/2}$.

Plot graphs of t against $\log(V_\infty - V_t)$. Set up a graph for Guggenheim method. The value of k can be obtained from the slope of the graph.

Result : The velocity constant for the studied reaction

$$= \dots \text{ min}^{-1}.$$

The half life period of the reaction = ... min.

Precautions : (i) The reactants are allowed to attain the temperature of the thermostat or water bath.

(ii) The zero time should only be noted when ice is added to the first 2 ml of the reaction mixture.

(iii) Distilled water used for preparing the solutions must be free from CO_2 , as the end points of the titration are very sharp, when no CO_2 is present. Similarly, for the same reason NaOH should also be free from CO_2 .

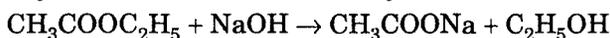
Note : To show graphically that the reaction is of the first order, plot the values of $\log(a - x)$, i.e., $\log(V_\infty - V_t)$ as ordinate against the corresponding values of time in minutes as abscissa. The curve must be a straight line.

EXPERIMENT No. 2

Object : To determine the order of saponification of ethyl acetate with sodium hydroxide.

Apparatus and Chemicals : Conical flasks of 100 ml and 200 ml capacity, burette, pipette, $M/40$ ethyl acetate, $M/40$ NaOH , $M/40$ HCl solutions.

Theory : The reaction between ethyl acetate and alkali takes place as follows:



The rate of the reaction is given by :

$$\frac{dx}{dt} = k [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{NaOH}]$$

Here we observe that the concentration of alkali also changes along with that of ester, during the course of the reaction. So, the reaction velocity is dependent on the concentration of the reactants and hence the reaction is of the second order. *This reaction differs from hydrolysis by acids in the respect that in the latter the concentration of hydrogen ions remains unchanged during the course of reaction and so the reaction is of the first order.* The reaction is quite fast and so the reactants may be taken in concentration of $M/40$ or even less, particularly in summer months.

Procedure : Take 50 ml of $M/40$ ester* solution and 100 ml of $M/40$ NaOH solution in two separate flasks and keep them in a water bath to attain same

*Molecular weight of ethyl acetate is 88 and its density is 0.9005 g/ml. Solution is made by weighing. If we dissolve 2 ml of ester in distilled water, the concentration of this solution will be 0.204M. Required solution can be prepared by dilution.

temperature. Meanwhile arrange eight 100 ml conical flasks containing 25 ml each of ice cold $M/40$ HCl. When the flasks have acquired the same temperature, the alkali is poured as rapidly as possible into the ester solution. Note the time (start the stop watch) when half the volume of the alkali has been poured into the ester. This is taken as zero time. Immediately pipette out 10 ml of the reaction mixture into a conical flask containing 25 ml of ice cold $M/40$ HCl. The mean point of the interval required for the pipette to deliver is taken as the time of stopping the reaction. **The excess of the acid is titrated back by means of a standard alkali solution.** 10 ml reaction mixture is then taken out of the reaction vessel after every 5, 10, 20, 40, 60 minutes. These solutions are then titrated against $M/40$ alkali solution as before. Let the titre value at any time t be V_t . The value will increase, as the concentration of NaOH in the reaction mixture gradually falls. The infinite reading is taken after 24 hours or after heating the reaction mixture on a water bath for about half an hour in the same way as described in preceding experiment. Let the titre value be V_∞ .

Let the initial concentration of alkali be a and that of ester be b . The value of a is calculated in 10 ml of the reaction mixture from the normalities of HCl and NaOH or by titration. Take 5 ml of alkali and add it to 10 ml HCl and titrate against the same solution of alkali, *i.e.*, $M/40$ NaOH. Let the titre value be V_0 . Similarly, titrate 25 ml of HCl against $M/40$ NaOH. Let the titre value be V . Therefore, $a \equiv V - V_0$ ml of $M/40$ NaOH.

Observations : Temperature = $t^\circ\text{C}$ (say)

Titre value when 25 ml HCl is titrated against $M/40$ NaOH = V ml (say).

Time (Minutes)	Volume of NaOH required (V_t ml)	$a - x = (V - V_t)$	$b - x = (V_\infty - V_t)$
0	$= V_0$		
...	...		
∞	V_∞		

Calculations : For a second order reaction, the value of k is given by the expression,

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

If a and b represent the initial concentrations of alkali and ester in 10 ml of the reaction mixture, then the values of a and b can be calculated in terms of volume of $M/40$ NaOH as follows :

$$a \equiv (V - V_0) \text{ ml}$$

$a - x =$ Amount of NaOH present at time t in 10 ml of the reaction mixture.

\equiv Amount of HCl used up from 25 ml of acid.

\equiv Difference of the amount of the acid present initially and the amount of acid present at time t .

$$\equiv (V - V_t) \text{ ml}$$

$$\therefore x = a - (a - x) \equiv (V_t - V_0) \text{ ml}$$

$(a - b) =$ Excess of NaOH over ester
 \equiv Amount of NaOH unused at the end of the reaction.
 $\equiv (V - V_{\infty}) \text{ ml}$

$$\therefore b = a - (a - b) \equiv (V_{\infty} - V_0) \text{ ml}$$

$$b - x = (V_{\infty} - V_0) - (V_t - V_0) \equiv (V_{\infty} - V_t) \text{ ml}$$

$$\therefore k = \frac{1}{t(a-b)} \log \frac{(V_{\infty} - V_0)(V - V_t)}{(V - V_0)(V_{\infty} - V_t)} \quad \dots (1)$$

The value of $(a - b)$ must be expressed in mole per litre of the reaction mixture. In the present case, $a = 0.025$ and $b = 0.025$.

The values of k calculated from equation (1) at different intervals of time come out to be constant, which shows that the saponification of ethyl acetate is of the second order.

Result : The order of saponification of ethyl acetate is two.

Precautions : Same as in preceding experiment.

Note : To show graphically, that the reaction is of the second order, plot the values of $\log \frac{b(a-x)}{a(b-x)}$, i.e., $\log \frac{(V_{\infty} - V_0)(V - V_t)}{(V - V_0)(V_{\infty} - V_t)}$ as ordinate against the corresponding values of time in minutes as abscissa. The curve must be a straight line.

EXPERIMENT No. 3

Object : To compare the strength of two acids, say hydrochloric acid and sulphuric acid, used in equal concentration for the hydrolysis of methyl acetate.

Apparatus and Chemicals : Same as in experiment 1, solutions of HCl and H_2SO_4 of same normality (0.5 N).

Theory : The rate of hydrolysis of an ester in presence of an acid is seen to be proportional to the concentration of the acid used as catalyst. The H^+ ions present in the solution act as catalyst. So, the specific reaction rate seen for the reaction will be proportional to the constant available concentration of H^+ ions. Therefore, the specific reaction rate of acid catalysed hydrolysis of an ester can be used to compare the concentration of hydrogen ions provided the solutions of the two acids are equi-normal.

So, if equal volumes of the two acids, say HCl and H_2SO_4 of equal normality are used for catalysing the hydrolysis of an ester and if k_1 and k_2 are the respective rate constants, then the ratio of strengths is given by,

$$\text{Strength of HCl} : \text{Strength of H}_2\text{SO}_4 = k_1 : k_2$$

Procedure : Perform the experiment as explained in experiment no. 1 and calculate the values of k_1 and k_2 separately in presence of HCl and H_2SO_4 , respectively.

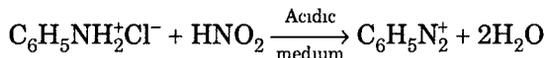
Result : The relative strengths of HCl and $\text{H}_2\text{SO}_4 = k_1/k_2 = \dots$

EXPERIMENT No. 4

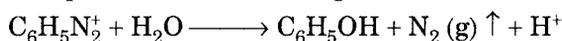
Object : To study the reaction kinetics of decomposition of benzene diazonium chloride in the temperature range 30°C to 60°C. Calculate the rate constant also.

Apparatus and Chemicals : 10 ml measuring cylinder, 1° thermometer, gas burette, aniline, concentrated HCl, sodium nitrite, starch-iodide papers.

Theory : The formation reaction of benzene diazonium chloride is as follows:



The decomposition reaction is expressed as :



So, the progress of the reaction is followed by measuring the volume of evolved nitrogen.

Procedure : [A] Preparation of benzene diazonium Chloride—Dissolve 1 ml of aniline in a mixture of 2.5 ml of concentrated HCl and 5.0 ml of water. Cool the solution to 5°C by keeping it in an ice bath. Add dropwise a solution of 0.8 g of sodium nitrite in 2 ml of water. The temperature of the mixture should not exceed 10°C. Keep the mixture well stirred. Addition of sodium nitrite solution is continued till a drop of the reaction mixture gives immediately a blue colour (spot) on a starch-iodide paper. The whole solution is needed for performing the experiment. The complete decomposition of the salt obtained will give nearly 250 ml of N₂(g). Lesser quantity can be used if the gas burette is of 50 ml capacity.

[B] Method and Observations : Place the diazonium salt solution with some broken glass pieces or pumice stone in a pyrex test tube fitted with a rubber cork and a delivery tube. (*Pumice stone helps in the steady evolution of the gas*). Connect the delivery tube to a gas burette. Put the test tube in a water bath of steady desired temperature. The reaction mixture quickly attains the temperature of the bath. The volume (*V*) of evolved nitrogen upto time *t* is measured with increasing time intervals. The volume readings are taken at intervals of one minute and finally when the reaction is complete. Record the temperature of the bath used for the reaction mixture.

Calculations : $V_\infty \propto [\text{C}_6\text{H}_5\text{N}_2^+]_0$

$$(V_\infty - V_t) \propto [\text{C}_6\text{H}_5\text{N}_2^+]_t$$

For a first order reaction (where A = reactant),

$$\log [A] = \log [A]_0 - \frac{k_1}{2.303} t$$

or
$$\log B (V_\infty - V_t) = \log BV_\infty - \frac{k_1 t}{2.303}$$

where *B* is a proportionality constant for changing (*V*_∞ - *V*_{*t*}) volumes to concentration of reactant.

$$\therefore \log (V_\infty - V_t) + \log B = \log V_\infty + \log B - \frac{k_1 t}{2.303}$$

$$\text{or} \quad \log(V_{\infty} - V_t) = \log V_{\infty} - \frac{k_1 t}{2.303}$$

So, a plot of $\log(V_{\infty} - V_t)$ against t should be a straight line with a slope of $-\frac{k_1 t}{2.303}$.

For a second order reaction,

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t$$

$$\text{or} \quad \frac{1}{\ln(V_{\infty} - V_t)} = \frac{1}{B(V_{\infty})} + k_2 t$$

$$\text{or} \quad \frac{1}{(V_{\infty} - V_t)} = \frac{1}{V_{\infty}} + Bk_2 t$$

So, a plot of $\frac{1}{(V_{\infty} - V_t)}$ against t should be a straight line of slope equal to Bk_2 .

Alternatively, the values of k_1 and Bk_2 may be calculated from the following expressions and their constancy verified.

$$\begin{aligned} k_1 &= \frac{2.303}{t} \log \frac{[A]_0}{[A]} \\ &= \frac{2.303}{t} \log \frac{V_{\infty}}{(V_{\infty} - V_t)} \end{aligned}$$

$$\begin{aligned} k_2 &= \frac{[A]_0 - [A]_t}{[A]_0 [A]_t} \times \frac{1}{t} \\ &= \frac{1}{B} \cdot \frac{V_t}{V_{\infty} (V_{\infty} - V_t)} \cdot \frac{1}{t} \end{aligned}$$

$$\text{or} \quad Bk_2 = \frac{V_t}{V_{\infty} (V_{\infty} - V_t)} \cdot \frac{1}{t}$$

Result : The reaction is found to be of the first order with rate constants of 0.0129, 0.0411 and 0.2098 at 35°, 45° and 55°C, respectively.

EXPERIMENT No. 5

Object : To study the reaction between acetone and iodine in presence of acids.

Apparatus and Chemicals : 100 ml volumetric flask, two 10 ml pipettes, burette, stop watch, thermostat, acetone, 0.10M iodine solution in 10% KI solution, 1M sodium acetate solution (or 0.05 M NaHCO₃ solution), standard 0.01 M hypo solution, 0.5 M H₂SO₄, starch solution.

Theory : Iodine reacts with acetone in presence of an acid (catalyst) according to the reaction :

the amount of residual iodine in the sample. Withdraw 10 ml of the reaction mixture after an interval of 5 minutes and proceed, as explained above.

Repeat the above process with varying amounts of acetone, iodine and acid to study the effect of the changes in their concentrations. Prepare the following mixtures :

Bottle number	Acetone (ml)	M/2 H ₂ SO ₄ (ml)	N/10 I ₂ solution (ml)	Water (ml)
1	10	20	10	60
2	10	20	5	65
3	5	20	10	65
4	10	10	10	70

Observations :

Bottle 1		Bottle 2		Bottle 3		Bottle 4	
Time (mts)	Vol. of hypo (ml)						

Calculations : Plot a curve between titre values as ordinate and time as abscissa for all the four bottles and find the slope of each curve. The slope will give the value of the velocity constant. *i.e.* k , [cf. eqn. (1)]. The straight line graph shows the reaction to be of zero order with respect to iodine.

From the value of rate constants for bottle 1 and 2 (concentration of iodine halved) sets, calculate the order of reaction with respect to acetone as follows :

When acetone and acid are taken in large excess,

$$-\frac{d(I_2)}{dt} = k_1 [I_2]^x$$

where $k_1 = k [\text{Acetone}]_1^y [\text{Acid}]^z \dots (1)$

When acetone concentration is halved (for bottles 1 and 3), the new value of k_1 is given by,

$$k_1' = k [\text{Acetone}]_2^y [\text{Acid}]^z \dots (2)$$

From equations (1) and (2),

$$\frac{k_1}{k_1'} = \left\{ \frac{[\text{Acetone}]_1}{[\text{Acetone}]_2} \right\}^y = (2)^y$$

So, calculate the value of y . Similarly, from the values of k for bottles (1) and (4), calculate the value of z , *i.e.*, order with respect to the acid used as a catalyst.

Result : The reaction is of zero order with respect to iodine.

Precautions : (i) Iodine solution should be prepared in minimum quantity of potassium iodide (solid or liquid).

(ii) Stop watch should be started when iodine solution has just been added to the mixture of acetone, acid and water already taken in the reagent bottle.

EXPERIMENT No. 6

Object : To study the kinetic characteristics of iodination of acetone using a colorimeter.

Apparatus : Colorimeter* etc.

Theory : See preceding experiment.

Procedure : The progress of the reaction between acetone and iodine can be easily followed colorimetrically by making use of the fact that the presence of iodine, mainly as the tri-iodide ion (I_3^-) gives a reddish brown colour to the reaction mixture. The colour fades to pale yellow as the reaction proceeds due to the consumption of iodine.

In this process, the isolation method can be easily used taking both acetone and acid in large excess. The order of the reaction is zero with respect to iodine and one with respect to acetone and the acid.

Procedure : Dilute 10 ml of pure acetone solution to 100 ml. Mix 5 ml of each of acetone solution, 0.5M H_2SO_4 and water. Add to it 10 ml of iodine solution and start the stop watch.

Set the wavelength at 565 nm in the calorimeter or set the selector to green LED if Delhi calorimeter is used. Transfer the reaction mixture to the cuvette of the calorimeter and note the absorbance against water (taken as blank) at suitable intervals of time.

Repeat the experiment three times by first changing the concentration of acetone, then iodine and then of sulphuric acid by a known amount. Prepare the following solutions for the experiment.

Bottle no.	Acetone (ml)	0.5M H_2SO_4 (ml)	0.05 M I_2 solution (ml)	Water (ml)
1	5	5	10	5
2	10	5	10	0
3	5	5	5	10
4	5	10	10	0

Plot the absorbance values or meter readings (ordinate) against time (abscissa) for different reaction mixtures. The plots are linear. The linear graph, i.e., a constant slope shows that reaction is of zero order with respect to iodine. The value of slope for bottle 3 too shows the reaction to be of zero order with respect to iodine.

For bottle 2, where the acetone concentration is doubled, the slope is twice that for bottle 1. This shows that the reaction is of first order with respect to acetone. The concentration of hydrogen ions is doubled for bottle 4 as compared to that for bottle 1. The slope of the plot for bottle 4, which is twice that for bottle 1, shows that the order is one with respect to the acid.

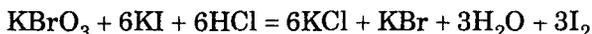
*A calorimeter co-relates the concentration of a coloured substance with the intensity of its colour. The intensity of colour is measurable in terms of absorbance of the solution for an absorbable monochromatic radiation of light. Even white light may be used with a suitable calibration curve.

EXPERIMENT No. 7

Object : To find out the order of reaction between potassium bromate and potassium iodide.

Apparatus : Same as in preceding experiments.

Theory : The reaction between potassium bromate and potassium iodide in presence of an acid takes place as follows :



As iodine is liberated during this reaction, the velocity of reaction can be studied by titrating the reaction mixture with sodium thiosulphate solution. The titre value at any time is a measure of KI oxidised or KBrO_3 used for oxidation at that time and so it gives the value of x at different intervals of time.

The reaction is of the second order, though the molecularity is much more. So, the rate expression is given by the following expression, if both the reactants have the same initial concentration.

$$k = \frac{1}{a.t} \cdot \frac{x}{(a-x)} \quad \dots (1)$$

Procedure : Take 25 ml of $N/10$ KBrO_3 solution in one flask and a mixture of 25 ml of $N/10$ KI, 100 ml of $N/10$ HCl and 100 ml distilled water in a separate flask. Keep both the flasks in a thermostat till they have attained constant temperature.

Now add the content (*i.e.*, KBrO_3) of the first flask into the second flask and note the mean time of mixing, as the starting point of the reaction. Now withdraw 25 ml of the reaction mixture and transfer it to a conical flask to which some pieces of ice have already been added. Titrate the liberated iodine against $N/100$ sodium thiosulphate solution and starch solution as an indicator. Withdraw the reaction mixture after 5, 10, 15, 20, 25 minutes and titrate it, as described above. Now carry a similar experiment with the following solutions :

12.5 ml $N/10$ KBrO_3 , 12.5 ml $N/10$ KI, 100 ml $N/10$ HCl and 125 ml distilled water.

Observations :

Experiment I		Experiment II	
Time (mts)	Vol. of hypo (ml)	Time (mts)	Vol. of hypo (ml)

Calculations : (i) Experiment I

From 25 ml of $N/10$ KBrO_3 solution, the total volume is made to 250 ml. Hence, normality of KBrO_3 in the reaction mixture becomes $N/100$. As 25 ml of the reaction mixture is taken for titration against hypo, hence from normality equation, we have,

$$N_1 V_1 = N_2 V_2$$

Reaction
Hypo
mixture

$$\frac{N}{100} \times 25 = \frac{N}{100} \times V_2$$

$$\therefore V_2 = 25 \text{ ml}$$

Therefore, $a = b \equiv 25 \text{ ml}$ of $\frac{N}{100}$ hypo

(i) *Experiment II*

Here, $a = b = 12.5 \text{ ml}$. of $N/100$ hypo

(The titre values directly give the values of x at different intervals of time).

The value of velocity constant (k) for both the experiments can be calculated vide equation (1) given in the theory of this experiment. The value of a in the expression $\frac{1}{a \cdot t}$ should be expressed in mole per litre of the reaction mixture. (In this case, however, the value of a is 0.1 and 0.05, for experiment I and II, respectively). The values of $\frac{x}{a-x}$ can be expressed in terms of volumetric readings.

We see that the values of k come out to be constant.

Result : The reaction between potassium bromate and potassium iodide is of the second order.

Precautions : Same as in preceding experiments.

ALTERNATE METHODS (GRAPHICAL METHOD) FOR CALCULATING THE ORDER OF REACTION

(1) Plot the values of x , i.e., titre values as abscissa and time (minutes) as ordinate for both the experiments. Draw smooth curves. From the graph, find out the times (t_1 and t_2) taken to complete any fraction, say half or one fourth of the reaction. Then calculate the order of reaction according to the equation,

$$n = 1 + \frac{\log t_1/t_2}{\log a_2/a_1}$$

(The value of a_2/a_1 is 2 in this particular case)

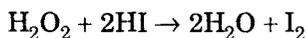
(2) Another way to show that the reaction is of the second order is to plot a curve between time as ordinate and $\frac{1}{a-x}$ as abscissa. The graph should be a straight line.

EXPERIMENT No. 8

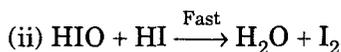
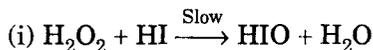
Object : To find out the rate constant and order of reaction between hydrogen peroxide and hydroiodic acid.

Apparatus : Same as in preceding experiments.

Theory : The reaction between hydrogen peroxide and hydroiodic acid takes place as follows :



The reaction is believed to occur in the following two stages :



As the slowest reaction determines the rate of reaction, so the first stage gives the order of reaction, which is thus two. The progress of the reaction is studied by titrating the liberated iodine against standard sodium thiosulphate solution. The titre values give the value of x , *i.e.*, amount of H_2O_2 decomposed by HI.

Procedure : Take 10 ml of $N/10$ H_2O_2 in one flask while a mixture of 10 ml of $N/10$ KI, 40 ml of $N/10$ HCl and 40 ml of distilled water is taken in a separate flask. Keep both the flasks in a thermostat till they have attained the constant temperature.

Now add H_2O_2 from the first to the second flask and note the mean time of mixing, as the starting point of the reaction. Now withdraw 5 ml of the reaction mixture in a conical flask to which some pieces of ice have already been added. Titrate the liberated iodine against $N/250$ sodium thiosulphate solution, using starch solution as an indicator. Withdraw the reaction mixture after 5, 10, 15, 20, 25 minutes and titrate it as described above. Now carry a similar experiment with the following solutions :

5 ml $N/10$ H_2O_2 , 10 ml $N/10$ KI, 40 ml $N/10$ HCl and 45 ml distilled water.

Observations : Same as in experiment 7.

Calculations : (i) *Experiment I.*

In this experiment, 10 ml of $N/10$ H_2O_2 are diluted to 100 ml so the normality of H_2O_2 in the reaction mixture becomes $N/100$. From normality equation, we have,

$$\begin{array}{ccc} N_1 V_1 & = & N_2 V_2 \\ \text{Reaction} & & \text{Hypo} \\ \text{mixture} & & \end{array}$$

$$\frac{N}{100} \times 5 = \frac{N}{250} \times V_2$$

$$\therefore V_2 = 12.5 \text{ ml}$$

If a and b be the initial concentrations of KI and H_2O_2 then,

$$a = b \equiv 12.5 \text{ ml of } \frac{N}{250} \text{ Na}_2\text{S}_2\text{O}_3$$

(ii) *Experiment II*

In this case, $a \equiv 12.5$ ml of $N/250$ $\text{Na}_2\text{S}_2\text{O}_3$.

$$b = 6.25 \text{ ml of } N/250 \text{ Na}_2\text{S}_2\text{O}_3.$$

The values of velocity constant can be calculated from the following equations;

$$k = \frac{1}{a \cdot t} \cdot \frac{x}{a - x} \quad (\text{For experiment I})$$

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)} \quad (\text{For experiment II})$$

Result : The reaction between hydrogen peroxide and potassium iodide is of the second order and the velocity constant is ...mole⁻¹ min⁻¹.

Precautions : Same as in preceding experiments.

ALTERNATIVE METHOD (GRAPHICAL METHOD) FOR CALCULATING THE ORDER OF REACTION.

(1) To show that the reaction is of the second order, plot a curve between values of $(a - x)$ as abscissa and time (minutes) as ordinate for experiment I, while plot a curve between values of $\log \frac{a-x}{b-x}$ as abscissa and time as ordinate for experiment II. Both the curves should be straight lines. Calculate the values of k from the slopes of the two curves.

(2) Another way of calculating order of reaction (n) is to plot a curve between titre values (x) and different intervals of time (t), for both the experiments. Then find the times (t_1 and t_2) for the completion of the same fraction of the reaction. Calculate the value of n , from the expression,

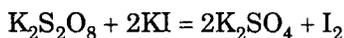
$$n = 1 + \frac{\log t_1/t_2}{\log a_2/a_1}.$$

EXPERIMENT No. 9

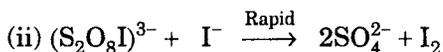
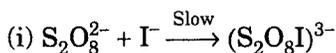
Object : To find out the velocity constant of the reaction between potassium persulphate and potassium iodide. Also calculate the activation energy and the influence of ionic strength on the rate constant.

Apparatus : Same as in preceding experiments.

Theory : The reaction between potassium persulphate and potassium iodide takes place as follows :



The mechanism of the reaction can be written as follows :



The reaction rate can be studied by measuring the rate of liberation of iodine. As the slowest reaction determines the reaction rate, therefore, step (i) gives the expression, which can be written, as

$$\begin{aligned} \frac{dx}{dt} &= k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-] \\ &= k (b - 2x) (a - x) \end{aligned} \quad \dots (1)$$

Hence, the reaction is of the second order. If we integrate equation (1), we get,

$$k = \frac{1}{2at} \cdot \frac{x}{a-x} \quad (\text{When } b = 2a) \quad \dots (2)$$

The terms a and b represent the initial concentrations of $\text{K}_2\text{S}_2\text{O}_8$ and KI in mole/litre in the reaction mixture. According to equation (2), the concentration of KI is to be made double that of $\text{K}_2\text{S}_2\text{O}_8$.

During the reaction, iodine is liberated and the progress of the reaction can be followed by titrating the liberated iodine in 5 ml of the reaction mixture against standard hypo solution at different intervals of time. The titre values are proportional to iodine formed and so gives the amount of persulphate which has disappeared by reaction from 5 ml of reaction mixture. They give the values of x at different intervals of time.

For a dilute solution, according to Bronsted-Bjerrum equation, we have,

$$\log k = \log k_0 + z_A z_B \sqrt{\mu},$$

where k is the rate constant at ionic strength* μ , k_0 is the rate constant at $\mu = 0$, z_A and z_B are the valencies of the ions in the reactions (In this case, $z_A \cdot z_B = 2$).

From the values of velocity constant at different temperatures, the activation energy (E) can be determined by applying Arrhenius equation, *i.e.*,

$$k = A \cdot e^{-E/RT}$$

where, A is the frequency factor.

On taking logarithm, we get,

$$\log k = \log A - E/RT \quad \dots (3)$$

Differentiating it with respect to temperature, we get

$$d \log k = \frac{E}{RT^2} \cdot dT$$

or
$$\int_{k_1}^{k_2} d \log k = \int_{T_1}^{T_2} \frac{E}{RT^2} \cdot dT$$

or
$$\log_{10} \frac{k_2}{k_1} = \frac{E}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots (4)$$

If the values of k_1 and k_2 are known (or determined at two different temperatures T_1 and T_2) then the value of E can be easily calculated.

Alternatively, the value of E can be evaluated graphically. If $\log_{10} k$ is plotted as ordinate against $1/T$ as abscissa, we get a straight line, according to equation (3), whose slope will be equal to $-E/2.303 R$ or $-E/4.576$ and knowing the slope, E can be evaluated easily.

Procedure : First a standard solution of 0.1N $K_2S_2O_8$ is prepared.* Prepare 0.1N KI solution accordingly. Take 100 ml of 0.1N $K_2S_2O_8$ in a reagent bottle and keep it in a thermostat for half an hour. Note the temperature of the thermostat. Then add to it 100 ml of 0.1N KI solution, already kept in thermostat. Start the stop watch at the time of half mixing. Now withdraw 5 ml of the reaction mixture into a conical flask, to which some pieces of ice have already been added. Now titrate it against 0.01N sodium thiosulphate solution. Similarly, withdraw 5 ml of the reaction mixture after 10, 20, 30, 40 minutes and titrate as usual.

*Lewis and Randall introduced the concept of ionic strength as a measure of the non-ideality that the solution imposes on any associated electrolyte in the solution. It is defined as, 'half the sum of the product of the concentration and square of valence terms.' If in a solution, there are a number of constituents represented by 1, 2, 3 ... i , whose concentration and valency is represented by c and z terms, then the ionic strength of the solution is given by

$$\begin{aligned} \mu &= \frac{1}{2} c_1 z_1^2 + \frac{1}{2} c_2 z_2^2 + \frac{1}{2} c_3 z_3^2 + \dots + \frac{1}{2} c_i z_i^2 \\ &= \frac{1}{2} \sum c_i z_i^2. \end{aligned}$$

Increase the temperature of thermostat by say 10°C and repeat the procedure by again taking the reactants, *i.e.*, 100 ml $0.1N$ $\text{K}_2\text{S}_2\text{O}_8$ and 100 ml of $0.1N$ KI.

Also repeat the procedure by taking solutions of $\text{K}_2\text{S}_2\text{O}_8$ and KI of different strengths in order to vary the ionic strength of the solution.

In order to obtain the titre value at infinite time, pipette out 40 ml of the reaction mixture into a clean flask, add 4 g of KI and place the flask in a beaker of hot water maintained at $50\text{--}60^{\circ}\text{C}$. The combined effect of raising the temperature and increasing the concentration of KI will cause the persulphate to react quickly to completion, liberating an equivalent quantity of iodine. After cooling, titrate 5 ml of this solution with $0.01N$ sodium thiosulphate solution to obtain the required titre value.

Observations : Initial concentration (a) corresponds to ...ml of $0.01N$ $\text{Na}_2\text{S}_2\text{O}_3$.

Time, t (mts)	Titre value x (ml)	$a - x$	$\frac{1}{a - x}$	$k = \frac{1}{t} \cdot \frac{x}{a(a - x)}$

Calculations : Initial concentrations of $\text{K}_2\text{S}_2\text{O}_8$ and KI in terms of $0.01N$ $\text{Na}_2\text{S}_2\text{O}_3$ may also be calculated as follows :

As equal volumes of $0.1N$ $\text{K}_2\text{S}_2\text{O}_8$ and $0.1N$ KI solutions are mixed, the normality of $\text{K}_2\text{S}_2\text{O}_8$ in the mixture is changed to $0.1N = 0.05N$.

When 5 ml of the reaction mixture is taken, then,

$$5 \times 0.05N = V \times 0.01N$$

or $V = 25$ ml

i.e., initial concentration of $\text{K}_2\text{S}_2\text{O}_8$ in the resultant 5 ml of reaction mixture is equivalent to 25 ml of $0.01N$ $\text{Na}_2\text{S}_2\text{O}_3$.

In this experiment, the initial concentrations of both the reactants are the same. So, the formula used is :

$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)}$$

The value of $x \equiv V_t$, titre value of $0.01N$ $\text{Na}_2\text{S}_2\text{O}_3$ at any time t .

$$\therefore k = \frac{1}{t} \cdot \frac{V_t}{25(25 - V_t)}$$

Now to find out the influence of ionic strength on rate constant, plot the values of $\log k$ as ordinate against $\sqrt{\mu}$ as abscissa. The curve will be a straight line, whose slope must be equal to $(z_A z_B)$, *i.e.*, two.

*The salt dissolves slowly and should be finely powdered before weighing. Dissolution may be accelerated by warming the flask under a hot water tap but stronger heating should be avoided.

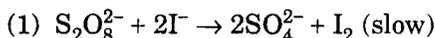
The activation energy can, however, be calculated from equation (4).

Result : The velocity constant of the studied reaction is ... mole⁻¹ min⁻¹ and the activation energy is ... cal mole⁻¹.

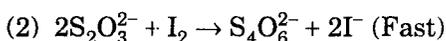
Precautions : Same as in preceding experiments.

CLOCK REACTIONS

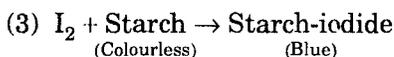
Consider a reaction of potassium persulphate with a solution of potassium iodide containing starch and a low concentration of sodium thiosulphate. The persulphate ions preferentially oxidise the iodide ions than thiosulphate ions.



However, the liberated iodine cannot turn the starch blue, because it reacts immediately with thiosulphate ions.



This reaction continues till all the thiosulphate ions have been consumed and then the solution at once turns blue due to the reaction between starch and iodine. Thus, thiosulphate acts as a monitor for this reaction.



The first reaction *i.e.*, (1) is known as **main reaction**, (2) as **monitor reaction** and (3) as **indicator reaction**. The time for the blue colour to appear depends on :

(i) Initial rate of formation of iodine. This, in turn, depends on the concentration of persulphate and iodide ions.

(ii) Amount of thiosulphate present.

For any specific conditions of temperature and concentration, the time for the appearance of the colour has a clock-like accuracy. This is, thus, called a **clock reaction**. The blue colour can be discharged by adding more of thiosulphate. Blue colour reappears after some time. This can be repeated a number of times by adding further quantities of the *monitor* till the persulphate ions are exhausted. Rewinding of chemical clock occurs due to the addition of the monitor. So, the subsequent time intervals will be larger even when thiosulphate additions are equal as the concentration of persulphate ion goes on decreasing and the main reaction becomes slower and slower.

EXPERIMENT No. 10

Object : To study the kinetics of iodine clock reaction.

Apparatus and Chemicals :

[I] SOLUTION A :

250 ml of 0.01 M potassium persulphate (mol. wt. = 270.3)

[II] SOLUTION B :

250 ml of 0.3 M KI + 0.0005M Na₂S₂O₃ + Starch solution, 10 ml in 250 ml of mixed solution.

Thermostat (or water bath), white glazed tile, two beakers (100 ml), two measuring flasks (250 ml), two pipettes (25 ml), thermometer (0.1°), stop watch.

Theory : The reaction involves the oxidation of iodide ions to iodine by persulphate ions. The reaction can be monitored by sodium thiosulphate solution and starch solution can be used as an indicator to time the reaction.

Procedure : Place both the solutions in a bath of water at constant temperature and swirl them from time to time (for nearly 20-25 minutes) till they attain the temperature of the bath. Check the temperature by means of a thermometer. Pipette out 25 ml of solution A in a dry 100 ml beaker. Rinse and drain a second 100 ml beaker with solution B and pipette out 25 ml of the solution into it. Pour solution B into solution A and start the stop watch. Mix the solutions and put the beaker on a white glazed tile (or a piece of white paper) if water bath is not used. Record the time when the blue colour first appears.

Repeat the mixing of standard solutions and note the time again for getting a concordant result.

Repeat the experiment by changing the concentration of $K_2S_2O_8$ solution as follows :

Bottle no.	Volume of solution A (ml)	Volume of solution B (ml)	Volume of water (ml)
1	25	25	0
2	20	25	5
3	15	25	10
4	10	25	15

If temperature is maintained at 20°C, the expected time for appearance of blue colour will be nearly 44, 56, 74 and 110 seconds, respectively. Use the initial rate method for analysing the experimental data.

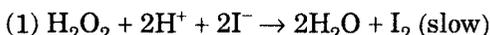
Repeat the experiment with double concentrations of KI and $Na_2S_2O_3$ and interpret the result.

EXPERIMENT No. 11

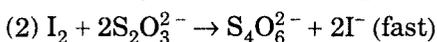
Object : To study the oxidation of iodide ions by H_2O_2 as an iodine clock reaction.

Apparatus : Same as in preceding experiment.

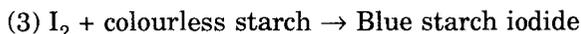
Theory : Consider the reaction of hydrogen peroxide with a solution of potassium iodide (liberating I^- ions) containing starch and a low concentration of sodium thiosulphate. The H_2O_2 oxidises iodide ions to iodine in preference to oxidising thiosulphate ions.



The liberated iodine cannot colour starch solution blue as it reacts instantaneously with the thiosulphate ions.



This goes on till thiosulphate is completely consumed and then the solution at once turns blue due to the action of iodine and starch.



The reactions (1), (2) and (3) are known as *main reaction*, *monitor reaction* and *indicator reaction*, respectively.

The time for the appearance of blue colour depends on (a) initial rate of formation of iodine, which, in turn, depends upon the concentration of iodide ions and H_2O_2 and (b) amount of thiosulphate present. For any specific condition of concentration and temperature, the time for the appearance of blue colour has a clock-like accuracy. This is the reason why the combination of the above three reactions is called **clock reaction**. The blue colour disappears by adding a quantity of thiosulphate, and it re-occurs after some time. Thus, Harcourt-Esson reaction can be treated as an iodine clock reaction. This can be repeated a number of times by adding more quantities of monitor, till all H_2O_2 is consumed. Addition of monitor can be compared to rewinding of the chemical clock. The subsequent time intervals will be larger even when thiosulphate additions are equal as the concentration of H_2O_2 goes on decreasing and the main reaction becomes slower.

The order of reaction with respect to H_2O_2 can be found by conducting experiment with a relatively large excess of I^- ion and H^+ ion, as the rate is given by

$$\text{Rate} = k [\text{H}_2\text{O}_2]^x [\text{I}^-]^y [\text{H}^+]^z \quad [\text{According to step (1)}]$$

Procedure : Take about 150 ml of distilled water in a conical flask and add about 20 ml of 1M KI solution, 10 ml of 2 M H_2SO_4 and 1 ml of starch solution into it. Add to it from the burette exactly 5 ml of 0.025M $\text{Na}_2\text{S}_2\text{O}_3$ solution. Keep the flask as well as 0.1M H_2O_2 solution in the water trough.

Now add 5 ml of 0.1M H_2O_2 solution with a pipette and start the stop watch half way through the addition. Shake the flask and keep it in a water trough. Note the time for the appearance of the blue colour without stopping the stop watch. Now add further 5 ml of 0.025 M $\text{Na}_2\text{S}_2\text{O}_3$ from the burette and shake well. Again note the time of disappearance of the blue colour. Repeat this procedure by adding 5 ml of 0.025 M $\text{Na}_2\text{S}_2\text{O}_3$ solution 4-5 times. Calculate the values of concentration of H_2O_2 , i.e., $(a - x)$ at the measured time intervals after taking into account increase in volume of solution due to $\text{Na}_2\text{S}_2\text{O}_3$ addition. The concentrations of H^+ and I^- ions change, but since the initial concentrations are high, the change is small and may be neglected.

Initial concentration of H_2O_2 can be calculated in terms of equivalent volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution. For this purpose, measure 10 ml of H_2O_2 solution and add slowly 10 ml of conc. H_2SO_4 and 8 g of KI dissolved in minimum quantity of water. The liberated iodine is then titrated against 0.025M $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Observations :

Time, t (secs)	t_∞
Volume (ml), V_t of 0.025 M $\text{Na}_2\text{S}_2\text{O}_3$	V_∞

Calculations : $V_{\infty} \propto [\text{H}_2\text{O}_2]_0$

$$V_{\infty} - V_t \propto [\text{H}_2\text{O}_2]_t$$

Plot a graph between values of V_t and time, t . Slopes of tangents to this curve at various times, t , represent rate of reaction at that time.

Plot 1st and 2nd order plots such as $\log (V_{\infty} - V_t)$ vs t and $\frac{1}{V_{\infty} - V_t}$ vs t .

The straight line if obtained will give the order of reaction.

Note : For finding the order of reaction with respect to iodide ions or H^+ ions, the concentration of these ions may be doubled or halved one at a time and the new values of the rate constant will determine the respective order of reaction.

EXPERIMENT No. 12

Object : To study the kinetics of bromination of phenol by bromide-bromate mixture in an acid medium as a clock reaction.

Apparatus and Chemicals : Pipettes (10 ml, 5 ml, 2 ml, 1 ml), two measuring flasks (100 ml), two beakers (100 ml), three burettes (50 ml), stop watch, white glazed tile, 0.005 M KBrO_3 , 0.01 M KBr , 0.001 M phenol, 1 M H_2SO_4 , Methyl orange solution (indicator bench reagent).

Theory : The clock reaction of bromination of phenol by bromide-bromate mixture (in acid medium) consists of the following steps:

- (1) $5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \rightarrow 3\text{H}_2\text{O} + 3\text{Br}_2$ (Main reaction)
- (2) $3\text{Br}_2 + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{Br}_3\text{C}_6\text{H}_3\text{OH} + 3\text{H}^+ + 3\text{Br}^-$ (Monitor reaction)
- (3) $\text{Br}_2 + \text{Methyl orange} \rightarrow \text{Colourless product}$ (Indicator reaction)

The study involves the changing concentrations of Br^- , BrO_3^- and H^+ ions.

Procedure :

[I] Change of Initial Rate with Br^- Ion Concentration

Immediately before starting the experiment, dilute the phenol solution with distilled water by making 5 ml of solution to 100 ml in a measuring flask. Thus, $5 \times 10^{-5} \text{ M}$ phenol solution (A) is obtained. Dilute 40 ml of 1M H_2SO_4 and 2 ml of methyl orange to 100 ml in another measuring flask (B). Using two 100 ml beakers, perform the following five or more observations. Before mixing the solutions, they are kept in a thermostat.

Beaker 1			Beaker 2			Time (see)
S. No.	KBr soln (ml)	Water (ml)	KBrO_3 soln (ml)	H_2SO_4 soln (B) (ml)	Phenol soln (A) (ml)	
1.	10	0	10	15	1	t_1
2.	8	2	10	15	1	t_2
3.	6	4	10	15	1	t_3
4.	5	5	10	15	1	t_4
5.	4	6	10	15	1	t_5

The times for disappearance of colour will be found to be inversely proportional to volume of KBr solution.

[II] Change of Initial Rate with BrO_3^- Ion Concentration

Beaker 1			Beaker 2			Time (see)
S. No.	KBrO_3 soln (ml)	Water (ml)	KBr soln (ml)	H_2SO_4 soln (B) (ml)	Phenol soln (A) (ml)	
1.	10	0	10	15	1	t_1
2.	8	2	10	15	1	t_2
3.	6	4	10	15	1	t_3
4.	5	5	10	15	1	t_4
5.	4	6	10	15	1	t_5

The solutions are first brought to a constant temperature. For the experiment solution from beaker 1 is added into solution in beaker 2 and the stop watch is started. The solution is poured rapidly between the two beakers and is set in the thermostat over a white glazed tile. Note the timing when the colour of methyl orange completely disappears (Practice is needed to be able to observe when the colour is first completely discharged).

The time will be found to be inversely proportional to the volume of KBrO_3 solution used.

[III] Change of Initial Rate with H^+ Ion concentration

In this case, sulphuric acid is made without methyl orange and the concentrations of KBr, KBrO_3 and other reactants are increased to greater values than of H_2SO_4 . Phenol solution used is the same solution (A). The new solutions required are $0.01 M \text{H}_2\text{SO}_4$, $0.2 M \text{KBrO}_3$ and $5 \times 10^{-5} M$ phenol.

The solution (C) contains 12.0 g KBr and 5 ml of bench methyl orange solution in 250 ml of solution. This solution is nearly $0.4 M$ in KBr. The following solutions are now arranged in beakers 1 and 2.

Beaker 1			Beaker 2			Time (sec)
S. No.	H_2SO_4 soln (ml)	Water (ml)	KBrO_3 soln (ml)	KBr soln (C) (ml)	Phenol soln (A) (ml)	
1.	10	0	10	15	1	t_1
2.	8	2	10	15	1	t_2
3.	6	4	10	15	1	t_3
4.	5	5	10	15	1	t_4
5.	4	6	10	15	1	t_5
6.	3	7	10	15	1	t_6

In case the initial rate is very fast when 10 ml of H_2SO_4 solution is used, carry out the experiments further with lesser concentrated solution than before. In this case also the time increases as sulphuric acid concentration is decreased but they are not inversely proportional to the volume of H_2SO_4 used.

Calculations and Discussion : The rate of the reaction can be expressed in terms of formation of bromine. The rate equation can be written as :

$$+ \frac{d[\text{Br}]}{dt} = k [\text{Br}^-]_t^x [\text{BrO}_3^-]_t^y [\text{H}^+]_t^z$$

The initial rate of reaction in each case is proportional to $[\text{Br}^-]_0^x [\text{BrO}_3^-]_0^y [\text{H}^+]_0^z$

As the two concentrations have been taken as constant in each series of experiments, the initial rate can be taken as proportional to the concentration factor of the reactant which is changed. For change in H_2SO_4 concentration $[\text{H}^+]_0$, we can express

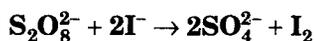
$$\text{Initial rate, } r_t \propto [\text{H}^+]_0^z$$

or
$$\log r_t = z \log [\text{H}^+]_0 + \log (\text{constant})$$

A plot of $\log r_t$ against $\log [\text{H}^+]_0$ should give a straight line with a slope equal to z . A non-integral slope will suggest a complex reaction kinetics and fractional orders for reactions.

EXPERIMENT No. 13

Object : To study the effect of change in ionic strength of solution on the kinetics of the reaction :



Apparatus and Chemicals : Burettes, pipettes, ten 250 ml conical flasks, stop watch, thermostat.

Stock Solutions :

- 0.1 M KI (250 ml)
- 10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$ (150 ml)
- 10^{-2} M $\text{K}_2\text{S}_2\text{O}_8$ (300 ml)
- 10^{-3} M HCl and 10^{-5} M EDTA (1 litre)
- 1 M KNO_3 (200 ml)
- Starch solution.

Theory : This reaction is a reaction between two ionic species and the effect of ionic strength on its kinetics can be studied by obtaining the values of specific reaction rate at different ionic strengths*.

The kinetics of this reaction can be studied as a clock reaction which is monitored by reaction of liberated iodine with a precalculated small amount of sodium thiosulphate using starch solution as an indicator.

Procedure : First test 5 ml of starch solution with a drop of iodine solution. Immediate deep blue colour should form if the solution is good for use. While preparing the following mixtures potassium persulphate solution should be added in the last and it is then that the stop watch is started. Solution d will be used as solvent.

Flask No.	Soln a, 0.1 M KI (ml)	Soln. b, 0.001 M $\text{Na}_2\text{S}_2\text{O}_3$ (ml)	Soln e, 1M KNO_3 (ml)	Soln-d, Solvent (ml)	Starch soln (ml)	Soln. c, 0.01 M $\text{K}_2\text{S}_2\text{O}_8$ (ml)
1	20	10	0	59	1	10
2	20	10	0	44	1	15
3	20	10	0	34	1	35
4	20	10	1	43	1	25
5	20	10	3	41	1	25
6	20	10	5	39	1	25
7	20	10	10	34	1	25
8	20	10	20	24	1	25
9	20	10	25	19	1	25
10	20	10	35	9	1	25

The solutions in reaction flasks should be mixed occasionally. The end of reaction in each case is indicated by the production of blue colour. First set up only the first three flasks and then the remaining seven flasks. True and apparent rate constants can be calculated from the first three flasks.

Then plot values of $\log k$ against $\mu^{1/2}$.

[Bronsted relationship is given by,

$$\log k = \log k_0 + 1.018z_1z_2 \mu^{1/2}$$

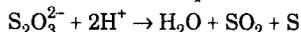
where $\mu = \frac{1}{2} \sum c_i z_i^2$.

*Ionic strength of a solution is usually denoted by μ and is given by

$$\mu = \frac{1}{2} \sum m_i z_i^2$$

where m_i represents molality (for dilute solutions molarities may be used) and z_i is the ionic charge for a species i and Σ is the addition symbol for all the ionic species involved including the reacting, non-reacting and the product ionic species.

The reaction between sodium thiosulphate and hydrochloric acid is an ionic reaction as follows :



If the reacting solutions are 0.1M and 2M, respectively, then.

$$\begin{aligned} \mu &= \frac{1}{2} \left\{ \left[2 \times 0.1 \times (+1)^2 + 0.1 \times (-2)^2 \right] + \left[2 \times (+1)^2 + 2 \times (-1)^2 \right] \right\} \\ &= \frac{1}{2} \{ (0.2 + 0.4) + [2 + 2] \} \\ &= \frac{1}{2} (0.6 + 4) = \frac{1}{2} 4.6 = 2.3. \end{aligned}$$

EXPERIMENT No. 14

Object : *To study the kinetics of depolymerisation of diacetone alcohol by means of a dilatometer.*

Apparatus and Chemicals : Dilatometer set up, 10 ml graduated pipette, thermometer, water bath, 250 ml beaker, 0.1 M NaOH (250 ml), diacetone alcohol (20 ml).

Theory : Dilatometer is a set up which can be used to measure dilation or change in volume of a liquid reaction mixture. It consists of a container of a fixed volume to which a uniform bore capillary tube is attached so that small changes in volume can be measured. The apparatus is made of glass. The rubber corks are used for tight fitting. The filling should essentially be air free. As a dilatometer also acts as a thermometer, expansion due to a change in temperature has to be strictly avoided. This is done by circulating water at constant temperature around the dilatometer.

For laboratory, dilatometer can be easily set up by taking a 50 or 100 ml separating funnel and fixing it in an aluminium pan as shown in figure (2). A glass capillary of about 1.5 mm to 2.5 mm bore and 60 cm to 100 cm length can be fixed to it by using a rubber cork. The dilatometer can be filled by suction using an ordinary pump. A metre scale is attached to the capillary for noting level of liquid in the capillary at different time intervals. The separating funnel dilatometer is filled directly by pouring liquid reaction mixture into it

Procedure : Put the boiling tube containing diacetone alcohol and 0.1 M NaOH solution flask in a bath of water or thermostat (for nearly 15-20 minutes) for obtaining equilibrium temperature. Measure 100 ml (200 ml) of 0.1 M NaOH solution into a beaker and add 5 ml (10 ml) of diacetone alcohol into it. Start the

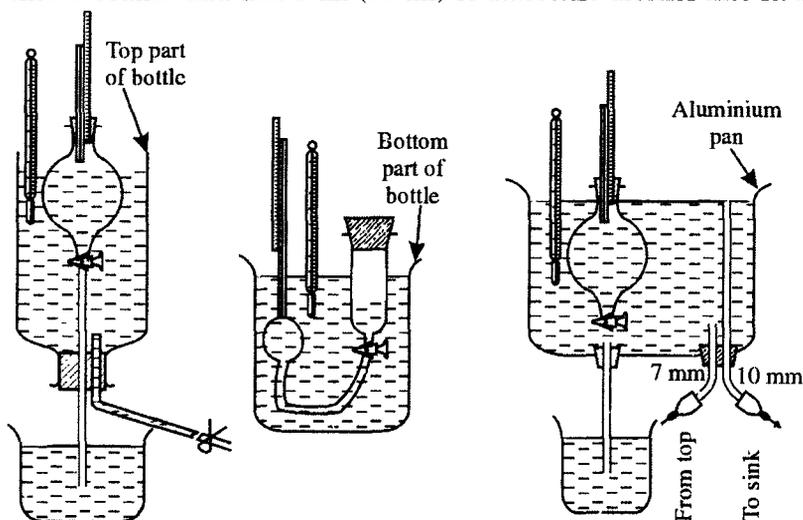


Fig. 2 : Dilatometer

stop watch immediately. Mix and then transfer the reaction mixture to a separating funnel and fill it to the brim. Invert the rubber cork carrying the capillary tube. As OH^- concentration remains constant, we can write

$$-\frac{d[\text{Alcohol}]}{dt} = k_1 [\text{Alcohol}]$$

Please check that there are no air bubbles in the dilatometer and the liquid stands in the capillary above the cork. The level of the liquid in the capillary is noted immediately and then it is noted after each 2 minutes interval for nearly 40 minutes (l_t) and then when the reaction is complete (l_∞).

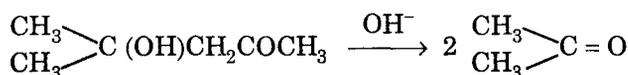
Calculations : We have

$$[\text{Alcohol}]_0 \propto (l_\infty - l_0)$$

$$[\text{Alcohol}]_t \propto (l_\infty - l_t)$$

The value of l_0 can be obtained by extrapolating l_t (ordinate) against t (abscissa) graph to $t = 0$. However, the value of l_0 need not be known as the kinetic study can be initiated from any stage of measurement.

Reaction Equation :



$$-\frac{d[\text{Alcohol}]}{dt} = k_1 [\text{Alcohol}] [\text{OH}^-]$$

As OH^- concentration remains constant, we can write

$$-\frac{d[\text{Alcohol}]}{dt} = k_1 [\text{Alcohol}]$$

where $k_1 = k_2 [\text{OH}^-]$.

Experimental measurement of k_1 as a first order rate constant can be used to calculate the second order rate constant, k_2 .

Note : This reaction is catalysed by OH^- ions and so this experiment can be used to compare the strengths of bases as well as for finding their dissociation constants.

Precautions : (1) The capillary tube and dilatometer should be thoroughly cleaned, rinsed with water, alcohol and ether and dried by sucking air through them.

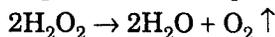
EXPERIMENT No. 15

Object : To study the decomposition of hydrogen peroxide catalysed by iodide ion.

Apparatus and Chemicals : Gas measuring apparatus including a 50 or 100 ml graduated gas tube or burette, conical flask (25 ml), pipettes (5 ml, 10 ml), stop watch, water bath, ice, hot water.

3% H_2O_2 , 0.1 M KCl, 0.1 M KI solutions.

Theory : Hydrogen peroxide decomposes as follows :



The rate of reaction is given by,

$$\begin{aligned} \text{Rate} &= -\frac{d[\text{H}_2\text{O}_2]}{dt} \\ &= k [\text{H}_2\text{O}_2]^x [\text{I}^-]^y \end{aligned}$$

In this experiment the volume (V) of oxygen gas at atmospheric pressure and temperature (both are constants) is measured as a function of time.

Procedure : Set up a reaction vessel with some glass beads, gas measuring apparatus and water bath. Transfer 5 ml of 3% H_2O_2 (for 50 ml gas burette, 1.5% H_2O_2 solution is used) by pipette to a reaction flask and replace the stopper. Put a stoppered test tube containing more than 10 ml of 0.1M KI solution in the water bath to equilibrate temperature to 25°C . Allow standing for nearly 15 to 30 minutes. The air leaks in the set up are checked by lowering the water bulb.

Remove the stopper for reaction vessel and level the water to stand at 0.0 ml in the gas burette. Now transfer 5 ml of 0.1M KI solution by means of a pipette to reaction vessel and shake thoroughly. Do not mind evolution of a small amount of oxygen at this stage. Stopper the reaction vessel and start the stop watch.

At set time intervals level the water in the gas burette and take the readings of gas volume to 0.01 ml (nearest) [For this a lens can be used] and time, mixing and shaking the solution in the reaction vessel. Continue till less than 1 ml of gas is formed in 60 seconds. Without disconnecting the reaction vessel, heat the reaction system in a boiling water bath for a few minutes so that H_2O_2 is completely decomposed. When no more gas is formed, cool the reaction system to 25°C , adjust the water level and record the values of V_{min} or V_{final} for oxygen.

Repeat the experiment by using 5 ml of 1:1 mixture of 0.1M KCl and 0.1M KI solutions instead of 5 ml of 0.1M KI solution. In this way the ionic strength remains constant and reduces the concentration of I^- ions. Repeat the experiment at temperatures 30° and 35°C .

Observations :

Time (min)	:	0	10	20	30	40	∞
Volume of O_2 gas (ml)	:	V_0	V_{10}	V_{20}	V_{30}	V_{40}	V_∞

Calculations : Since the decomposition of H_2O_2 is a first order reaction, the rate equation is given by,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$= \frac{2.303}{t} \log \frac{V_\infty}{(V_t - V_0)}$$

Result : The order of reaction is **one**.

Precautions : (1) If a 50 ml gas burette is used, use only 1.5% H_2O_2 solution.

(2) Some glass beads are kept in the flask to minimise the supersaturating of the solution with oxygen.

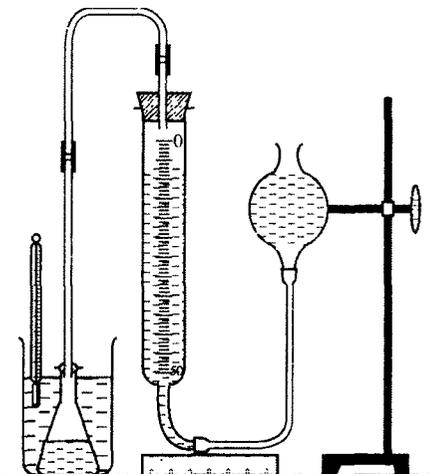


Fig. 3 : Set up for reactions involving evolution of gases.

(3) The reaction vessel be kept shaking at a slow rate to dislodge the gas bubbles accumulating on the flask surface under solution.

(4) The bath temperature should be kept adjusted to a working temperature of 25°C.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 16

Object : *To find out the order of reaction of the hydrolysis of canesugar.*
Proceed as in experiment 1.

EXPERIMENT No. 17

Object : *To study the kinetics of bromination of acetone in presence of acid as catalyst.*

Proceed as in experiment 5. The bromine concentration can be determined by adding fixed amounts of KI in each aliquot and then titrating the liberated iodine against sodium thiosulphate solution.

EXPERIMENT No. 18

Object : *To determine the relative strengths of HCl, HNO₃ and H₂SO₄ by studying the kinetics of hydrolysis of methyl acetate.*

Proceed as in experiment 1. Take equinormal solutions of each acid turn by turn and determine the velocity constants as usual. Therefore, strength of HCl : strength of HNO₃ : strength of H₂SO₄ = $k_1 : k_2 : k_3$.

EXPERIMENT No. 19

Object : *To determine the relative strength of mono- chloroacetic acid (4N) and trichloroacetic acid (4N) by studying the kinetics of hydrolysis of methyl acetate or cane sugar.*

Proceed as in experiment 1.

EXPERIMENT No. 20

Object : *To determine the degree of hydrolysis of urea hydrochloride (A) by studying the hydrolysis of methyl acetate by an acid and A.*

The degree of hydrolysis is given by the ratio of the concentration of free acid and amount which would be present if the salt were completely hydrolysed.

The concentration of free acid that would be present after complete hydrolysis is measured by the rate constant (k_1) of the hydrolysis of methyl acetate by pure acid solution. The free acid actually present in the solution is measured by the rate constant (k_2) obtained after the addition of an equinormal and equivalent solution of urea hydrochloride. The degree of hydrolysis is then given by k_1/k_2 .

EXPERIMENT No. 21

Object : *To find out the order of reaction between sodium thiosulphate and ethyl bromoacetate.*

Mix 100 ml of $M/100$ solution of each reactant and titrate 5 ml of reaction mixture with a standard solution ($M/150$) of iodine using starch solution as an indicator. The value of k for a second order reaction is given by :

$$k = \frac{1}{at} \cdot \frac{x}{a-x} = \frac{2}{0.005 \times t} \cdot \frac{V_0 - V_t}{V_t}$$

EXPERIMENT No. 22

Object : *To find out the order of reaction between chromic acid and oxalic acid.*

EXPERIMENT No. 23

Object : *To find out the effect of adding an indifferent electrolyte to the system between potassium persulphate and potassium iodide.*

Add solutions of any electrolyte, say potassium chloride of different strengths and determine the rate constants and evaluate the results as in experiment 9.

EXPERIMENT No. 24

Object : *To study the reaction between potassium persulphate and potassium iodide in presence of an excess of latter.*

The reaction becomes of the first order with respect to the persulphate. The reaction is started by adding 100 ml of 0.4 M KI into 100 ml of 0.025 M persulphate, withdrawing 10 ml samples at intervals of 5 minutes to obtain the thiosulphate titre (V_t). An infinite titre (V_∞) is obtained as explained in experiment 9, but the addition of KI may be omitted. Now put the values of a and $(a-x)$ in the first order rate expression *viz.*,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} = \frac{2.303}{t} \log \frac{V_t}{V_\infty - V_t}$$

EXPERIMENT No. 25

Object : *To investigate the velocity of muta-rotation of α -D-glucose in water polarimetrically.*

This is a first order reversible reaction which undergoes general acid-base catalysis. Before explaining the procedure, one must know the method for the preparation of α -D-glucose. (Dissolve 500 g of pure D-glucose in 250 ml of distilled water. Warm slightly on a water bath till the dissolution is complete. Remove the syrup from the bath and add 100 ml of cold glacial acetic acid. Stir the syrup to prevent caking during crystallisation. Filter on a Buchner funnel under suction. Wash the residue with 90% alcohol followed by absolute alcohol in which the β -form is more soluble). Weigh 2 g of α -D-glucose accurately into a dry 100 ml measuring flask. Dissolve the glucose in distilled water and make up the solution to 100 ml. The stop watch should be started when the flask is half full. Now fill the polarimeter tube with this solution and start taking readings (r_t) after suitable intervals of time. After taking readings for an hour, transfer the solution

from the polarimeter tube to the flask. Keep it for a week to measure the equilibrium angle of rotation (r_e).

Plot r_t against the values of t and draw a curve. For a first order reversible reaction, we have

$$\log (r_t - r_e) = \frac{-(k_1 + k_2) t}{2.303} + \log (r_0 - r_e)$$

where, k_1 and k_2 are the velocity constants for the forward and backward reactions, r_0 is the initial angle of rotation. Plot another curve between $\log (r_t - r_e)$ and t . Obtain $(k_1 + k_2)$ from the slope and r_0 from the appropriate intercept.

EXPERIMENT No. 26

Experiment 26 : To study the autocatalytic reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ ions catalysed by Mn^{2+} ions.

The reaction between potassium permanganate and oxalic acid in presence of a mineral acid occurs according to the following reaction.



The reaction is catalysed by Mn^{2+} ions formed during the reaction. The progress of the reaction can be followed by estimating the residual MnO_4^- (permanganate ions) concentration from time to time. This is done by running the samples of the mixture to excess of KI and then titrating the liberated iodine with standard hypo solution.

Prepare three reaction mixtures (total volume 200 ml) as follows :

(I) 100 ml 0.1M $\text{H}_2\text{C}_2\text{O}_4$ + 30 ml 0.02 M KMnO_4
+ 10 ml 1M H_2SO_4 + 0 ml 0.2 M MnSO_4 + 60 ml H_2O

(II) 100 ml 0.1 M $\text{H}_2\text{C}_2\text{O}_4$ + 30 ml 0.02 M KMnSO_4
+ 20 ml 0.2M MnSO_4 + 10M ml 1M H_2SO_4 + 40 ml H_2O

(III) 100 ml 0.2 M $\text{H}_2\text{C}_2\text{O}_4$ + 15 ml 0.02 M KMnO_4
+ 20 ml 0.2M MnSO_4 + 10 ml 1M H_2SO_4 + 55 ml water

For each experiment, add 50 ml of 0.2 M KMnO_4 to the mixture and start the stop watch. Shake well and after 30 seconds, withdraw 10 ml of the reaction mixture into a conical flask. Note the time and immediately add about 10 ml of 0.1 M KI solution. This reacts with KMnO_4 and stops the reaction. Iodine is liberated with 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ adding 4-5 drops of starch (indicator). Remove 10 ml of the reaction mixture after every 5 minutes, till the titre values become smaller than 3.0 ml. Now plot a graph between titre values (ordinate) and time in minutes (abscissa).

Calculations : Plot the titre values of $\text{Na}_2\text{S}_2\text{O}_3$ (ordinate) against time (abscissa) for both mixtures (I) and (II). The catalytic effect of Mn^{2+} can be observed from the shape of the curve [Curve (a), figure (4)] for reaction mixture (I). As is clear, from the graph, the reaction in the beginning is very slow but the rate

increases rapidly due to the formation of Mn^{2+} ions. In mixtures (II) and (III) containing an excess of Mn^{2+} ions [Curve (b) and (c) figure (4)], the auto-catalysis disappears, the concentration of $KMnO_4$, *i.e.*, the titre value falls rapidly from the very beginning. From the time concentration graph for mixture (II) and (III) determine the time required for the half change and determine the order of reaction with respect to $KMnO_4$ by using the equation

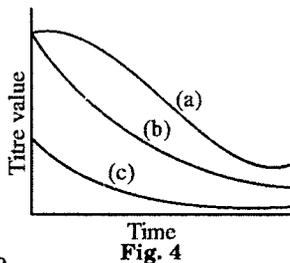


Fig. 4

$$n = 1 + \frac{\log t_1 - \log t_2}{\log a_2 - \log a_1}$$

EXPERIMENT No. 27

Object : *To determine the temperature coefficient of hydrolysis of methyl acetate and its energy of activation.*

Proceed as in experiment 1. Determine the velocity constant at two temperatures, differing by $10^\circ C$. From these values, the energy of activation can be calculated as in experiment 6. The temperature coefficient is given by k_{t+10}/k_t .



TRANSPORT NUMBER

EXPERIMENT No. 1

Object : To determine the transport numbers of silver and nitrate ions in a solution of silver nitrate by Hittorf's method.

Apparatus : Transport number cell with electrodes, copper or silver voltameter, milli-ammeter, variable resistance, 30V battery or D.C. mains with large resistance, burette, pipette, big glass vessel etc.

Theory : We know that when an electric current is passed through an electrolytic solution, there is a change of concentration at the two electrodes. The change may or may not be equal. Electricity is carried by both types of ions. The quantity of electricity carried by each ion is directly proportional to the speed of the concerned ion, *i.e.*,

Amount of electricity carried by anion \propto speed of anion, u_a and, amount of electricity carried by cation \propto speed of cation, u_c

\therefore Total amount of electricity carried \propto (speed of anion + speed of cation)
 $\propto (u_a + u_c)$

The transport number of an ion is defined, 'as the fraction of the total current carried by that ion'. It is represented by the symbol t or n .

Transport number of anion, n_a

$$= \frac{\text{Amount of electricity carried by anion}}{\text{Total amount of electricity carried}} = \frac{u_a}{u_a + u_c}$$

Transport number of cation, n_c

$$= \frac{\text{Amount of electricity carried by cation}}{\text{Total amount of electricity carried}} = \frac{u_c}{u_a + u_c}$$

$$\therefore n_a + n_c = \frac{u_a}{u_a + u_c} + \frac{u_c}{u_a + u_c} = 1$$

Therefore, if the transport number of one ion is known, then that of the other can be calculated. We know that the fall in concentration round an electrode is proportional to the speed of the ion moving away from that electrode, *i.e.*,

Fall in concentration round anode \propto Speed of cation (u_c)

Fall in concentration round cathode \propto Speed of anion (u_a)

We have :

$$n_a = \frac{u_a}{u_a + u_c} = \frac{\text{Fall in concentration around cathode}}{\text{Fall in concentration around (cathode + anode)}}$$

$$= \frac{\text{Fall in concentration around cathode}}{\text{Total fall in concentration around both electrodes}}$$

If concentration is measured in gram equivalent, then

$$n_a = \frac{\text{Number of g equiv. lost from cathode}}{\text{Total number of g eqivs lost}}$$

But we know that the total number of gram equivalents lost is equal to the gram equivalents deposited at each electrode. Therefore,

$$n_a = \frac{\text{Number of g equiv. lost from cathode}}{\text{Number of g equiv. deposited on each electrode}}$$

If a silver voltameter is taken, then the number of g equivalents deposited on each electrode must be equal to the amount of silver deposited in the silver voltameter. Therefore,

$$n_a = \frac{\text{Number of g equiv lost from cathode}}{\text{Number of g equiv of silver deposited in voltameter}}$$

Similarly,

$$n_c = \frac{\text{Number of g equiv lost from anode}}{\text{Number of g equiv of silver deposited in voltameter}}$$

Suppose x faraday of electric current is passed between two silver electrodes, then x equivalent of silver ions are formed in the anodic chamber due to the electrode reaction. But the actual increase in the concentration of silver ions in the anodic chamber is, say z equivalents. We see that $z < x$, because silver ions have migrated away from anodic chamber towards the cathodic chamber. Thus, the fall in concentration of silver ions due to its migration is $(x - z)$ equivalents. Therefore, transport number of silver ion is given by :

$$n_{\text{Ag}^+} = \frac{x - z}{x}$$

$$\therefore n_{\text{NO}_3^-} = 1 - n_{\text{Ag}^+}$$

Procedure : Before we discuss the procedure, the students must understand the construction of the apparatus used. The apparatus shown in figure (1) consists

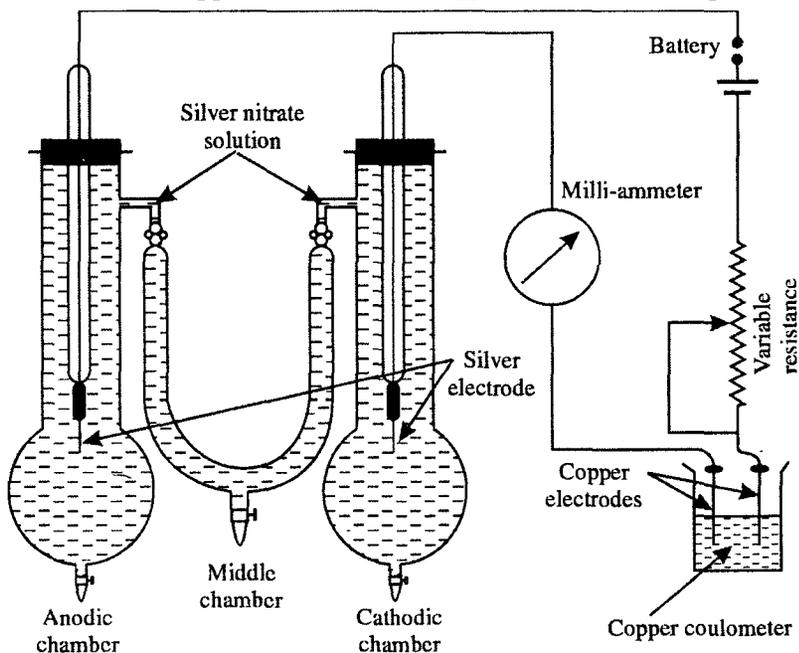


Fig. 1 : Hittorf apparatus

of two vertical glass tubes connected together through a U-tube in the middle. The end tubes are known as anodic and cathodic chambers, as anode and cathode are contained in them. The U-tube is known as middle chamber. Each chamber is provided with a stop-cock at the bottom. The electrodes are made of suitable metal, say in this case they are of silver. The electrodes are sealed in glass tubes which pass through rubber stoppers as shown. Mercury is placed in the tubes to make electrical contacts.

The copper voltameter consists of a vessel or a large beaker containing a solution of copper sulphate of the following composition :

Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) crystals = 150 g

Sulphuric acid (conc.) = 50 g

Alcohol = 50 g

Distilled water = 1000 g

The electrodes are made of copper (1.5 cm \times 2 cm) cut from a copper sheet. They are dipped in the copper sulphate solution. The copper plate to be used as cathode must be cleaned, dried and weighed.

Fill the three chambers with an exact $N/10$ solution of AgNO_3 . The three limbed electrolytic cell is then connected in series with a copper voltameter, a battery, milli-ammeter and a variable resistance. A current of about 0.02 ampere is passed for about 2-3 hours (Note the exact time period by means of a watch) through the solution. The variable resistance should be changed occasionally, if need arises, so that the current should be about 0.02 ampere. *The object is to get an appreciable, but not too large a change in the concentration around the electrodes. If the change is large, diffusion will set in.* The two pinch cocks should be kept open while passing electric current.

After the experiment, the pinch cocks are closed by means of clips. Now withdraw about 30 ml of the anodic solution by means of the stop cock of the anodic chamber. Then pipette out 25 ml of this solution in a previously weighed clean conical flask. Weigh the whole solution. Now titrate it with a standard $N/10$ KCNS solution, using 1 ml of ferric ammonium sulphate solution, until a permanent red colour is obtained.

Now take some solution from the middle chamber and titrate it against $N/10$ KCNS solution, as described above. See that the composition of the solution remains unchanged in the middle chamber. If it changes, repeat the whole procedure.

Remove the cathode (which has been previously cleaned, dried and weighed) from the voltameter and wash it first with distilled water and finally with alcohol. Heat it in an oven at 110° and then cool it in a dessicator and weight it.

Observations : Current strength used = ... amp

Time for electrolysis = ... sec

(1) Observations before electrolysis

Weight of empty flask = W_1 g

Weight of flask + 25.0 ml of AgNO_3 solution = W_2 g

25 ml of AgNO_3 solution required, say V_1 ml of $N/10$ KCNS

(2) Observations after electrolysis

(a) Anodic chamber : Weight of empty flask = W_3 g

Weight of flask + 25 ml anodic solution = W_4 g

25 ml of anodic solution required, say V_2 ml of $N/10$ KCNS.

(b) *Middle chamber* : 25 ml of the solution of this chamber required, say V_3 ml of $N/10$ KCNS.

(3) Voltmeter readings

Initial weight of cathode = W g

Final weight of cathode = W' g

Calculations : (1) Before electrolysis

Weight of solution = $(W_2 - W_1)$ g = W_5 g (say)

Concentration of AgNO_3 (by using normality equation)

$$= \frac{N}{x} \text{ (say)}$$

$$\therefore \text{Amount of } \text{AgNO}_3 = \frac{169.89}{x} = W_6 \text{ g (say)}$$

Amount of water = $(W_5 - W_6)$ g

Therefore, before electrolysis, $(W_5 - W_6)$ g of water contains

$$\begin{aligned} &= \frac{W_6 \times 107.88}{169.89} \text{ g of Ag} \\ &= \frac{W_6}{169.89} \text{ g equiv of Ag} \end{aligned}$$

(2) After electrolysis

Weight of anodic solution = $(W_4 - W_3)$ g = W_7 g (say)

Concentration of AgNO_3 (by using normality equation)

$$= \frac{N}{y} \text{ (say)}$$

$$\therefore \text{Amount of } \text{AgNO}_3 = \frac{169.89}{y} = W_8 \text{ g (say)}$$

$$\therefore \text{Amount of water} = (W_7 - W_8) \text{ g}$$

After electrolysis, $(W_7 - W_8)$ g of water contains W_7 g of silver nitrate or $\frac{W_7}{169.89}$ g equiv of silver.

Before electrolysis, $(W_7 - W_8)$ g of water would have contained

$$= \frac{W_6 \times (W_7 - W_8)}{169.89 \times (W_5 - W_6)} \text{ g equiv of Ag}$$

Therefore, the increase in the number of gram equivalents of silver ions in the anodic chamber

$$= \left[\frac{W_7}{169.89} - \frac{W_6 \times (W_7 - W_8)}{169.89 \times (W_5 - W_6)} \right] = z \text{ (say)}$$

Increase in weight of cathode in copper voltameter

$$= (W' - W) \text{ g of copper}$$

$$= \frac{(W' - W)}{31.78} \text{ g equiv of copper}$$

$$= \frac{(W' - W) \times 107.88}{31.78} \quad \text{g equiv of silver} = x \text{ (say)}$$

Had there been no migration of Ag^+ ions from the anode during the electrolysis, the increase in concentration in anodic chamber would have been equal to x , but the actual increase is z .

\therefore Fall in concentration around anode due to the migration of Ag^+ ions = $(x - z)$ g equiv of Ag^+ .

$$\therefore n_{\text{Ag}^+} = \frac{x - z}{x}$$

Knowing the values of x and z , we can calculate the value of n_{Ag^+} . The value of $n_{\text{NO}_3^-}$ can also be calculated, as $n_{\text{NO}_3^-} = 1 - n_{\text{Ag}^+}$.

Result : The transport numbers of silver and nitrate ion are ... and ..., respectively.

Precautions : (i) The estimations should be made with a known weight and not with a known volume of the solution, before and after electrolysis.

(ii) A small current should be passed for 2-3 hours, otherwise diffusion will set in, on passing high current.

(iii) The concentration of the AgNO_3 solution in the middle chamber should not be changed. If it changes, the whole experiment should be started anew.

EXPERIMENT No. 2

Object : To find out the transport numbers of potassium and chloride ions by moving boundary method.

Apparatus : Electrolytic cell with electrodes, battery, variable resistance, milli-ammeter etc.

Theory : The principle of this method is based on measuring the actual speed of ions, as suggested by Lodge and Whethan. If the velocities of both ions can be measured by means of a moving boundary, it is evident that the transport numbers can be measured directly.

Suppose we want to measure the transport number of any cation, say K^+ ion in KCl . The electrolyte is known as **principal electrolyte**. We now choose another suitable electrolyte, called the **indicator electrolyte**, which has a common ion with the principal electrolyte. The other condition which must be fulfilled is that the cation of indicator electrolyte must be slow as compared to the cation of the principal electrolyte. As Li^+ ion moves slower than K^+ ion, we can take LiCl as the indicator electrolyte. The disadvantage in taking the indicator ion faster than the principal ion is that the boundary becomes blurred.

Suppose a current of I ampere is passed for t second, then the quantity of electricity carried by K^+ ion

$$= n_{\text{K}^+} \cdot I \cdot t \text{ coulomb}$$

Therefore, the amount of K^+ ions that has migrated upwards from one known position to another is given by,

$$\frac{n_{\text{K}^+} I \cdot t}{F} \text{ g equivalent} \quad \dots (1)$$

where, F = faraday.

Suppose during the passage of electric current, the K^+ ion has migrated or moved through a distance l cm in a tube of area of cross-section a cm².

∴ Volume of solution between a distance of l cm.

$$= (l \cdot a) \text{ ml}$$

∴ Amount of K^+ ions in the specified volume of the solution

$$= l \cdot a \cdot c \cdot \text{g equivalent} \quad \dots (2)$$

where, c = concentration of K^+ ions in g equivalent per ml.

From equations (1) and (2), we have,

$$\frac{n_{K^+} l \cdot t}{F} = l \cdot a \cdot c.$$

$$n_{K^+} = \frac{l \cdot a \cdot c \cdot F}{I \cdot t} \quad \dots (3)$$

Therefore, the transport number of K^+ ion can be calculated from equation (3) and that of Cl^- ion by means of the relation $n_{Cl^-} = 1 - n_{K^+}$.

Procedure : The apparatus used consists of an electrolytic cell of the shape, shown in figure (2). The middle point of the left hand portion is a vertical tube of uniform area of cross-section. The indicator electrolytic solution, *i.e.*, LiCl is placed in the lower half of this tube. The experimental or principal solution, *i.e.*, KCl is

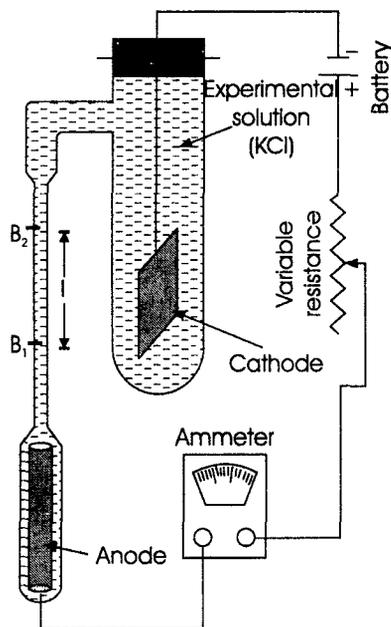


Fig. 2 : Moving boundary apparatus

made to float on it, so as to produce a sharp boundary. The anode is dipped in the indicator solution and the cathode in the principal solution.

In order to obtain a sharp boundary, we use a cadmium anode which, on electrolysis, gives cadmium chloride which, in turn, acts as an indicator solution. This will bring automatically an autogenic and sharp boundary.

The electrodes are connected to a variable resistance, battery, ammeter as shown in figure (2). A constant current of about 0.02 ampere is passed for about

5–6 hours. (Note the exact time period by means of a watch). This will cause K^+ ions to move upwards towards the cathode, closely followed by Li^+ or Cd^{2+} ions. The sharp boundary thus moves gradually upwards. The initial level (B_1) of the boundary is noted and after the end of the experiment, the final level (B_2) of the boundary is also noted.

Observations : Current strength used = I amp

Time of electrolysis = t sec

Initial reading of the boundary = h_1 cm

Final reading of the boundary = h_2 cm

Diameter of the tube = d cm

Concentration of KCl solution = ... equivalent per ml

Calculations : The distance through which the boundary has moved in t sec = $(h_2 - h_1)$ cm.

Area of cross-section of the tube = $\pi r^2 \text{ cm}^2$ ($\because r = d/2$)

Therefore, from equation (3), the transport number of K^+ ion can be calculated as follows :

$$n_{K^+} = \frac{l \cdot a \cdot c \cdot F}{I \cdot t}$$

or

$$n_{K^+} = \frac{(h_2 - h_1) \times \pi r^2 \times \text{concentration of KCl solution} \times 96,500}{\text{current strength} \times \text{time}}$$

$$\therefore n_{Cl^-} = 1 - n_{K^+}$$

Thus, the transport numbers of K^+ and Cl^- ions can be easily calculated.

Result : Transport numbers of K^+ and Cl^- ion are ... and ..., respectively.

Precautions : (i) The boundary should be quite sharp.

(ii) Only a small current should be passed through the electrolytic solution.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 3

Object : To determine the transport numbers of copper and sulphate ions in 0.5M solution of copper sulphate by Hittorf's method.

This experiment is similar to experiment no. 1. In the transport number apparatus, we fill 0.5M solution of copper sulphate crystals (A.R.). The electrodes are of stout pure copper wire. The copper ions are estimated iodometrically using an excess of KI solution and standard sodium thiosulphate solution (0.05M). The electrodes are cleaned with concentrated nitric acid and finally washed with water before use. Solution from either the anodic or cathodic chamber may be taken out for analysis.

EXPERIMENT No. 4

Object : To determine the transport number of silver and chloride ions by moving boundary method.

Proceed as in experiment no. 2.

EXPERIMENT No. 5

Object : To determine the transport number of chloride ions in a solution of 0.5N HCl by moving boundary method.

The suitable indicator ion in this experiment is lithium ion. The transport numbers of H^+ and Li^+ ions are ~ 0.8 and 0.3 , respectively, so the ratio of concentration of $LiCl$ to that of HCl should be about $0.3/0.8 \approx 0.4$. Proceed as in experiment no. 2.



When a beam of light which is vibrating in all planes perpendicular to its direction of propagation [fig. 1(a)] is passed through a Nicol prism, it emerges out with all its vibrations taking place in only one plane. Such a light is said to be *plane polarised* and the Nicol prism is known as *polariser*. The plane in which vibrations occur is known as *plane of vibration* of the polarised ray, while the plane perpendicular to it is known as *plane of polarisation* [fig. 1(b)]. If the plane polarised light is passed through a second Nicol prism (*analyser*), then it is observed that on rotating the second prism, the light will pass through and will be completely stopped alternately as the prism is rotated. If two Nicol prisms are arranged with their planes of polarisation parallel to one another, the rays of light passing out from the first prism will go through the second prism and the field of

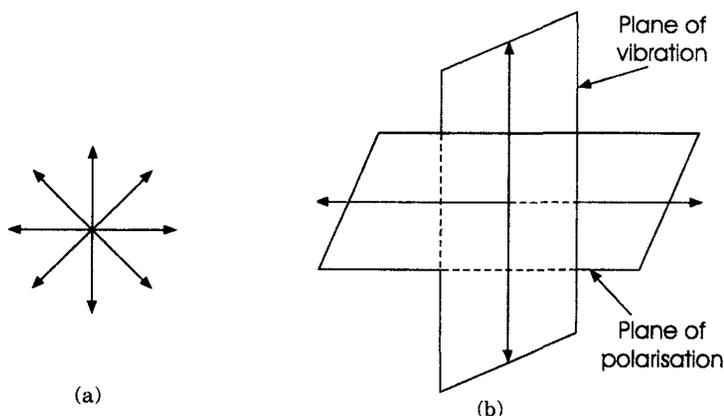


Fig. 1 : Vibrating beam of light

view will be lighted [fig. 2(A)]. Twice during the complete revolution of the second Nicol prism, will all the light be stopped and twice will all of it get through. In other words, the fields observed in the second Nicol prism will be alternately dark and bright, the maximum and minimum brightness occurring at positions 90° apart.

If the two Nicol prisms are placed with their axes at right angles [fig. 2(B)] to one another, *i.e.*, in a position that when light is entering the first prism, the field observed in the second prism is dark, then such position is known as position of

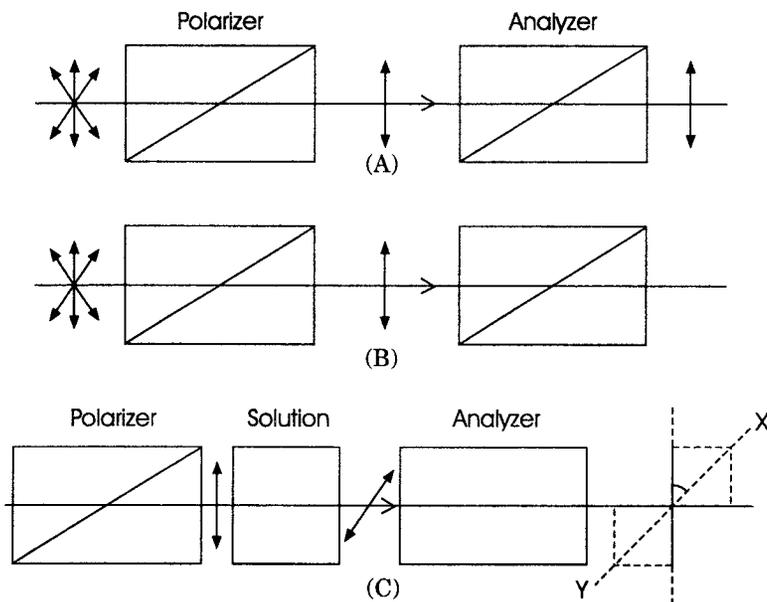


Fig. 2.

complete extinction of the prism. If a tube containing water is placed horizontally between the two, the field observed in the second prism will still be dark. If instead of water, we put a solution of sucrose then it is observed that the field in the second prism becomes bright [fig. 2(C)]. This means that water did not rotate the polarised beam, while sucrose had rotated the plane of the polarised light. The second prism has to be rotated through a certain angle for obtaining a dark field again. Therefore, **substances which cause rotation of the plane polarised light are said to be optically active substances**. The rotation may be to the right or left. When the second prism has to be rotated to the right, *i.e.*, clockwise to reproduce the dark field, the substance is said to be **dextro-rotatory** and when it has to be rotated to the left, the substance is said to be **laevo-rotatory**.

From the above, it is obvious that a position of darkness could be regained by rotating the second prism in either direction, since there are two positions of complete darkness 180° apart. However, a direction is chosen, when the angle through which the prism must be rotated is less than 90° .

The angle of rotation, *i.e.*, angle through which the plane of the polarised beam of light is rotated, is dependent upon (i) the nature of the substance, (ii) length of the column through which the light passes, (iii) temperature, (iv) concentration of the solution and (v) the wavelength of light used. The last factor makes it necessary to use monochromatic light for all such measurements.

The rotation R , is thus given by,

$$R = [\alpha]_{\lambda}^t \cdot l \cdot \frac{m}{v} \quad \dots (1)$$

where, l is the length of the column in decimeter through which the light passes, m is the weight in gram of the optically active substance dissolved in a volume of v ml and $[\alpha]_{\lambda}^t$ is a constant which depends upon the nature of the substance,

temperature and wavelength of light. The constant $[\alpha]_{\lambda}^t$ is known as **specific rotation** of the substance. It has a fixed value for a given substance under similar conditions.

From equation (1), we get,

$$[\alpha]_{\lambda}^t = \frac{R.v}{l.m}$$

If $l = 1$ dm, $v = 1$ ml, $m = 1$ g, then,

$$[\alpha]_{\lambda}^t = R$$

Hence, specific rotation is defined, *as the angle of rotation of plane polarised light produced by a solution containing 1 g of the substance in 1 ml of solvent, when the length of the column through which the light passes is one dm.* Values of specific rotation are measured in units of angle per decimetre per g per ml ($\text{deg dm}^{-1} \text{g}^{-1} \text{cm}^3$).

As $\frac{m}{v}$ is density, d of the solution, therefore,

$$[\alpha]_{\lambda}^t = \frac{R}{l.d}$$

In case of solution of an optically active substance,

$$[\alpha]_{\lambda}^t = \frac{100R}{l.c}$$

where, c is the number of grams of the substance present in 100 ml of the solution. For comparison of rotating power of different substances, molecular rotation $[M]_{\lambda}^t$ function is defined by the equation,

$$[M]_{\lambda}^t = \frac{M[\alpha]_{\lambda}^t}{100} = \frac{MR}{l.c}$$

Polarimeter : The instrument used to measure the angle of rotation caused by an optically active substance is known as *polarimeter*. Sometimes, the scale of the polarimeter is so graduated that the concentration of sugar solution is directly given, the instrument is then known as *saccharimeter*.

Now-a-days, two types of polarimeters are in use, one designed by Lippich and the other by Laurent. The difference between the two designs is the difference between the mode of producing half shadows. In the former design, a homogeneous light of any wavelength can be used, while in the latter design the half shadow plate is for one wavelength of light only. Therefore, Laurent's type of polarimeter cannot be readily used for all wavelengths, but it is best suited for the present purpose.

Laurent polarimeter is diagrammatically shown in figure (3). It consists of two metal tubes A and B, which are fixed rigidly on a stand and are separated by a through in which the observation tube O containing the required solution is placed. The tube A carries a lens C which renders the light coming from the source parallel. The light then passes into the first Nicol prism (*polariser*) D, which polarises it. The light then passes through the observation tube O and into the second tube B, which contains another Nicol prism (*analyser*) E and a telescope FG. At H, the opening of the tube A is half covered by a semi-circular plate of quartz q , of such

a thickness that the phase of light passing through it is changed by half a wavelength. If the optical axis of the quartz plate is parallel with the plane of polarisation, no effect will be observed in the telescope, due to half the light passing through the quartz plate, *i.e.*, the intensity of light in both halves of the field will be the same. On the contrary, if the polariser is rotated through an angle θ , then that portion of light which passes through the quartz plate will be rotated by an equal amount in the opposite direction, *i.e.*, there will be two beams of polarised light emerging from the tube A. The planes of these beams are inclined at an angle 2θ to one another. On observing the light through the telescope, one half of the field will be dark and other half bright and if the analyser is rotated, the bright

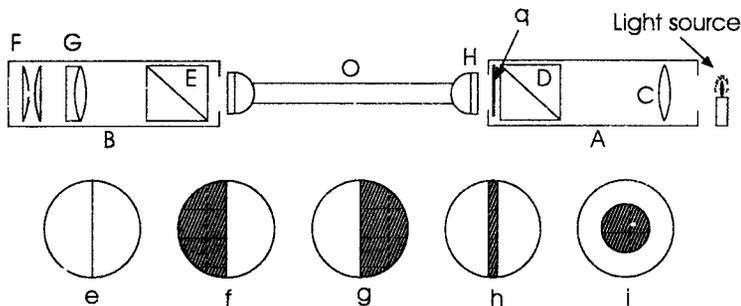


Fig. 3 : Laurent polarimeter.

and dark halves will interchange. Thus, there will be an intermediate position at which both halves of the field are equally illuminated. **This is the position at which all observations are made.** The angle 2θ is known as **half shadow angle**. It can be made larger or smaller by rotating the polariser.

By diminishing the half-shadow angle, the sensitivity of the polarimeter can be increased, but with increasing sensitiveness, a difficulty arises in deciding when the field is uniformly illuminated. In practice, however, a half-shadow angle of $4^\circ - 6^\circ$ is most suitable and simpler polarimeters are provided with the polariser set to give this angle.

In modern instruments, [fig. (4)] the half-shadow is produced by having a strip of quartz h in place of semi-circle g or f. This divides the field into three parts, of which the two outer are bright whilst the central one is dark and vice versa. This arrangement helps us to find the position of equal illumination very easily. Other type of quartz piece consists of a semi-circular piece of quartz i in place of g or f. The effect in this case is to produce a dark centre surrounded by a bright ring or vice-versa. The plate e represents the portion of equal illumination of uniform brightness.

The Laurent polarimeter is shown in figure (4). The end A is directed towards the source of light and contains a lens for

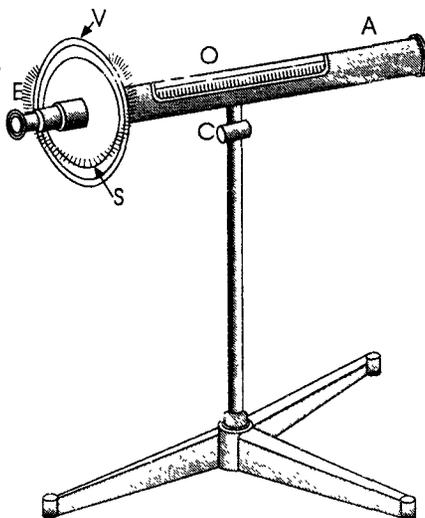


Fig. 4 : Laurent polarimeter

rendering the light parallel, the polariser is situated a little farther along the tube A. The observation tube O lies in the through between the polariser and the analyser, and is usually protected from extraneous light by a closed type of box. The analyser is placed in the tube E close to the graduated disc S. The analyser tube is fastened to the graduated disc and on rotating this tube, the disc moves past a vernier V. The graduated disc S is divided into degrees and the vernier is divided into 25 divisions which are equal to 24 divisions of the disc, so that the angle can be read upto 0.1° . The graduation varies with different types of polarimeters.

A suitable source of monochromatic light is to be used and in most of the experiments sodium flame is used.

The tube in which the liquid is taken is known as polarimeter tube [fig. (5)]. It is made of stout glass, a, with accurately ground ends. Then circular plates of glass, c serve to close the tube and these are secured by metal screw caps b and rubber washers, d. The polarimeter tubes are generally made in lengths of 0.5, 1, 2 or 4 decimeters, as the decimeter is the unit of length for all polarimetric determinations.

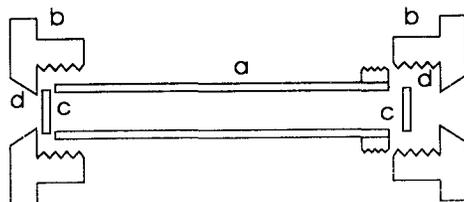


Fig. 5 : Polarimeter tube.

The following changes occur in the field on turning the analyser through 360° . To perform this, place a sodium lamp about 6 inches from the opening at the polariser end of instrument. Set the zero of the vernier on the zero of the scale. Look into the telescope. Turn the analyser slowly and continuously in the same direction and note the changes as they occur. Soon after the start, the field will be half dark and half bright. Assume that the left half is dark. On turning, the brightness of the two halves slowly approaches one another and somewhere about 90° , they attain nearly equal illumination. As the analyser is turned further, the brightness of the two halves recedes from one another and the right half becomes dark and the left bright. By this time, the tube will have been turned about 180° . At this point, the left half will become dark again and the right half bright again, but this time the change from bright to dark will be rapid. The slow change will occur again at 270° and the rapid change at 360° . Thus, there are two positions of rapid change and two of slow change. A position of rapid change should be selected for measurements, because it is easier and more accurate to judge the position of equal illumination of the field in these positions than at the position of slow change. To ascertain the position of rapid change, if an equally illuminated field is present, then a small movement of the analyser to the right will produce bright and dark halves of the field. In other words, the position of dark and bright halves will be interchanged by a very small movement of the analyser and the position of equal illumination lies between these two positions.

Determination of Zero Point of the Polarimeter : A sodium lamp is placed about 6" from the end of the polarimeter. Clean the polarimeter tube with a solution of chromic acid and then with distilled water. Fill the tube with distilled water and place it in position. While filling the tube, care must be taken to avoid the presence of air bubbles in the tube. Screw the metal cap very lightly.

The analyser tube is moved about the zero position, as marked on the graduated scale, until the field of vision is equally illuminated. It is advisable to approach this position from either side. Thus, the left half of the field may be dark and the right half bright and a small movement of the analyser tube will cause the field to become uniformly illuminated. This position is read on the scale with the help of a vernier. If the tube is now twisted a little more, the right half becomes dark, while the left half becomes bright and on turning the tube back again equal illumination is observed and the position read again. Several measurements of zero positions should be made from either side till the same value is obtained for the zero from both sides.

If the zero of the instrument does not lie exactly at the zero graduation, all readings must be corrected from the displacement of the zero. The angle by which the zero is displaced must be added to all laevo-rotations and subtracted from all dextro-rotations.

EXPERIMENT No. 1

Object : To find the specific rotation and molecular rotation of cane sugar polarimetrically and also find the concentration of the unknown solution (concentration lies between 1% and 5%). Calculate the intrinsic rotation for cane sugar.

Apparatus : Polarimeter, beaker, chemical balance, sodium vapour lamp etc.

Theory : The specific and molecular rotation of a substance are given by the following equations :

$$[\alpha]_{\lambda}^t = \frac{100R}{l.c} \quad \dots (1)$$

$$[M]_{\lambda}^t = MR/l.c \quad \dots (2)$$

where all letters have their usual significance.

The concentration of the unknown solution can be determined by means of a calibration curve, drawn between the concentration (abscissa) and rotation (ordinate).

Since specific rotation in concentrated solutions has been seen to be different from that in dilute solutions, another concentration independent function, known as *intrinsic rotation* has been given. The intrinsic rotation of a solute in a given solvent for a given wavelength of light and given temperature is the limiting value of specific rotation when concentration (c) approaches zero. This is found by extrapolating the $[\alpha]$ versus c graph to $c = 0$. So,

$$\begin{aligned} [\alpha] &= a + bc \\ &= \{\alpha\} + bc \end{aligned}$$

where $\{\alpha\}$ stands for intrinsic rotation.

Procedure : Weigh 5 g of cane sugar and dissolve it in distilled water in a 100 ml measuring flask. Now make the solution upto the mark. The solution must be absolutely clear and if necessary, it should be filtered. Then rinse the polarimeter tube with this solution and fill it, as explained before. After placing the tube, focus it as explained before.

Obtain the zero reading in the polarimeter by filling the tube with distilled water. If on placing the tube filled with solution of cane sugar, the field is dark on

the right, the substance is dextro-rotatory and if it is dark on the left, it is laevo-rotatory. Now rotate the analyser tube and obtain the position when the two halves are equally illuminated. Note this reading. Take 2 or 3 more readings and take their mean.

Now prepare 1%, 2%, 3%, 4% solutions of cane sugar, as we have already prepared a 5% solution. Determine the angle of rotation for each of these solutions. It must be kept in mind that before filling the polarimeter tube with any solution, it must be rinsed with it.

Similarly, note the angle of rotation for the unknown solution.

Observations : Room temperature = $t^{\circ}\text{C}$

Zero reading with distilled water = r°

Length of the polarimeter tube = ... dm.

S. N.	Solution of cane sugar	Reading in degrees (r_1°)	Angle of rotation, R ($R = r_1^{\circ} - r^{\circ}$)
1.	1%
2.	2%
3.	3%
4.	4%
6.	Unknown solution

Calculations : The specific and molecular rotation of cane sugar can be calculated from any solution, by using relations (1) and (2). For a 5% solution, $c = 5$.

A curve [figure (6)] is plotted between concentration (abscissa) and angle of rotation in degrees (ordinate). As seen, a straight line is obtained. From the rotation of the unknown solution, we can find out its concentration, as evident from the curve.

The intrinsic rotation is obtained from the $[\alpha]_{\lambda}^t$ versus concentration graph extrapolated to $c = 0$.

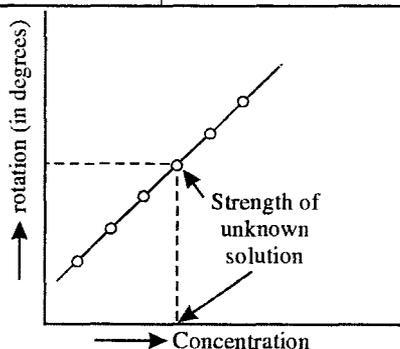


Fig. 6

Result : (1) Specific rotation of cane sugar at $t^{\circ}\text{C} = \dots$ degree.

(2) Molecular rotation of cane sugar at $t^{\circ}\text{C} = \dots$ degree.

(3) Concentration of unknown solution = ... %.

(4) Intrinsic rotation of cane sugar = ... degree.

Precautions : (i) There should be no air bubbles in the polarimeter tube.

(ii) The metal caps should be screwed very lightly, lest it may press the plate too much and strain the glass.

(iii) The glass plates must be clean and the outer surface must be dry.

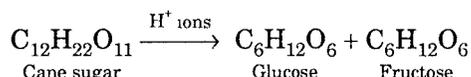
(iv) The solution should be absolutely clear.

EXPERIMENT No. 2

Object : To find out the order of reaction and velocity constant for the inversion of cane sugar by acids.

Apparatus : Polarimeter, sodium vapour lamp, beaker, stop watch etc.

Theory : Cane sugar is hydrolysed in presence of an acid giving rise to glucose and fructose.



The solution of cane sugar is dextro-rotatory in the beginning. On hydrolysis in presence of an acid say hydrochloric acid, it gives glucose (*d*-rotatory) and fructose (*l*-rotatory) in equal amounts. The laevo rotation of fructose is -92° , which is larger than the dextro rotation of glucose ($+52.5^\circ$). The mixture is thus laevo-rotatory. That is why, the hydrolysis of cane sugar is known as inversion of cane sugar.

The progress of the reaction is followed by measuring the change in the angle of rotation by means of a polarimeter. The change in rotation produced in time t , gives a measure of x , i.e., the amount of cane sugar hydrolysed. The total change in rotation produced at the end of the reaction gives a measure of a , the initial concentration of cane sugar.

The reaction is of the first order, as only the concentration of cane sugar changes during the course of reaction (**pseudo unimolecular reaction**). The concentration of water does not change appreciably, as it is present in large excess. The rate expression for a first order reaction is given by,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

where, k is the velocity constant, a is the initial concentration of cane sugar, x is the amount of cane sugar hydrolysed in time t .

For the inversion of cane sugar, we have,

$$a = r_0 - r_\infty \text{ and } x = r_0 - r_t$$

where, r_0 , r_t and r_∞ are the rotations at the start of the reaction, after time t and at the completion of the reaction, respectively.

$$\therefore k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty} \quad \dots (1)$$

Procedure : Prepare 100 ml of 5% solution of cane sugar. Now mix 100 ml of this solution with 100 ml of $N/2$ HCl in a reaction vessel. Immediately fill the polarimeter tube with this solution and start taking readings. As soon as the first reading is taken, start the stop watch. This value will correspond to the reading, r_0 , i.e., rotation value at the start of the reaction. (*The zero reading is to be taken with distilled water, before starting the actual experiment*).

Now go on taking the readings after 5, 10, 20, 30, 40, 50 minutes. Keeping the polarimeter tube as such, take the final reading after keeping the reaction mixture for 24 hours. This reading will correspond to r_∞ , i.e., reading at the completion of the reaction.

Observations : Room temperature = $t^{\circ}\text{C}$

Zero reading with distilled water = r°

S. N.	Time in minutes	Reading in degrees (r_1°)	Angle of rotation, r ($r_1^{\circ} - r^{\circ}$)	Velocity constant k in min^{-1}
1.	0
2.	5
3.	10
4.	20
5.	30
6.	40
7.	50
8.	∞

Calculations : The velocity constant for the reaction is calculated according to the equation (1). The mean of all the values is taken. This gives the velocity constant of the reaction.

The value of k is calculated for every interval of time and it is seen that the value comes out to be constant, which shows that the reaction is of the first order.

Result : (1) Order of reaction = one.

(2) Velocity constant at $t^{\circ}\text{C} = \dots \text{min}^{-1}$.

Precautions : Same as in preceding experiment.

EXPERIMENT No. 3

Object : To find out the percentage of two optically active substances such as *d*-sugar and *d*-tartaric acid in a given solution polarimetrically.

Apparatus : Same as in experiment 1.

Theory : When two solutes A and B do not interact and are optically active, the specific rotations due to the two solutes are additive. So,

$$\begin{aligned} [\alpha]_M &= c_A [\alpha]_A + c_B [\alpha]_B \\ &= c_A [\alpha]_A + (1 - c_A) [\alpha]_B \end{aligned}$$

where, c terms are the mole fractions of the solute and $[\alpha]$ terms the specific rotations. Thus,

$$\begin{aligned} [\alpha]_M &= c_A [\alpha]_A + [\alpha]_B - c_A [\alpha]_B \\ &= c_A \{[\alpha]_A - [\alpha]_B\} + [\alpha]_B \end{aligned}$$

$$\text{or} \quad c_A = \frac{[\alpha]_M - [\alpha]_B}{[\alpha]_A - [\alpha]_B} \quad \dots (1)$$

$$\text{Similarly,} \quad c_B = 1 - c_A \quad \dots (2)$$

Thus, determining the specific rotations of solutes A, B and mixture, we can calculate the amount of each solute in the mixture.

Procedure : Prepare standard solutions of *d*-sugar and *d*-tartaric acid. Determine their specific rotations as well as that of the given mixture, as described in experiment 1.

Observations : Same as described in experiment 1.

Calculations : The value of $[\alpha]_A$, $[\alpha]_B$ and $[\alpha]_M$ are calculated as described in experiment 1. From these values, the values of c_A and c_B are determined from equations (1) and (2).

Result : The mixture contains ... % sugar and ... % tartaric acid.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 4

Object : *To determine the specific rotation of turpentine oil, tartaric acid.*

This experiment can be performed as described in experiment 1.

EXPERIMENT No. 5

Object : *To determine the relative strength of acids.*

An acid is a substance which gives H^+ ions in solution. It is observed that the rate of inversion of cane sugar is affected by changing the concentration of H^+ ions, which is a measure of its strength.

The inversion of cane sugar is studied (as in experiment 2) by taking equinormal solution of acids say HCl , H_2SO_4 , HNO_3 etc. The velocity constants are calculated in each case. Suppose the values are k_1, k_2, k_3 for the reaction while using HCl , H_2SO_4 , HNO_3 . Then,

Strength of HCl : Strength of H_2SO_4 : Strength of $HNO_3 = k_1 : k_2 : k_3$

EXPERIMENT No. 6

Object : *To determine the specific rotation of camphor in benzene or carbon tetrachloride.*

Proceed as in experiment 1.

EXPERIMENT No. 7

Object : *To determine the intrinsic rotation of a solution of cane sugar polarimetrically.*

Since specific rotation in concentrated solutions has been found to be different from that in dilute solutions, another concentration independent function known as intrinsic function has been defined. *Intrinsic rotation of a solute in a specified solvent for a specified wavelength of light and temperature is the limiting value of specific rotation when c approaches zero.* Thus, a graph is plotted between specific rotation values (Y -axis) and concentration of the solute (X -axis) and the curve is extrapolated to $c = 0$, as

Intrinsic rotation = $\lim_{c \rightarrow 0}$ Specific rotation.

Proceed as explained in experiment 1.

EXPERIMENT No. 8

Object : *To study the influence of solvent on the optical rotation of a solute.*

For this purpose, take 50 ml of 5% cane sugar solution and add to it 50 ml of any solvent, say alcohol, acetone etc. Measure the angle of rotation of this solution and calculate the specific rotation of cane sugar. Similarly, find the specific rotation of a 2.5% solution of cane sugar and compare the values.

EXPERIMENT No. 9

Object : *To study the influence of added impurity on the rotation of a solute.*

This can be studied by taking a number of electrolytes and non-electrolytes and mixing them with cane sugar solution one by one and finding the angle of rotation in each case.

Proceed as in experiment 1 and tabulate the results accordingly.



An electric current flowing through an electrolyte, like a current flowing through a metallic conductor is governed by Ohm's law, according to which, '*the current strength (I) is directly proportional to the difference of potential (E) between the two ends of the conductor through which the current is flowing.*' Thus, mathematically,

$$I \propto E \text{ or } I = A.E \text{ or } I.R = E$$

where, R and A are constants. The ratio $\frac{E}{I}$ is the resistance of the circuit to the passage of electric current and so the constant R is known as *resistance*. The term A is known as **conductance**. It is clear, that $A = \frac{1}{R}$.

If a unit current is driven by unit electromotive force through a circuit, then according to Ohm's law, the circuit has unit resistance. The units of *current strength*, *electromotive force* and *resistance* will be *ampere*, *volt* and *ohm*, respectively.

The conductance of a substance, *i.e.*, its power of conducting an electric current, is thus reciprocal of the resistance. The resistance R of a conductor at a fixed temperature is directly proportional to its length l cm and inversely proportional to its area of cross-section a cm². Thus,

$$R \propto \frac{l}{a} \text{ or } R = \rho \cdot \frac{l}{a}$$

where, ρ is a constant, known as *specific resistance* which is dependent on the nature of the substance.

If $l = 1$ cm and $a = 1$ cm², then $\rho = R$ ohm. Thus, specific resistance is defined as, '*the resistance in ohm offered by a cube of 1 cm dimensions or by a conductor of 1 cm length and 1 cm² area of cross-section.*'

It will be observed that a conductor of low resistance will have a high conductivity. So, the conductance of a column of material 1 cm long and 1 cm² cross-section is known as the **specific conductivity** of the substance.

$$\therefore \text{Conductance} = \frac{1}{\text{Resistance}}$$

$$\therefore \text{Specific conductance } (\kappa) = \frac{1}{\text{Specific resistance } (\rho)}$$

Since conductance is reciprocal of ohm, therefore, its unit will be **ohm⁻¹** or **mho⁻¹**.

A knowledge of the conductivity of solution does not lead very far in physico-chemical work, because the conductivity of a solution is not due to the whole of the material lying between the electrodes, but it is also due to the dissolved substance. Hence, to obtain conductivity which must be comparable, it should be represented as function of the concentration of the dissolved substance. Thus, there are two such quantities which are generally used, *viz.*, equivalent conductivity and molecular conductivity.

Equivalent Conductivity : It is the conductivity of a solution containing one gram equivalent of an electrolyte, when measured between electrodes one cm apart. It is represented by the symbol λ .

Molecular Conductivity : It is the conductivity of a solution containing one mole of an electrolyte, when measured between electrodes one cm apart. It is represented by the symbol μ .

The specific conductivity, equivalent conductivity and molecular conductivity of an electrolyte are connected by the following relations :

$$(i) \lambda_v = \kappa_v \times V, \quad (ii) \mu_v = \kappa_v \times V$$

where, in equation (i), λ_v is the equivalent conductivity of a solution at any dilution $V \text{ cm}^3$, and κ_v is the specific conductivity and V is the dilution in cm^3 containing one gram equivalent of an electrolyte. In equation (ii), μ_v is the molecular conductivity and V is the volume in cm^3 containing one gram mole of an electrolyte.

Measurement of Conductivity of a Solution : The resistance of a metallic conductor, say a wire, is measured by means of a Wheatstone bridge, which consists of a system of resistance R , S and AC [fig. (1)], connected as shown. R represents a known resistance, usually a resistance box, S is an unknown resistance and AC is a uniform meter wire, B is a battery connected to the two ends A and C of the wire.

The current may flow along two paths ABC and ADC . The total fall of potential along the two paths is the same, so there must be a point D on the wire AC at which the potential is the same as that at B , the point of contact between the unknown resistance S and known resistance R .

Such a point can be found by joining one terminal of the galvanometer G to B , and the other to a sliding contact, called *jockey*, which can be moved along the wire AC . At every point other than D , the current will flow through the galvanometer and so there will be a deflection. But at D , the potential is the same as at B , therefore, no current will flow through the galvanometer. Thus, there will be no deflection in the galvanometer. At this stage, according to Wheatstone's principle,

$$\frac{\text{Resistance } R}{\text{Resistance } S} = \frac{\text{Resistance of wire } AD}{\text{Resistance of wire } DC}$$

Since the wire is uniform, the resistance of the wire will be proportional to its length, therefore,

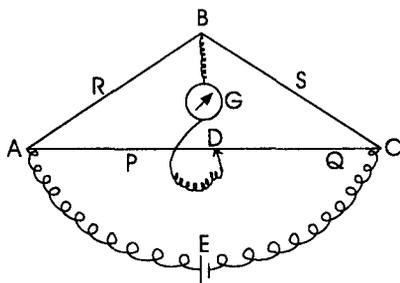


Fig. 1 : Wheatstone bridge

$$\frac{\text{Resistance R}}{\text{Resistance S}} = \frac{\text{Length AD}}{\text{Length DC}}$$

$$\therefore \text{Resistance S} = \frac{\text{Length DC}}{\text{Length AD}} \times \text{Resistance R}$$

Thus, the unknown resistance S can be calculated, as all the quantities on the right side are known.

The above arrangement is somewhat modified while measuring the resistance of a solution. When a direct current is passed through a solution, the following two difficulties arise :

(a) The electrodes are polarised, i.e., the products of the electrolysis accumulate on them.

(b) The passage of current involves the composition of a portion of the solute, so the concentration of this substance changes during the passage of electric current.

In order to remove the above difficulties, we use alternating current in place of direct current. It is obtained in laboratory from the secondary coil of a small induction coil. The galvanometer becomes useless while using alternating current, which is then replaced by a head phone. The arrangement is shown in fig. (2). The sliding contact is moved slowly along the wire AB, till a point X is reached at which

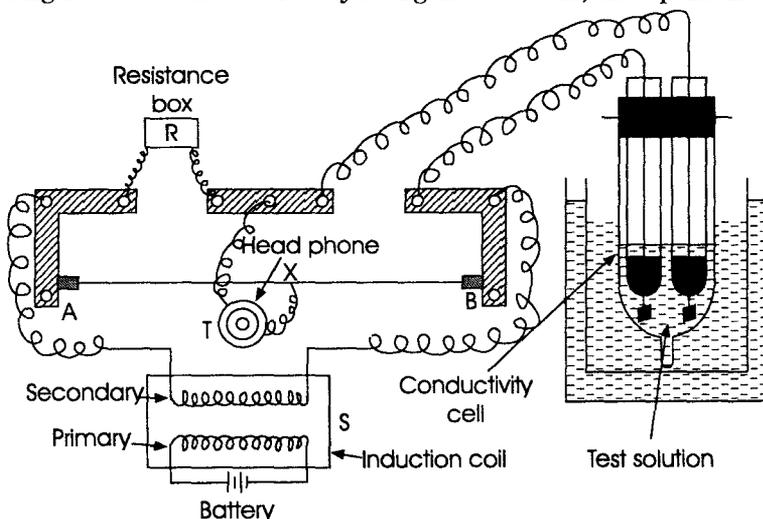


Fig. 2 : Measurement of conductivity

the potential becomes equal to that of R. Under such condition, minimum current will flow through the head phone and it will give a minimum sound. At all other points, a buzzing sound can be heard in the head phone. *In actual practice, it is not usually possible to obtain complete silence in the head phone so, the point of minimum sound is taken as the null point of the experiment.* The low sound in the headphone is due to imbalance between the capacitance factors of the cell and the resistance box.

The source of electric power is usually an oscillator which is operated by a battery or mains. However, these days built up direct reading units are available for determining conductance, as mentioned below. These units may be used for titration purposes and approximate measurement of conductance but are not so

good for accurate measurements of conductance as the assembled *Kohlrausch bridge* (described above) or modified forms like *Wayne-Kerr bridge*.

Magic Eye Type Conductivity Bridge : In the Kohlrausch type bridge, headphone is used as detector and the apparatus is kept in a room free from noise. Now-a-days, the headphone detector has been replaced by visual devices such as *magic eye* or an *electronic detector*. Several manufacturers like Elico, Toshniwal, Philips market conductivity bridges by incorporating a magic eye circuit. (*The method of operation of an instrument depends on its make and so the manual supplied by the manufacturers must be read thoroughly or the teacher must be consulted before handling such an instrument*).

The usual controls provided on these units are shown in figures [3(a) and 3(b)].

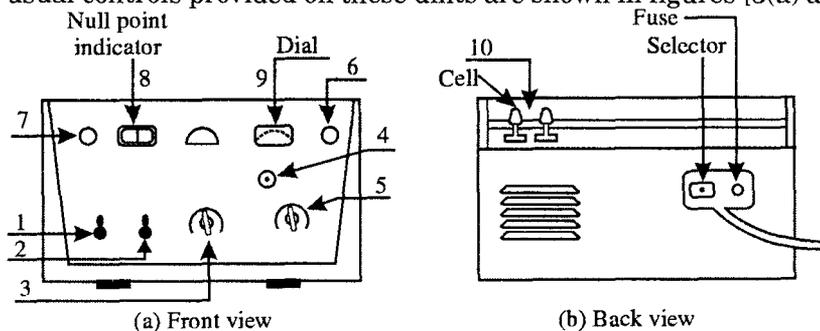


Fig. 3 : A conductivity bridge.

[I] Description of Controls

1. Off/On switch : In figure [3(a)], there is a knob which when turned clockwise, makes the instrument switched on. The fuse and mains voltage selector are usually situated at the back of the instrument [fig. 3(b)]. This switch is marked 'bridge source'.

2. Frequency selector switch : By means of this switch the bridge can be made to work on a frequency of 50 or 1000 cycles sec^{-1} . For low conductance measurements ($< 10^{-5}$ mho) set it on 50 cycles sec^{-1} , while for high conductance measurements (0.1 to 10^{-5} mhos) set it on 1000 cycles sec^{-1} .

3. Range multiplier or range selector switch : This is a ten position rotatory switch. By means of this switch, any one of the 5 resistance multiplication ranges or the corresponding 5 conductance multiplication ranges can be selected. In order to get the actual resistance (or conductance), the dial reading should be multiplied by the indicated factor set in on the range multiplier.

4. Coarse balance control : By rotating this knob, the bridge is balanced to nearest 0.1 division marking on the dial.

5. Fine balance control : By rotating this knob, a finer balance can be obtained and its full rotation corresponds to $- 0.1$ to $+ 0.1$. This reading should be added to or subtracted from the main dial reading.

6. Zero correction or phase control : This control corrects the resistance unbalance. By rotating this knob, a variable capacitor can be changed to obtain a sharp balance indication or the sharp edges of the green glow in the magic eye.

This is not effective in high conductances and at the lower bridge frequency (50 cycles sec^{-1}) setting. However, this will be effective only for very low conductance measurements and for solutions of high dielectric constant.

7. Sensitivity control : This knob varies the sensitivity of the null detecting amplifier. The control should be set near the minimum position while obtaining rough balance and then the sensitivity should be increased for getting a sharp balance.

8. Null point indicator or magic eye : This panel window shows the *magic eye* null detector. The minimum glow shows null point or in other words the maximum gap between the two sharp ends of green glow is the null point (maximum shadow position).

9. Dial : This graduated dial can be seen through the other panel window. The dial is divided into 110 equal divisions of 0.1 each (from 0.5 to 10.5).

10. Conductivity cell terminals : The conductivity cell is to be connected to the terminals marked 'cell'.

On the back side of the instrument, a connecting lead with three-pin mains plug is provided. It is to be connected to the 220–230 V, 50 c/s. Two terminals marked 'Battery' are also placed on the back side so as to operate the instrument with battery.

[II] Operation

For starting the operation, connect the three-pin mains plug to 220-230V, 50 c/s. Connect the terminal marked 'Earth' to a water tap or any other good electrical earth connection. This prevents the fluctuation in the magic eye null point detector with voltage fluctuations. To reduce the voltage fluctuations, a voltage stabiliser may be used. Now switch on the instrument by turning slightly the off/on switch clockwise. Allow the instrument to warm up for nearly 30-45 seconds. A green glow in the magic eye shows that the instrument is ready for use.

Connect the well cleaned cell to the terminals marked *cell*. Take the sample solution in a small (100 ml capacity) clean beaker and immerse the cell so that the platinum electrodes of it are dipped about 1 cm below the surface of the solution. Set the 'Sensitivity' control switch at a position where a slight parting of the green glow, i.e., small shadow in the magic eye is seen. Turn the range selector switch step-by-step and set in on a range where the parting of the green glow (shadow) is maximum. Now increase the sensitivity of null detection and obtain a more precise balance. This can be done by putting dial on nearest 0.1 division marking and adjusting 'Fine Balance' control till the balance is obtained.

Now adjust the 'Zero Correction' control to balance off the reactance component. This operation is effective for higher frequency use and for high resistance readings only. Rotate this control till a sharp edge of the green glow towards the shadow is obtained.

The 'Fine Balance' indication should be added or subtracted, as the case may be, from the main dial reading. The resulting value is then multiplied by the factor shown by the 'Multiplier' to give the resistance (or conductance) of the sample solution.

To obtain the specific conductance of the solution, the measured conductance is multiplied by the cell constant. So,

Specific conductance (in micro mho cm^{-1} or micro siemen cm^{-1})

$$= \text{Cell constant} \times \text{Measured conductance (in micro mho)}$$

$$= \text{Cell constant} \times \frac{10^6}{\text{Measured resistance (in ohm)}}$$

The above measurement can be easily explained by considering the following example.

Example : A 0.1 normal solution when measured on the bridge with a cell of cell constant 0.4 cm^{-1} gave the following results.

Main Dial (Coarse Balance) = 3.5

Fine balance reading = + 0.05

Multiplier range = 10^4 in conductance (micro mho).

Calculations :

$$\begin{aligned} \text{Observed conductance} &= (3.5 + 0.05) \times 10^4 \\ &= 3.55 \times 10^4 = 35500 \text{ micro mho} \end{aligned}$$

$$\begin{aligned} \text{Specific conductance} &= 0.4 \times 35500 \\ &= 14200 \text{ micro mho cm}^{-1} \\ &= 0.0142 \text{ ohm}^{-1} \text{ cm}^{-1} \\ &= 0.0142 \text{ siemen cm}^{-1} \end{aligned}$$

Induction Coil : The coil [fig. (4)] used for the determination of the resistance of the solutions should be small and should have comparatively less windings. If large coil is used, large current will be sent through the solution which will then set up polarisation. The hammer should be light and should vibrate very rapidly, thus producing a high pitched note in the head phone, which is more easily distinguished than a low pitched note. The coil may be worked from a small accumulator or dry cell.

Sometimes, it becomes difficult to differentiate between the noise of the hammer and the sound in the head phone. This difficulty can, however, be removed with a little practice and even if it persists, the induction coil can be covered with a felt-lined box or the coil may be removed from the operator as far away as possible.

Conductivity Cells : The vessel in which the measurement of conductivity of solution is to be made is known as *conductivity cell*. These are of various shapes and sizes depending upon the nature of the solution taken. They are made of some form of *resistance glass* and are provided with a pair of platinum electrodes fused into glass tubes and supported by an ebonite cover, which is fitted into the vessel, so that the distance between the electrodes may not change. Some cells are shown in figures (5), (6) and (7).

For ordinary measurements, the cells can be of the types shown in figures (5), (6) and (7). The type [5 (a)] is used for solutions of electrolytes which conduct well, while type [5 (b)] is for poorly conducting solutions. Electrical connections are made

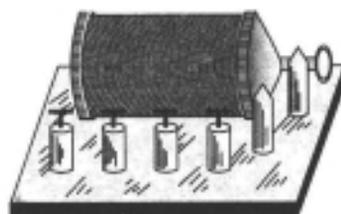


Fig. 4 : Induction coil

by means of mercury which can be poured into the glass tubes. Cell of type shown in fig. (6) can be used for liquids which conduct very well. In this type, the electrodes are moveable, thus making the cell suitable for solutions of conductance extending over a wide range. For example, if a very good conductor such as hydrochloric acid is used, then the electrodes are placed such that a long column of liquid lies between them. On the contrary, for solutions which conduct less, but still are good conductors, the electrodes are moved down the glass tubes, thus shortening the column of liquid between them. Another form of conductivity cell is also shown in figure (7).

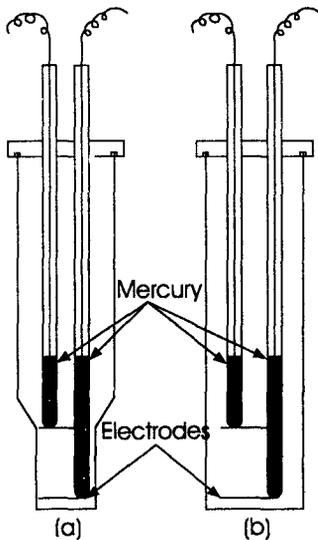


Fig. 5 : Conductivity cell.

Since conductivity varies with temperature, it increases about 2% per degree, it is advisable to keep the cell containing the solutions in a thermostat or a constant temperature bath, while making observations.

Platinising the Electrodes : The electrodes used in conductance measurement must be prepared with utmost care. Bright platinum electrodes give satisfactory results when the conductance of the solution is less than $4 \times 10^{-4} \text{ ohm}^{-1}$. For solutions of higher conductance, the electrodes must be coated with platinum black. Such coated electrodes give satisfactory results when the conductance of the solution varies from 0.2 to 0.04 ohm^{-1} . It is advisable to use platinum electrodes in all conductivity measurements, except where the platinum black is likely to catalyse the decomposition of the solutions.

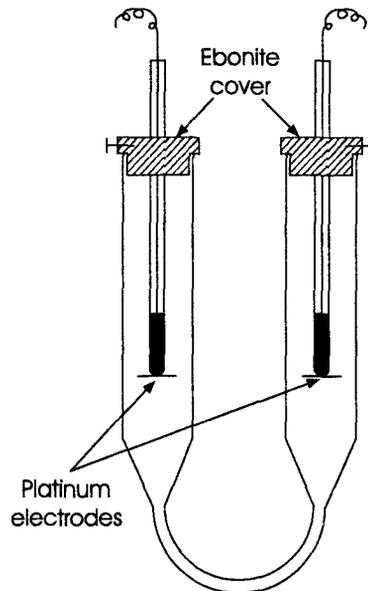


Fig. 6 : Conductivity cell.

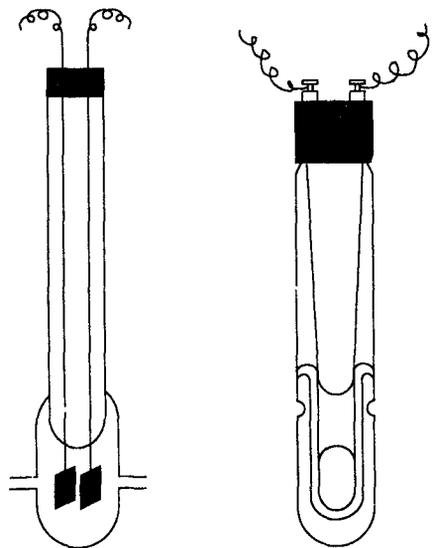


Fig. 7 : Conductivity cell.

Before platinising the electrodes they are first washed with warm chromic acid to remove all greasy matter and then with distilled water. They are then immersed in solution consisting of 3 gram of chloroplatinic acid and 0.02 – 0.03 gram of lead acetate in 100 ml of distilled water. The electrodes are then placed in an inclined position to facilitate the removal of any gas formed during electrolysis. The electrodes are connected through a variable resistance and a reversing switch with a battery of two lead accumulators, so that they serve as electrodes in the electrolysis of platinum solution. The current is passed for 15-20 minutes, its direction being reversed every half a minute. The current should be so regulated that the rate of evolution of gas from the electrodes is not very rapid. The electrodes will then be coated with a black, velvety, coherent deposit of platinum black. The electrodes thus prepared will contain gases and small quantities of the platinising liquid, occluded in the platinum black. To remove this, the electrodes are placed in dilute sulphuric acid and current is passed for about half an hour, its direction being reversed every minute. The electrodes are then washed with warm distilled water and left standing in it till they are required for use.

Conductivity Water : Ordinary distilled water possesses so large a conductance due to the materials dissolved from the container and due to carbon dioxide and ammonia dissolved from the air, that it is quite unsuitable to prepare solution for conductivity measurements. Hence, water is specially purified before it can be used. Such water is known as **conductivity water**. It should have a conductivity not more than 2 to $3 \times 10^{-8} \text{ ohm}^{-1}$. The purest water obtained has been found to have a conductivity $5.54 \times 10^{-8} \text{ ohm}^{-1}$, but it loses its high resistivity on standing in air for a long time or by dissolving materials from the walls of the closed vessel.

Conductivity water can be prepared in laboratory by distillation process. An apparatus similar to that for steam distillation is shown in figure (8). The inner tube of the condenser D must be of jena or silica glass. The turn down joint C

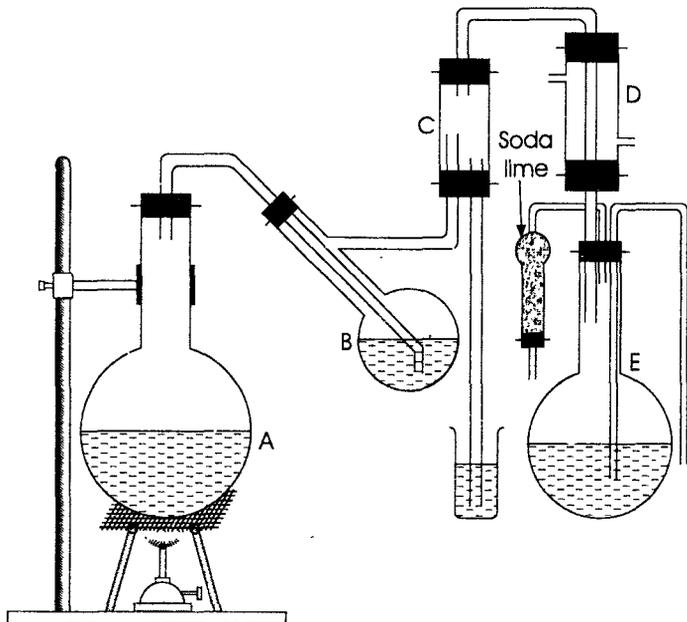


Fig. 8 : Preparation of conductivity water

prevents the contamination of the distillate by drainage from the bung of the condenser tube. If a silica tube is used in the condenser, a straight type of joint C will be necessary and the flask B must then be of hard glass. To increase the speed of distillation, connecting tubes must be lagged.

To about 2 litre of distilled water, add 8–10 crystals of potassium permanganate and 2–3 crystals of sodium hydroxide. Boil the solution for 10–15 minutes before connecting it to the flask B. After connecting, continue boiling but allow the distillate to condense in B until a sufficient quantity (75–100 ml) is obtained which then can serve as a trap for alkaline splash. Subsequent condensation in B should be prevented by placing a small flame below it. The water should be received from the condenser in hard glass flask, which has been thoroughly steamed out, and which is closed by a cork that has been soaked in molten paraffin wax, carrying a soda lime tube and a syphon to transfer the water, as required. Conductivity water should not be preserved for more than a week. It is, however, advisable to use conductivity water which has been freshly prepared.

EXPERIMENT No. 1

Object : *To find out the cell constant of the conductivity cell and find out the equivalent conductivity of a solution of barium chloride at various dilutions. Also infer the results obtained.*

Apparatus : Conductivity cell, Wheatstone bridge with all components, beakers, burette etc.

Theory : We know that the specific conductivity of a solution is the conductivity of 1 cm^3 of the solution. The observed conductivity will be equal to the specific conductivity, if the distance between the electrodes is 1 cm and their area of cross-section is 1 cm^2 as,

$$R = \rho \times \frac{l}{a}$$

or

$$\frac{1}{R} = \frac{1}{\rho} \times \frac{1}{l/a}$$

$$\therefore \text{Observed conductivity} = \text{Specific conductivity} \times \frac{1}{l/a}$$

If $l = 1 \text{ cm}$, and $a = 1 \text{ cm}^2$, then,

Specific conductivity = Observed conductivity.

If, however, the above conditions are not fulfilled (which are very difficult in actual practice), then the observed conductivity must be multiplied by a factor $\frac{l}{a}$, say x in order to get the value of specific conductivity. The values of l and a are constants for a particular cell and so, $\frac{l}{a}$ is constant which is known as **cell constant**.

$$\therefore \text{Specific conductivity} = \text{Observed conductivity} \times \text{Cell constant}$$

The cell constant is determined by taking a solution of known specific conductivity in the cell and from the observed conductivity measured, the value of

x can be calculated. Solutions of potassium chloride of known concentration and known conductivity are used in the determination of cell constant.

If we take $N/50$ potassium chloride solution in a conductivity cell, say at a temperature 25°C , then,

$$\text{Cell constant} = \frac{\text{Specific conductivity}}{\text{Observed conductivity}} = \frac{0.002768}{\text{Observed conductivity}} \quad \dots (1)$$

Specific conductivity of KCl solutions in $\text{ohm}^{-1} \text{cm}^{-1}$

Temperature ($^{\circ}\text{C}$)	N	0.1N	0.02N	0.01N
0	0.0654	0.00716	0.001522	0.000776
5	0.0740	0.00822	0.001752	0.000895
10	0.0832	0.00932	0.001995	0.001019
15	0.0925	0.01048	0.002243	0.001147
20	0.1020	0.01167	0.002501	0.001278
25	0.1120	0.01289	0.002768	0.001412
30	0.01412	0.003036	0.001552

The equivalent conductivity of a solution of barium chloride is calculated from the formula ($\lambda_v = \kappa_v \times V$), where V is the volume in cm^3 containing one gram equivalent of an electrolyte. Similar experiments are performed at various dilutions and we see that the equivalent conductivity increases with dilution.

Procedure : Set up and connect the apparatus as shown in figure (2). The conductivity cell is first cleaned and supported in a thermostat in such a way that it is immersed upto within 1" of the top. The connections are made as shown.

Prepare $N/50$ solution of potassium chloride. Now wash the electrodes with this solution and then introduce it till the electrodes are immersed in the solution. Any air bubbles sticking to the side of the cell or electrodes are removed. The cell is then immersed in a large beaker of 2-3 litre capacity, which can work as a water thermostat.

Now some resistance is taken out from the resistance box R, which is approximately equal to the resistance of the solution in the cell. This can be observed by getting the null point nearly at the centre of the meter wire, AB. The point of minimum sound in the head phone is now obtained by sliding the jockey along the wire AB. Now measure the lengths AX and BX or simply note the position of the jockey X.

Take 2-3 more readings by changing the resistance in the box R, but see that the null point lies somewhere in the middle of the wire.

After determining the cell constant, remove the potassium chloride solution and wash the electrodes with conductivity water several times. Then prepare a normal solution of barium chloride (stock solution).

Also prepare $N/10$, $N/20$, $N/50$, $N/100$... $N/10000$ solutions of barium chloride by diluting the stock N -solution accordingly.

Rinse the cell with N -solution of barium chloride and introduce it in the cell till the electrodes are completely immersed. Allow the solution to reach the constant temperature of the water thermostat. Then determine its observed conductivity, as explained before.

Empty the cell and then wash the electrodes and the cell with distilled water and finally with $N/10$ solution of barium chloride. Introduce this solution into the cell, till the electrodes get immersed. Again determine its observed conductivity, as usual. Now repeat the process of emptying the cell, washing the electrodes and cell with distilled water and then with that solution which is to be taken in it. Then take the readings for observed conductivity as usual, in the case of all other solutions.

After finishing the experiment, wash the cell with conductivity water and keep it immersed in it. Note that the cell must never be left dry.

Observations : (1) For the determination of cell constant

Temperature = $t^\circ\text{C}$

Strength of KCl solution	Resistance (R)	Reading of the jockey (length AX)	Length BX (100—AX)	Observed conductivity, $C = \frac{AX}{BX} \times \frac{1}{R}$
$N/50$
	Mean value
	= ...

(2) For equivalent conductivity of BaCl_2 solutions

Cell constant =

S.N.	Strength	V (cm ³)	Observed conductivity	Specific conductivity	Equivalent conductivity
1	N	1,000
		

Calculations : (i) Calculation of cell constant : The cell constant is calculated according to equation (1).

The value of specific conductivity of $N/50$ KCl solution at the room temperature can be noted from the table. On substituting the mean value of observed conductivity, we can easily calculate the cell constant.

(ii) Equivalent conductivity of BaCl_2 solutions : The calculated observed conductivity for say N solution is multiplied by the cell constant to get its specific conductivity. On multiplying the specific conductivity by V , volume in cm³ containing one gram equivalent of the electrolyte (in this case, $V = 1000$), we get the value of equivalent conductivity. Similarly, the values of the equivalent conductivity can be calculated for other dilutions. From the values we infer that the equivalent conductivity of barium chloride solution increases with dilution.

Results : (i) Cell constant = ...

(ii) The equivalent conductivity of an electrolyte increases with dilution.

Precautions : (i) The electrodes must be platinised.

(ii) The cell should never be kept dry.

(iii) The electrodes must always be washed with that solution which is to be filled in it.

(iv) The point of minimum sound should be very carefully found in the head phone.

Important : Now-a-days, the Wheatstone bridge is seldom used in laboratories. In its place automatic conductivity bridges are in vogue now, which directly give the value of either observed conductivity or observed resistance. Whole of the system is built in. Some conductivity bridges are A.C. mains operated and some are battery operated. In India, several firms are supplying conductivity bridges and to mention a couple of them they are Philips, Toshniwal etc. as discussed earlier. There are also Serfass conductivity bridge, Pye conductivity bridge etc, which are, of course, imported articles.

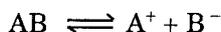
In the following experiments, we will be working with the help of built-in conductivity bridge, instead of using a Wheatstone bridge. However, the equations and principles remain the same. If any student wants to perform the succeeding experiments by the older Wheatstone bridge, he can do so by, using the same equations.

EXPERIMENT No. 2

Object : To determine the dissociation constant of acetic acid and verify Ostwald's dilution law.

Apparatus : Mains operated conductivity bridge, thermostat, beakers, measuring flasks, burette etc.

Theory : The ionisation of a weak electrolyte AB can be represented as:



On applying the law of mass action, we get,

$$K = \frac{[A^+][B^-]}{[AB]} \quad \dots (1)$$

where, K is the dissociation constant of the substance AB. If we start with 1 mole of an electrolyte and if α be its degree of ionisation, (fraction of the total salt ionised), then the amounts of A^+ , B^- and undissociated AB at equilibrium will be α , α and $(1 - \alpha)$, respectively. If V litres be the total volume of the system, then,

$$[A^+] = \frac{\alpha}{V}; [B^-] = \frac{\alpha}{V}; [AB] = \frac{1 - \alpha}{V}$$

Hence, from equation (1), we have,

$$K = \frac{\alpha^2}{(1 - \alpha)V} \quad \dots (2)$$

For a weak electrolyte, the value of α can be neglected in comparison to unity, hence $(1 - \alpha) \approx 1$. Therefore,

$$K = \frac{\alpha^2}{V} \quad \dots (3)$$

Equations (2) and (3) are known as expressions of **Ostwald's dilution law**.

The value of dissociation constant (K) of a weak electrolyte can be calculated from equation (2) or (3), provided the degree of ionisation at a particular dilution is known. The value of α is calculated from conductivity value, as it is given by,

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

where, λ_v = equivalent conductivity at any dilution $V \text{ cm}^3$

λ_∞ = equivalent conductivity at infinite dilution.

The value of λ_∞ , according to Kohlrausch's law is given by,

$$\lambda_\infty = \lambda_a + \lambda_c$$

where λ_a and λ_c are the ionic conductances of the anion and cation of the substance in question. These values are fixed for an ion and can be seen from the tables.

In order to verify Ostwald's dilution law, we find the dissociation constant of the given substance at several dilutions. If the values come out to be constant, then the law is verified, otherwise not.

Procedure : First the cell constant is determined as described in experiment 1. An approximate $N/2$ solution is first prepared by diluting the glacial acetic acid (The strength of the acid should be more than $N/2$). It is then titrated against $N/2$ NaOH solution and exact strength determined. It is then diluted to get exact $N/2$ solution. It can be treated as a stock solution. Clean and dry the conductivity cell. It is then washed with $N/2$ acetic acid solution and its observed resistance determined, as usual. Then we prepare $N/4$, $N/8$, $N/16$, $N/32$, $N/64$, $N/128$ solutions of acetic acid from the stock $N/2$ solution by proper dilution by using conductivity water. The cell is then washed with each solution in turn and observed resistance is measured, as usual.

Observations : Cell constant, $x = \dots\dots$

$$\lambda_\infty \text{ for } \text{CH}_3\text{COOH} = \lambda_{\text{H}^+} + \lambda_{\text{CH}_3\text{COO}^-} = \dots$$

S.N.	Strength of acetic acid	V (litres)	Observed resistance (R)	Observed conductivity (1/R)	Equivalent conductivity (λ_v)	Degree of ionisation (α)
1.	$N/2$		2	
2.	$N/2$		4	
...	

Calculations : The degree of ionisation, α of acetic acid at any dilution is calculated as,

$$\alpha = \frac{\lambda_v}{\lambda_\infty} = \frac{\lambda_v}{\lambda_a + \lambda_c}$$

Once the value of α is known, we can calculate the values of K , the dissociation constant of acetic acid at every dilution from expression (3).

We see that the values of K come out to be constant which proves the validity of Ostwald's dilution law.

Result : The dissociation constant of acetic acid is $\dots\dots$ and Ostwald's dilution law is applicable to it.

Precautions : Same as in preceding experiment.

EXPERIMENT No. 3

Object : To find out the equivalent conductivity of strong electrolytes at different dilutions and from them find out the equivalent conductivity of a weak electrolyte at infinite dilution.

Apparatus : Same as in preceding experiments.

Theory : Strong electrolytes are those substances which are practically completely ionised at all dilutions, whilst weak electrolytes are slightly ionised at low dilutions. The conductivity of an electrolytic solution changes with dilution due to an increase in the number of ions and their mobility.

The conductivity of strong electrolytes increases with dilution and this is mainly due to the increased mobility of the ions. Debye, Huckel and Onsager gave the following expressions for the conductance of strong electrolytes.

$$\lambda_v = \lambda_\infty - [A + B \lambda_\infty] \cdot \frac{1}{\sqrt{V}}$$

or
$$\lambda_v = \lambda_\infty - [A + B \lambda_\infty] \cdot \sqrt{C} \quad \dots (1)$$

or
$$\lambda_c = \lambda_0 - [A + B \lambda_0] \sqrt{C}$$

where, A and B are constants, which depend upon temperature and nature of the solvent, V is the volume in litre containing one gram mole of an electrolyte and C is the concentration in mole per litre. If we plot a curve between λ_v and \sqrt{C} at different dilutions, we get a straight line, whose intercept is equal to λ_∞ at $C = 0$. The values of A and B for uni-univalent electrolytes are 59.78 and 0.2273, respectively.

In case of weak electrolytes, the value of λ_∞ cannot be obtained directly by extrapolation to infinite dilution of results obtained at finite concentrations. However, it can be calculated from the λ_∞ values of strong electrolytes, according to Kohlrausch's law. For example, the value of λ_∞ for a weak electrolyte, say CH_3COOH can be easily determined from λ_∞ values of strong electrolytes, *e.g.*, HCl , NaCl and CH_3COONa , which can be calculated from equation (1).

$$\lambda_\infty (\text{CH}_3\text{COOH}) = \lambda_\infty (\text{HCl}) + \lambda_\infty (\text{CH}_3\text{COONa}) - \lambda_\infty (\text{NaCl}) \quad \dots (2)$$

Procedure : The cell constant is determined as usual (cf. expt. 1). Stock solution ($N/10$) of each electrolyte HCl , NaCl and CH_3COONa can be prepared as usual. From this stock solution, $N/20$, $N/40$, $N/80$, $N/160$, $N/320$ solutions of each electrolyte are prepared by dilution method. The conductivity cell is washed with each electrolytic solution in turn and observed resistance measured, as usual.

Observations : Cell constant, $x = \dots$

Electrolyte	Concentration in mole/litre	Observed resistance	Observed conductivity	Equivalent conductivity
HCl	...			}
	...			
NaCl	...			
	...			
CH_3COONa	...			
	...			

Calculations : A curve is plotted with equivalent conductivity of say HCl , as ordinate against \sqrt{C} as abscissa. The curve, which is a straight line is extrapolated

to $C = 0$. The value of the intercept on the ordinate gives the value of λ_{∞} for HCl. Similarly, find the values of λ_{∞} for NaCl and CH_3COONa .

Now calculate the values of λ_{∞} for CH_3COOH , with the help of equation (2).

Result : Equivalent conductivities at infinite dilution of :

(i) HCl =

(ii) NaCl =

(iii) CH_3COONa =

(iv) CH_3COOH =

Precautions : As in preceding experiments.

EXPERIMENT No. 4

Object : To determine the equivalent conductivity of a strong electrolyte (say KCl, NaCl, AgNO_3 , HCl) at several concentrations and verify the applicability of Debye-Huckel- Onsager equation.

Apparatus : Same as in preceding experiments.

Theory : Same as in experiment no. 3.

Procedure : Prepare 200 ml of 0.1N (exact) solution of any electrolyte, say KCl in conductivity water. Then prepare 0.02, 0.01, 0.002, 0.001, 0.0005N solutions by appropriately diluting 0.1N solution. The conductance of the solutions can be measured by using cells of high and low cell constants for concentrated and dilute solutions, respectively as described in experiment no. 1.

Observations and Calculations : The equivalent conductances of all solutions are calculated as described in preceding experiments. Plot a curve between λ_c (Y-axis) and \sqrt{C} (X-axis). The curve will be a straight line at high dilutions. It is then extrapolated to zero concentration. The intercept on Y-axis gives the value of λ_0 and the slope of this line will be $-(A + B \lambda_0)$. Its value can be compared by using the standard values of A (59.78) and B (0.2273).

Result : Debye-Huckel-Onsager equation is valid for KCl at high dilutions.

EXPERIMENT No. 5

Object : To determine the basicity of an acid, say citric acid conductometrically.

Apparatus : Same as in preceding experiments.

Theory : Ostwald showed that the equivalent conductivity of sodium salt of monobasic acids increases by approximately 10.8 units when diluted from $N/32$ to $N/1024$. Similarly, the equivalent conductivity of the normal sodium salt of dibasic acid increases by 21.6 units and that of tribasic acid by 32.4 units. In general, the equivalent conductivity of the normal sodium salts increases by $10.8B$ units when they are diluted from $N/32$ to $N/1024$, where B is the basicity of the acid.

$$\therefore B = \frac{\lambda_{1024} - \lambda_{32}}{10.8} \quad \dots (1)$$

Thus, by measuring the equivalent conductivity of a normal sodium salt of the given acid at dilutions $N/32$ and $N/1024$, we can calculate the basicity of the acid.

Procedure : Prepare $N/16$ exact solution of NaOH by titrating it against $N/16$ oxalic acid solution. Also prepare a concentrated solution (of unknown concentration, of course) of the given acid, say citric acid.

Take 100 ml of $N/16$ sodium hydroxide solution in a 200 ml measuring flask. Add to it one drop of phenolphthalein indicator. Then add concentrated solution of citric acid from the burette, till sodium hydroxide is just neutralised, *i.e.*, until the pink colour is discharged. **It is always preferable to have a drop too much of the acid solution rather than have any of the alkalis un-neutralised.** Add conductivity water to the measuring flask and make the volume 200 ml. This is $N/32$ solution of sodium salt of the acid. Also prepare $N/1024$ solution of the sodium salt of the acid from $N/32$ solution by diluting it accordingly.

The conductivity cell is washed with both $N/32$ and $N/1024$ solutions in turn and their observed resistances noted, as usual.

Observations : Cell constant, $x = \dots$

Solution of sodium salt of acid	Dilution (cm ³)	Observed resistance	Observed conductivity	Equivalent conductivity
$N/32$	32,600
$N/1024$	10,24,000

Calculations : After calculating the equivalent conductivity of $\frac{N}{32}$ and $\frac{N}{1024}$ solutions, we can calculate the basicity, according to equation (1). The value of B will come out to be 3 for citric acid.

Result : The basicity of the given acid, say citric acid is three.

Precautions : (i) While titrating the NaOH solution by the acid solution, it is advisable to have a drop too much of the acid solution.

EXPERIMENT No. 6

Object : To find the solubility and solubility product of sparingly soluble salt, say barium sulphate, conductometrically.

Apparatus : Same as in preceding experiments.

Theory : Salts like silver chloride, barium sulphate, lead chromate are very slightly soluble in water and are thus known as **sparingly soluble salts**. Their solubility is so small that it cannot be determined from ordinary analytical methods. It is, however, possible to determine the extremely small solubilities by conductance measurements.

As the solubility of such salts is extremely low, the minute quantity that is dissolved may be regarded as present at infinite dilution and, therefore, measured equivalent conductivity is taken as equivalent conductivity at infinite dilution.

$$\therefore \lambda_v = \lambda_\infty = \lambda_a + \lambda_c$$

The specific conductivity (κ_v) is related to the equivalent conductivity (λ_v) by the relation :

$$\lambda_v = \kappa_v \times V$$

where, V is the volume in cm³ containing one gram equivalent of the electrolyte.

After knowing the value of V , we can calculate the value of solubility (S) of sparingly soluble salt, which is the amount in gram equivalent present in 1000 cm^3 of the solution. From the solubility value, we can also calculate its solubility product (K_s) as, $K_s = S^2$.

Procedure : The determination is carried out in a conductivity cell with fairly large electrodes which are not far apart. Measure the cell constant, as usual.

Measure the observed resistance conductivity water (A resistance of 10^4 ohm will be required in the resistance box, if one is using Wheatstone bridge). Grind 2 g of barium sulphate to a fine powder. Add barium sulphate into a beaker containing conductivity water. Shake well and allow the solid to settle down. Pour the liquid out and repeat the operation three to four times with fresh quantities of water to dissolve out all the soluble impurities. Add about 100 ml of conductivity water to the solid and shake well for about 5 minutes. During this time the solution will become saturated. Allow the heavier particles to settle down and wash the cell with the still turbid solution and measure its resistance. Repeat the procedure till two portions of the solution give same value of resistance.

Liquid	Observed resistance	Observed conductivity
Conductivity water
Solution of BaSO_4

Calculations : Observed conductivity (R_s) of the solution due to the dissolved salt

$$= \text{Observed conductivity of the solution} \\ - \text{Observed conductivity of conductivity water.}$$

The specific conductivity of solution due to the dissolved salt

$$= R_s \times x = \kappa_v \text{ (say)}$$

$$\text{Now, } \kappa_v \times V = \lambda_a + \lambda_c$$

The values of λ_a and λ_c (in this case $\lambda_{\text{Ba}^{2+}}$ and $\lambda_{\text{SO}_4^{2-}}$) can be seen from the tables.

The value of V is thus calculated.

$\therefore V$ ml of the solution contain 1 g equiv. of the salt,

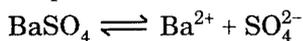
\therefore 1000 ml of the solution will contain $\frac{1000}{V}$ g equiv. of the salt.

\therefore Solubility of the salt = $\frac{1000}{V}$ g equiv/litre.

$$= \frac{1000 \times E}{V} \text{ g/litre}$$

$$= \frac{1000 \times E}{V \times M} \text{ g mole/litre}$$

where, E and M are the equivalent weight and molecular weight of the salt, respectively. Barium sulphate which has dissolved in solution ionises as :



Therefore, if S g mole/litre be the solubility of barium sulphate, then the solubility product is given by,

$$K_s = [\text{Ba}^{2+}] [\text{SO}_4^{2-}] = S \times S = S^2$$

$$\therefore \text{Solubility product} = \left(\frac{1000 \cdot E}{V.M} \right)^2$$

Result : (i) Solubility of barium sulphate at $t^\circ\text{C}$

$$= \dots \text{ g/litre}$$

(ii) Solubility product at $t^\circ\text{C} = \dots$

Precautions : Same as in preceding experiments, along with that the sparingly soluble salt must be absolutely pure, otherwise the results will be affected.

EXPERIMENT No. 7

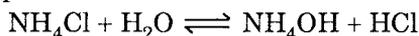
Object : *To determine the degree of hydrolysis and hydrolysis constant of ammonium chloride at room temperature.*

Apparatus : Same as in preceding experiments.

Theory : Hydrolysis of a salt may be regarded as the interaction of the ions of the salt with the corresponding ions of water to produce either acidity or alkalinity. When salt of a weak acid or a weak base or both is dissolved in water, it gets hydrolysed to produce either acidity or alkalinity. The conductivity of the solution is due to the formation of ions of the unhydrolysed salt and ions of acid or base, when the salt is hydrolysed.

The degree of hydrolysis (h) is defined as, 'the fraction of the total salt hydrolysed on the attainment of equilibrium'.

Consider a salt of weak base and strong acid, say ammonium chloride. If h be the degree of hydrolysis, then for every mole of the salt, the number of moles of every species at equilibrium will be as shown below :



(Initially)	1	0	0
-------------	---	---	---

(At equilibrium)	$1 - h$	h	h
------------------	---------	-----	-----

Ammonium hydroxide, being a weak base, may be taken as completely un-ionised and contribute little or nothing towards the total conductivity of the solution. The equivalent conductivity (λ) of this solution as determined experimentally will be the sum of the conductivity of $(1 - h)$ gram equivalent of unhydrolysed ammonium chloride and h gram equivalent of hydrochloric acid. Therefore,

$$\lambda = (1 - h) \lambda_c + h \lambda_\infty (\text{HCl}) \quad \dots (1)$$

where, λ_c is the equivalent conductivity of the unhydrolysed salt and $\lambda_\infty (\text{HCl})$ is the equivalent conductivity of hydrochloric acid at infinite dilution. HCl is a strong electrolyte and is assumed to be completely ionised at all dilutions. From equation (1), we get,

$$h = \frac{\lambda - \lambda_c}{\lambda_\infty (\text{HCl}) - \lambda_c} \quad \dots (2)$$

The value of λ_c is obtained by adding excess of non-conducting ammonium hydroxide to the salt solution. This suppresses the hydrolysis of ammonium chloride to such a large extent that the equivalent conductivity of the mixture can be taken

as λ_c , the conductivity of the unhydrolysed salt. The value of hydrolysis constant K_h , is given by,

$$K_h = \frac{h^2}{(1-h)V} \quad \dots (3)$$

Procedure : First determine the cell constant as usual. Prepare $N/32$ solution of ammonium chloride in water and determine its observed conductivity as usual. Dilute the $N/32$ solution with conductivity water to get $N/64$ and $N/128$ solutions. Determine their observed conductivities as usual.

Now prepare $N/32$ solution of ammonium chloride not in water but by dissolving the salt in $N/32$ solution of ammonia ($N/32$ solution of ammonia can be prepared by titrating a concentrated solution of ammonia with hydrochloric acid). Prepare $N/64$ and $N/128$ solutions of ammonium chloride by diluting the $N/32$ solution with $N/32$ ammonia solution. Determine the observed conductivity of each solution.

Observations : Room temperature = $t^\circ\text{C}$

Cell constant, $x = \dots$

Solution	Strength	Observed resistance	Observed conductivity	Equivalent conductivity
NH ₄ Cl in water	$N/32$	} Value of λ
	$N/64$	
	$N/128$	
NH ₄ Cl in ammonia	$N/32$	} Value of λ_c
	$N/64$	
	$N/128$	

The values of λ_∞ for HCl are seen to be as follows :

For $N/32, \lambda_\infty = 393 \text{ ohm}^{-1}$

For $N/64, \lambda_\infty = 399 \text{ ohm}^{-1}$

For $N/128, \lambda_\infty = 401 \text{ ohm}^{-1}$

Calculations : The degree of hydrolysis of ammonium chloride can be calculated, from equation (2). Thus, the values of degree of hydrolysis can be calculated at each dilution, viz., $N/32, N/64, N/128$.

The hydrolysis constant K_h , can now be calculated at each dilution according to equation (3). V is the volume in litres containing one gram mole of the salt, e.g., for $N/32, N/64, N/128$ solutions, the values of V will be 32, 64 and 128, respectively. It is seen that the values of K_h come out to be practically constant.

Result : (i) Degree of hydrolysis of ammonium chloride at different dilutions, viz., $N/32, N/64, N/128$ is ... percent.

(ii) Hydrolysis constant of ammonium chloride = ...

Precautions : Same as in preceding experiments.

EXPERIMENT No. 8

Object : To determine the order of reaction of the saponification of ethyl acetate by sodium hydroxide. Also determine the rate constants at different temperatures and from them calculate the energy of activation of the reaction.

Apparatus : Same as in preceding experiments.

Theory : For a reaction of the n th order, the time ($t_{0.5}$) taken to complete a definite fraction, say one half of the reaction is given by,

$$t_{0.5} \propto \frac{1}{a^{n-1}}$$

provided all the reactants are at the same initial concentration, a . If in two different experiments, t_1 and t_2 are the corresponding half life periods, when the initial concentrations of the reactants are a_1 and a_2 , respectively, then,

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1} \right)^{n-1}$$

$$\text{or} \quad n = 1 + \frac{\log(t_1/t_2)}{\log(a_2/a_1)} \quad \dots (1)$$

The values of t_1 and t_2 can be obtained by plotting x , the extent of the reaction against the corresponding time t .

The saponification of ethyl acetate by sodium hydroxide is represented by the equation,



It is a second order reaction, whose rate expression is given by,

$$kt = \frac{x}{a(a-x)}$$

(If both reactants have same initial concentrations)

$$\text{or} \quad kt = \frac{1}{a-x} - \frac{1}{a}$$

The rate constant k is equal to the slope of the curve drawn between $\frac{1}{a-x}$ and t .

In the saponification reaction, the fast moving OH^- ions are replaced by slow moving CH_3COO^- ions, hence the conductance will decrease as the reaction progresses. If R_0, R_t, R_∞ be the resistances of the reaction mixture at time zero, t and infinity, respectively, then,

$$x \propto \left(\frac{1}{R_0} - \frac{1}{R_t} \right) \propto C_0 - C_t$$

$$a \propto \left(\frac{1}{R_0} - \frac{1}{R_\infty} \right) \propto C_0 - C_\infty$$

$$a - x \propto \left(\frac{1}{R_t} - \frac{1}{R_\infty} \right) \propto C_t - C_\infty$$

The total change in conductivity, *i.e.*, $C_0 - C_\infty$ is evidently proportional to the initial concentration of ethyl acetate, the change in conductivity at any time t , *i.e.*, $C_0 - C_t$ is evidently proportional to the amount of ethyl acetate hydrolysed.

Thus, a plot of $\frac{1}{1/R_t - 1/R_\infty}$ or $\frac{1}{C_t - C_\infty}$ against t will give a straight line, whose slope will be equal to the rate constant k .

We know that the rate constant k , is related to the activation energy E , according to the expression,

$$k = Ae^{-E/RT} \quad \dots (2)$$

where, A is the frequency factor.

Taking logarithm of equation (2), we get,

$$\log k = \log A - E/RT$$

Differentiating it with respect to temperature, we get,

$$\frac{d \log k}{dT} = \frac{E}{RT^2}$$

$$d \log k = \frac{E}{RT^2} \cdot dT$$

Integrating it between the limits T_1 and T_2 when the values of rate constants are k_1 and k_2 we get,

$$\log_{10} \frac{k_2}{k_1} = \frac{E}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad \dots ()$$

Thus, by measuring the rate constants at two different temperatures, we can evaluate E , the energy of activation.

Procedure : (i) Prepare $M/50$ solutions of ethyl acetate and sodium hydroxide. Take 25 ml of $N/50$ sodium hydroxide solution in a reaction vessel and keep it in a thermostat. Now add 25 ml of $N/50$ ethyl acetate by means of a pipette into the reaction vessel and the stop watch is started at the time of half discharge of the pipette. The mixture is well shaken and taken in a beaker in which the conductivity cell is immersed. The resistance of the solution is observed. The reaction mixture is allowed to be kept in the beaker and resistance measured after every five minutes for the first twenty minutes and then after ten minutes for the next thirty minutes. The reaction mixture is then kept overnight for observing the R_∞ reading.

(ii) Take another reaction vessel containing 50 ml of distilled water. Now add 25 ml each of $M/50$ ethyl acetate and sodium hydroxide in it and start the stop watch at the time of half discharge of the pipette. The reaction mixture is quickly transferred to a beaker in which the cell is dipped. The resistance of the solution is noted at the same intervals of time, as above. It is also kept overnight for observing the R_∞ reading.

(iii) Take 25 ml each of $M/50$ ethyl acetate and $M/50$ sodium hydroxide in a reaction vessel. Before mixing the two reactants, both sodium hydroxide and ethyl acetate solutions are kept in a thermostat whose temperature has been raised by at least 10°C over that of the previous set. The reaction mixture is continuously kept in the thermostat while observing the resistance of the solutions after different intervals of time. The process is repeated as in step (i).

Observations : (A) Temperature = $t^\circ\text{C}$.

Reaction mixture I				Reaction mixture II			
Time (min)	R (ohm)	1/R	$1/R_0 - 1/R_t$	Time (min)	R (ohm)	1/R	$1/R_0 - 1/R_t$
...
...

(B)

Temp (°C)	Time (min)	R (ohm)	$\frac{1}{R}$	$\frac{1}{R} - \frac{1}{R_\infty}$	$\frac{1}{a-x} = \frac{1}{1/R_t - 1/R_\infty}$
t°	0
	∞
t_1°	0
	∞

Calculations : (A) Determination of order of reaction from the first set of observations.

From set (A) of observations, plot $\frac{1}{R_0} - \frac{1}{R_t}$ against time t , for both the reaction mixtures I and II. From each graph, find out the time during which the value of $\frac{1}{R_0} - \frac{1}{R_t}$ falls to half. This value will give the time for half decomposition. From the graph, we have,

Half time for reaction mixture I = T_1 (say)

Half time for reaction mixture II = T_2 (say)

$$\therefore \text{Order of reaction} = 1 + \frac{\log T_1/T_2}{\log a_1/a_2} = 1 + \frac{\log T_1/T_2}{\log (1/2)}$$

(B) Calculation of rate constant and energy of activation from the second set of observations.

The values of $\frac{1}{C_0 - C_\infty}$ are plotted as ordinate against time t as abscissa at each temperature (*i.e.*, t° and t_1° C). The slope of each curve will give the values of k_1 and k_2 at two different temperatures. From the values of k_1 and k_2 , we can calculate E , the energy of activation (The temperature in centigrade is to be converted into absolute degrees) with the help of equation (3).

Result : (i) Order of reaction = 2

(ii) Rate constant at t° C = ... mole⁻¹ min⁻¹

(iii) Energy of activation = ... cal mole⁻¹.

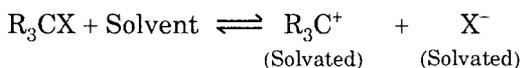
Precautions : The stop watch should be started just before measuring the first resistance reading of the reaction mixture. This time should be taken as zero time. However, for approximation purposes, we can start the stop watch at the time of half discharge of ester solution from the pipette.

EXPERIMENT No. 9

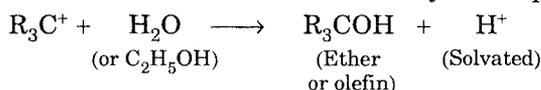
Object : To study the kinetics of hydrolysis of a tertiary aliphatic halide conductometrically

Apparatus and Chemicals : Conductivity set, dip type conductivity electrode mounted on a suitable cork, burette, graduated pipette (1 ml), stop watch, thermostat, 80% ethanol, tertiary butyl (or amyl) iodide.

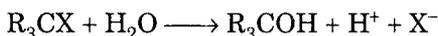
Theory : The hydrolysis of tertiary aliphatic halide is a two step process:



The carbonium ion reacts fast with any nucleophilic reagent present.



The net reaction is as follows :



The formation of ions increases the conductivity and makes it possible to follow the reaction kinetics conductometrically. The suitable substances for this purpose are tertiary butyl chloride and tertiary amyl iodide. As the solubility of the above chlorides in water is not sufficient, 80% aqueous ethanol is used as solvent. So, a dip type cell and direct reading conductivity bridge are needed.

Procedure : Take 50 ml of aqueous ethanol in a cylinder and the conductivity electrode in another cylinder. Keep both the cylinders in a thermostat. Take 5 ml of tertiary amyl iodide in a test tube and place it also in the thermostat. Set the conductivity bridge. After the equilibrium of temperature is obtained, transfer 0.3 ml of tertiary amyl iodide by means of a 1 ml pipette into aqueous alcohol. Start the stop watch. Mix and set the electrode in it and start taking conductivity readings every half minute for five minutes and then every minute for about 25 minutes. Transfer the electrode to the empty cylinder. Remove the cylinder with reaction mixture. Transfer its contents to a loosely corked conical flask. Heat the solution at nearly 60-65°C for about 20 minutes. Cool it and transfer the contents to the cylinder for reaction mixture and determine conductivity. Repeat the heating step for nearly 5 minutes and determine the conductivity again. In case the last two readings are the same, it means that the reaction has been completed.

Repeat the above experiment with 0.4 ml and 0.2 ml of tertiary amyl iodide. Find the half change times or 25% change time graphically. These will be independent of volume of ester used. This shows that the reaction conforms to first order. If the conductivity values are expressed by C terms, then

$$a \propto C_\infty - C_0 ; x \propto (C_t - C_0)$$

$$\therefore (a - x) \propto (C_\infty - C_t)$$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

or
$$\log \frac{(C_\infty - C_0)}{(C_\infty - C_t)} = \frac{kt}{2.303}$$

Alternatively, we can analyse the experimental data by using the difference formula.

$$k = \frac{2.303}{(t_2 - t_1)} \log \left(\frac{a - x_1}{a - x_2} \right)$$

or
$$\log \left(\frac{a - x_1}{a - x_2} \right) = \frac{k(t_2 - t_1)}{2.303} \dots (1)$$

= Constant [if (t₂ - t₁) is kept constant]

$$\therefore \left(\frac{a - x_1}{a - x_2} \right) = \text{constant, } I \dots (2)$$

or
$$(a - x_1) = aI - x_2I$$

or

$$x_1 = x_2 I - a(I - 1)$$

The above equation suggests that from a plot of x_1 values against x_2 values, the constant, I can be calculated from the slope. Taking equations (1) and (2) together, we may write

$$\log I = \frac{k(t_2 - t_1)}{2.303}$$

Thus, the value of k can be evaluated from the above equation. Initially, plot a graph of conductivity against time. From this graph, find the values of conductivity at fixed intervals of time say 5 minutes and plot them as x_1 and x_2 factors

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 10

Object : *To compare the relative strengths of different acids; say acetic acid and monochloroacetic acid.*

We know that the strength of an acid depends upon the number of H^+ ions it can give at any dilution, *i.e.*, degree of ionisation at that dilution. Therefore, the relative strength of the acids will be in the ratio of their degrees of ionisation and according to Ostwald's dilution law, the ratio of the degree of ionisation of weak electrolytes is in the ratio of the square root of dissociation constants.

$$\therefore \frac{\text{Strength of one acid}}{\text{Strength of other acid}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\left(\frac{K_1}{K_2}\right)}$$

Thus, if we want to determine the relative strengths of two acids say acetic acid and monochloroacetic acid, then determine the dissociation constant of each acid (cf. experiment 2).

EXPERIMENT No. 11

Object : *To determine the basicity of tartaric acid, oxalic acid etc.*

Proceed as in experiment 5.

EXPERIMENT No. 12

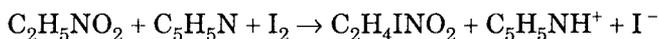
Object : *To find out the degree of dissociation and dissociation constant of monochloroacetic acid.*

Proceed as in experiment 2.

EXPERIMENT No. 13

Object : *To study the kinetics of ionisation of nitroethane in presence of pyridine in 80% alcohol solution.*

The reaction involved in kinetics is :



The conductance increases as the reaction proceeds due to the formation of ionic species.



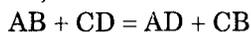
CONDUCTOMETRIC TITRATIONS

In such titrations, the variation of equivalent conductivity by the addition of titrant is measured. It is, however, not necessary to measure the actual equivalent conductivity—any quantity proportional to conductivity can be used. This results in great simplification.

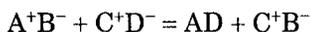
Conductometric titrations have special advantages, especially when the solutions are coloured or turbid, because in such titrations no indicator is required. In conductometric titrations, advantage is taken of the fact that the conductivity of a solution is dependent upon the number of ions and their mobility.

The addition of one electrolytic solution to another electrolytic solution, producing no appreciable change in volume will alter the conductivity of the solution, according to whether ionic reactions are occurring or not. If no ionic interaction takes place as in the titration of KCl and KNO₃, the conductivity will not change. If, on the contrary, ionic interaction occurs, conductivity also changes, *e.g.*, the titration of HCl and NaOH. In this type of titration, the addition of a base to a strong acid will cause the conductivity to change due to the replacement of high mobility hydrogen ions by lower mobility sodium ions. Thus, the principle of conductometric titration is the substitution of ions of one mobility by ions of another mobility.

For example, consider the reaction between two electrolytic solutions AB and CD. If the product AD of the reaction is relatively insoluble or only slightly ionised, the reaction is written as,



Writing this equation in the form of ions, we have,



In the reaction between A⁺ ions and D⁻ ions, the former ions are replaced by C⁺ ions during the titration. Therefore, the conductivity increases or decreases, depending on the fact whether the mobility of C⁺ ions is greater or less than that of A⁺ ions.

In conductometric titrations, the titrant is added from the burette and the conductivity readings corresponding to various increments of titrant are plotted against the volume of the titrant. The plots consist of two curves which intersect at a particular point known as **end point** or **equivalence point**.

If the reaction is not quantitative then in the proximity of the end point, there is a curvature in the curve. Several phenomena like hydrolysis, dissociation of the product or appreciable solubility in case of precipitation reactions, give rise to a

curvature in the curves. The acuteness of the angle at the point of intersection of the two branches will be a function of the individual ionic conductance of the reactants.

The titrant should be at least ten times as concentrated as the solution being titrated in order to keep the volume change small. If it is not so, then a correction to the readings must be applied, *i.e.*,

$$\text{Actual conductivity} = \left(\frac{v + V}{V} \right) \times \text{Observed conductivity}$$

where, v is the volume of titrant or reagent added and V is the original volume of the solution.

This method can be employed to very dilute solutions, say about $10^{-4} M$. Since every ion contributes to the conductivity, therefore, extraneous substances may be removed as far as possible. It is essential for calculating absolute conductivities, but not so in conductometric titrations. The end point is measured with an error of $\pm 0.5\%$ and it also takes a very short time to perform the complete titration.

The conductivity cell for conductometric titrations should be such that continuous stirring of the contents can be made. The contents of the mixture should be preferably placed in a thermostat and in case it is not available, the contents are then placed in a large beaker or any other beaker containing water, so that the contents may acquire the room temperature.

EXPERIMENT No. 1

Object : *To find out the strength of hydrochloric acid solution (approximate strength N/10) by titrating it against standard sodium hydroxide solution conductometrically.*

Apparatus : Conductivity bridge, beaker, thermostat, measuring flask, stirrer etc.

Theory : Consider that the acid is taken in a conical flask, while the base is taken in the burette. The solution at first contains H^+ and Cl^- ions. Since H^+ ions possess the greatest mobility, hence it follows that the conductivity of this solution is mainly due to H^+ ions. The addition of sodium hydroxide is represented by the equation.



As sodium hydroxide is added, the H^+ ions are removed as slightly ionised water. Therefore, the conductivity will decrease, as Na^+ ions do not possess much mobility. At the neutralisation point, the solution contains Na^+ and Cl^- ions and has a considerably less conductivity than the original value. If a drop of sodium hydroxide is added after the neutralisation point, there will be a small concentration of OH^- ions and, therefore, the conductivity increases, as OH^- ions have the second highest mobility. As more and more sodium hydroxide is added, the conductivity goes on increasing continuously. Hence, on plotting the conductivity values as ordinate against milli-litres of titrant added as abscissa, we get two straight lines, the point of intersection of which gives the equivalence point.

Procedure : Prepare exact N/10 sodium hydroxide solution. (Its exact solution is prepared by first preparing N/8 sodium hydroxide by weighing. It is then titrated

against exact $N/10$ oxalic acid solution and the normality of alkali solution is calculated. It is then diluted accordingly by distilled water to get an exact $N/10$ solution. This procedure is followed, because pellets of sodium hydroxide absorb moisture while weighing).

Rinse and fill the burette with $N/10$ sodium hydroxide solution. Now take 10 ml of the unknown acid solution in a 400 ml beaker and add about 100 ml of distilled water to it. (*This will change the strength of the acid solution*). Now clamp the conductivity cell in the beaker, so that the electrodes are dipped in the solution. Also introduce a stirrer in the beaker.

Measure the resistance of the solution by means of a conductivity bridge or Wheatstone bridge. Now add 1 ml of alkali solution from the burette and stir the contents thoroughly. Again measure the resistance of the solution. Repeat this procedure till you have added 9 ml of alkali solution. Now start adding the alkali solution at an increment of 0.2 ml instead of 1 ml (as done before 9 ml) till you have added 11 ml of it. (*This is done to get as many readings as possible near the end point in order to get an accurate curve*). Now, after adding 11 ml of the alkali solution, add 1 ml of it in each addition and continue it upto 15 ml. Shake well and measure the resistance after each addition.

Observations : Volume of unknown acid solution taken
= 10 ml

S. N.	Volume of sodium hydroxide added (ml)	Observed resistance (ohm)	Observed conductivity (ohm^{-1})

Calculations : The values of observed conductivity are plotted as ordinate against volume of sodium hydroxide added as abscissa. The curve obtained is as shown in figure (1). Suppose the end point (A) lies at V_2 ml of $N/10$ sodium hydroxide. Therefore, from normality equation ($N_1V_1 = N_2V_2$), we have,

$$\text{Strength of HCl} = \frac{36.5 \times V_2}{10 \times 10} \text{ g/litre}$$

Result : The strength of HCl solution = ... g/litre.

Precautions : (i) After each addition of the titrant from the burette, the solution should be thoroughly stirred for about a minute and then the reading should be taken.

(ii) Just before and after the end point, the addition of titrant should be in as small fractions as possible.

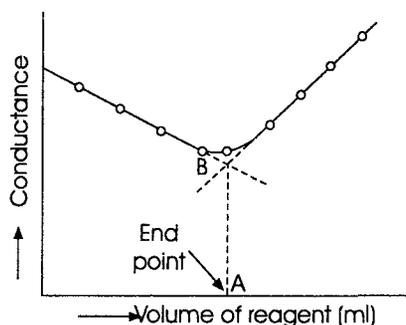


Fig. 1 : Titration curve for strong acid and strong base

EXPERIMENT No. 2

Object : To find out the strength of given ammonium hydroxide solution (approximate strength $N/10$) by titrating it against hydrochloric acid conductometrically.

Apparatus : Same as in preceding experiment.

Theory : If we take ammonium hydroxide solution in the burette and the acid solution in the conical flask, then each addition of the solution from the burette will cause the conductivity to decrease, as the H^+ ions are replaced by OH^- ions. After the equivalence point, however, the conductivity will almost remain constant, as a solution of ammonium hydroxide has a very small conductivity compared with that of the acid or the salt. If we plot the conductivity of the solution as ordinate against volume of alkali added as abscissa, we get two curves. The point of intersection of these two curves gives the equivalence point. At the end point, the curves are not straight lines but are slightly curved due to hydrolysis of the salt, ammonium chloride.

Procedure : Prepare $N/10$ hydrochloric acid solution. (Its exact solution is prepared by titrating a slightly concentrated acid solution against $N/10$ sodium hydroxide solution, whose exact solution is prepared as described in experiment 1).

Now take 10 ml of $N/10$ hydrochloric acid solution in a 400 ml beaker. Rinse and fill the burette with the unknown ammonium hydroxide solution. Add about 100 ml of distilled water in the beaker and dip the electrodes of the cell in the solution. Measure the resistance of the solution before adding any alkali solution. Now add 1 ml of alkali solution from the burette and stir the contents thoroughly. Measure the resistance of the solution. Repeat the process of adding alkali solution and stirring till 9 ml of it has been added. Now from 9 ml to 11 ml add the alkali solution at an increment of 0.2 ml. Now again add 1 ml of alkali solution in each addition from 11 ml to 15 ml. Measure the resistance of the solution as usual after stirring the contents well.

Observations : Same as in preceding experiment.

Calculations : A curve is plotted with observed conductivity as ordinate against volume of ammonium hydroxide solution added as abscissa. The curve is of the shape shown in figure (2). From the curve, suppose the end point lies at V_1 ml of ammonium hydroxide solution. The strength of NH_4OH can be calculated from the normality equation.

Result : The strength of the given NH_4OH solution = ... g/litre.

Precautions : Same as in preceding experiment.

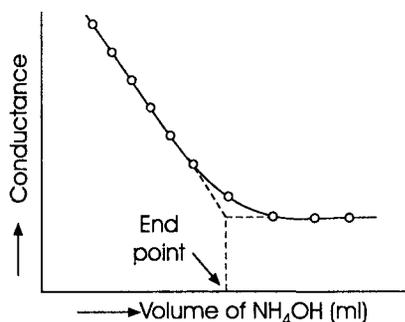


Fig. 2 : Titration curve for strong acid and weak base.

EXPERIMENT No. 3

Object : To find out the strength of the given acetic acid solution (approximate strength $N/10$) by titrating it against sodium hydroxide solution conductometrically.

Apparatus : Same as in preceding experiments.

Theory : During the titration of CH_3COOH with $NaOH$, the salt CH_3COONa is formed. Owing to the effect of the common ion [i.e., neutral salt

(CH_3COONa), which is formed during the first part of titration, tends to repress the ionisation of CH_3COOH still present], the conductivity increases because the conducting power of the highly ionised salt exceeds that of weak acid. Conductivity increases more rapidly after the end point is just passed, because of the presence of hydroxyl ions from the alkali added.

Procedure : Rinse and fill the burette with standard $N/10$ sodium hydroxide solution (prepared as described in experiment 1). Now take 10 ml of the acid solution in a 400 ml beaker. Add about 100 ml of distilled water and dip the electrodes of the cell in the solution. Now proceed as explained in preceding experiments. Add small increments of the titrant near the end point.

Observations : Same as in preceding experiments.

Calculations : Plot a curve between observed conductivity as ordinate and volume of alkali added as abscissa. The shape of the curve is as shown in figure (3). Suppose the end point lies at V_2 ml of $N/10$ sodium hydroxide solution. Then, the strength of CH_3COOH can be calculated from the normality equation.

Result : The strength of acetic acid solution = ... g/litre.

Precautions : Same as in preceding experiments.

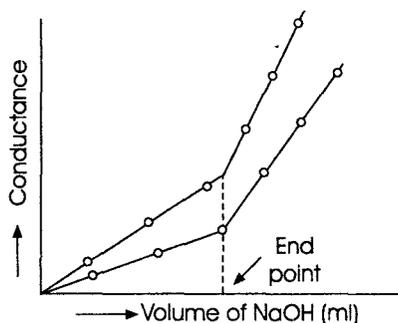


Fig. 3 : Titration curve for weak acid and strong base

EXPERIMENT No. 4

Object : To determine the strength of a moderately strong acid (like salicylic acid, mandelic acid or malonic acid) in the given solution conductometrically.

Apparatus : Same as in preceding experiments.

Theory : Salicylic, mandelic and malonic acids are considered as moderately strong acids. Their dissociation constants lie in the range $10^{-2} - 10^{-4}$. They possess a relatively high degree of dissociation and their dissociation is not completely suppressed by the addition of their salts. When such acids are titrated with a base like NaOH , the conductivity falls due to the removal of H^+ ions already present and a partial suppression of further ionisation of the remaining acid. At the same time, the conductivity increases due to the formation of the salt which tends to be completely ionised. Due to all these interactions, we see that the graph of conductivity against titrant volume (abscissa) is a curved loop, rising part of which merges into the rising linear part of the curve due to an excess of alkali after the end point. The end point of titration is fixed with difficulty. Two methods are employed to find out the end point.

[I] Salt Line Method

In this method, use is made of the fact that at equivalence point, the conductivity is mainly due to the salt formed. The method consists of the following steps :

(a) A definite volume (say V ml) of the acid solution is titrated against standard alkali solution (say x -N NaOH or KOH) in the usual way and the titration curve is plotted.

(b) A solution of pure salt of the acid with titrant alkali is prepared (concentration of alkali is equal to that of the titrant, *i.e.*, x .N salt).

(c) V ml of pure water is taken in the conductance cell and salt solution is added to it in steps. After each addition, the solution is thoroughly shaken and conductance is measured. The water-salt titration curve, which is a straight line, known as **salt line** is plotted on the acid-alkali titration graph. The point where the salt line meets the acid-alkali curve tangentially will determine the end point. At the end point, the salt concentration for both titrations is the same. If the experimental salt line does not meet the acid-alkali curve tangentially, a parallel line touching the acid curve is drawn.

Thread technique of drawing the salt line : We know that the salt line is a straight line tangential to the acid-alkali curve, the salt line can also be located without carrying actual water-salt titration. The conductance of water used in preparing solutions is measured and a point on the conductance axis (ordinate) for the titrant (salt solution) volume equal to zero is plotted. Now fix a thumb and a thread loop at this point and stretch the thread to a tangential position for the acid-alkali titration curve. Mark few points along the thread and draw a tangent line. The point where this line meets the titration curve, gives the end point of the titration.

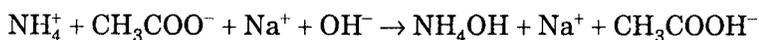
Procedure : Titrate 5 ml 0.01 N acid solution with 0.1 N NaOH solution as usual. Prepare 0.1 N solution of sodium salt of the acid and carry out the water-salt titration taking 50 ml of pure water in the conductivity cell.

Preparation of standard solution of sodium salt of the acid : Take NaOH solution of normality strength equal to that of the titrant and add to it increasing amounts of the acid in powdered form till the resulting solution stops to impart pink colour to phenolphthalein paper (A slight excess of acid will not cause any significant error in the salt line method).

Alternatively, take NaOH solution in double strength and titrate it with a concentrated solution of the given acid to the end point. Then dilute the resulting solution to double volume of the initial volume of NaOH solution.

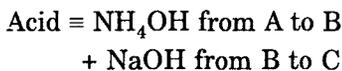
[II] Double Alkali Method

This method consists in first titrating with ammonia solution upto an extent of 80% neutralisation and then with standard sodium hydroxide solution. If the conductivity values are plotted during the addition of ammonia and alkali solutions, the curve is similar to the acid-NaOH curve (loop form), till the acid is completely neutralized. When all the acid has been used, the ammonium ion formed starts to react with hydroxyl ions to form NH_4OH .



During this reaction, the conductivity of the solution falls slightly due to the replacement of NH_4^+ ($\lambda_{\text{NH}_4^+}^+ = 73.0$) by Na^+ ($\lambda_{\text{Na}^+}^+ = 50.1$) or remains unchanged in case

KOH is used. When the replacement is complete, a sharp rise in the conductivity occurs due to an excess of alkali. The titration curve will be as shown in fig (4). Point A is the starting point of titration with NH_4OH . At point B, addition of NaOH starts. At point C, the first break in the titration curve, the acid is completely neutralised and replacement of NH_4^+ ions by Na^+ ions starts. At point D, the second break point, replacement of NH_4^+ by Na^+ ion is complete. Therefore,



As NH_4OH from A to B \equiv NaOH from C to D

\therefore Acid \equiv NaOH from B to D

Procedure : Prepare 0.1N NaOH and 0.1N NH_4OH solutions. First titrate the 50 ml of 0.01N acid solution with NaOH solution in the usual way and from the titration curve obtain the approximate titre value. Then repeat the titration of 50 ml acid solution, first with NH_4OH solution upto an extent of nearly 80% neutralisation and then with NaOH solution. Plot the conductance (ordinate) values against the volume of titrants (abscissa) added and get the titration curve. The volume of NaOH solution added to get the sharp break in the curve will give the titre value.

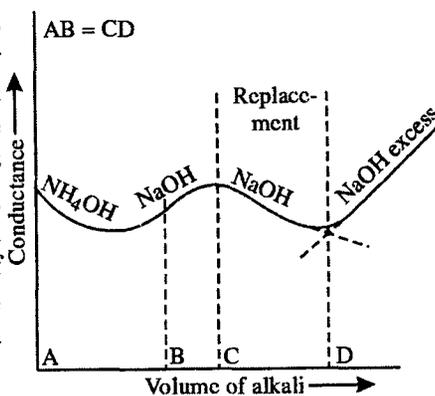


Fig. 4

EXPERIMENT No. 5

Object : To find out the strength of hydrochloric acid and acetic acid in a mixture of both (approximate strength of each acid is $N/10$) by titrating it against sodium hydroxide solution conductometrically.

Apparatus : Same as in preceding experiments.

Theory : This type of titration is just a combination of two separate titrations, *viz.*, HCl against NaOH and CH_3COOH against NaOH. By adding alkali to the mixture, the conductivity of the solution decreases due to the replacement of H^+ ions from the strong acid. It then increases as the weak acid is converted into salt and finally rises more steeply as excess of alkali is added.

A curve is plotted with conductivity as ordinate against volume of alkali added as abscissa. It is observed that there is a rounding off at both the end points. Usually extrapolation of the straight lines of the three branches would lead to a definite location of the end points. It must be noted that the first end point will be that of hydrochloric acid (strong) while the second that of acetic acid (weak).

Procedure : Prepare an exact $N/10$ solution of sodium hydroxide (method described in experiment 1). Rinse and fill the burette with the alkali solution. Now take 5 ml of the mixture of HCl and CH_3COOH in a 400 ml beaker. Add about 100 ml distilled water. Dip the electrodes of the conductivity cell in the solution of the

mixture. (The first end point will lie near about 5 ml, while the second will be near about 10 ml of sodium hydroxide solution).

Note the resistance of the solution before adding the alkali. Now add 1 ml, 2 ml, 3 ml and 4 ml of alkali from the burette and shake the contents of the beaker thoroughly. Note the resistance readings after each addition. Now add alkali at an increment of 0.2 ml upto 6 ml and then again between 9 ml and 11 ml. After adding 11 ml of alkali solution, add 1 ml in each addition till you have added 15 ml. Note the resistance of the solution after each addition and thoroughly stir the contents of the beaker.

Observations : Volume of mixture taken = 5 ml.

S. N.	Volume of alkali added (ml)	Observed resistance (ohm)	Observed conductivity (ohm^{-1})

Calculations : A curve is now plotted with observed conductivity as ordinate against volume of alkali added as abscissa. The shape of the curve will be as shown in figure (5). Suppose the first end point lies at V_2 ml, while the second lies at V_4 ml of NaOH

$$(i) \quad N_1 V_1 = N_2 V_2$$

HCl NaOH

$$N_1 \times 5 = \frac{N}{10} \times V_2$$

or

$$N_1 = \frac{N \times V_2}{5 \times 10}$$

Strength of HCl

$$= \frac{36.5 \times V_2}{5 \times 10} \text{ g/litre}$$

$$(ii) \quad N_3 V_3 = N_4 V_4$$

CH₃COOH NaOH

$$N_3 \times 5 = \frac{N}{10} \times V_4$$

or

$$N_3 = \frac{N \times V_4}{5 \times 10}$$

$$\therefore \text{Strength of CH}_3\text{COOH} = \frac{60 \times V_4}{5 \times 10} \text{ g/litre.}$$

Result : The strength of each acid in the given mixture is :

(i) Hydrochloric acid = ... g/litre.

(ii) Acetic acid = ... g/litre.

Precautions : Same as in preceding experiments.

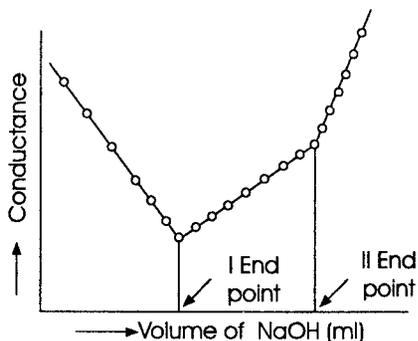


Fig. 5 : Titration curves for mixture of acids.

EXPERIMENT No. 6

Object : *Estimate oxalic acid by carrying out suitable conductometric titrations in the following solutions :*

(a) *A solution of pure oxalic acid*

(b) *A solution of oxalic acid and HCl*

(c) *A solution of oxalic acid and CH₃COOH.*

Apparatus : Same as in preceding experiments.

Theory and Procedure : (a) When a solution of oxalic acid is titrated conductometrically against NaOH solution, the two dissociations of oxalic acid operate one after the other. The first dissociation is similar to that of strong acid, while the second is similar to that of weak acid. Thus, the titration curve shows two marked inflexion points as are observed from a mixture of HCl and CH₃COOH. However, the volumes of alkali needed for titration of oxalic acid to sodium hydrogen oxalate and for titration of the latter to sodium oxalate will be equal.

(b) When a mixture of oxalic acid and HCl are titrated against NaOH, the first break point is observed when all HCl is neutralised and oxalic acid is converted to sodium hydrogen oxalate. The second break point in the titration curve occurs when sodium hydrogen oxalate is converted completely to sodium oxalate. If V_1 and V_2 be the volumes of NaOH required upto the first and second break points, respectively, then

$$\text{Oxalic acid} \equiv 2 (V_2 - V_1) \text{ ml of NaOH}$$

$$\text{HCl} \equiv V_1 - (V_2 - V_1) \text{ ml of NaOH}$$

$$\equiv (2V_1 - V_2) \text{ ml of NaOH}$$

(c) In the titration of a mixture of oxalic acid and CH₃COOH against NaOH, the first break point in the titration curve corresponds to the conversion of oxalic acid to sodium hydrogen oxalate, while the second break point corresponds to CH₃COOH and the conversion of sodium hydrogen oxalate to sodium oxalate. If V_1 and V_2 be the volumes of NaOH required upto the first and second break points in the curve, respectively, then,

$$\text{Oxalic acid} \equiv 2V_1 \text{ ml of NaOH}$$

$$\text{CH}_3\text{COOH} \equiv (V_2 - 2V_1) \text{ ml of NaOH}$$

Observations and Calculations : As described above.

Result :

EXPERIMENT No. 7

Object : *To estimate conductometrically, nitric acid and sulphuric acid in a mixture of both the acids.*

Apparatus : Same as in preceding experiments.

Theory and Procedure : Since both HNO₃ and H₂SO₄ are strong acids, titration against NaOH clearly shows one break point. If, however, after the first break point has been reached with NaOH, addition of NaOH may be stopped after adding 1 ml in excess after the first break point, the resulting solution may be

titrated against a standard solution of BaCl_2 . During this titration, SO_4^{2-} ions in the solution are replaced by Cl^- ions and BaSO_4 is precipitated. (All precipitation titrations should be carried out at low concentrations slowly). This does not appreciably change the conductance value. When the precipitation is complete, an increase in conductance occurs. Thus, the BaCl_2 equivalent of H_2SO_4 present in the original mixture can be found out. The amount of HNO_3 is then estimated as difference.

Observations and Calculations : As described in preceding experiments.

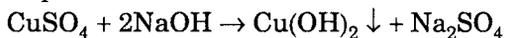
Result : The strengths of H_2SO_4 and HNO_3 in the given mixture are ... and ...

EXPERIMENT No. 8

Object : To titrate a given mixture of sulphuric acid, acetic acid and copper sulphate against 0.1 M NaOH solution conductometrically.

Apparatus : Same as in preceding experiments.

Theory and Procedure : In this titration, CH_3COOH and H_2SO_4 will get neutralised as weak and strong acids, respectively. This will be followed by precipitation reaction :



Thus, copper ions will get replaced by an equivalent amount of sodium ions. The ionic conductances of Cu^{2+} and Na^+ ions are nearly equal and so the conductance of the solution remains constant during this part of titration. The solutions should be dilute and readings should be taken after thorough stirring of the contents.

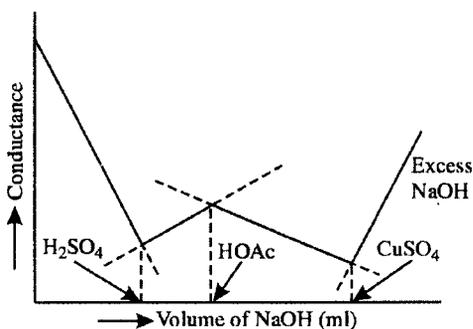


Fig. 6

Observations and Calculations :

Same as in preceding experiments.

Result : The concentrations of various components are :

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 9

Object : To determine the strength of acetic acid by titration with ammonium hydroxide.

Proceed as in experiment 3. The curves will be obtained as shown in figure (7).

EXPERIMENT No. 10

Object : To determine the strength of boric acid by titrating it with sodium hydroxide.

Proceed as in experiment 3. The curves will be obtained as shown in figure (8)

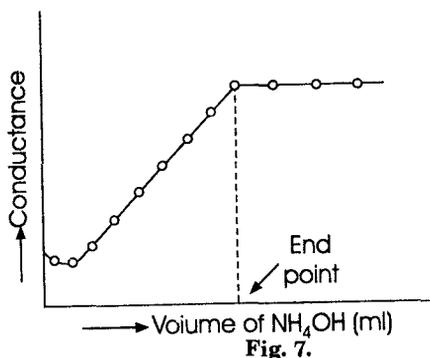


Fig. 7.

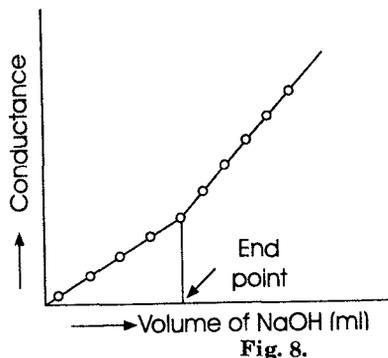


Fig. 8.

EXPERIMENT No. 11

Object : To perform the conductometric titration between a salt and alkali (or acid), e.g., between magnesium sulphate and barium hydroxide. (Displacement titration).

In this titration, the sparingly soluble salt, BaSO_4 separates out from the solution. Thus, the conductivity of the solution decreases at first till the end point is reached. After the end point has been reached, conductivity increases rapidly on adding barium hydroxide solution.

EXPERIMENT No. 12

Object : To study the complex formation between two species, e.g., potassium iodide and mercuric iodide.

Conductivity measurements give us an idea about the existence of complex compounds. A series of solutions is prepared in which mole fractions of the components are varied and the total molarity is kept constant. The conductivity of each solution is measured and plotted against mole fraction of one of the components. If the curve is linear, there is no complex formation. The existence of a maxima indicates the complex formation.

EXPERIMENT No. 13

Object : To study the conductometric titration of a Lewis acid (stannic chloride) with a Lewis base (benzophenone) in a non-aqueous medium (thionyl chloride).

Lewis acid is a substance which can accept one or more pairs of electrons from an electron donor (Lewis base). Take 20 ml of $N/20$ stannic chloride solution prepared in thionyl chloride in a glove-box. Note the resistance of this solution. Now add about 50 mg of benzophenone in the solid state to the stannic chloride solution and note the resistance. Repeat the process after adding various amounts of solid benzophenone. Note that all additions in various titrations should be made at equal intervals of time.

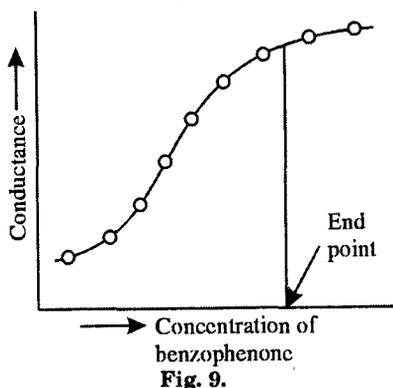


Fig. 9.

Plot a curve with conductivity as ordinate against concentration of benzophenone as abscissa. We see that the curve is of the shape as shown in figure (9).

EXPERIMENT No. 14

Object : To determine the strength of silver nitrate by titration with sodium chloride or potassium thiocyanate (precipitation titration).

Proceed as performed in preceding experiments of simple titrations. Take (N/10) AgNO₃ solution in the burette and 10 ml of sodium chloride or potassium thiocyanate solution in a 400 ml beaker. Add 100 ml of distilled water and dip the conductivity cell in the solution note the conductance readings as usual. Then plot a curve [fig. (10)] between conductance (ordinate) and volume of AgNO₃ solution (abscissa). The point of intersection will give the end point. The strength of AgNO₃ is calculated by using normality equation.

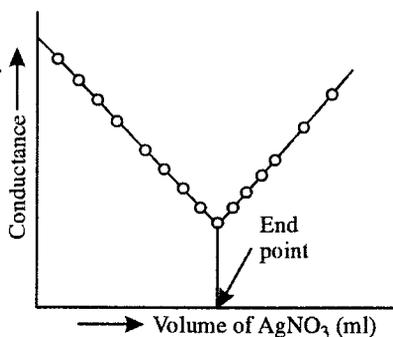
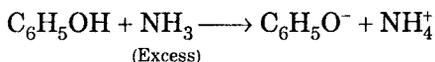
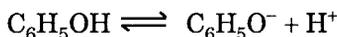


Fig. 10.

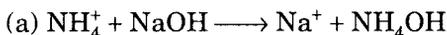
EXPERIMENT No. 15

Object : To titrate a given solution of phenol with NaOH.

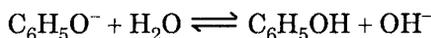
Theory : If a large excess of ammonia is added the dissociation equilibrium of an acid e.g., phenol will shift in the direction of complete dissociation



If a strong base like NaOH is added the following reaction (a) occurs and reaction (b) does not occur.



Reaction (a) does not suffer from formation of OH⁻ ions by hydrolysis as in the case with reaction (b), in which hydrolysis occurs prominently.



The solution of phenol in ammonia can be taken as an acid, for which dissociation constant is,

$$K = \frac{[\text{NH}_4^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{NH}_3][\text{C}_6\text{H}_5\text{OH}]} = \frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{H}^+]} \times \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]}$$

$$\left(\frac{1}{K_a} \text{ for } \text{NH}_4^+\right) \quad (K_a \text{ for } \text{C}_6\text{H}_5\text{OH})$$

$$\approx \frac{1}{10^{-9}} \times 10^{-10} \approx 10^{-1}$$

This shows quite a strong acidic character. When NaOH begins to be in excess, a sharp rise in the conductance occurs and, therefore, the conductance curve exhibits a sharp break.

Apparatus and Chemicals : 1M NaOH, 0.3M phenol, burette, pipette, titration flask etc.

Procedure : Take 20 ml of phenol solution in a titration flask. Add to it, about 150 ml CO₂ free water and 10 ml of liquid ammonia. Titrate it against 1 M NaOH solution taken in the burette and find the end point.

EXPERIMENT No. 16

Object : *A commercial sample of vinegar is suspected of having H₂SO₄. Show conductometrically if it is so and estimate the impurity of mineral acid, if present.*

This can be carried out as described in experiment 5, as the mixture is of a strong acid and a weak acid.

EXPERIMENT No. 17

Object : *To estimate conductometrically sodium acetate and ammonium chloride in 50 ml of a mixture of both.*

Sodium acetate can be titrated first against 0.5N HCl. Acetic acid obtained by displacement does not contribute to conductivity. The break in the conductance curve gives the end point. After the first break point titrate against 0.5N NaOH solution to estimate ammonium chloride as it displaces NH₄⁺ ions forming NH₄OH.

EXPERIMENT No. 18

Object : *To estimate conductometrically the quantities of HCl and NH₄Cl in a given mixture.*

The titration can be carried out by titrating directly with NaOH as done in experiment 5. HCl will act as a strong acid and NH₄Cl as a weak acid component.

EXPERIMENT No. 19

Object : *To estimate conductometrically NH₄OH and NH₄Cl in their mixture.*

The mixture is titrated separately with HCl (NH₄OH gets titrated to the end point) and NaOH (NH₄Cl gets titrated to the end point).

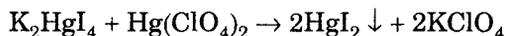
EXPERIMENT No. 20

Object : *To titrate 10 ml of 0.1N KI solution after dilution to 150 ml with 0.1N Hg(ClO₄)₂ solution. Repeat the titration with 0.05M HgCl₂ solution.*

Mercuric perchlorate solution is prepared by saturating 0.1N perchloric acid solution with mercuric oxide. The observed conductances will need volume corrections.

$$\text{Corrected conductance} = \frac{V+v}{V} \times \text{Observed conductance.}$$

A small break occurs in the titration curve when KI is converted to K_2HgI_4 (50% titration). A major break occurs when the precipitation is complete.



EXPERIMENT No. 21

Object : To find out the concentration of H_2SO_4 , HCl and HClO_4 in a given mixture by conductometric titration.

Titrate against NaOH solution for total acidity of the solution. Now titrate the resulting solution against barium nitrate solution to find out the concentration of H_2SO_4 . Then neutralise another portion with CaCO_3 and estimate chloride ions by titration against AgNO_3 .

EXPERIMENT No. 22

Object : To determine the strength of NaOH and NH_4OH in a given solution by titrating it against HCl .

A mixture of NaOH and NH_4OH solution can be titrated against HCl as usual. The curves will be as shown in figure (11). The curves are of the same shape as obtained for a mixture of acids [Fig. 11(a)].

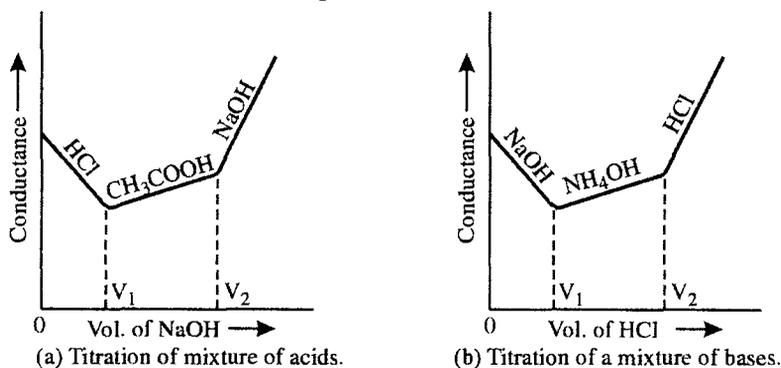


Fig. 11



current flowing through the resistance is amplified and then passed through a milli-ammeter; the deflection of the needle on a scale graduated in pH units corresponds to the pH of solution directly. It is basically a valve (vacuum tube) voltmeter. The pH meter is particularly useful in following changes of pH that occur during an electrometric titration and is readily adapted for the convenience of A.C. operation.

(1) **Glass Electrode** : This electrode was designed by Haber and Klemensiewicz. It is based on the principle that when a thin glass membrane separates two solutions having different pH values, there develops a potential difference between the two surfaces of the membrane. The value of this potential difference for a given variety of glass varies with the concentration of hydrogen ions and at 25°C is given by the expression,

$$E_G = E_G^\circ + 0.0591 \text{ pH}$$

where, E_G is the potential of the glass electrode and E_G° is a constant for the given glass electrode, depending upon the nature of the glass.

The glass electrode [fig. (1)] consists of a special glass of relatively low melting point and high electrical conductivity. It is made in the form of a thin walled glass bulb, which is sealed to the bottom of a glass tube. A solution of 0.1M HCl which furnishes a constant hydrogen ion concentration is placed inside the bulb and an Ag/AgCl electrode or a platinum wire is inserted to make electrical contact. This bulb dips in a solution of unknown pH.

Glass electrode can be used both in oxidising and reducing solutions and is also immune to poisoning. It can be used upto pH 0–9 using ordinary electrodes, but for pH onwards, electrodes of special glass are to be used.

Two solutions of same hydrogen ion concentration with the glass membrane interposed, should show no potential difference. However, glass electrodes usually show a small potential, (*i.e.*, asymmetric potential due to the different states inside & outside the glass electrode bulb) under these conditions. That is why, pH meter is standardised by using a buffer of known pH before starting the experiment.

(2) **Reference Electrode** : A cell is formed in which the glass electrode is combined with another electrode known as reference electrode. It is generally a calomel electrode [fig. (2)] which consists of a platinum wire dipping in mercury over which a paste of Hg_2Cl_2 and KCl is taken. The tube is then filled with potassium chloride solution. The electrode is represented as :

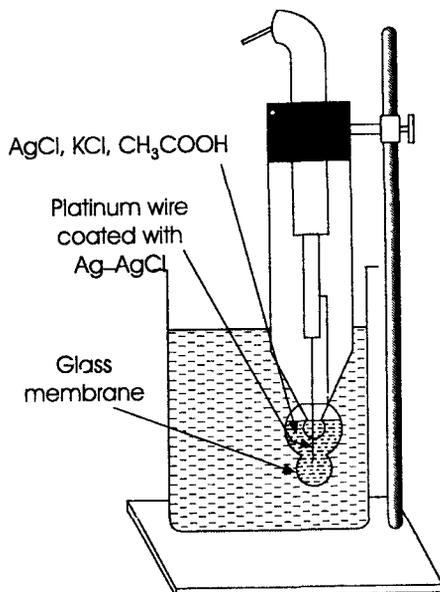


Fig. 1 : Glass electrode.

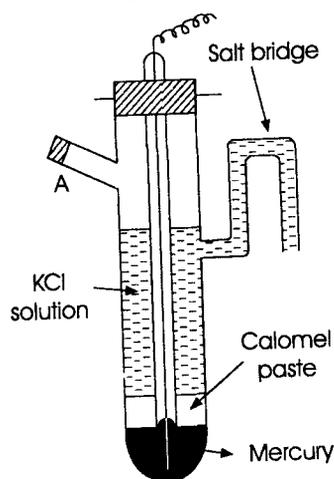
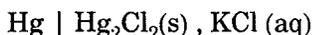
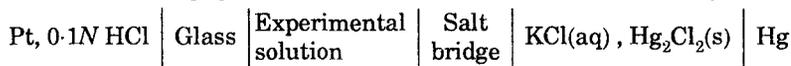


Fig. 2 : Calomel electrode.



On combining glass electrode with calomel electrode, we get the following cell :



EXPERIMENT No. 1

Object : To find out the strength of the given hydrochloric acid solution (approximate strength $N/10$) by titrating it against sodium hydroxide. Use a pH meter.

Apparatus : pH meter, glass electrode, reference electrode, beaker (400 ml), burette, stirrer etc.

Theory : When an alkali is added to an acid solution, the pH of the solution increases slowly, but at the vicinity of the equivalence point, the rate of change of pH of the solution is very rapid. From the sharp break in the curve, we can find the equivalence point, from which the strength can be calculated by normality equation.

Procedure : First standardise the pH meter against a buffer of known pH. (The detailed working instructions of the pH meter are supplied along with the instrument).

Now first wash the glass electrode and reference electrode with distilled water and then with the acid solution. Take 5 ml of HCl solution in a 400 ml beaker. Add sufficient water so that the glass electrode

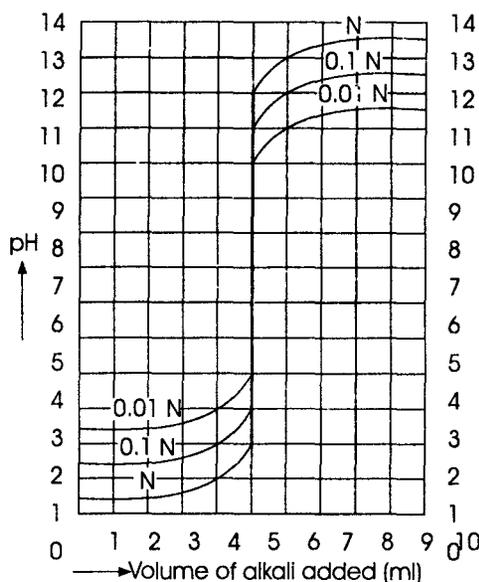


Fig. 3.

as well as the reference electrode are completely dipped. Note the pH of pure acid solution. Now add 1 ml of 0.1N NaOH (prepared exactly 0.1N by dilution method) from the burette in the acid solution taken in the beaker. Stir the contents well. Note the pH of the solution. Now go on adding NaOH solution from the burette and note the pH of the solution, upto say 9—10 ml of NaOH. Near the equivalence point *i.e.*, between 4.0 and 6.0 ml, the alkali should be added in fractions.

Observations : Volume of acid taken = 5 ml (say)

Volume of alkali added (ml)	0.0	1.0	2.0	3.0	4.0	4.5	4.7	4.9	5.1	5.3	5.5	6.0	7.0	8.0	9.0	10.0
pH																

Calculations : A curve is plotted with pH values as ordinate and the volume of alkali added (ml) as abscissa. It will be of the type as shown in figure (3). Find

out the end point. Suppose it is equivalent to x ml of $N/10$ NaOH. From normality equation,

$$\begin{array}{c} N_1 V_1 = N_2 V_2 \\ \text{Acid} \quad \text{Alkali} \\ N_1 \times 5 = \frac{N}{10} \times x \end{array}$$

or
$$N_1 = \frac{N \times x}{10 \times 5}$$

$$\therefore \text{Strength of HCl solution} = \frac{36.5 \times x}{10 \times 5} \text{ g/litre}$$

Result : The strength of the given acid solution is ... g/litre.

Precautions : (i) The temperature control knob of the pH meter should be adjusted to the room temperature.

(ii) After the addition of the alkali, the solution should be thoroughly stirred.

(iii) The pH meter should be first standardised by taking a buffer of known pH.

EXPERIMENT No. 2

Object : To find out the strength of hydrochloric acid and acetic acid in a mixture of both (approximate strength of each acid is 0.1N) by titrating it against sodium hydroxide solution. Use a pH meter.

Apparatus : Same as in preceding experiment.

Theory : Same as in preceding experiment. Here the stronger acid (HCl) will be neutralised first, while the weaker acid (CH_3COOH) will be neutralised afterwards. So, the first end point will be due to HCl, while the second due to CH_3COOH .

Procedure : Same as in preceding experiment. It is advisable to take 5 ml of the mixture in the beaker. This is to avoid taking a large number of readings by the pH meter. Add fractional amounts of alkali, first between 4 and 6 ml and then between 9 and 11 ml and proceed adding the alkali upto 16 ml.

Observations : Same as in preceding experiment.

Calculations : Plot a curve between the pH values as ordinate and the volume of the alkali added as abscissa. The shape of the curve will be as shown in figure (4).

Suppose the first end point corresponds to x ml of NaOH, while the second to y ml of NaOH. From normality equations :

$$\begin{array}{c} N_1 V_1 = N_2 V_2 \\ \text{HCl} \quad \text{NaOH} \end{array}$$

$$N_1 \times 5 = \frac{N}{10} \times x$$

or
$$N_1 = \frac{N \times x}{10 \times 5}$$

$$\therefore \text{Strength of HCl} = \frac{36.5 \times x}{10 \times 5} \text{ g/litre.}$$

Similarly,
$$\begin{array}{c} N_3 V_3 = N_4 V_4 \\ \text{CH}_3\text{COOH} \quad \text{NaOH} \end{array}$$

$$N_3 \times 5 = \frac{N}{10} \times y$$

$$\therefore N_3 = \frac{N \times y}{10 \times 5}$$

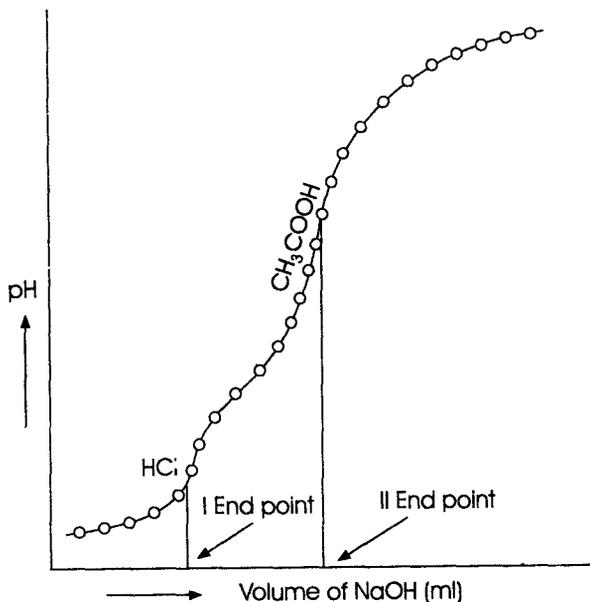


Fig. 4.

$$\therefore \text{Strength of CH}_3\text{COOH} = \frac{60 \times y}{10 \times 5} \text{ g/litre.}$$

Result : The strengths of HCl and CH₃COOH in the given mixture of both are ... and ... g/litre, respectively.

Precautions : Same as in preceding experiment.

EXPERIMENT No. 3

Object : To determine the pH of a solution with indicators.

Apparatus : About 30 test tubes of same size.

Theory : The following table gives different indicators in use and their working range in pH units.

Indicator	Colour change		pH range	pK _{In}
	Acid	Alkali		
Thymol blue (Acid)	Red	Yellow	1.2–2.8	1.7
Methyl yellow	Red	Yellow	2.8–4.0	3.3
Methyl orange	Red	Yellow	3.1–4.4	3.7
Methyl red	Red	Yellow	4.2–6.3	5.1
Bromothymol blue	Yellow	Blue	6.0–7.6	7.1
Phenol red	Yellow	Red	6.8–8.6	7.8
Cresol red (Base)	Yellow	Red	7.2–8.8	8.2
Phenolphthalein	Colourless	Red	8.3–10.0	9.7

Instead of taking an appropriate indicator, several companies have marketed a mixture of indicators under the trade names as **universal indicators**. From the

colour developed with the **universal indicator**, we can easily fix the approximate pH of an unknown solution.

Procedure : Take the unknown solution to be tested and add to it drops of the universal indicator as advised by the manufacturer. Compare the colour developed with the colour chart of the universal indicator. The colour of the solution shows the approximate pH value.

Select an indicator from the above table, whose pK_{In} value is equal or nearly equal to the approximate pH of the solution. Suppose the pH shown by the indicator is 5. The indicator of choice will be methyl red with a pK_{In} value of 5.1.

Set up two sets of nine test tubes of equal size and shape and number them serially. Take 10 ml of a strong solution of an acid in each test tube in first set and 10 ml of an alkali solution of similar concentration in the other set of test tubes. Pair the tubes of acid and alkali marked with same number.

Now put one drop of the selected indicator in the acid and nine drops in the alkali solution in first pair. Similarly, in the second pair add two drops of indicator solution in acid and eight drops in alkali solution and so on. Thus, the ninth pair will contain nine drops of indicator solution in acid tube and one drop in alkali tube. So, each pair of tubes contains ten drops of the indicator solution. Now take 10 ml of the solution of unknown pH in a similar tube and to it add ten drops of the indicator. Pair it with a test tube having 10 ml of water. Compare its colour with the mixed colour of the paired acid-alkali tubes.

Suppose the colour of the solution under test matches with test tube pair number 5. According to the set up, this means that the indicator acquires 5 parts of acid form and 5 parts of the base form.

Calculations : Using the Henderson's equation

$$pH = pK_{In} + \log \frac{[\text{Base form}]}{[\text{Acid form}]}$$

Here $pK_{In} = 5.1$

$$\therefore pH = 5.1 + \log \frac{5}{5} = 5.1$$

Result : *The pH of the unknown solution is 5.1.*

EXPERIMENT No. 4

Object : *To determine the pH (varies between 6 and 9) of a given solution by comparator method or buffer solution method.*

Apparatus : Tintometer or comparator, B.D.H. universal indicator etc.

Theory : The colour of an indicator changes with a change in the pH value of the solution containing it. The solution to be examined is mixed with a suitable indicator and the colour obtained is compared with the colours of a series of mixture of the same indicator with buffer solutions of known pH values. The buffer solution which gives the same colour as the test solution will have the same pH. For accurate pH determination, we employ indicators with short ranges so that the colour changes are very distinct. By suitably mixing a series of indicators, the colour change may be made to extend from pH 1 to 12. Such indicators are known as **universal indicators**. Such indicators give only approximate values of pH.

In comparator method, comparison is made with a series of permanent glass colour standards. Nine glass colour standards are fitted into a disc fitted into a

Acid	Alkali
①	①
②	②
③	③
④	④
⑤	⑤
⑥	⑥
⑦	⑦
⑧	⑧
⑨	⑨

Fig. 5

comparator. It consists of four compartments to receive rectangular glass cells. It is also provided with an opal glass screen. The disc revolves in the comparator and each colour standard passes in turn in front of an aperture through which the solution in the cell can be observed. The colour is matched which gives an idea about the pH of the solution.

Procedure and Observations :

(1) **Buffer Solution Method** : Take 10 ml of the given solution and add 0.5 ml of the universal indicator and note the colour change. Then comparing the colour with the colour chart, the approximate pH of the solution within 1 to 2 units is obtained. Suppose the value lies between 7 and 8.6. Now an indicator is selected whose pH range lies within these values. Phenol red indicator is found to be suitable within this range, as its pH range is 6.8 – 8.4. It has yellow colour at pH 6.8 and red at pH 8.4.

A series of buffer solutions of 0.2M KH_2PO_4 and 0.2M NaOH is selected, differing successively in pH by about 0.2 unit, covering the pH range of the solutions under study. Now take 9 test tubes of pyrex glass of exactly the same dimensions and take 1 ml of buffer solution of definite pH value in each test tube, i.e., 7.0, 7.2, 7.4, 7.6, 7.8, 8.0, 8.2, 8.4 and 8.6. Mark the pH on each tube. Add 0.5 ml of phenol red (indicator) in each tube. The tube marked 7.0 will have yellow colour and that marked 8.4 and 8.6, a red colour. The other tubes will have colours intermediate between yellow and red.

Now take 10 ml of the test solution in a tube of the same type and size and add 0.5 ml of phenol red (indicator). The resultant colour is then matched with that of the coloured standard buffer solution. When a complete match is found, the solution and the corresponding buffer solution will have the same pH. In case, complete match is not found, i.e., the colour lies between those of two successive standards, then the pH of the solution will be between those two standards. Special stands having holes for keeping the buffer solutions are available in the market.

(2) **Comparator Method** : The approximate pH of the test solution is determined by buffer solution method, using a B.D.H. universal indicator.

Now select a suitable disc within this range and fit it into a comparator. Take 10 ml of the test solution in a rectangular cell and add 0.5 ml of suitable indicator (say, phenol red in this case). The disc is rotated and the colour of the solution is matched against the colour standard of the disc. From this the pH of the solution is determined. As the disc revolves, the value of the colour standard visible in the aperture appears in a special indicator recess.

Note : By this method, visual colour matching is carried out and the accuracy is about ± 0.1 pH unit. For higher accuracy, photoelectric colorimeter is used.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 5

Object : To find out the strength of acetic acid by titrating it against sodium hydroxide.

Proceed as in experiment 1. The curve (AB) will be of the type as shown in figure (6).

EXPERIMENT No. 6

Object : To find out the strength of ammonia solution by titrating it against acetic acid solution.

Proceed as in experiment 1. The curve (CD) will be of the type shown in figure (6).

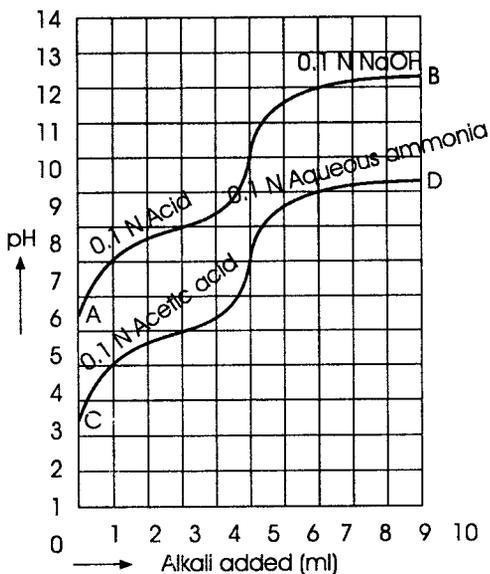


Fig. 6 : pH curve for weak acid and strong base as well as for weak acid and weak base.

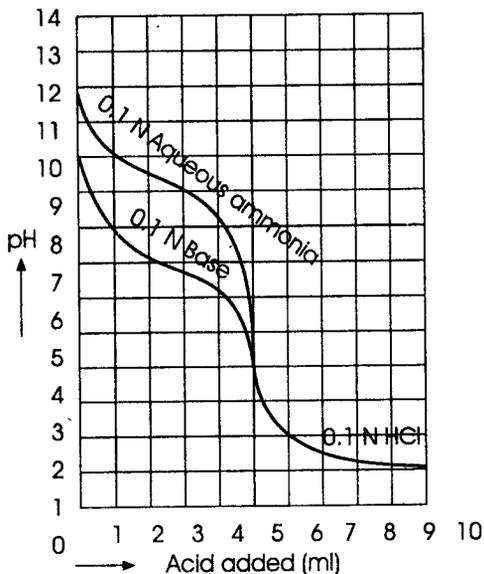


Fig. 7 : pH curve for strong acid and weak base.

EXPERIMENT No. 7

Object : To find out the strength of ammonia solution by titrating it against hydrochloric acid.

Proceed as in experiment 1. In this case, take ammonia solution in the beaker and the acid solution in the burette. The curve will be of the type shown in figure (7).

EXPERIMENT No. 8

Object : To find out the strength of borax solution by titrating it against hydrochloric acid.

Proceed as in experiment 1.

EXPERIMENT No. 9

Object : To find out the strength of sodium carbonate solution by titrating it against hydrochloric acid.

The shape of the curve will be as shown in figure (8).

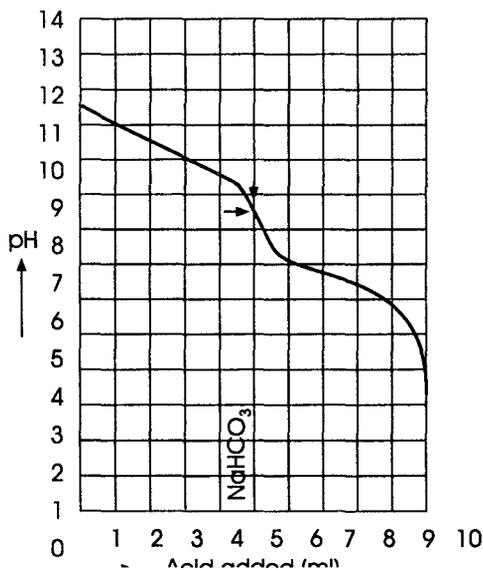


Fig. 8 : pH curve for HCl and Na_2CO_3 .

EXPERIMENT No. 10

Object : To find out the dissociation constants of a polybasic acid, say phosphoric acid by titrating it against sodium hydroxide solution.

See experiment no. 5 (Potentiometry) for reference.

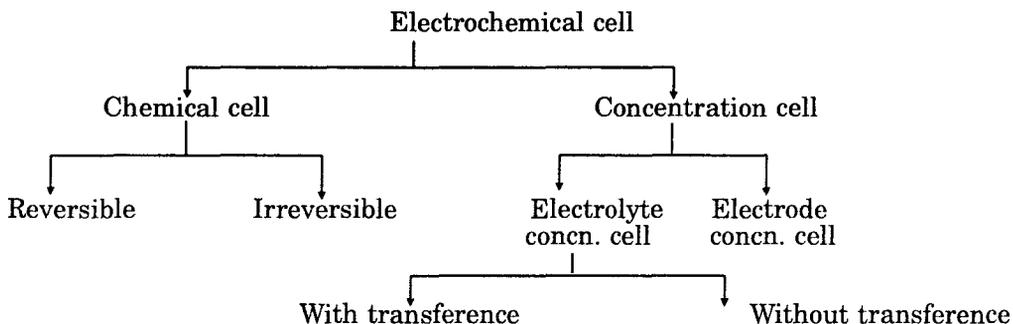


POTENTIOMETRY

A galvanic cell is a device which converts chemical energy into electrical energy. This process is the reverse of the transformation brought about during electrolysis in an electrolytic cell. Galvanic cells, usually consist of one or two electrolytic solutions into which are dipped two electrodes of the same or different metals, *e.g.*, in a Daniell cell, a zinc electrode is dipped in a solution of zinc sulphate and a copper electrode is dipped in a solution of copper sulphate. The two solutions are separated by means of a porous partition.

Electrochemical Cells : When two half elements or cells are connected, we get an electrochemical cell. When the solutions are brought in contact with one another, the ions pass between them. If the two solutions are the same, there is no liquid junction and we get a cell without transference. However, if the solutions are different, the transport of ions across the junction will produce irreversible changes and a cell with transference is obtained.

A cell in which electrical energy arises from the energy change, accompanying a chemical reaction or from a chemical change, is known as a **chemical cell**. The other type of cell is known as **concentration cell**, in which the electrical energy arises from the energy change accompanying the transfer of solute or material from one concentration to another. The other varieties of electrochemical cells are classified as follows :



Measurement of e.m.f. : During the passage of electric current, the e.m.f. of an electrochemical cell is altered, because,

(a) *Internal resistance of the cell may absorb some of the available potential difference.*

(b) *Chemical change may involve polarisation.*

Hence, the e.m.f. of the cell cannot be measured by a voltmeter directly. It can, however, be measured by means of a potentiometer, in which we measure the external potential difference required to stop the passage of current in the cell. Since at the time of measurement, no current flows, hence the above mentioned both errors are eliminated. The applied e.m.f. is equal in magnitude to the e.m.f. of the cell.

The principle generally used in potentiometer is that of *Poggendorff compensation method*. A working cell *C* usually an accumulator of constant e.m.f. (2 volt) and larger than the e.m.f. of the cell to be measured, is connected to the two ends of a uniform wire *AB*, known as potentiometer wire, made of platinum or platinum-iridium of high resistance. The cell *S* whose e.m.f. is to be measured is connected to *A*, with the poles in the same direction, as those of the cell *C* and then through a galvanometer *G*, to a sliding contact (or jockey) *J*, which can be moved along the wire *AB*. By means of a two way key, the cell *S* may be replaced by a standard cell *W* [fig. (1)].

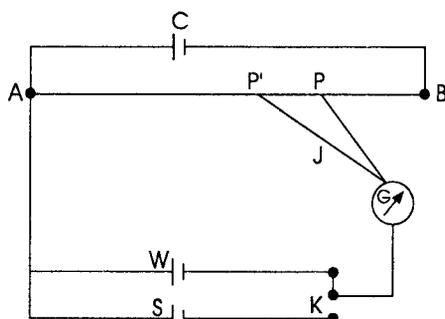


Fig. 1 : Principle of potentiometer

First, the sliding contact is moved till at a certain point there is no deflection in the galvanometer, *i.e.*, no current flows through it. Say the point is *P*, then the e.m.f., of the cell (E_s) would be exactly equal to the potential difference between points *A* and *P*.

Then the cell *S* is replaced by the standard cell *W* and a point (say *P'*) is again found when no current flows through the galvanometer. Now, the e.m.f. of the cell *W*, *i.e.*, E_w will be equal to the potential difference between points *A* and *P'*. Therefore,

$$\frac{E_S}{E_w} = \frac{\text{Potential difference between A and P}}{\text{Potential difference between A and P'}}$$

If *e* be the fall in potential per unit length of the wire, then

$$\frac{E_S}{E_w} = \frac{\text{Length AP} \times e}{\text{Length AP}' \times e} = \frac{\text{Length AP}}{\text{Length AP}'} \quad \dots (1)$$

Knowing the e.m.f. of the standard cell, we can calculate the e.m.f. of the given cell by means of equation (1).

A number of special laboratory potentiometers may be obtained from the market, which allow e.m.f.'s to be read off directly within an accuracy of ± 0.1 millivolt and in which the Poggendorff compensation principle is employed.

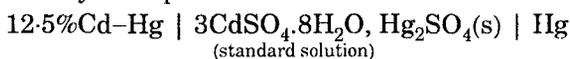
There are a number of sensitive galvanometers such as multiflex galvanometer, Pye galvanometer (moving spot type) etc.

Standard Cells : A cell to be used as a standard of e.m.f. should be (a) readily reproducible from well defined materials, (b) chemically and physically stable over long periods when out of use, (c) as far as possible unpolarisable. In addition to

these essential qualities, it is desirable that its e.m.f. should have a low temperature coefficient. The Weston cadmium cell (cadmium amalgam cell) is generally held to satisfy the above requirements better than any other yet devised.

Weston cadmium cell [fig. (2)] consists of an H shaped glass vessel with a platinum wire sealed through the bottom of each limb. One limb contains a layer of pure mercury (1 cm deep) which is covered with a paste of sparingly soluble salt, mercurous sulphate (paste made with saturated solution of cadmium sulphate), which constitutes an anode. The other limb constituting the cathode is covered with a layer of cadmium sulphate crystals ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$). The electrolyte is a saturated solution of cadmium sulphate.

The cell may be represented as :



This cell has a definite e.m.f. given by,

$$E_t = 1.018300 - (t - 20) \times 4.06 \times 10^{-6} - (t - 20)^2 \times 9.5 \times 10^{-7} + (t - 20)^3 \times 1 \times 10^{-8} \text{ volt.}$$

At 20°C , therefore, the cell will have an e.m.f. of 1.0183 volt. The temperature coefficient of this cell is negligibly small.

Potentiometer : Now-a-days direct reading potentiometers are used in laboratories. These are built up units in which the stretched wire of a metre bridge is replaced by a series of equal resistances and one circular slide wire step equal

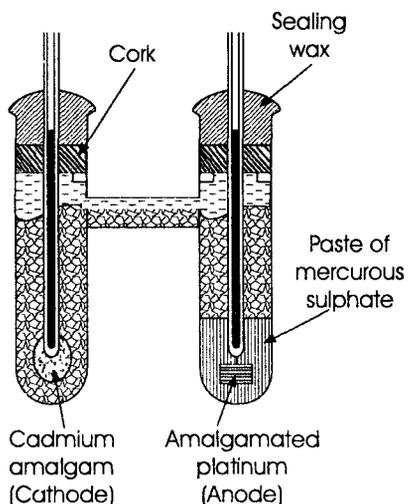


Fig. 2 : Standard cell.

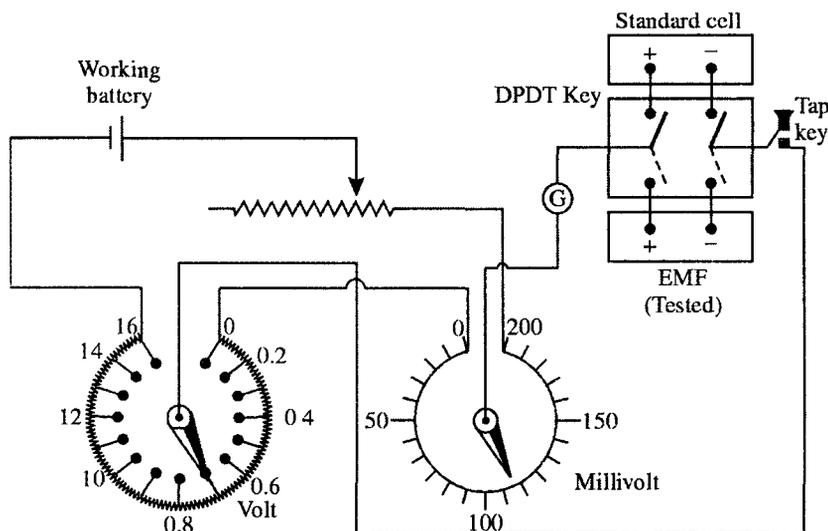
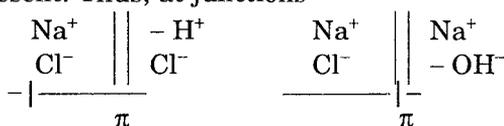


Fig. 3 : Direct reading potentiometer.

in resistance to one step in the resistance series. Variable resistances are fitted to cut off the extra battery potential. Separate terminals are fitted for connecting the working battery, standard cell, galvanometer and the EMF to be examined. A selector switch connects the potentiometer separately for standardisation and measurement steps, a tap key and a sensitive galvanometer are fitted in series with the cell whose potential is to be measured by balancing against known potentials from the potentiometer potential divider.

Diffusion Potentials : When two different electrolytic solutions are brought with one another, a boundary potential is set up due to the unequal mobilities of the ions present. Thus, at junctions



the high mobility possessed by H^+ or OH^- ions relative to the mobilities of the other ions, results in a strong tendency for these ions to diffuse to the left solution. A diffusion potential (π) is set up as shown. These potentials may be as high as 50 mV, but owing to their sensitiveness to the conditions at the junction, they are very difficult to calculate. They may be minimised to a very small extent by connecting the half cells with a concentrated or saturated solution of a salt whose ions have nearly equal mobilities, e.g., potassium chloride, ammonium nitrate etc.

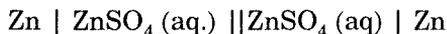
Salt Bridge : To minimise the diffusion potential, the two electrodes are connected by means of a **salt bridge**, which consists of an inverted U-tube containing a jelly of agar-agar or gelatin. The jelly contains a little potassium chloride or ammonium nitrate, which can be added during its preparation.

To prepare a salt bridge make a bent tube, bent at right angles at two places. Take 3 g of agar-agar in a beaker containing about 100 ml of distilled water. Heat it till the agar-agar completely dissolves. Add 15 g of solid potassium chloride or ammonium nitrate to this solution and stir till the solute completely dissolves. Fill the U-tube or bent tube with this solution and keep it in an upright position, till the jelly sets completely on cooling. If the jelly shrinks in the tube on cooling, then break the ends of the tube with a file, so that the jelly comes on the surface of the two ends. Care should also be taken that no air bubbles are present in the tube after they have been filled with the jelly.

Conventions with Regard to Cell Diagrams, Signs of Electrode Potential :

(1) A single vertical line | represents the junction of an electrode and a solution, say $\text{Cu} | \text{CuSO}_4(\text{aq.})$.

(2) A double vertical line || represents a salt bridge between the two solutions, e.g.,



(3) A long arrow embracing the whole cell diagram, gives the direction of the current inside the cell. A short line with indication of positive end (+—) gives the direction of potential difference (electrode of diffusion potential).

(4) The letter E usually represents the e.m.f. of the cell. The sign, e.g., $E_{\text{M}^+}^\circ$ will be used only when the activity of the reversible ion in solution is unity; the potential $E_{\text{M}^+}^\circ$, is thus known as standard potential.

(5) Diffusion potential will be represented by the symbol π .

(6) All electrode potentials are assumed to be measured on the hydrogen scale ($a_{\text{H}^+} = 1$).

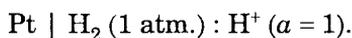
(7) An electrode potential is positive when the electrode is positive to the solution with which it is in equilibrium.

Construction of Electrodes : There are two types of electrodes :

(a) *Primary reference electrode*, such as hydrogen electrode.

(b) *Secondary reference electrode*, such as calomel electrode, silver-silver chloride electrode etc.

1. Hydrogen Electrode : Hydrogen gas at one atmosphere pressure in contact with solution of hydrogen ions constitutes a hydrogen electrode. It is represented as :



On account of hydrogen being a gas, a special device is made in order to make the potential difference between the gas and the solution measurable. This device consists in placing a small strip of platinised platinum foil such that it is half immersed in the solution and half surrounded by the gas. The finely divided platinum on platinum foil adsorbs hydrogen and in that condition behaves as if it were a solid electrode of the gas. It freely permits the change from the gaseous state to the ionic state and vice versa. Different forms of hydrogen electrodes are used, but the one devised by Hildebrand is much used in practice.

(a) **Gas bubbling type hydrogen electrode :** A rectangular piece of platinum foil, which is platinised, is connected to a piece of platinum wire sealed in a glass tube. The foil is first cleaned by keeping it standing overnight in chromic acid or more quickly by immersing it in hot concentrated nitric acid. It is washed with water and lightly platinised by electrolysis (as done for conductivity cells). A glass jacket encloses the tube carrying the platinum foil. The jacket is closed at the top and widened at the bottom. A side tube attached to the jacket admits hydrogen at normal atmospheric pressure which escapes through two holes made in the widened part of the jacket at level midway up the platinum foil. The whole apparatus [fig. (4)] stands in a tall beaker containing hydrochloric acid, having effective concentration of hydrogen ions equal to one gram hydrogen ions per litre, i.e., $a_{\text{H}^+} = 1$.

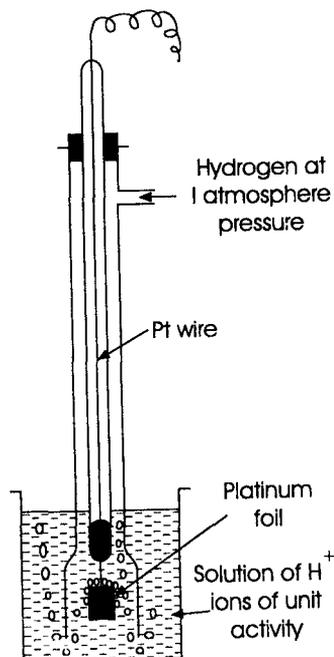


Fig. 4 : Hydrogen electrode.

This particular electrode is known as standard, hydrogen electrode, for hydrogen gas and hydrogen ions are in their both standard states. The convention is that this electrode is arbitrarily assigned a potential of ± 0.0000 volt at all

temperatures. All other potentials expressed on this basis are referred to as potentials on the hydrogen scale.

Note : Setting this electrode in its final position before cleaning and platinising is not recommended, as it is then usually difficult to secure an even coating of deposit. The electrode should not be allowed to dry after its final preparation and it should be kept immersed in distilled water or dilute sulphuric acid, when not in use.

(b) **The enclosed type of hydrogen electrode :** The first type of electrode is essential for electrometric titrations and some other purposes, but for the determination of the pH of a single solution of fixed composition, it is unnecessarily

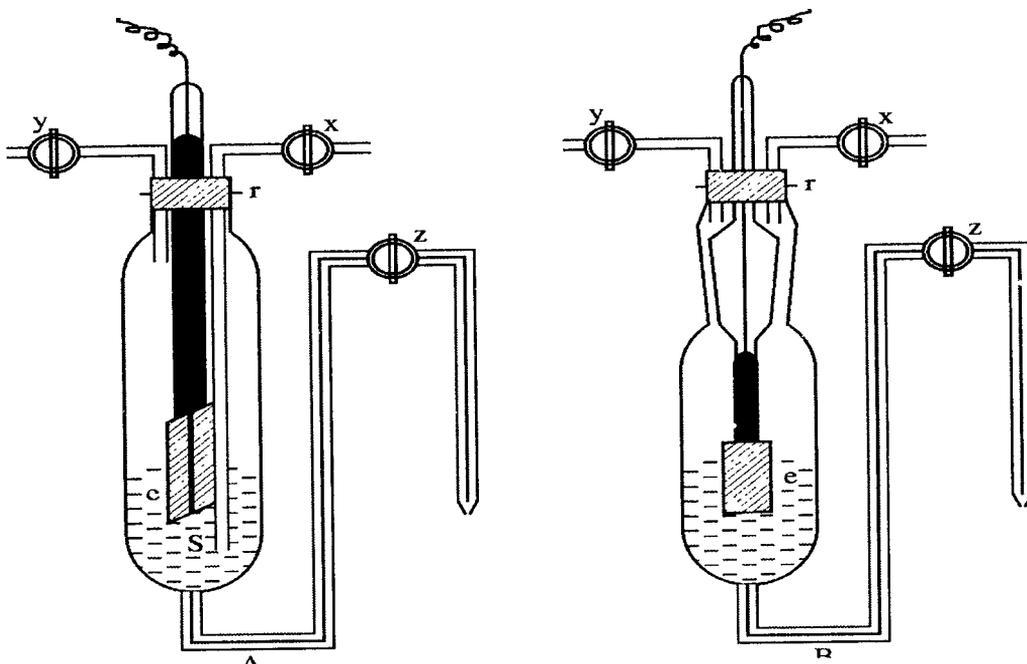
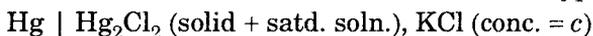


Fig. 5 : Hydrogen electrode (enclosed type)

wasteful of hydrogen. Enclosed type of electrode is shown in figure (5). The platinum foil is first cleaned and platinised as before. The vessel is first completely filled with the solution under examination and the bung carrying the electrode and tapped tubes x and y are then set in place with tap y open, so that a little of the solution issues from it, and no air bubble is left under the bung. The tap z is shut and y opened, hydrogen thus continues to bubble through the solution for some time to remove dissolved air.

2. Calomel Electrode : This electrode is of the type :



The electrode shown in figure (6) may be conveniently set up in a glass boiling tube of about 70-80 ml capacity. A small quantity of pure mercury is first placed in a thoroughly cleaned tube to give a layer about 1 cm deep. A tube T containing mercury and with fused platinum wire at its lower end to serve as contact with the mercury of the electrode is then introduced. The tube should contain sufficient mercury to sink the platinum contact to rest on the base of the boiling tube.

Pure calomel is first prepared by dissolving mercury in mercuric chloride in a mortar pestle. To this pure calomel, add a few drops of mercury and shake it in a

separate bottle with two successive portions of the prepared solution of potassium chloride to be used in the electrode, to remove traces of mercuric compounds. The solution is decanted and rejected before adding the second portion of potassium chloride. The calomel is then washed for the third time, but this time keep the decanted potassium chloride solution for the final filling of cell. This pasty calomel is carefully poured onto the mercury in the tube. Great care is taken that no liquid paste intrudes between the contact wire and the mercury. *It is, however, not recommended to grind the calomel in a mortar with potassium chloride solution and mercury.* If a saturated calomel electrode is to be prepared, crystals of pure potassium chloride should be added to the paste after it has been poured into the boiling tube. The tube is then filled with the decanted potassium chloride solution (decanted after washing the pure calomel for the third time), by drawing in the solution through the tube and then closing the rubber tube A with a clip. The middle end of the boiling tube is connected to a side tube carrying an agar-agar jelly, which is dipped in the beaker constituting the salt bridge.

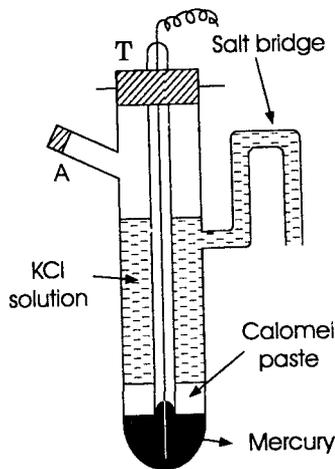


Fig. 6 : Calomel electrode.

Other types of calomel electrodes are shown in figures (7) and (8). The second type is suitable for precision work. It has a three way stop cock for removing the contaminated potassium chloride after it has been employed in a titration.

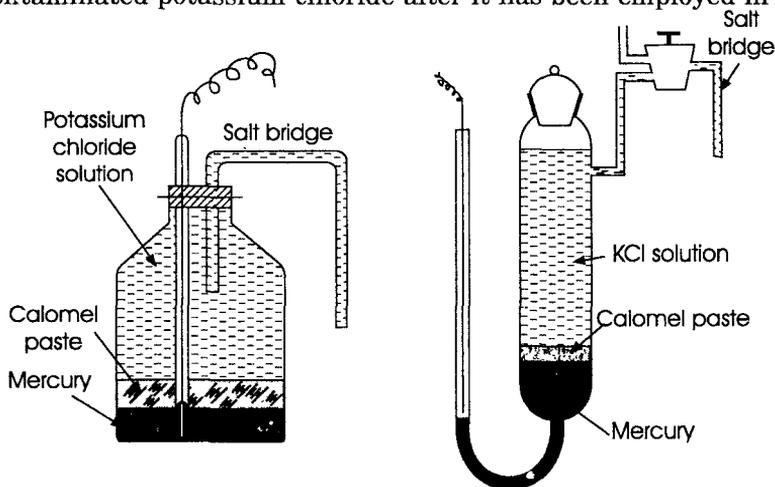


Fig. 7 : Calomel electrode. Fig. 8 : Calomel electrode

Normal or decinormal calomel electrodes can be prepared by using normal or decinormal potassium chloride solutions instead of its saturated solution.

3. Silver-Silver Chloride Electrode : In recent years, the silver-silver chloride electrode has been frequently used as a reference electrode due to its

simplicity and robustness. The electrode shown in fig. 9 (a) consists of a strip of pure silver. (It is washed with acetone to remove greasy matter). A connecting silver wire is attached by binding into a small hole, bored at the extremity of the narrow part, which is then inserted into a length of glass tubing and the connecting wire bent over the top of the tube so as to retain the silver strip firmly in place.

The silver strip is coated with a film of chloride by electrolysis in which the strip is taken as an anode and platinum foil as a cathode. The electrolytic solution is normal hydrochloric acid through which a current of 5 milli-ampere is passed for about an hour. The electrode (silver strip) should acquire a uniform purplish colour.

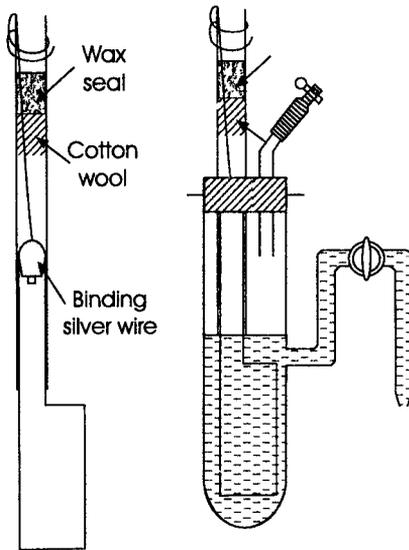


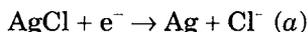
Fig. 9 (a)

Fig. 9 (b)

The electrode can then be used for experimental purposes by dipping it in a solution of molar or decinormal solution of potassium chloride or hydrochloric acid, taken in a tube. The complete set up of the electrode is shown in figure 9 (b).

The standard electrode potential of silver-silver chloride is given by $E^\circ = 0.22239 - 645.32 \times 10^{-6} (t - 25) - 3.284 \times 10^{-6} (t - 25)^2 + 9.948 \times 10^{-1} (t - 25)^3$

Nernst equation for the reduction electrode potential based on the reaction



is
$$E = E^\circ - \frac{2.303 RT}{F} \log a_{\text{Cl}^-}$$

Caution : Silver chloride dissolves in high concentration of chloride ions by forming a soluble complex. It makes use of this electrode in one molar or stronger solutions of chloride ions unsafe unless these solutions are already saturated with silver chloride.

Silver Electrode : For accurate work, a silver electrode is prepared with a fresh film of silver as follows :

Take nearly 0.4% solution of AgNO_3 and add to it dilute KCN solution with constant stirring till the precipitate of AgCN first formed redissolves. Clean the silver electrode with emery paper and dip it in 1:1 HNO_3 solution till gas evolution starts and bubbles are formed freely. Take the electrode out and wash it with water. Support the electrode in the cyanide electroplating bath and make it cathode. Use another silver electrode as anode. Now pass a current of 0.2 mA for sufficient time to get a thin deposit of silver. Wash thoroughly with distilled water. Store the electrode in water. A silver wire of 0.5 to 1.0 mm diameter will serve for experimental purposes.

EXPERIMENT No. 1

Object : To determine the electrode potential of copper and zinc electrodes in 0.1M and 0.01M solutions and to calculate the standard electrode potential of these electrodes.

Apparatus : Copper and zinc rods, glass tubes, potentiometer, saturated calomel electrode etc.

Theory : The saturated calomel electrode (SCE) is connected with the copper or zinc electrode and the e.m.f. of the cell (E) is determined by means of a potentiometer. Thus,

$$E = E_R - E_L$$

The standard electrode potential (E°) is given by,

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{a_{red}}{a_{ox}}$$

Procedure : Take copper or zinc rods or thick wires about 2.5 cm long and solder each to an insulated connecting wire. Clean the copper rod with emery paper or dip it in dilute HNO_3 . Wash it and deposit a thin layer of copper electrolytically (by taking CuSO_4 solution in voltameter and a strip of pure copper as anode and passing a current of 0.5 amp). The zinc rod, on the other hand, is amalgamated by rubbing mercury over it in presence of dil. H_2SO_4 . Wash it thoroughly with water and dry it before putting it in a solution of zinc sulphate. The process of amalgamation makes the surface impurities ineffective and eliminates local action.

The electrodes are cemented into glass tubes with glass wax or araldite. Now fill the zinc electrode vessel in turn with 0.1M or 0.01M solution of ZnSO_4 and similarly the copper electrode is dipped in a solution of 0.1M or 0.01M CuSO_4 as shown in figure (10)

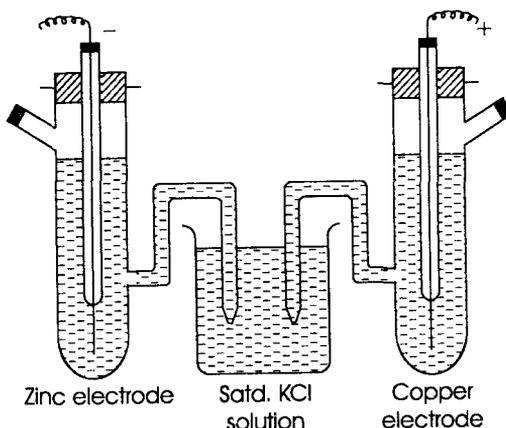
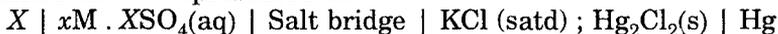


Fig. 10 : Daniell Cell

The single electrode is then coupled with standard calomel electrode (SCE) (reference electrode) by means of salt bridge (satd. KCl solution) and the cell thus obtained can be represented as :



where, $X = \text{Zn}$ or Cu and $x = 0.1$ or 0.01 .

When the two electrodes have been combined to form a cell, it is not known as which of the electrodes will form the positive or negative pole. In order to determine this, one of the electrodes is connected to the end A of the potentiometer wire AB [fig. (11)] and the other electrode to the galvanometer G through a single pole double throw (SPDT) key and then to the jockey C. Move the jockey on the wire AB and tap the tap key. If the galvanometer pointer moves in one direction for all positions of the jockey, it means that wrong end (negative electrode) has been

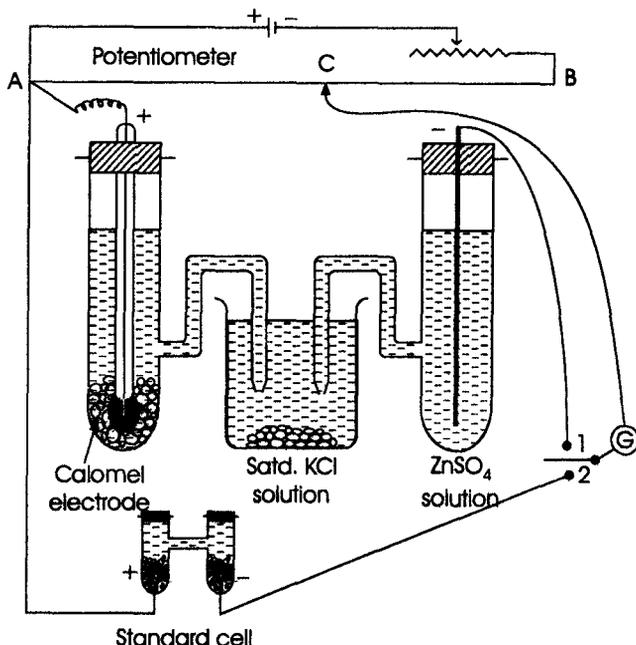
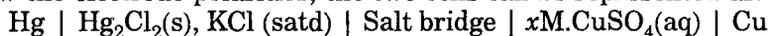


Fig. 11

connected to point A. Change the electrodes accordingly*. Now the null point is detected on the wire from which e.m.f. of the cell can be calculated. Keeping in view the electrode polarities, the two cells can be represented as:



Let for Zn—SCE(I) and Cu—SCE (II) cell, the wire distance for null points be represented by AC, AD and AC' (standard cell).

Then,

$$\frac{\text{E.M.F. of cell I } (E_1)}{\text{E.M.F. of standard cell } (E_s)} = \frac{AC}{AC'}$$

$$\therefore \text{E.M.F. of cell I, } E_1 = \frac{AC}{AC'} \times E_s \quad \dots (1)$$

Similarly,

$$\text{E.M.F. of cell II, } E_2 = \frac{AD}{AC'} \times E_s \quad \dots (2)$$

Observations :

Distance AC for cell I	Distance AD for cell II	Distance AC' for standard cell
...

*In case of Zn—SCE cell, the Zn will act as negative, while Hg will act as positive electrode. But for Cu—SCE cell, Cu will act as positive and Hg acts as negative electrode.

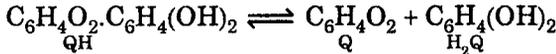
where, a_Q , a_{H_2Q} and a_{H^+} are the activities of quinone, hydroquinone and hydrogen ions, respectively, E° is the standard electrode potential referred to normal hydrogen electrode. If the solution contains equimolecular amounts of quinone and hydroquinone, the ratio $\frac{a_Q}{a_{H_2Q}}$ may be taken as unity. Therefore,

$$E = E^\circ + \frac{RT}{F} \log a_{H^+}$$

or
$$E = E^\circ + 0.0591 \log a_{H^+}, \text{ at } 25^\circ \text{ C} \quad \dots (2)$$

(At 25°C or 298K ; $\frac{RT}{F} = 0.0591$ volt)

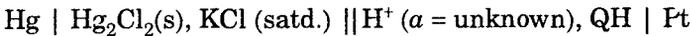
Quinhydrone (QH) is an equimolecular compound of quinone and hydroquinone and is slightly soluble in water and dissociates into its two components as follows :



It follows, therefore, that in the pH range over which the compound quinhydrone is stable, expression (2) holds good. The value of E° has been determined by direct reference to normal hydrogen electrode and it has a value of -0.704 volt and -0.6994 volt at 18°C and 25°C , respectively.

The quinhydrone electrode can be set up very easily. A pinch of quinhydrone (1 g per 100 ml of solution) is added to the solution, taken in a beaker. A clean platinum electrode is then inserted in it for making the electrical contact.

Suppose quinhydrone electrode is combined with a saturated calomel electrode for carrying out the titration. A cell of the following type will result in :



In this cell, the calomel electrode undergoes oxidation, while the quinhydrone electrode undergoes reduction. The observed e.m.f. of the cell will be :

$$E_{obs} = E_R - E_L = E_R - E_L$$

where, E_L = Electrode potential of the left electrode, i.e., saturated calomel electrode and is equal to 0.2415 volt and E_R is given by equation (2).

$$\begin{aligned} \therefore E_{obs} &= E^\circ + 0.0591 \log a_{H^+} - 0.2415 \\ &= 0.6994 - 0.2415 + 0.0591 \log a_{H^+} \\ &= 0.6994 - 0.2415 - 0.0591 \text{ pH} \end{aligned}$$

$$\therefore \text{pH} = \frac{0.4579 - E_{obs}}{0.0591} \quad \dots (3)$$

Important : Quinhydrone electrode cannot be used in alkaline solution having pH more than 9, for then the ratio $\frac{a_Q}{a_{H_2Q}}$ does not remain unity. This is partly due to the oxidation of hydroquinone in alkaline solution and partly due to the hydroquinone ionising as acid under these conditions.

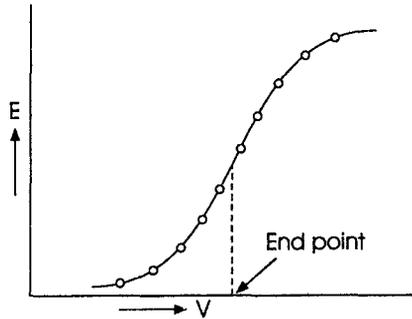


Fig. 12

Thus, with changing values of pH, the observed e.m.f. varies. Hence, in practice, the potential is measured after successive addition of small volumes of titrant. Then a curve [fig. (12)] is plotted between E_{obs} or pH as ordinate and volume of titrant (V) as abscissa. The equivalence point will, thus, be indicated by a sudden change in the value of E_{obs} or pH.

Greater the steepness of the slope of the inflexion in the curve, greater will be the precision of the experiment. The steepness of the slope of the curve will decrease, if the solution is dilute or if either the acid or base or both are weak substances. In case the slope is not steep, it is advisable to plot a curve between $\Delta E/\Delta V$ and V ; where ΔE is the change in potential of the solution due to small change ΔV of the titrant. Such a curve shown in figure (13) is known as **differential curve**. The equivalence point in such a curve lies at the maxima of the curve.

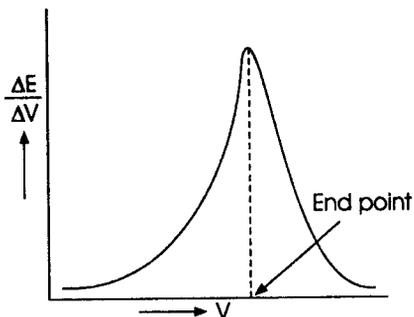


Fig. 13

Sometimes a curve shown in figure (14) is obtained by plotting $\Delta^2 E/\Delta V^2$ against V . It is based on the principle that $\Delta^2 E/\Delta V^2$ is zero at a point where the slope of the curve, $\Delta E/\Delta V$ is maximum. Such a curve is known as **analytical curve**.

According to Henderson's equation, we have,

$$\text{pH} = \text{pH}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

where, K_a is the dissociation constant of the acid ($\text{pK}_a = -\log K_a$). At a point when the acid is half neutralised, we have,

$$[\text{Salt}] = [\text{Acid}]$$

$$\therefore \text{pH} = \text{pK}_a$$

Hence, the dissociation constant of the acid can be calculated from the pH at the half-neutralization point.

Procedure : Take 10 ml of acetic acid in a 400 ml beaker and add 100 ml of distilled water. Now add about 0.5 g of quinhydrone and stir the solution vigorously to obtain a saturated solution. Now immerse a platinised platinum electrode and also one arm of the salt bridge apparatus. Also immerse in the beaker, the bent tube of the saturated calomel

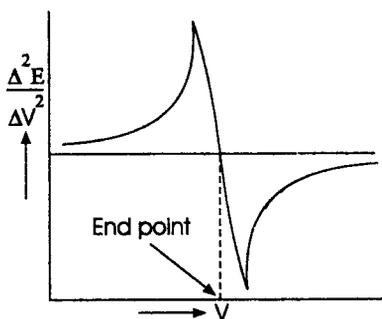


Fig. 14

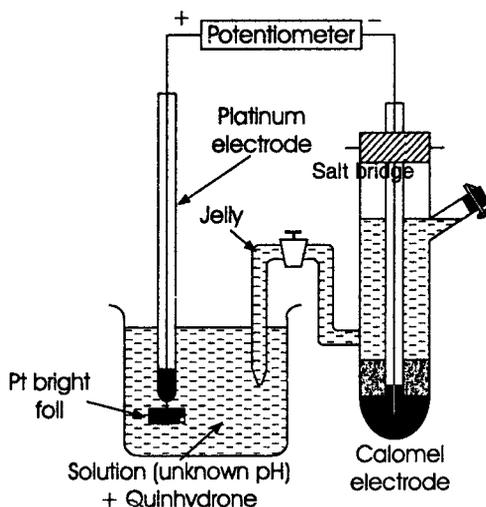


Fig. 15

electrode. The two electrodes are connected to a potentiometer, battery etc. as shown in figure (15).

Add $N/10$ NaOH (prepared exactly by dilution method) and shake the contents vigorously by means of a stirrer. Note the e.m.f. of the solution directly by means of the potentiometer. **The potentiometer should be first standardised by a Weston cadmium cell and then the reading of the potential should be taken.** Add 1 ml titrant in each addition, but add only 0.2 ml of it just before and after the end point. (In this case, add 0.2 ml from 9 ml to 11 ml). Continue addition of NaOH till you have added 18 ml of it.

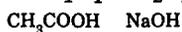
Observations : Volume of acid taken = 10 ml (say).

Volume of NaOH added (ml)	E_{obs} (volt)	$\Delta E/\Delta V$	$\Delta^2 E/\Delta V^2$

Calculations : Plot the values of E_{obs} as ordinate against volume of NaOH as abscissa. The point of inflexion [Fig. (12)] will indicate the equivalence point. If it is not sharp, then plot a curve between $\Delta E/\Delta V$ (ordinate) and volume of NaOH (abscissa) and find the equivalence point [Fig. (13)]. If need be, also plot a curve between $\Delta^2 E/\Delta V^2$ and volume of NaOH [Fig. (14)].

Suppose the end point lies at x ml of NaOH. Then, according to normality equation,

$$N_1 V_1 = N_2 V_2$$



$$N_1 \times 10 = \frac{N}{10} \times x$$

$$\therefore N_1 = \frac{N \times x}{10 \times 10}$$

$$\therefore \text{Strength of CH}_3\text{COOH} = \frac{60 \times x}{10 \times 10} \text{ g/litre.}$$

From any of the curves, find the pH at the neutralisation point. Hence, find the pH at half neutralisation point, from which we can calculate the dissociation constant of the acid as,

$$\text{pH}_{1/2} = \text{p}K_a$$

Result : The strength of acetic acid is ... g/litre and the dissociation constant of acetic acid is ...

Precautions : (i) It is necessary to clean the platinum electrode from time to time. This can be done by heating the wire in an alcohol flame.

(ii) In the solution, quinhydrone should be present in excess.

(iii) The pH of the solution should not go beyond 9.0.

(iv) The stirring should be vigorous after each addition of the titrant.

(v) Always take acid in the beaker containing the electrode and the base should be taken in the burette.

(vi) Connect quinhydrone electrode to the positive end and calomel electrode to the negative end of the potentiometer.

(vii) Standardisation of the potentiometer should be done after noting every reading.

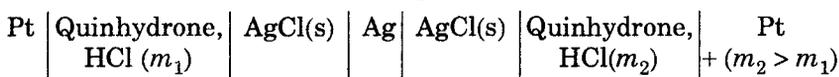
EXPERIMENT No. 3

Object : (a) To determine the mean ionic activity coefficient of hydrochloric acid solution at different concentrations.

(b) To study the effect of ionic strength on mean activity coefficient of hydrochloric acid in a given solution.

Apparatus and Chemicals : Potentiometer set, two platinum electrodes, two Ag-AgCl electrodes, quinhydrone, 0.01M HCl solution, solid KNO₃.

(a) **Theory :** The experiment is carried out by setting up the following concentration cell without transport.



Quinhydrone electrode is reversible with respect to H⁺ ions and Ag - AgCl electrode is reversible with respect to Cl⁻ ions. For such a cell, the emf is given by,

$$E = \frac{2RT}{F} \ln \frac{(m_{\pm} f_{\pm})_2}{(m_{\pm} f_{\pm})_1}$$

$$m_{\pm}^{\nu} = m_{+}^{\nu_{+}} \cdot m_{-}^{\nu_{-}}$$

where ν = total number of ions per molecule

ν_{+} = number of cations per molecule

ν_{-} = number of anions per molecule

If the cell emf is measured by changing m_1 and keeping m_2 constant, the activity coefficient for any acid concentration may be measured by extrapolation method.

From Debye-Huckel equation for dilute solutions of electrolytes, f_{\pm} is given by,

$$\log f_{\pm} = z_{+} z_{-} A \sqrt{\mu} - C \mu \quad \dots (1)$$

where z_{+} and z_{-} are the valencies of the positive and negative ions of the electrolyte. μ is the ionic strength of the solution, A and C are constants.

For a 1 : 1 electrolyte, $z_{+} = z_{-} = 1$, so

$$\begin{aligned} \mu &= \frac{1}{2} \sum m_i z_i^2 \\ &= \frac{1}{2} (m_{+} \times 1^2 + m_{-} \times 1^2) \\ &= \frac{1}{2} (m_{+} + m_{-}) = \frac{1}{2} (m + m) = m \end{aligned}$$

(In this case m is taken as m_1 , which is varied)

Thus for a 1 : 1 electrolyte, equation (1) can be written as,

$$-\log (f_{\pm})_1 = A \sqrt{m_1} - C m_1 \quad \dots (2)$$

Combining equation (2) with the identity

$$-\log (f_{\pm})_1 + \log (f_{\pm})_2 = \log \frac{(f_{\pm})_2}{(f_{\pm})_1}$$

or
$$-\log (f_{\pm})_1 = -\log (f_{\pm})_2 + \log \frac{(f_{\pm})_2}{(f_{\pm})_1}$$

we get,

$$A \sqrt{m_1} - C m_1 = -\log (f_{\pm})_2 + \log \frac{(f_{\pm})_2}{(f_{\pm})_1}$$

On rearrangement, we have

$$\log \frac{(f_{\pm})_2}{(f_{\pm})_1} - A \sqrt{m_1} = \log (f_{\pm})_2 - C m_1 \quad \dots (3)$$

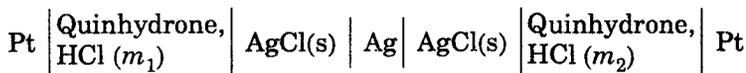
A plot of L.H.S values of equation (3) against m_1 values will give a straight line with a slope of $-C$ and intercept of $\log (f_{\pm})_2$.

On the left hand side of equation (3), A is seen to have a value of 0.509 at 25°C, m_1 is known directly. The values of $\log \frac{(f_{\pm})_2}{(f_{\pm})_1}$ can be known from E_{cell} measurements vide E_{cell} equation,

$$\begin{aligned} E_{\text{cell}} &= \frac{2RT}{F} \ln \frac{(m_{\pm} f_{\pm})_2}{(m_{\pm} f_{\pm})_1} \\ &= \frac{2 \times 2.303 RT}{F} \log \frac{(m_{\pm})_2}{(m_{\pm})_1} + \frac{2 \times 2.303 RT}{F} \log \frac{(f_{\pm})_2}{(f_{\pm})_1} \quad \dots (4) \end{aligned}$$

So, $\log (f_{\pm})_2$ can be evaluated for any solution of HCl.

Alternately, when the molality of m_2 solution is held constant ($m_{\pm})_2$ and $(f_{\pm})_2$ can be treated as constants. The half cell on the RHS in the cell



will have a constant emf. The cell emf's measured by changing m_1 will show changes due to the changing emf of the left electrode.

$$\begin{aligned} E_{\text{cell}} &= \frac{2 \times 2.303 RT}{F} \log \frac{(m_{\pm} f_{\pm})_2}{(m_{\pm} f_{\pm})_1} \\ &= \frac{2 \times 2.303 RT}{F} \log (m_{\pm} f_{\pm})_2 - \frac{2 \times 2.303 RT}{F} \log (m_{\pm})_1 - \frac{2 \times 2.303 RT}{F} \log (f_{\pm})_1 \end{aligned}$$

or
$$E_{\text{cell}} + \frac{2 \times 2.303 RT}{F} \log (m_{\pm})_1 = \frac{2 \times 2.303 RT}{R} \log (m_{\pm} f_{\pm})_2 - \frac{2 \times 2.303 RT}{F} \log (f_{\pm})_1 \quad \dots (5)$$

In equation (5), the LHS is completely known and can be plotted as ordinate. The first term on the RHS is constant during the study, while the second term involves the variable $(f_{\pm})_1$ which is not known. Hence,

$$-\log (f_{\pm})_1 = A \sqrt{m_1} - C m_1$$

This situation permits an approximation

$$-\log (f_{\pm})_1 \approx A \sqrt{m_1} \quad \dots (6)$$

If the above approximation (which becomes increasingly valid as m_1 is decreased) in equation (5), a graph can be plotted between $E_{\text{cell}} + \frac{2 \times 2.303RT}{F} \log (m_{\pm})_1$ values as ordinate and $\sqrt{m_1}$ values as abscissa. On extrapolating this straight line to $\sqrt{m_1}$ equal to zero will give the value of $\frac{2 \times 2.303 RT}{F} \log (m_{\pm} f_{\pm})_2$ as an intercept on the ordinate. On substituting this value in equation (5), the values of $\log (f_{\pm})_1$ can be calculated for different values of m_1 . However, dilution of m_1 up to $0.0001m$ will be sufficient.

Procedure : (a) Set up the potentiometer and standardise it using a standard cell. The two silver-silver chloride electrodes and two platinum electrodes in common solutions of chloride ion and hydrogen ion with quinhydrone are checked. The emf difference for each pair of electrodes should not exceed $0.5mV$. Set up the two beakers. Take nearly 25 ml of $0.01N$ HCl in m_2 beaker and 25g of water in m_1 beaker. Add quinhydrone (0.2 – 0.3 g) to each beaker. Dip one platinum electrode in each beaker. The solutions in the beakers are inter-connected by placing the two Ag – AgCl electrodes from the two silver wires externally. After setting, add 0.5 g of $0.002M$ HCl solution to the water beaker (m_1). Stir and note the constant value of E_{cell} .

Add further 0.5 g of $0.002M$ HCl solution step-by-step. After each addition stir the solution and record the E_{cell} value. Continue till 5.0 g of $0.002M$ HCl solution has been added. Record the temperature.

Use the above data in calculating $(f_{\pm})_2$ in $0.01 M$ HCl solution.

(b) In order to study the effect of ionic strength on the mean ionic activity coefficient of HCl, the concentration (molality) of HCl is fixed and the concentration of KNO_3 is varied. In each of the two compartments of the cell mentioned above, place 2 ml of $0.002 m$ HCl. Also prepare a concentrated solution ($2 m$) of KNO_3 in $0.002 m$ HCl solution. Add successively 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 ml of this solution to one compartment (connected to negative terminal of the potentiometer), stir the mixture well and measure the emf after each addition. In this way, the concentration of HCl ($0.002M$) remains constant, whereas that of KNO_3 is changed.

Calculations : (a) Following the extrapolation method as explained, calculate the mean ionic activity coefficient of HCl at each concentration. The activity coefficient will increase with decrease in concentration.

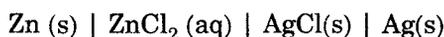
(b) Determine the mean ionic activity coefficient of HCl for a fixed concentration ($0.002 m$) at different concentrations of KNO_3 . The value decreases with increase in ionic strength, *i.e.*, with increasing concentration of KNO_3 .

EXPERIMENT No. 4

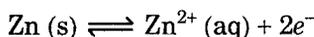
Object : To find the mean ionic activity coefficient in a solution of zinc chloride.

Apparatus and Chemicals : Potentiometer set, Calomel electrode, silver-silver chloride electrode, zinc rod, 1 *m* ZnCl₂ solution, 1% HgCl₂ solution.

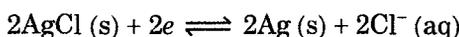
Theory : The following cell may be set up :



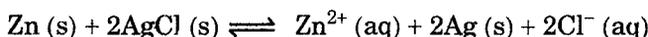
The anode reaction is :



The cathode reaction is



The cell reaction will thus be :



The cell potential according to Nernst equation is given by,

$$\begin{aligned} E &= (E^\circ_{\text{Ag, AgCl}} - E^\circ_{\text{Zn, Zn}^{2+}}) - \frac{RT}{2F} \ln (a_{\text{Zn}^{2+}} \times a_{\text{Cl}^-}^2) \\ &= E^\circ_{\text{cell}} - \frac{RT}{2F} \ln a_{\text{ZnCl}_2} \end{aligned}$$

By electrochemical convention, activity relationship between activity of an electrolyte and activity of its ions is given by the following equation:

$$a_{\text{ZnCl}_2} = a_{\text{Zn}^{2+}} \times a_{\text{Cl}^-}^2$$

The mean activity coefficient of Zn²⁺ and Cl⁻ ions in a solution of ZnCl₂ is given by

$$a_{\pm} = (a_{\text{Zn}^{2+}} \times a_{\text{Cl}^-}^2)^{1/3} = (a_{\text{ZnCl}_2})^{1/3}$$

Likewise,

$$f_{\pm} = (f_{\text{ZnCl}_2})^{1/3} = (f_{\text{Zn}^{2+}} \times f_{\text{Cl}^-}^2)^{1/3}$$

In terms of molality and activity coefficients, the cell potential will be given by,

$$E = E^\circ_{\text{cell}} - \frac{RT}{2F} \ln (m_{\text{Zn}^{2+}} \cdot m_{\text{Zn}^{2+}}) \times [(m_{\text{Cl}^-}^2 f_{\text{Cl}^-}^2)]$$

or

$$E = E^\circ_{\text{cell}} - \frac{RT}{2F} \ln [m_{\text{Zn}^{2+}} \times m_{\text{Cl}^-}^2] - \frac{RT}{2F} \ln f_{\pm}^3$$

On rearrangement,

$$E + \frac{RT}{2F} \ln (m_{\text{Zn}^{2+}} \times m_{\text{Cl}^-}^2) = E^\circ_{\text{cell}} - \frac{RT}{2F} \ln f_{\pm}^3$$

If a graph is plotted between LHS (ordinate) and molality (abscissa) of solutions, its extrapolation to $m = 0$ gives E°_{cell} because then f_{\pm} will be equal to one and $\ln f_{\pm}^3$ will be zero. Once we calculate E°_{cell} (this could be different from the

calculated value on the basis of tabulated values of standard electrode potentials due to imperfection in Ag – AgCl electrode and temperature being different), values of f_{\pm} can be calculated for different values of m from the corresponding values of E_{cell} .

Procedure : Prepare Ag – AgCl electrode by anodising a silver wire in a concentrated HCl solution. Standardise the prepared electrode against a saturated calomel electrode. Amalgamate a zinc electrode by dipping it in a 1% HgCl₂ solution for a few minutes. Remove it and wash it with water and rub it with a filter paper to remove any oxide layer and to get a shining surface. For such an electrode, activity of zinc is the same as in pure metal. Use zinc chloride solution between 0.001 m and 1.0 m . These should be known accurately and may be prepared gravimetrically. Set up the cell with different molalities and determine emf's. Keep

Result : The mean ionic activity coefficient =

Precautions : (i) Use a cell of small size, (ii) Add 1-2 drops of conc. HCl to the stock solution of ZnCl₂ to prevent hydrolysis. (iii) Mercury and mercuric chloride are both extremely poisonous and should be handled with care and with covered hands.

EXPERIMENT No. 5

Object : To determine the transport numbers in HCl and ZnSO₄ solutions potentiometrically. Use 0.01 M and 0.1 M HCl and 0.1M and 0.5M ZnSO₄ solutions.

Apparatus and Chemicals : Two platinum electrodes, two platinum contact electrodes, two zinc electrodes, two electrode vessels, quinhydrone, 0.1M and 0.01M HCl solutions saturated with calomel, 0.5M and 0.1M ZnSO₄ solutions saturated with mercurous sulphate.

Theory and Procedure : Determination of transport number requires comparison of potential of a concentration cell with transference involving a liquid-liquid junction and the potential of a concentration cell without transference from which liquid junction potential is eliminated. The electrode vessels as shown in figure (16) are used to set up alternate cells. Three alternate cell arrangements will be available as follows :

(a) A U-tube bridge of less dense solution is employed with an asbestos or cotton plug on the side of the denser solution. This allows the liquid-liquid junction with junction potential in operation.

(b) A salt bridge of saturated KCl-agar jelly taken in a U-tube is employed for interconnecting the two electrode vessels. This allows the liquid-liquid junction but the liquid junction potential is eliminated.

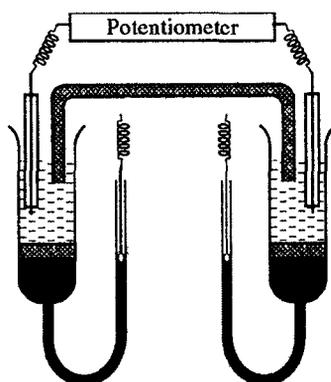
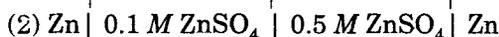
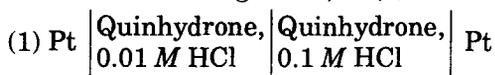


Fig. 16

(c) A U-tube bridge is not used and the mercury layers in the two limbs are joined externally, using contact electrodes. Thus, the liquid-liquid junction does not exist and the concentration cell without transference is operative.

For the first arrangement, *i.e.*, (a) the two cells will be :



$$E_1 = \frac{2}{1} (+1) t_{Cl^-} \cdot \frac{RT}{1 \cdot F} \ln \frac{(a_{\pm})_{0.1}}{(a_{\pm})_{0.01}}$$

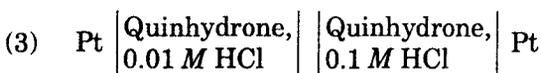
or
$$E_1 = 2t_{Cl^-} \cdot \frac{RT}{F} \ln \frac{(a_{\pm})_{0.1}}{(a_{\pm})_{0.01}}$$

Similarly,

$$E_2 = \frac{2}{1} (+1) t_{SO_4^{2-}} \cdot \frac{RT}{2F} \ln \frac{(a_{\pm})_{0.5}}{(a_{\pm})_{0.1}}$$

or
$$E_2 = t_{SO_4^{2-}} \cdot \frac{RT}{F} \ln \frac{(a_{\pm})_{0.5}}{(a_{\pm})_{0.1}}$$

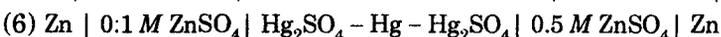
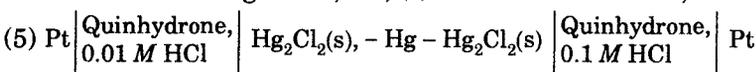
For the second arrangement *i.e.*, (b) two cells will be



∴
$$E_3 = \frac{RT}{1 \cdot F} \ln \frac{(a_{\pm})_{0.1}}{(a_{\pm})_{0.01}}$$

$$E_4 = \frac{RT}{2F} \ln \frac{(a_{\pm})_{0.5}}{(a_{\pm})_{0.1}}$$

For the third arrangement, *i.e.*, (c) the two cells will be,



∴
$$E_5 = \frac{2}{1} (+1) \frac{RT}{1 \cdot F} \ln \frac{(a_{\pm})_{0.1}}{(a_{\pm})_{0.01}}$$

or
$$E_5 = \frac{2RT}{F} \ln \frac{(a_{\pm})_{0.1}}{(a_{\pm})_{0.01}}$$

$$E_6 = \frac{2}{1} (+1) \cdot \frac{RT}{2F} \ln \frac{(a_{\pm})_{0.5}}{(a_{\pm})_{0.1}}$$

or
$$E_6 = \frac{RT}{F} \ln \frac{(a_{\pm})_{0.5}}{(a_{\pm})_{0.1}}$$

From the measured cell potentials,

$$t_{Cl^-} = \frac{E_1}{E_5} = \frac{E_1}{2E_3} (t_{H^+} = 1 - t_{Cl^-})$$

$$t_{SO_4^{2-}} = \frac{E_2}{E_6} = \frac{E_2}{2E_4} (t_{Zn^{2+}} = 1 - t_{SO_4^{2-}})$$

The activity factors will cancel out when we take ratios of cell potentials. So, a knowledge of activity coefficients will not be required.

Result : The transport numbers of H^+ , Cl^- , Zn^{2+} and SO_4^{2-} are,, and, respectively.

Precautions : Liquid junction should not be kept for more than a few minutes because diffusion of solutes changes the concentration of solutions.

EXPERIMENT No. 6

Object : To find the strengths of HCl and CH_3COOH in a given mixture potentiometrically.

Theory and Procedure : Quinhydrone electrode is used as an indicator electrode while calomel electrode is used as a reference electrode. The titration curve will show two inflexion points, the first when the stronger acid is neutralised and the second when the weaker acid is neutralised. The relative vertical separation of the titration curve portions for the two acids will depend on the orders of tens by which the dissociation constants of the two acids differ. If the ratio of the dissociation constants of the two acids is 10^2 or less the two portions are not clearly marked and separable. The horizontal separation of the segments of the titration curve depends on the concentration of the two acids.

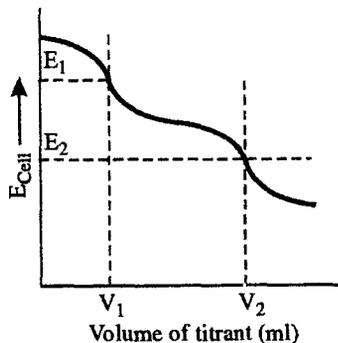


Fig. 17.

A graph is plotted between E_{cell} (ordinate) and volume of titrant (abscissa). Strong acid, *i.e.*, $HCl \equiv V_1$ ml of $NaOH$

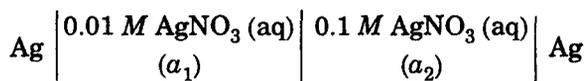
Weak acid *i.e.*, $CH_3COOH \equiv (V_2 - V_1)$ ml of $NaOH$.

Result : The strengths of HCl and CH_3COOH are and g/litre, respectively.

EXPERIMENT No. 7

Object : To determine the transport number of Ag^+ and NO_3^- ions in solutions of $AgNO_3$ in the concentration range $0.01 M$ to $0.1 M$ (Mean activity coefficients of silver nitrate in $0.01 M$ and $0.1 M$ solutions are 0.89 and 0.73).

Theory and Procedure : The following concentration cell is constructed :



Use two 100 ml beakers half filled with the respective solutions. Measure the emf's of the cell using bridges of 0.1 M AgNO₃ (E_1) and saturated KNO₃ (E_2) solutions. The measurements are repeated with fresh solutions to check for the errors due to diffusion of solutes. We have,

$$E_1 = 2t_{\text{NO}_3^-} \left(\frac{2.303 RT}{F} \right) \log \frac{a_2}{a_1}$$

$$E_2 = \left(\frac{2.303 RT}{F} \right) \log \frac{a_2}{a_1}$$

Calculate the value of $t_{\text{NO}_3^-}$ using activity coefficients data from E_1 and compare it with the value obtained from the relation

$$t_{\text{NO}_3^-} = \frac{E_1}{2E_2}.$$

Result : The transport numbers of Ag⁺ and NO₃⁻ ions are and, respectively

EXPERIMENT No. 8

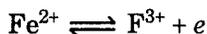
Object : To find out the strength of the given ferrous ammonium sulphate solution (approximate strength N/10) by titrating it against potassium dichromate solution potentiometrically. Also find the redox potential of the ferrous-ferric system.

Apparatus : Same as in preceding experiment.

Theory : The oxidation potential of any redox system is given by

$$E = E^\circ + \frac{RT}{nF} \log \frac{[\text{Oxidised state}]}{[\text{Reduced state}]}$$

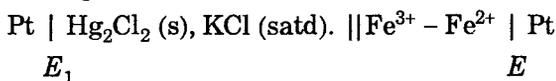
For a ferrous-ferric system, we have,



$$\therefore E = E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}} + \frac{RT}{nF} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

where, $E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}}$ is the redox potential of the ferrous-ferric system.

The following cell is constructed :



The observed e.m.f. (E_{obs}) of such a cell is given by,

$$E_{\text{obs}} = E - E_1$$

$$= \left\{ E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}} + \frac{RT}{nF} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right\} - E_1 \quad \dots (1)$$

When potassium dichromate solution is added, ferrous ions are removed and the concentration of ferric ions increases. From equation (1), we can say that gradual addition of potassium dichromate will cause the observed e.m.f. to increase slowly. At the end point, there will be a sharp change due to the sudden removal of all ferrous ions.

At half equivalence point, $[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$

∴ From equation (1), we have,

$$(E_{obs})_{1/2} = E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^{\circ} - E_1$$

$$\therefore E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^{\circ} = (E_{obs})_{1/2} + E_1 \quad \dots (2)$$

Procedure : The connections of the potentiometer are made as in experiment no. 2. Take 10 ml of the given ferrous ammonium sulphate solution in a 400 ml beaker. Add about 100 ml distilled water. Now add 10 ml of dilute H_2SO_4 . Place a bright platinum electrode in the solution and connect it to a saturated calomel electrode by means of a salt bridge.

Now standardise the potentiometer against the standard cell. Measure the e.m.f. of the cell as usual. Now add 1 ml of $N/10 \text{ K}_2\text{Cr}_2\text{O}_7$ solution from the burette and record the e.m.f. of cell as usual. The solution should be thoroughly stirred before measuring the e.m.f. Go on adding $\text{K}_2\text{Cr}_2\text{O}_7$ solution and note the e.m.f. after stirring. The readings should be at an interval of 1 ml upto 9 ml, but between 9 ml and 11 ml the interval should be 0.2 ml. Then again add $\text{K}_2\text{Cr}_2\text{O}_7$ solution at an interval of 1 ml after adding 11 ml of this solution and continue it upto 17 ml.

Observations : Volume of ferrous ammonium sulphate solution taken = 10 ml (say)

Table should be made as in experiment 1.

Calculations : Plot the values of E_{obs} as ordinate against volume of $N/10 \text{ K}_2\text{Cr}_2\text{O}_7$ solution as abscissa. The point of inflexion will indicate the equivalence point. If the point of inflexion is not sharp, then plot the values of $\Delta E/\Delta V$ against volume of titrant added. The strength of ferrous ammonium sulphate is calculated from normality equation.

Also find the volume of E_{obs} at half equivalence point and then after noting the value of E_1 of saturated calomel electrode from the table, we can calculate the redox potential of the ferrous-ferric system, from equation (2).

Result : (i) Strength of ferrous ammonium sulphate = ... g/litre.

(ii) Redox potential of $\text{Fe}^{2+}|\text{Fe}^{3+}$ system = ... volt.

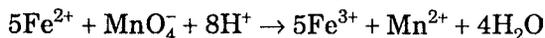
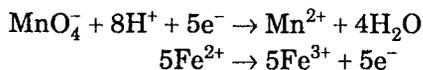
Precautions : Same as in preceding experiments.

EXPERIMENT No. 9

Object : To find out the strength of the given ferrous ammonium sulphate solution, (approximate strength 0.1N) by titrating it with 0.1N KMnO_4 solution, potentiometrically. Also find the redox potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$ system.

Apparatus : Potentiometer, SCE, bright platinum electrode etc.

Theory : The involved reaction in the titration is,



The electrode potential in this titration depends on the concentration of H^+ ions besides the concentration of Fe^{2+} and Fe^{3+} ions. To avoid the effect of change in H^+ ion concentration on electrode potential, titration is carried out in presence of

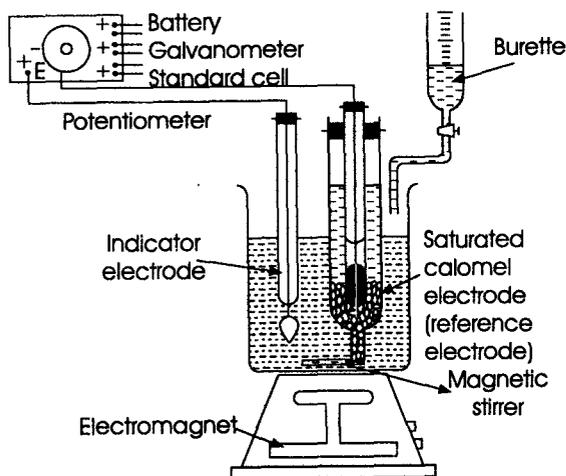


Fig. 18 : Titration cell.

a large excess of H^+ ions by making the solution $2N$ or $4N$ in respect of the acid (H_2SO_4). The plot between e.m.f. (E) or $\Delta E/\Delta V$ (ordinate) and volume of titrant (V) is drawn and the equivalent point V_0 is found. The e.m.f. of the cell at the point where the titre reading is $V_0/2$ gives the value of redox potential of Fe^{2+}/Fe^{3+} system.

Procedure : Set up the titration cell as shown in figure (18). Take 10 ml of ferrous ammonium sulphate solution in conical flask and dilute it with an equal volume of $4N H_2SO_4$. Now add 1 ml of $0.1N KMnO_4$ solution from the burette, mix thoroughly and determine the cell potential by means of a potentiometer. Again add 1 ml of $KMnO_4$ solution and repeat the measurement of cell potential. When the difference between successive values of cell e.m.f. goes beyond 10 mV, add titrant in steps of 0.5 ml and when the change of potential exceeds 20 mV, the titrant should be added in steps of 0.1 ml and if the change of potential exceeds 30 to 40 mV, the titrant should be added only in drops. When the sudden rapid change of cell potential is over, add the titrant with increasing volumes in each step. The titration should be stopped after adding 5-6 ml of titrant in excess.

Observations : The values of cell e.m.f. and the corresponding volumes of titrant are noted in a tabular form.

Calculations : Plot a graph between E_{cell} (ordinate) and V (abscissa) and $\Delta E/\Delta V$ against V . The point of inflexion gives the end point (V_0), from which the strength of $KMnO_4$ solution is determined by using normality equation. The e.m.f. at $V_0/2$ gives the redox potential of ferrous-ferric system.

Result : The strength of $KMnO_4$ solution is ... g/litre and redox potential of Fe^{2+}/Fe^{3+} system is ... volt.

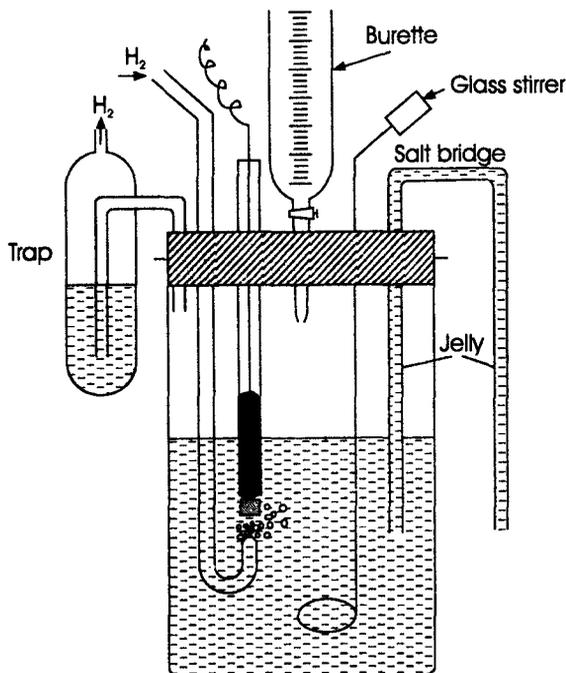


Fig. 19

Observations : Volume of phosphoric acid = V ml (say)

S.N.	Volume of NaOH (ml)	E_{obs} (volt)	$\Delta E / \Delta V$	$\Delta^2 E / \Delta V^2$	pH
					The value of pH after each addition of NaOH is calculated, vide equation (1).

Calculations : A curve is plotted with pH as ordinate and volume of NaOH as abscissa and its shape is as shown in figure (20). We can now calculate the dissociation constants of phosphoric acid as follows :

(i) pH at first point of inflexion = ...

$\therefore pK_1 = \dots$

(pH at half neutralisation point gives the value of pK)

(ii) pH at second point of inflexion = ...

$\therefore pK_2 = \dots$

Results : The dissociation constants of phosphoric acid are ... and ..., respectively.

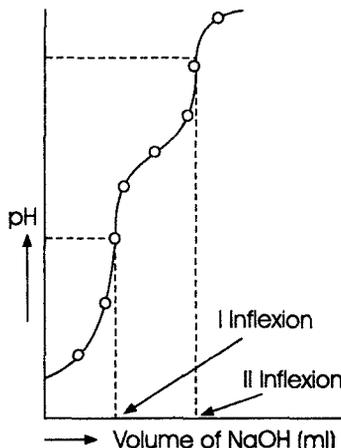


Fig. 20 : Titration curve for phosphoric acid

Precautions : (i) Only slight currents should be allowed to pass, as otherwise the hydrogen electrode will become polarised.

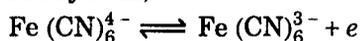
(ii) The hydrogen gas should be purified. This is done by passing it through wash bottles containing solutions of alkaline pyrogallol, potassium permanganate and distilled water.

EXPERIMENT No. 11

Object : To find the strength of cobalt sulphate solution (approximate strength N/10) by titrating it against a standard solution of potassium ferricyanide potentiometrically.

Apparatus : Same as in preceding experiments.

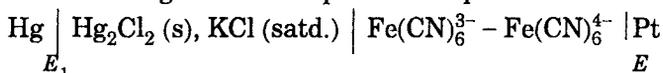
Theory : Co^{II} can be estimated by means of potassium ferricyanide solution in strongly alkaline medium in presence of ammonium citrate. In alkaline medium, $\text{Co}^{\text{II}}(\text{NH}_3)_6$ formed is oxidised to $\text{Co}^{\text{III}}(\text{NH}_3)_6$ by ferricyanide. The oxidation potential of the redox system,



is given by,

$$\begin{aligned} E &= E^\circ + \frac{RT}{nF} \log \frac{[\text{Oxidised state}]}{[\text{Reduced state}]} \\ &= E^\circ + \frac{RT}{F} \log \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]} \end{aligned}$$

The following cell is set up for the experiment :



The observed e.m.f. of the cell is given by,

$$\begin{aligned} E_{\text{obs}} &= E - E_1 \\ &= \left\{ E^\circ + \frac{RT}{F} \log \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]} \right\} - E_1 \end{aligned} \quad \dots (1)$$

When cobalt(II) sulphate solution is added to the system, $\text{Fe}(\text{CN})_6^{3-}$ is removed and the concentration of $\text{Fe}(\text{CN})_6^{4-}$ is increased. From expression (1), it is clear that the value of observed e.m.f. will decrease by the gradual addition of cobalt(II) sulphate solution. At the equivalence point, there will be a sharp fall in the e.m.f. due to the removal of all ferricyanide ions.

Procedure : First prepare an exact N/10 potassium ferricyanide solution. It is done by first preparing its concentrated solution and then titrating it with a standard sodium thiosulphate solution. The required solution is prepared by dilution process.

Take 10 ml of N/10 $\text{K}_3\text{Fe}(\text{CN})_6$ solution in a 400 ml beaker. Add to it 10 ml of ammonium citrate (ammonium citrate is prepared by mixing 10 g citric acid, 20 ml distilled water and 13.5 ml of liquid ammonia) and 50 ml of 5N ammonia solution. The mixture is then covered with sufficient petroleum ether. This is done to prevent atmospheric oxidation of $\text{Co}(\text{II})(\text{NH}_3)_6$ as also to prevent evaporation of

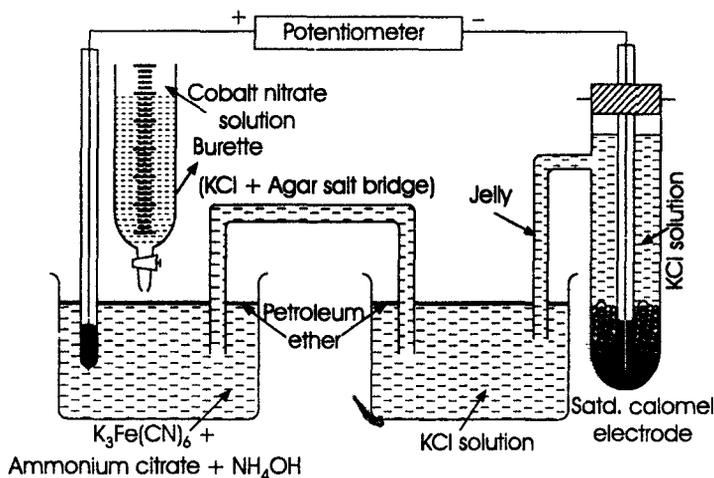


Fig. 21

ammonia. Dip a platinum electrode in this solution and complete the circuit of the potentiometer by a saturated calomel electrode and a salt bridge.

First standardise the potentiometer against the standard cell. Then note the e.m.f. of the solution. Now add 1 ml of cobalt(II) sulphate solution from the burette in the beaker. Stir the contents well and note the e.m.f. of the cell. Continue adding 1 ml of the Co (II) solution, till the end point is approached, *i.e.*, upto 9 ml. Now take readings at an interval of 0.1 or 0.2 ml of Co(II) solution and continue it upto 11 ml, beyond which take readings after adding 1 ml of the solution from the burette. Continue it to say 17 ml.

Observations : The e.m.f. of the cell is measured potentiometrically and the corresponding volumes of titrant are noted.

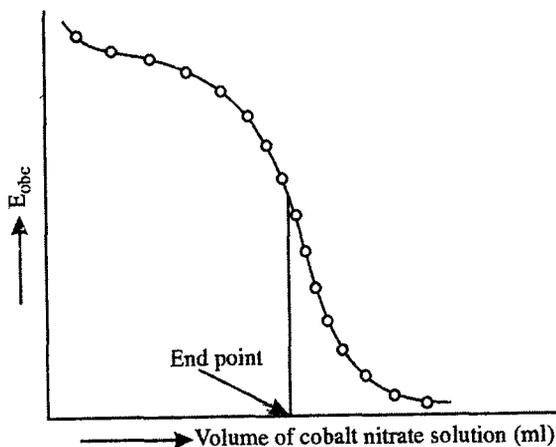


Fig. 22

Calculations : Plot a curve with E_{obs} as ordinate and volume of Co(II) solution as abscissa. The shape of the curve will be as shown in figure (22). Suppose the end point lies at x ml of Co(II) solution. Then according to normality equation, we can calculate the strength of cobalt sulphate solution.

Result : The strength of the given cobalt sulphate solution is ... g per litre.

Precautions : As in preceding experiments.

EXPERIMENT No. 12

Object : To find the strength of the given halide solution (approximate strength N/10) by titrating it against a standard silver nitrate solution potentiometrically.

Apparatus : Silver wire, saturated calomel electrode, potentiometer and its accessories, beaker, burette, stirrer etc.

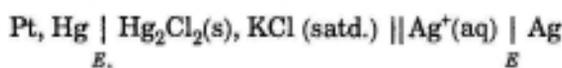
Theory : Silver ionises to give silver ions to produce the following redox system:



The potential of the above system is given by,

$$\begin{aligned} E &= E^* + \frac{RT}{nF} \log \frac{[\text{Oxidised state}]}{[\text{Reduced state}]} \\ &= E^* + \frac{RT}{F} \log [\text{Ag}^+] \quad (\because n = 1) \end{aligned}$$

The following cell is constructed,



The e.m.f. of the above cell is given by,

$$\begin{aligned} E_{\text{obs}} &= E - E_1 \\ &= \left\{ E^* + \frac{RT}{F} \log [\text{Ag}^+] \right\} - E_1 \end{aligned}$$

At 25°C,

$$\begin{aligned} E_{\text{obs}} &= 0.798 + 0.0591 \log [\text{Ag}^+] - 0.2415 \\ &= 0.5565 + 0.0591 \log [\text{Ag}^+] \quad \dots (1) \end{aligned}$$

Therefore, when any halide, say potassium chloride is added to the system, Ag^+ is removed as AgCl . So, from equation (1), it is clear that at the end point there will be a sudden fall in E_{obs} due to the removal of all Ag^+ ions.

Procedure : Prepare a standard N/10 silver nitrate solution. Now take 10 ml of it in a 400 ml beaker and add to it about 100 ml distilled water. Dip a silver electrode in it, which has been previously cleaned by nitric acid. Now make the connections as shown in figure (23). Now add halide solution from the burette at regular intervals.

Now repeat the procedure adopted in preceding potentiometric titrations. In this titration, the salt bridge must be free from halides and hence an ammonium nitrate salt bridge is used.

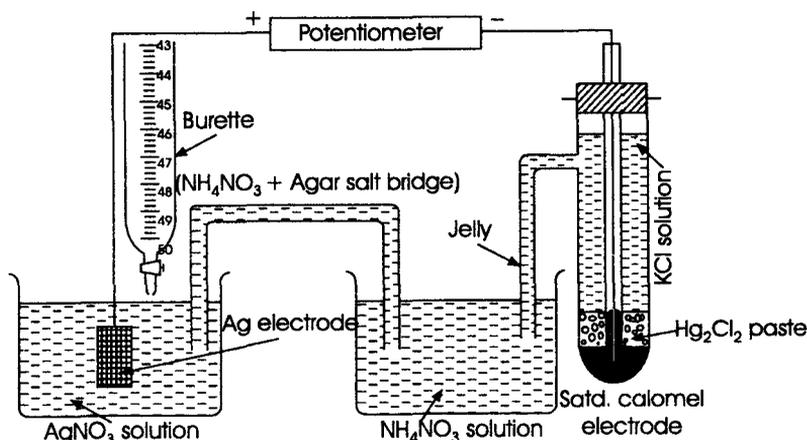


Fig. 23

Observations : Same as in preceding experiments.

Calculations : Plot E_{obs} against volume of titrant and find the point of inflexion. The curve is as shown in figure (24). The strength of the solution is calculated from normality equation.

Result : The strength of the given halide (KCl) solution is ... g/litre.

Precautions : (i) The salt bridge should be of ammonium nitrate.

(ii) If possible, near the equivalence point, the halide solution should be added at an interval of 0.1 ml.

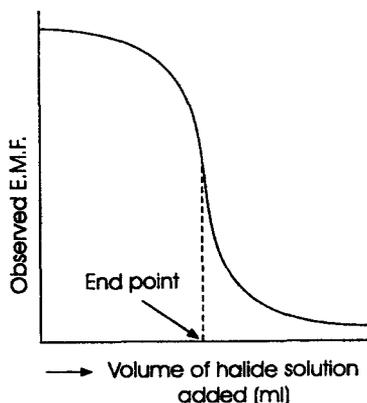


Fig. 24

EXPERIMENT No. 13

Object : To find the strength of a mixture of halides (approximate strength $N/10$) by titrating it against silver nitrate solution potentiometrically.

Apparatus : Same as in preceding experiment.

Theory : Same as in preceding experiment.

Procedure : Take 5 ml of the mixture of halides (say KI and KCl) in a 400 ml beaker and add to it about 100 ml distilled water. Now repeat the procedure as carried out in the previous experiment. *The first end point will be observed at about 5 ml of $N/10$ $AgNO_3$ and the second at about 10 ml of $N/10$ $AgNO_3$.* Hence, fractions of silver nitrate solution should be added first between 4 and 6 ml and then again between 9 and 11 ml.

Observations : Same as in preceding experiments.

Calculations : Plot E_{obs} and volume of titrant and obtain a graph as shown in figure (25). Suppose the first and second point of inflexion lie at x and y ml of $N/10$ $AgNO_3$. Therefore,

$$N_1 V_1 = N_2 V_2$$

$KI \quad AgNO_3$

$$N_1 \times 5 = \frac{N}{10} \times x$$

$$\therefore N_1 = \frac{N \times x}{10 \times 5}$$

$$\therefore \text{Strength of KI} = \frac{166 \times x}{10 \times 5} \text{ g/litre}$$

$$(\text{Eq. wt. of KI} = 166)$$

Similarly,

$$N_3 V_3 = N_4 V_4$$

$KCl \quad AgNO_3$

$$N_3 \times 5 = \frac{N}{10} \times (y - x)$$

$$\therefore N_3 = \frac{N \times (y - x)}{10 \times 5}$$

$$\therefore \text{Strength of KCl} = \frac{74.5 \times (y - x)}{10 \times 5} \text{ g/litre} \quad (\text{Eq. wt. of KCl} = 74.5)$$

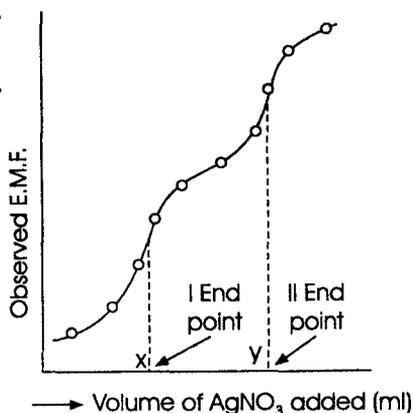


Fig. 25

Result : The strengths of KI and KCl in the given mixture are

(a) KI =g/litre.

(b) KCl = g/litre.

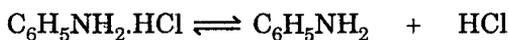
Precautions : Same as in preceding experiments.

EXPERIMENT No. 14

Object : To determine the hydrolysis constant of aniline hydrochloride by *e.m.f. method*.

Apparatus : Same as in preceding experiments.

Theory : Aniline hydrochloride is a salt of a weak base and a strong acid. It hydrolyses as follows :



$$\begin{array}{ccc} 1 & 0 & 0 \\ (1-h)c & ch & ch \end{array} \quad \begin{array}{l} \text{(Initially)} \\ \text{(At equilibrium)} \end{array}$$

The hydrolysis constant K_h , is given by the expression,

$$K_h = \frac{[C_6H_5NH_2][HCl]}{[C_6H_5NH_2 \cdot HCl]}$$

$$\frac{= (ch) \cdot (ch)}{(1-h)c} = \frac{c^2 h^2}{(1-h)c} \quad \dots (1)$$

where, h is the degree of hydrolysis and c is the total concentration of the salt in mole per litre. The concentration of the free acid ch , may be taken as equal to c_{H^+} , because hydrochloric acid is completely ionised. Therefore, from equation (1), we have,

$$K_h = \frac{c_{H^+}^2}{c - ch} = \frac{c_{H^+}^2}{c} \quad \dots (2)$$

Thus, from equation (2) it is clear that by measuring the hydrogen ion concentration of the salt in the solution, we can easily calculate the hydrolysis constant. For this purpose, we construct the following cell :



The observed e.m.f. is given by,

$$E_{obs} = 0.0591 \text{ pH} + E_1 \quad (\text{cf. experiment 10})$$

$$\therefore \text{pH} = \frac{E_{obs} - 0.2415}{0.0591} = -\log c_{H^+}$$

Procedure : Prepare solutions of aniline hydrochloride at different strengths, say $M/10$, $M/50$, $M/100$, $M/200$, $M/250$ etc. Now measure the pH of each solution, as described in experiment 10.

Observations : Note the e.m.f. of all solutions. For example, the value of c (mole/litre) for $M/10$ solution will be 10.

Calculations : Calculate the values of the hydrolysis constant K_h , vide equation (2). Take the mean of all the values of K_h .

Result : The hydrolysis constant of aniline hydrochloride is ...

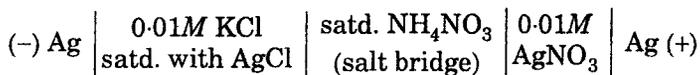
Precautions : (i) Aniline hydrochloride should be freshly prepared. It can be prepared by adding concentrated HCl to freshly distilled aniline. Cool and stir the solution in ice. Filter the salt and dry it.

EXPERIMENT No. 15

Object : To determine the solubility and solubility product of a sparingly soluble salt, say AgCl in water, potentiometrically.

Apparatus : Two silver electrodes, potentiometer, glass tubes etc.

Theory : The following cell is constructed :



The above cell is a concentration cell reversible with respect to silver ions. One Ag electrode is in contact with a solution of Ag^+ ions of known concentration, say $0.01M$, assuming AgNO_3 to be completely ionised at this dilution. The other electrode is in contact with a solution of much lower concentration of Ag^+ ions (furnished by the ionisation of sparingly soluble salt, AgCl) which is unknown. The e.m.f. (E_{cell}) of the cell is determined. Therefore,

$$E_{cell} = \frac{2.303 RT}{nF} \log \frac{(a_{Ag^+})_r}{(a_{Ag^+})_l}$$

$$= 0.0591 \log \frac{(a_{Ag^+})_r}{(a_{Ag^+})_l}$$

or

$$E_{cell} = 0.0591 \log \frac{0.01}{a_{Ag^+}}$$

$$= 0.0591 \times \log 0.01 / c_{Ag^+} \quad \dots (1)$$

Thus, knowing the value of E_{cell} , we can easily calculate the value of a_{Ag^+} or c_{Ag^+} , from which solubility product (K_s) can also be calculated.

Procedure : Take two strong silver foils or wires and cement them into tubes, as explained in experiment 1. These Ag electrodes* should be coated with fresh electrolytic deposit of silver. Now fill 0.01M KCl solution in one of the electrodes and add 2-3 drops of $AgNO_3$ solution to it to form a precipitate of AgCl. This gives a saturated solution of AgCl in 0.01M KCl solution. The other electrode is dipped in a solution of 0.01M $AgNO_3$ †.

Observations and Calculations : The e.m.f. of the cell is observed from potentiometer. The concentration, c_{Ag^+} of Ag^+ ions in 0.01M KCl solution is calculated from equation (1). The concentration of Cl^- ions in this solution is nearly equal to 0.01 g ion/litre. The solubility product K_s , of AgCl is given by,

$$K_s = [Ag^+] [Cl^-] = [Ag^+] \times 0.01$$

In pure aqueous solution, the concentration of Ag^+ ions is equal to the concentration of Cl^- ions, so the concentration of either of them will be equal to $\sqrt{K_s}$, as AgCl ionises to give one Ag^+ and one Cl^- ion. The concentration of dissolved AgCl in water can also be taken to be equal to concentration of Ag^+ or Cl^- ions, i.e., $\sqrt{K_s}$.

Result : The solubility and solubility product of AgCl are ... mole/litre and ..., respectively.

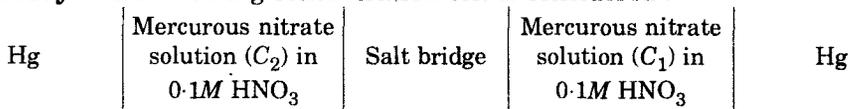
Precautions : Same as in preceding experiments.

EXPERIMENT No. 16

Object : To determine the valency of mercurous ions potentiometrically.

Apparatus : Same as in preceding experiments.

Theory : The following concentration cell is considered :



The e.m.f., E_{cell} at 25°C of the above cell can be written as,

*Old silver electrodes can be sensitized by dipping them into 1 : 1 HNO_3 containing a little $NaNNO_3$, till the formation of gas starts.

†The value of mean activity coefficient (γ_{\pm}) in 0.01 M $AgNO_3$ is 0.892 and in 0.1M solution 0.733. Similarly, for 0.01M KCl solution $\gamma_{\pm} = 0.902$.

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_1}{C_2} \quad \dots (1)$$

If the value of C_1 and C_2 is known, we can calculate n , valency of mercurous ion.

Procedure and Observations : Prepare a solution of mercurous nitrate of known concentration (C_1) in 0.1M HNO₃. The second solution of concentration (C_2) is prepared by diluting the first solution 10 times with 0.1M HNO₃, so that $C_2 = C_1/10$. After constructing the cell, its e.m.f. is determined potentiometrically, as described in preceding experiments.

Calculations : If $C_2 = C_1/10$, equation (1) can be written as,

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_1}{C_1/10} = \frac{0.0591}{n} \log 10 = \frac{0.0591}{n}$$

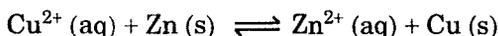
or
$$n = 0.0591/E_{cell}$$

Result : The valency of mercurous ion as calculated is 2. It should thus be represented as Hg₂²⁺.

Precautions : Same as in preceding experiments.

EXPERIMENT No. 17

Object : To determine the heat of reaction, equilibrium constant and other thermodynamic functions for the following reaction, potentiometrically.



Apparatus : Two platinum contact electrodes, potentiometer etc.

Theory : The fundamental relations used in electrochemistry are :

$$\Delta G = - nFE \text{ joule}$$

where, ΔG is the change in free energy produced by the passage of n faradays, i.e., nF coulomb of electricity, where $F = 96,500$ coulomb. The heat of reaction, ΔH is given by,

$$\Delta H = nFT \left(\frac{\partial E}{\partial T} \right)_P - nFE$$

The change in entropy, ΔS and equilibrium constant, K_p is given by,

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_P$$

$$nFE^\circ = RT \log K_p$$

Procedure : To calculate all functions we need to determine the values of E , E° and $(\partial E/\partial T)_P$. The apparatus is set as shown in figure (26). 3% zinc and copper amalgams are preferred to pure metals as electrodes, because they give reproducible potentials more easily. The contact electrodes of platinum must dip

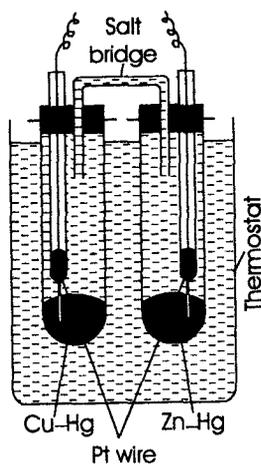


Fig. 26

completely in the respective amalgams. A large beaker of water serves as a thermostat. The polarities of the electrodes are recorded and cell potentials are measured from 0°C upwards at intervals of five degree.

Calculations : The values of ΔG , ΔH , ΔS and K_p are easily calculated from the above expressions.

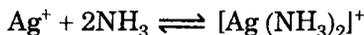
Result : The respective values of thermodynamic functions are

EXPERIMENT No. 18

Object : To determine the equilibrium constant for the formation of complex ion $[\text{Ag}(\text{NH}_3)_2]^+$, potentiometrically.

Apparatus : Two silver electrodes, half cell vessels, potentiometer etc.

Theory : The complex ion $[\text{Ag}(\text{NH}_3)_2]^+$ is formed as follows



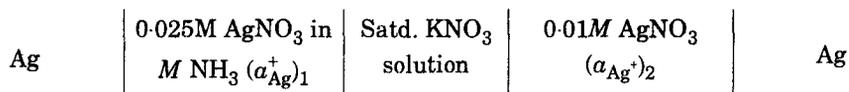
The equilibrium or formation constant (K) is given by,

$$K = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{\alpha_{\text{Ag}^+} \times \alpha_{\text{NH}_3}^2} \quad \dots (1)$$

The value of α_{Ag^+} is obtained experimentally from the measurement of electrode potential of the electrode dipped in a solution of complex, by using the equation,

$$E_{\text{Ag}} = E^\circ_{\text{Ag}} + 0.0591 \log \alpha_{\text{Ag}^+}$$

For the above measurement, the following cell is set up :



The e.m.f. at 25°C is given by,

$$E = 0.0591 \log \frac{(\alpha_{\text{Ag}^+})_2}{(\alpha_{\text{Ag}^+})_1} \quad \dots (2)$$

where, $(\alpha_{\text{Ag}^+})_2$ and $(\alpha_{\text{Ag}^+})_1$ are the activities of Ag^+ ions in 0.01M AgNO_3 solution and in solution of the complex. Since $(\alpha_{\text{Ag}^+})_2$ is known, $(\alpha_{\text{Ag}^+})_1$ can be calculated.

Procedure : Take silver nitrate solution in one vessel and dilute it with an equal volume of ammonia solution. The other vessel is filled with AgNO_3 solution diluted with four volumes of water. The cell is constructed and the polarity of electrode is recorded. The experiment is repeated with other concentrations of Ag^+ ions in the two vessels, changing to half concentration, one at a time. The e.m.f. of the cell is measured experimentally in each case.

Calculations : By measuring the e.m.f. of the cell, the activity of Ag^+ ions in the solution containing complex, $(\alpha_{\text{Ag}^+})_1$ is calculated. The activity coefficient of Ag^+ ions in 0.025M solution is taken to be 0.9.

$$\therefore [\text{Ag}^+] = \alpha_{\text{Ag}^+} \gamma_{\pm} = \alpha_{\text{Ag}^+} / 0.9$$

$$\therefore [\text{Ag}(\text{NH}_3)_2]^+ = 0.025 - [\text{Ag}^+] = 0.025 - \alpha_{\text{Ag}^+} / 0.9$$

The concentration of NH_3 entering into complexation,

$$= 2 \times [\text{Ag}(\text{NH}_3)_2]^+ = 2 \times [0.025 - a_{\text{Ag}^+}/0.9]$$

\therefore Concentration of NH_3 at equilibrium, *i.e.*,

$$[\text{NH}_3] = 1 - 2 \times [0.025 - a_{\text{Ag}^+}/0.9]$$

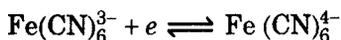
As $\gamma_{\text{Ag}^+} \approx \gamma_{[\text{Ag}(\text{NH}_3)_2]^+} \approx \gamma_{\text{NH}_3} \approx 1$, concentrations can be used in place of activities in expression (1), to calculate the value of K .

EXPERIMENT No. 19

Object : To find the composition of zinc ferrocyanide precipitate on adding zinc sulphate to acidified potassium ferrocyanide solution, potentiometrically.

Theory : If we take a solution containing $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions, it will show a redox potential on a bright platinum electrode. This potential will suffer a change on adding zinc ions which remove $[\text{Fe}(\text{CN})_6]^{4-}$ ions from the solution. The change in potential will be very rapid as the end point of the titration approaches.

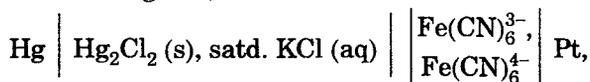
The reduction electrode potential for the ferric-ferrous ions system



is given by,

$$E = E^\circ - \frac{2.303RT}{F} \log \frac{[\text{Fe}(\text{CN})_6^{4-}]}{[\text{Fe}(\text{CN})_6^{3-}]}$$

For the following cell,



we have,

$$E_{\text{cell}} = E^\circ - 0.0591 \log \frac{[\text{Fe}(\text{CN})_6^{4-}]}{[\text{Fe}(\text{CN})_6^{3-}]} - E_{\text{SCE}}$$

Hence, as zinc ions are added, the cell emf will gradually increase and it increases abruptly at the end point. After the end point, the added zinc ions and $\text{Fe}(\text{CN})_6^{3-}$ ions remain in solution without any reaction from the end point, we can find the volumes of $\text{K}_4\text{Fe}(\text{CN})_6$ and Zn^{2+} solution, from which we can calculate the number of moles of Zn^{2+} ions reacting with the initial moles of $\text{Fe}(\text{CN})_6^{4-}$ ions and hence the composition of the complex. Suppose for every mole of $\text{Fe}(\text{CN})_6^{4-}$ ions, 1.5 mole of Zn^{2+} ions react. Then the reaction can be written as



Since the precipitate is always a neutral substance, it will have the composition $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.

The titration can be carried out in the reverse way also.

(i) Take 20 ml of 0.1M $K_4Fe(CN)_6$ in 1M HCl in a small beaker. Add to it nearly 1-2 ml of dilute $K_3Fe(CN)_6$ solution. Set up a cell by dipping a platinum and a calomel electrode in the beaker and measure its emf connecting the electrodes to a standardised potentiometer. Then, titrate ferrocyanide solution with $ZnSO_4$ in the usual way and find the end point by plotting a differential curve.

Calculate the number of moles of $K_4Fe(CN)_6$ in 20 ml of the solution taken and that of $ZnSO_4$ in the volume needed for 20 ml of ferrocyanide solution. The ratio of the moles of the latter to those of the former must be 1 : 5.

TITRATIONS WITHOUT REFERENCE ELECTRODES

EXPERIMENT No. 20

Object : To titrate a solution of silver nitrate with potassium chloride by the differential titration technique.

Apparatus and Chemicals : Potentiometer set, magnetic stirrer, two silver electrodes (one sheltered in a dropper), burette, pipette, standard 0.05M KCl solution, nearly 0.05M $AgNO_3$ solution.

Theory : In this technique, the differential titration curve is determined directly, instead of being calculated from the potential-volume curve. Two silver electrodes (X and Y) are set up in silver nitrate solution and connected to a potentiometer. One silver electrode (A) is enclosed in a tube (dropper) which temporarily holds back a portion of $AgNO_3$ solution and the other silver electrode (B) is directly put in the solution [See fig. (27)]. Initially the electrodes do not exhibit any potential difference (In case there is a small potential difference of a few mV, it should be recorded. However, it will not interfere in the experimental result). When KCl solution is added to $AgNO_3$ solution, precipitate of $AgCl$ is formed which results in the decrease in concentration of Ag^+ ions around electrode B. The concentration around electrode A in the dropper remains unchanged as the trapped solution has not mixed with the bulk solution. Thus, a potential difference is developed between the two electrodes which is noted. Now the sheltered solution is mixed with the bulk by pressing the teat of the dropper several times to give again a zero emf. This process is repeated after each addition of KCl solution. Near the end point, the measured emf increases sharply, thereafter its value becomes small or negligible. The addition of the titrant must be made in small amounts, particularly near the end point.

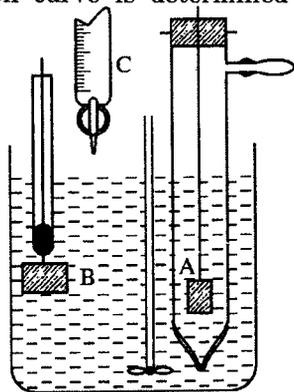


Fig. 27 : Apparatus for differential titration

Procedure : Take a measured volume (20 ml) of $AgNO_3$ solution in a beaker and add to it about 2-3 ml of dilute HNO_3 and about 50 ml of water. Support the free and sheltered electrodes in the solution and connect them to the potentiometer set. Measure the emf (which should be zero).

Now add a small amount of KCl solution, stir well and measure the emf. Pressing the dropper teat, mix the sheltered solution thoroughly with the bulk so that the emf value again becomes zero. Continue to measure the emf after each addition of KCl solution in small quantities, till its value increases sharply and then falls back.

A plot of measured emf /volume increment, *i.e.*, $\Delta E/\Delta V$ (ordinate) against volume (V) of titrant added (abscissa) will be similar to $\Delta E/\Delta V$ versus V curve with a peak corresponding to the end point.

Calculations : Plot $\Delta E/\Delta V$ (of KCl solution added) against volume of titrant (abscissa). The peak of the curve gives the end point.

EXPERIMENT No. 21

Object : To titrate ferrous ammonium sulphate solution with potassium dichromate solution potentiometrically using a bimetallic electrode pair.

Apparatus and Chemicals : Potentiometer set, bright platinum and tungsten electrodes, burette, pipette, standard 0.1M ferrous ammonium sulphate solution and nearly 0.02M potassium dichromate solution (both solutions should be prepared in 1M sulphuric acid).

Theory : The redox titration can be easily carried out by using an attackable internal reference electrode paired with platinum as the indicator electrode. Tungsten, which undergoes slow oxidation in presence of most oxidising agents, is a suitable electrode for such titrations. At the start of the titration, *i.e.*, in the reducing solution there is usually a large emf between the electrodes. On addition of the titrant (oxidising agent) the emf falls to a very small value, remains at this value till very close to the end point, it increases slightly. At the end point, there is a rapid change of emf. (This titration is not suitable for dilute solutions of concentrations less than 0.001M).

Procedure : First clean the tungsten electrode either by polishing with emery paper or by dipping it into just molten sodium nitrite for a few second and finally washing it with distilled water. Take 20 ml of ferrous ammonium sulphate solution, about 5 ml of concentrated H_2SO_4 and about 50 ml of water in a beaker. Support the two electrodes in the solution and connect them to the standardised potentiometer (platinum electrode is positive). Measure the emf between the electrodes.

Now add $K_2Cr_2O_7$ solution from the burette into the beaker, stir well and measure emf after each addition. Make small additions as the end point approaches.

Calculations : Plot the values of emf (ordinate) against volume of titrant (abscissa) The maximum point of the curve will show the end point of titration.

EXPERIMENT No. 22

Object : To titrate iodine solution with sodium thiosulphate by the dead stop end point or polarisation method.

Apparatus and Chemicals : A wire potentiometer of about 1 k Ω ; a resistor of about 100 k Ω , a galvanometer of sensitivity 50-200 mm/mA, two bright platinum electrodes, battery, mechanical stirrer, standard 0.1M sodium thiosulphate

solution, about $0.5M$ iodine solution in $0.1M$ KI solution.

Theory : This method consists in using two identical bright platinum electrodes dipped in the solution across which a small potential is applied through a large resistor, a battery and a galvanometer in series. The applied potential is balanced with the back emf due to polarisation so that no current flows through the galvanometer. At the end point, there is sudden change from polarisation of at least one electrode to depolarisation of both or vice versa. Polarisation occurs due to adsorbed film of hydrogen on the cathode and oxygen film on the anode. The anode and the cathode may be depolarised by suitable reducing or oxidising agents, respectively. Two cases may thus arise.

[I] Only one electrode is depolarised, when the added reagent is present in excess the other also gets depolarised. During the titration of sodium thiosulphate with iodine solution, the thiosulphate acts as anode depolariser. The iodide formed also acts as depolariser till the end point is reached, when free iodine acts as a cathode depolariser. At this moment, there is a sudden flow of current through the solution, due to which deflection in galvanometer occurs.

[II] Both electrodes are depolarised till the point is reached when one gets polarised in presence of excess of the reagent. In the present titration, both the electrodes are depolarised before the end point and there is a flow of current in the solution. When the end point is obtained, the cathode becomes polarised due to complete removal of iodine from the solution. Thus, at and beyond the end point, there is no flow of current.

It should be noted that after each addition of reagent, there is a movement of galvanometer needle due to momentarily high local concentration around an electrode. The magnitude of this effect which depends on the rate of titration and the efficiency of stirring is due to partial polarisation or depolarisation of an electrode.

Procedure : Take a measured volume, about 50 ml of $0.1 M$ sodium thiosulphate solution in a small beaker and support the two electrodes in the solution. Connect the electrodes to a battery through a resistor (R_1) about $100 \text{ k}\Omega$ and galvanometer in series as shown in figure (28). Press the tap key and set the galvanometer reading to zero by adjusting the potentiometer, R_2 .

Keep the key pressed and add iodine solution in small volumes. Stir the solution thoroughly and note the galvanometer deflection after each addition. The galvanometer will show zero deflection till the end point is obtained when it is permanently showing deflection on adding more of iodine solution.

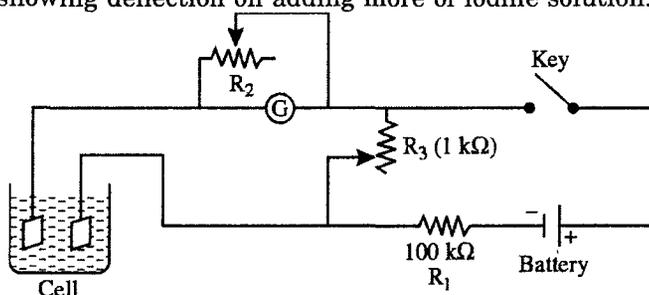


Fig. 28.

Repeat the experiment by now taking iodine solution in the beaker and adding sodium thiosulphate solution to it. For doing this, first adjust the zero position of the galvanometer with the sodium thiosulphate solution in the beaker using R_2 . Now take out the sodium thiosulphate solution from the beaker and wash the beaker and electrodes thoroughly with distilled water and place a measured volume of iodine solution (50 ml) in the beaker. Press the tap key momentarily. The galvanometer deflection will be off the scale. Then bring the deflection on the scale by adjusting the sensitivity control R_3 (a shunt).

Now add sodium thiosulphate solution in small amounts with constant shaking. Note the galvanometer deflection after each addition. As the concentration of free iodine decreases, the deflection decreases due to the decrease in current. The sensitivity of the galvanometer is increased as required and addition of sodium thiosulphate solution is continued till there is no deflection in the galvanometer. This gives the end point. After the end point is reached, subsequent addition of sodium thiosulphate solution will have no effect on the deflection of the galvanometer.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 23

Object : *To find the strength of KI or KBr solution (approximate strength N/10) by titrating it against silver nitrate solution.*

Proceed as in experiment no. 12.

EXPERIMENT No. 24

Object : *To find the strength of KI and KBr (or KCl and KBr) solutions (approximate strength N/10) in a given mixture by titrating against silver nitrate solution.*

Proceed as in experiment no. 13.

EXPERIMENT No. 25

Object : *To find the strength of KI, KBr and KCl solution (approximate strength N/10) in a given mixture by titrating it against silver nitrate solution.*

Here in this case, we will get three points of inflexion which will correspond to KI, KBr and KCl, respectively. If we take 5 ml of the mixture then the three end points will approximately be at 5 ml, 10 ml and 15 ml of N/10 AgNO_3 solution, if the strength of the mixture is N/10 (approximately).

Proceed as in experiment no. 13.

EXPERIMENT No. 26

Object : *To find the strength of KCNS solution by titrating it against silver nitrate solution.*

Proceed as in experiment no. 12.

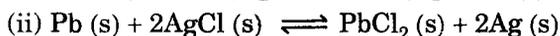
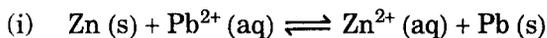
EXPERIMENT No. 27

Object : *To determine the standard oxidation potential of $Fe(CN)_6^{4-} - Fe(CN)_6^{3-}$ system.*

Proceed as in experiment no. 9.

EXPERIMENT No. 28

Object : *To determine potentiometrically the thermodynamic function for the reactions :*



Proceed as in experiment no. 17. In the first reaction, zinc and lead amalgams are preferred to pure metals as electrodes because they give more reproducible potentials. The contact electrodes of platinum must dip completely in the respective amalgams. Record the polarities of electrodes and measure the cell potentials from 0°C upwards at intervals of five degree.

The second reaction is simpler as all reactants are solids ($\alpha = 1$) and any solution of HCl saturated with $PbCl_2$ can be used as an electrolyte.

EXPERIMENT No. 29

Object : *To titrate 0.1M solution of oxalic acid, malonic acid and tartaric acid against 0.1M NaOH solution potentiometrically.*

The polybasic acids serve in the same way as mixtures of monobasic acids. Inflexion points for individual dissociation steps are well marked in case the corresponding dissociation constants decrease by a factor of 10^3 or more. The breaks in the titration curve are well marked for malonic acid. In case of oxalic acid, the first break is not well marked, while in case of tartaric or succinic acid, the first break is hardly to be seen.

Each dissociation stage can be taken to be a separate monobasic acid. The pH values corresponding to 1/4th and 3/4th completions of titration of a dibasic acid equal the pK_1 and pK_2 values of the acid, respectively.



When a beam of light is passed through a medium, a portion there of gets absorbed. The extent of absorption depends upon the wave length of radiation, thickness of the medium and concentration, if solution is used. Thus, by measuring the intensity of radiation we can qualitatively and quantitatively identify the species present. This technique is known as **photometry**. In case the analysis is made by measuring the intensity of colours, the technique is known as **colorimetry**. In colorimetry, the intensity of colour due to a species is compared with the intensity of colour in its solutions of known concentration, known as **standard**.

LAWS OF COLORIMETRY :

There are certain laws governing the absorption of light by a species. These are :

(1) **Lambert's law** : *When light radiation travels through an absorbing medium, the rate of decrease of intensity of radiation with the distance (x) travelled is proportional to the initial intensity of radiation (I). Mathematically,*

$$-\frac{dI}{dx} = k'I$$

or

$$\frac{dI}{I} = -k' dx$$

or

$$\int_{I_0}^{I_x} \frac{dI}{I} = - \int_0^x k' dx$$

or

$$\log_e \frac{I_x}{I_0} = -k'x$$

or

$$I_x/I_0 = e^{-k'x}$$

or

$$I_x = I_0 \cdot e^{-k'x} \quad \dots (1)$$

On changing the natural logarithm to common logarithm, the base e will be changed to the base 10 and thus the value of k' will be changed to another constant k . Thus,

$$I_x = I_0 \cdot 10^{-(k'/2.303)x} = I_0 \cdot 10^{-kx} \quad \dots (2)$$

(2) **Beer's law** : In case of solutions, the intensity absorption of a radiation also depends on the concentration (c) of light absorbing species. Thus, for solutions Lambert's law can be written as,

$$I_x = I_0 \cdot 10^{-\epsilon c x} \quad \dots (3)$$

Equation (3) is known as Beer's law equation. The constant k of equation (2) is thus replaced by its equivalent, ϵc , where c is the molar concentration of the solution in mole per litre. The constant ϵ is characteristic of the solute but it is independent of the concentration of solution. It is known as **molar absorptivity, molar extinction coefficient, molar absorbancy index or molecular absorption coefficient**. Equation (3) can be put in the form,

$$\log \frac{I_0}{I_x} = \epsilon c x = D, E \text{ or } A \quad \dots (4)$$

The fraction $\log(I_0/I_x)$ is called **optical density (D), extinction (E) or absorbancy (A)** of the solution. The fraction of the transmitted light, I_x/I_0 is known as **transmittancy** of the solution. Thus, optical density is logarithm of the reciprocal of transmittancy.

Validity of Beer's Law : For the Beer's law to hold good, the following conditions are necessary :

(1) The solute must not undergo solvation, association, dissociation, polymerisation or hydrolysis in the solvent.

(2) When absorption depends upon pH of the medium, the acid-base buffers used should not cause any interference in absorbance.

(3) Clear solutions free from any foreign substances should be used as a blank or test solution.

(4) The absorption should be stable and reproducible, *i.e.*, factors like temperature, pH and time affecting the nature of the solute chemically must be fixed.

The experimental measurement of concentration of coloured species can be carried out in the following two ways :

[A] Visual matching of colours in the unknown solution with colour of a known solution.

[B] Photometrically measuring the absorption of selected radiation by using Beer's law. For this, a colour calibration curve is set up for a series of solutions of known concentrations.

[A] **Visual Comparison of Colours :** This can be done as follows :

1. Matching method : In this method, colour intensities of unknown and known solutions are matched to equal values by seeing through different depths of the two solutions. Under these conditions, both the solutions should have the same extinction (E). Therefore,

$$\epsilon c_1 x_1 = \epsilon c_2 x_2$$

or

$$\frac{c_1}{c_2} = \frac{x_2}{x_1}$$

Knowing x_1 , x_2 and c_2 , we can calculate c_1 .

2. Standard series method : In this method, a series of standard solutions of a definite thickness is prepared, in which colour intensity differs by 10%. Then a layer of unknown solution of the same thickness is compared with the standard series. The unknown concentration will be equal to that of any of the standard solutions whose colour coincides with that of the unknown solution. If the colour is intermediate between two neighbouring standards, a new intermediate series of

standard concentration is prepared to match with the colour of the unknown solution. This is only an approximate method.

3. Colorimetric titrations : In this method, a definite volume of the unknown coloured solution and an equal volume of distilled water are taken in Nessler's tubes of same size and shape. A more concentrated standard solution of the species to be estimated is taken in the burette. Then equal volumes of colour producing reagent and water are added to water and unknown solutions, respectively from the burette. The solutions are thoroughly shaken and colours compared. The addition from burette is stopped as soon as the colours in the two tubes are exactly matched. Thus, the concentration in the water tube is calculated, which gives the concentration of the species in the unknown solution.

Suppose c mole/litre is the concentration in the titrant and x ml there of are added to y ml of water. The final concentration (c_1) in water tube is given by,

$$c_1 = c \times \frac{x}{x+y}$$

The initial concentration of species in the unknown solution will thus be given by $c_1 \times \frac{(x+y)}{y}$. If $x \ll y$, then correction is not necessary, and in that case $c_1 = c$.

This method is generally employed for estimating Pb^{2+} , Fe^{2+} ions in water. The colours are thus developed by using sodium sulphide and potassium thiocyanate solution, respectively.

[B] Photoelectric Colorimetry : In this method, human eye is replaced by a photoelectric cell coupled with a sensitive galvanometer for measuring the radiant power of the transmitted beam. The main advantage of these methods lies in that almost monochromatic light is used and the analysis of the mixture containing more than one constituent can be carried out. The instruments are known as *photoelectric colorimeters* or *spectrophotometers*. The essential parts of the instrument are :

(1) A source of light of constant intensity. Usually, a tungsten filament electric lamp operated on a low voltage is used.

(2) A set of suitable light filters to obtain nearly monochromatic light complementary in colour to the colour of the solution under investigation.

(3) An adjustable shutter to control the intensity of light incident on the solution cell.

(4) A cell with transparent walls for the solution.

(5) A photoelectric cell to be excited by the radiation coming out of the solution cell.

(6) A very sensitive galvanometer or any other device to measure the photoelectric current.

Spectrophotometers are of two types :

(1) **Non-recording type spectrophotometer :** Among this type, a few important null point instruments are : Unicam SP 500, Beckmann Model DU, Hilger Upspek. Among the direct reading instruments are Unicam model SP 600, Beckmann model B, Bosch and Lomb Spectronic 20 colorimeter, Optica CF-4 and Perkin-Elmer Hitachi model.

(2) Recording type spectrophotometer : A few commonly used instruments of this type are Beckmann model DK-A and DB, Perkin-Elmer model 350, Unicam SP 700, Bosch-Lomb Spectronic 505 type.

A mention of all types of instruments is beyond the scope of this book. We shall, however, describe Bosch and Lomb Spectronic 20 model in the visible range 340-650 nm (range can be extended to 950 nm by a change of phototube). It is a direct reading single channel spectrophotometer shown in figure (1).

The dispersing device is a small reflection replica grating which, in conjunction with fixed slits, passes band of 20 nm. A vacuum phototube acts as a detector, the

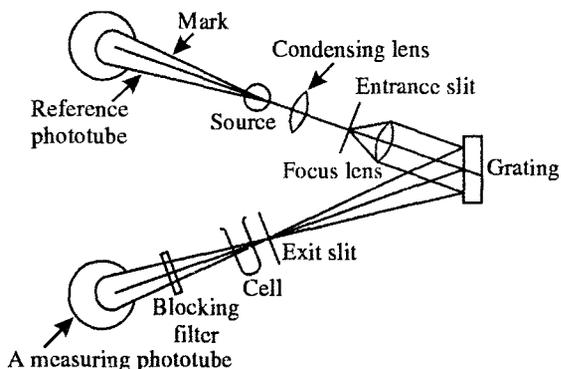


Fig. 1 : Schematic optical diagram of Bosch and Lomb Spectronic 20 colorimeter.

signal from which is passed through a special amplifier, compensated to reduce the effects of drift and non-linearity. There are only three controls in the instrument viz., wavelength selector, zero adjustment control (or dark current control) and 100% transmittance adjustment control or light control. The fluctuations in the source are eliminated by a magnetic or electric regulator consisting of an auxillary phototube which receives the light directly from the source.

When the cuvette containing the solution or solvent is removed from the instrument, an occluder falls in the path of light and the phototube does not receive

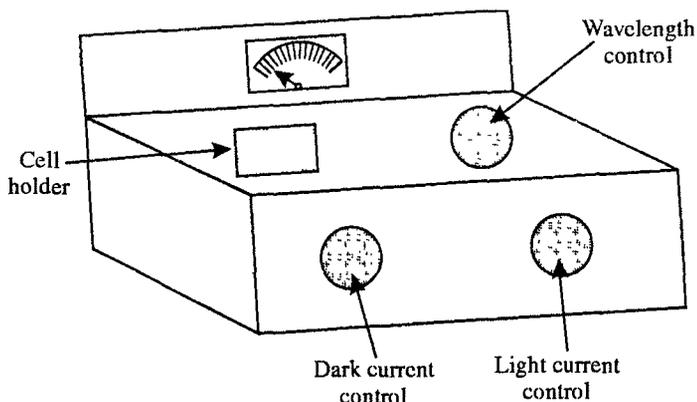


Fig. 2 : Bosch and Lomb Spectronic 20 colorimeter. (Exterior view)

any light. The amplifier control is adjusted to get a zero reading on the transmittance scale. The instrument is again adjusted for 100% transmittance in the dispersed beam of light by using the light control.

General Techniques of Spectrophotometer : While doing colorimetric estimations, we should follow the following series of steps :

(1) First thoroughly clean the absorption cells. Handle them subsequently on the frosted sides.

(2) Prepare a 'test' solution in which the colour developed gives an extinction of nearly zero or slightly more. To obtain this, prepare the solution having the concentration of the test material slightly more than half the maximum of the recommended range. Also prepare a 'blank' solution similar to test solution in all respects except for the absence of test solute.

(3) Fill both the absorption cells nearly to the top with the 'blank' solution, dry it by wiping carefully the outer side with tissue paper and put them side-by-side in the cell holder. Set the wavelength to the required value corresponding to maximum absorption (if known) or to some other value anywhere in the suspected region of absorption. The galvanometer is set to zero, if it has zero setting, otherwise with the shutter closed, *i.e.*, with no light falling on the photocell, adjust the zero control to obtain zero deflection of the galvanometer. Now put one of the cells in the path of light and with light passing through (shutter open), adjust the percentage transmittance to 100% (In some spectrophotometers, this step consists in bringing the galvanometer needle to zero by keeping the selector at 'check' and adjusting the check control). Slide the second cell in the path of light and observe the percentage transmittance. If the cells are accurately matched, this should again be 100. If not, clean the cells again and repeat the above method. In case, a difference is still found, note this difference in terms of extinction and subtract it from the subsequent readings.

(4) Replace 'blank' of one of the cells with 'test' solution, slide the cell into the beam of light and note the optical density or transmittance readings. Change the wavelength at intervals of 5 nm (or $m\mu$), adjust the transmittance through 'blank' to 100% for each new wavelength and note the absorbance or transmittance for the test solution.

(5) Plot the absorption curve between the absorbance (optical density) (ordinate) and wavelength (abscissa) and obtain the value of λ_{\max} , at which maximum absorption occurs.

(6) Now prepare the stock solution (standard solution) of the substance to be analysed having concentration greater than that to be used in the final analysis. By quantitative dilution of the stock solution prepare a series of solutions of different concentrations. Measure the absorbance of each solution at λ_{\max} .

(7) Plot the absorbance against the concentration and obtain the calibration curve. If Beer's law is obeyed, this calibration curve should be a straight line.

EXPERIMENT No. 1

Object : *To determine iron in the given sample of water (or to determine the concentration of the unknown solution) using Duboscq colorimeter.*

Apparatus : Duboscq colorimeter, graduated pipettes, measuring flasks, graduated cylinder etc.

Theory : The Duboscq colorimeter is shown in figure (3). Light from a uniform source of illumination is reflected from a mirror or a white glass plate, M, through two cells containing the solutions to be compared. The light then passes through two fixed glass plungers P_1 and P_2 having flat ends, from which it is finally reflected and collected by a prism system to a common axis so that the two beams appear in the eye lens, E, in the shape of two juxtaposed semi-circular patches. Each cell is mounted on a rack and pinion arrangement and can be raised or lowered relative to the stationary plungers to adjust the length of the light beam through each solution. The heights of the cells are adjusted so that the colours are matched and the dividing line between the two halves of the field of view in the eye piece disappears.

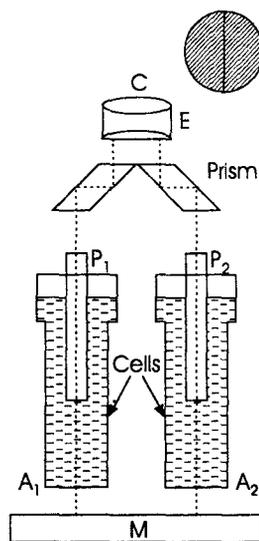


Fig. 3 : Duboscq colorimeter

To start the experiment with Duboscq colorimeter, the cells and plungers are first thoroughly washed with distilled water and then with the standard solution to be used. Then both cells are filled with the standard solution and their heights adjusted till the length of the light beam through each cell is the same. Now adjust the relative position of the lamp and instrument so that the two halves of the field of view in the lens are completely matched. Now rinse one cell with the test solution and fill it with it. Adjust the thickness of the standard solution to 2-6 mm and set the other cell such that the two halves are completely matched.

Procedure : Prepare $M/1000$ solution of ferric alum $[\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}]$ in distilled water as a stock solution. Now prepare a standard $1 \times 10^{-4} M$ solution as an experimental liquid. Now take 5 ml of $1 \times 10^{-4} M$ solution in a 25 ml measuring flask and add 5 ml of sulphosalicylic acid solution, 5 ml NH_3 solution and thoroughly mix the solution. The solution should not be made to 25 ml at this stage.

Take 5 ml of unknown solution or water containing iron in another 25 ml measuring flask and similarly add 5 ml of sulphosalicylic acid solution and 5 ml of NH_3 solution and mix thoroughly. (Do not make upto 25 ml).

The colour intensities of the two solutions are compared visually. If one or the other solution is found to be of deeper colour, its colour intensity should be reduced by taking the working standard solution or volume of water (or volume of the unknown solution) in less amount compensating the rest of the volume by adding distilled water. When the two solutions acquire nearly equal colour intensity, dilute the solution with distilled water to 25 ml mark in each measuring flask.

Take 10 ml of the prepared unknown solution and prepare standard solutions in the Duboscq cylinders separately. Set a definite level of the plunger in the standard solution and the position of the plunger in the unknown solution side is adjusted till the two halves of the field in the eye piece are of the same colour

intensity. Repeat the observations and take about 8—10 readings and find the average value of the plunger position in the unknown solution. Similarly, repeat the observations for two or three positions of the plunger in the standard solution.

Observations : Concentration (c_1) of the standard solution in 25 ml of the solution = ... mg/litre.

S. N.	Position of plunger in standard solution, x_1	Position of plunger in unknown solution, x_2
1.	...	(i), (ii), (viii) Mean = ...
2.	...	(i), (ii), (viii) Mean = ...
3.	...	(i), (ii), (viii) Mean = ...

Calculations : The concentration (c_2) of unknown solution or amount of iron in water is given by,

$$\frac{c_1}{c_2} = \frac{x_1}{x_2} \quad \text{or} \quad c_1 = c_2 \times \frac{x_1}{x_2}$$

Result : The amount of iron in water = ... mg/litre.

EXPERIMENT No. 2

Object : To verify Beer's law for solution of $KMnO_4$ and $K_2Cr_2O_7$ using absorptionmeter and to determine concentration in their solutions of unknown concentration.

Apparatus : Absorptionmeter, proper filters, burettes, pipettes etc.

Theory : See preceding pages.

Procedure : Switch on the absorptionmeter and wait for about 15 minutes for the instrument to acquire temperature stability. The intensity of light from the lamp depends upon the external temperature.

Choice of proper filter : Fill the cell with the pure solvent. Now select filter of complementary colour visually as shown in the following table.

Colour of solution	Complementary colour of filter	Wavelength ($m\mu$) transmitted by filter
Yellow	Blue	435—480
Orange	Greenish blue	480—490
Red	Bluish green	490—500
Blue	Yellow	580—595
Violet	Yellowish green	560—580
Purple	Green	500—560
Bluish green	Red	610—650
Yellowish green	Violet	400—435

Now insert selected filter in the right place. Adjust the shutter to a setting of 100% transmittancy for the solvent and filter. Now remove the solvent from the cell and rinse it with the solution to be measured and fill it with this solution. Note

the transmittancy of this solution. Repeat the above steps for all possible filters. 100% transmittancy setting will be adjusted each time and the filter for which the given solution shows the maximum optical density or least transmittancy is the most absorbing for it and is selected for further work.

The proper filter is mounted in the absorptionmeter and the shutter setting for 100% transmittancy with the pure solvent is not changed during the course of experiment.

Prepare a standard solution, say A of $2 \times 10^{-3}M$ $K_2Cr_2O_7$ or $KMnO_4$. Dilute it as follows :

Solution I — 50 ml of solution A + 50 ml of distilled water.

Solution II — 50 ml of solution A + 50 ml $0.1M$ H_2SO_4 .

Now mix, 0, 2, 4, 6, 8, 10 ml of solution I with 10, 8, 6, 4, 2, 0 ml of distilled water. Similarly, prepare diluted solutions for solution II. Now fill all these solutions one-by-one in the cell and note the percent transmittance and optical density of each solution. Repeat the experiment for solutions of each substance in water and in presence of $0.1 M$ H_2SO_4 .

Draw a graph between optical density (absorbance) or transmittancy against concentration.

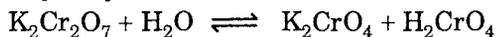
Observations : Temperature = ... °C.

Solution No.	Concentration (C) in mole/litre	Optical density (A)	Transmittance (T)
I
II

Calculations : A curve is plotted between absorbance (ordinate) and concentration (abscissa) and if a straight line is obtained, Beer's law is applicable (A curve between T and C will be an exponential curve).

Similarly, concentration of unknown solution can be found by intrapolation from the graph.

Result : (i) It is observed that $KMnO_4$ solution in water and in acid medium obey Beer's law, but an aqueous solution of $K_2Cr_2O_7$ does not obey Beer's law because of its hydrolysis.



On adding excess of acid, however, $K_2Cr_2O_7$ solution obeys Beer's law.

(ii) The concentration of the unknown solution = ... mg/litre.

EXPERIMENT No. 3

Object : To test the validity of Beer-Lambert's law using photoelectric absorptionmeter and to determine the unknown concentration of the solution.

Apparatus and Chemicals : Photoelectric absorptiometer, filters, methylene blue.

Theory : In a photoelectric instrument in which the cells containing the reference and unknown samples are of the same size, we have

$$A = \log I_0/I = \text{constant} \times C$$

i.e., absorbance A varies proportionately with concentration of the solution. A plot of A versus C must be linear if the Beer-Lambert's law is valid. From the calibration curve so obtained the concentration of the unknown solution can be determined by measuring its absorbance.

Procedure : Prepare a stock solution of methylene blue containing 0.01 g dm^{-3} , *i.e.*, 10 ppm (parts per million). Dilute this solution quantitatively so as to get 8, 6, 4, 2 and 1 ppm. To obtain this, mix 8, 6, 4, 2 and 1 cm^3 of the stock solution with 2, 4, 6, 8, and 9 cm^3 of distilled water.

Measure the absorbance of one of the above solutions against a water "blank" using each of the filters in turn given with the instrument. The filter giving the maximum absorbance will be most suitable for measuring the absorbance.

Determine the absorbance of a solution against a water 'blank'. Carry out replicate measurements so as to get concordant readings.

Repeat the experiment using other solutions.

Calculations and Result : Plot absorbance (ordinate) against concentration (abscissa). A linear curve must be obtained if the Beer-Lambert's law is valid. Obtain the concentration of the unknown solution from this curve by determining its corresponding absorbance.

EXPERIMENT No. 4

Object : To scan a spectral absorption curve of a given substance using a spectrophotometer (Bausch-Lomb Spectronic-20 colorimeter) and also determine the wavelength of maximum absorption.

Apparatus and Chemicals : Bausch-Lomb Spectronic-20 colorimeter, a pure sample of the given substance and the solvent.

Procedure : Prepare a known solution of the given substance in a suitable solvent. Usually 0.01 to 0.001 M solution is sufficiently concentrated for the lowest absorption range.

With the shutter closed, *i.e.*, when no light falls on the photo cell, adjust the "dark current control" to zero.

Clean the absorption cells thoroughly, fill one of the cells with the solvent used and place it in the cell holder of the instrument. Set the wavelength control to $20 \text{ m}\mu$ (nm) and then adjust 'light control' to percentage transmission equal to 100.

Remove the cell containing the solvent and place another cell filled with the test solution in the cell holder. Observe and record both the absorbance and the transmittance. Scan the wavelength range at intervals of $10 \text{ m}\mu$ (nm) and record the absorbance and the transmittance for each wavelength. Transmission through the blank (solvent) must be adjusted to 100%, because the absorbance of the blank also changes with wavelength. Re-scan the region at smaller intervals where structural features are clear.

Calculations and Result : Plot the data in two ways : (i) absorbance (optical density) as ordinate versus wavelength in millimicrons (nm) as abscissa and (ii) transmittance as ordinate versus wavelength in millimicrons as abscissa. The maximum of the curve in the former case, whereas the minimum in the latter gives the wavelength, λ_{max} , at which there is maximum absorption.

EXPERIMENT No. 5

Object : To obtain the calibration curve for a given compound (methylene blue, potassium permanganate, copper sulphate, etc.) using Bausch-Lomb Spectronic 20 colorimeter and hence (i) verify the Beer-Lambert's law and (ii) determine the unknown concentration of the compound.

Apparatus and Chemicals : Bausch-Lomb Spectronic-20 colorimeter, 0.01 g/dm⁻³, i.e., 20 p.p.m. solution of the given compound in water.

Procedure : Prepare a standard stock solution 0.01 g/dm³ of the compound in distilled water. Then obtain separately 9, 8, 7, 6, 5, 4, 3, 2 and 1 ppm. solutions by mixing 9, 8, 3, 2, 1 cm³ of the stock solution and 1, 2 8, 9 cm³ of distilled water, respectively.

Determine the wavelength, λ_{\max} of maximum absorption for the compound as in previous experiments.

Set the wavelength to λ_{\max} , and adjust the percentage transmission through the "blank" (distilled water in the cell) for 100. Fill another absorption cell with one of the test solutions and place it in the cell holder. Observe and record the absorbance. Similarly, measure the absorbances of the compound.

Calculations and Result : Plot the absorbance (ordinate) against concentration (abscissa) of the compound in the solution. This gives the calibration curve for the compound. If a linear curve is obtained, this will prove the validity of Beer-Lambert law. Obtain the concentration of the unknown solution of the compound from the calibration curve corresponding to its absorbance.

EXPERIMENT No. 6

Object : To obtain a spectral absorption curve of a given substance using spectrophotometer and also to find the wavelength of maximum absorption.

Apparatus : Spectrophotometer (Lomb-Bausch type), pipettes, burettes, etc.

Theory : See preceding experiments.

Procedure : Prepare 0.01–0.001M solution of the given substance. When the shutter is closed, adjust the current control to zero. Clean the cell and fill it with solvent used and keep it in the cell holder. Set the wavelength knob to 360 m μ and adjust the transmittancy to 100%. Now remove the solvent cell and fill it with the test solution and place it in the cell holder. Note the optical density and transmission. Now change the wavelength by 10 m μ and note the optical density (or absorbance) and transmission for each wavelength. Transmission through the pure solvent (blank) is always adjusted to 100% as the extinction of the blank also changes with wavelength. The wavelength reading can be reduced to 5 m μ or even less where structural features are observable.

Observations : Same as in preceding experiment.

Calculations : Plot either (a) absorbance (ordinate) against wavelength in millimicrons (abscissa) or (b) transmission (ordinate) against wavelength

(abscissa). The maxima and minima in the former and later curves, respectively give the value of wavelength of maximum absorption, λ_{\max} .

Result : $\lambda_{\max} = \dots \text{ m}\mu$.

EXPERIMENT No. 7

Object : To determine the phosphate concentration in a soft drink.

Apparatus and Chemicals : Colorimeter, potassium hydrogen phosphate, ammonium molybdate, sodium hydrogen sulphite, sodium sulphate, 1-amino-2-naphthol-4-sulphonic acid and the sample of soft drink.

Theory : The procedure is based on the formation of complex ion, phosphomolybdate between phosphate ion and molybdic acid. The phosphomolybdate ion on reduction leads to the formation of another complex molybdenum blue which can be monitored colorimetrically. The reduction can be effected in a number of ways, e.g., by using sodium hydrogen sulphite and 1-amino-2-naphthol-4-sulphonic acid mixture, stannous chloride, ascorbic acid, etc.

Procedure : Preparation of ammonium molybdate solution : Dissolve 2.5 g of ammonium molybdate in about 50 cm³ of water. In a separate vessel, add 13.6 cm³ of concentrated sulphuric acid to about 35 cm³ of water and allow the solution to cool. Now mix the two solutions and make the volume to 100 cm³.

Reducing solution : Dissolve 15.0 g of sodium hydrogen sulphite in about 40 cm³ of water. Add 3.0 g of sodium sulphate and 0.25 g 1-amino-2-naphthol-4-sulphonic acid and make the volume to 100 cm³.

The reducing solution can be stored in a glassstoppered dark bottle placed in a refrigerator. The solution should be allowed to warm to room temperature before use.

Standard solution of potassium hydrogen phosphate : Dissolve 20 mg of potassium hydrogen phosphate in 100 cm³ of molybdate solution + 0.2 cm³ of reducing solution + x cm³ of phosphate (stock) solution + y cm³ of distilled water, where $x + y = 9.3 \text{ cm}^3$ and $x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 1.9$ and 2 cm^3 .

Also prepare a blank or reference solution by mixing 0.5 cm³ of ammonium molybdate solution, 0.2 cm³ of reducing solution and 9.3 cm³ of water.

Set the wavelength to 635 nm and adjust the meter reading to zero with the reference solution in the cuvette. Place each standard solution of PO_4^{3-} in turn in the cuvette and record the absorbance.

Dilute the soft drink sample by 10 times. Mix 1 cm³ of this diluted solution with 0.5 cm³ of ammonium molybdate solution, 0.2 cm³ of reducing solution and 9.3 cm³ of water so as to prepare the test solution. Measure the absorbance for the test solution.

Calculations : Plot a graph between the meter reading and the volume of phosphate (stock) solution in different standard solutions and obtain the calibration curve. From this curve determine the amount of phosphate in the test solution (in terms of cm³ of the stock solution) corresponding to the meter reading for it.

Let this volume be $V \text{ cm}^3$. Then the amount of phosphate in the sample of soft drink is $10 \times 0.14 V = 1.4 V \text{ mg cm}^{-3}$.

Result : The amount of phosphate in soft drink = mg cm^{-3}

Precautions : The reduction of phosphomolybdate complex is a sluggish reaction. The blue colour, therefore, develops slowly which takes about 20-30 minutes.

EXPERIMENT No. 8

Object : To determine the composition of a binary mixture containing, say $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 , spectrophotometrically.

Apparatus : Same as in preceding experiment.

Theory : The quantitative analysis of mixture containing two or more components can be carried out as follows :

(i) If the absorption bands of different components do not overlap, we can select a set of wavelengths, such that at a particular wavelength the absorption for one component is very high as compared to others. Thus, the absorption of each component can be measured independently. If D_1 and D_2 be the absorbance of the mixture wavelengths λ_1 and λ_2 at which the absorption of first and second component is very high, then

$$D_1 = \epsilon_1 C_1 \text{ and } D_2 = \epsilon_2 C_2$$

where, ϵ_1 and ϵ_2 are the respective extinction coefficients. Thus, the concentration (C_1 and C_2) of various components in the mixture can be calculated.

The concentration of a component can also be measured from calibration curve obtained by plotting values of absorbances against concentration. The absorbance of the mixture at the wavelength of maximum absorption of a particular component will correspond to the concentration of that component.

(ii) If the absorption bands of different components overlap each other, the absorbance of the mixture containing n components is measured at n suitably chosen wavelengths and thus n simultaneous expressions are obtained. Let C_1 and C_2 be the concentration of the components 1 and 2 in the given mixture and D_1 and D_2 be the absorbance of the mixture at two wavelengths λ_1 and λ_2 . Let at wavelengths λ_1 and λ_2 , D_1' and D_1'' be the absorbance of a solution of pure component 1, its concentration being C_1' . Similarly, let D_2' and D_2'' be the respective values of a solution of pure component 2, its concentration being C_2' . Assuming Beer's law to be valid, we get,

Absorbance of mixture

$$= \frac{\text{Absorbance due to 1}}{C_1'} \times C_1 + \frac{\text{Absorbance due to 2}}{C_2'} \times C_2$$

$$\therefore D_1 = \frac{D_1' \cdot C_1}{C_1'} + \frac{D_2' \cdot C_2}{C_2'} \quad (\text{At wavelength } \lambda_1) \dots (1)$$

$$\text{and } D_2 = \frac{D_1'' \cdot C_1}{C_1'} + \frac{D_2'' \cdot C_2}{C_2'} \quad (\text{At wavelength } \lambda_2) \dots (2)$$

Thus, by measuring the absorbances of the mixture and solutions of pure components of known concentration at two suitably selected wavelengths, we calculate the concentrations, C_1 and C_2 of the components in the given mixture.

The two wavelengths chosen should be such that at each wavelength one component shows stronger absorption than the other. It is done by measuring absorbance of the solution of pure components at different wavelengths. The ratio (absorbance)₁ / (absorbance)₂ at a series of wavelengths is obtained and

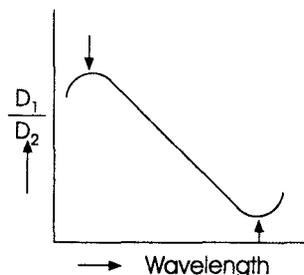


Fig. 4

plotted as shown in figure (4). The wavelengths corresponding to the maxima and minima in the curve will give the values of the two optimum wavelengths.

Procedure : Prepare $10^{-3}M$ solutions of $K_2Cr_2O_7$ and $KMnO_4$ in $0.1M$ H_2SO_4 . Obtain the spectral absorption curves for each substance and from these obtain the values of optimum wavelengths, say λ_1 and λ_2 as explained in the 'theory'.

Then measure the absorbances of the mixture and known solutions of pure components against a blank (pure solvent) at wavelengths λ_1 and λ_2 .

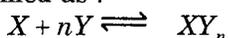
Observations : Same as in preceding experiment.

Calculations : The values of concentration of $K_2Cr_2O_7$ and $KMnO_4$ are calculated with the help of equations (1) and (2).

Result : The composition of the binary mixture is ...

COMPOSITION OF COMPLEXES

The formula of a single compound or a complex ion formed by mixing two substances in the solution state can be determined by means of **Job's method**. According to it, *when equimolecular solutions of components are mixed in varying proportions, the maximum amount of complex at equilibrium is formed when two components are present in the same ratio as required for complex formation.* Consider a complex formed as :



where, X is a metallic ion and Y is either an anion or a neutral molecule. The value of n can be determined by measuring the transmittance or optical density (absorbance) of a series of mixtures of X and Y of equimolar concentrations. The difference between each observed value of absorbance and that calculated on the basis of no reaction is then plotted against the composition of the mixture. The ratio of the molar concentrations of components corresponding to minima or maxima in the curve will give the value of n . If the maxima or minima is obtained as a point of intersection of two straight lines, the reaction is complete and if the curves are continuous, it shows a reversible reaction.

Suppose a parts of solution of X and $(1 - a)$ parts of solution of Y (molarity, M , being equal) are mixed. If C_X , C_Y and C_{XY_n} be the equilibrium concentrations of X , Y and XY_n , then,

$$C_X = Ma - C_{XY_n} \quad \dots (1)$$

$$C_Y = M(1 - a) - nC_{XY_n} \quad \dots (2)$$

and

$$K = C_{XY_n} / C_X \cdot C_Y^n \quad \dots (3)$$

where, K is known as *stability constant of the complex*. The reciprocal of K , i.e., $1/K$ is known as *instability constant*.

For obtaining a maxima in the curve of C_{XY_n} and a , we should have,

$$\frac{dC_{XY_n}}{da} = 0 \quad \dots (4)$$

Differentiating equations (1), (2), (3) and combining them with equation (4), we get,

$$n = (1 - a)/a \quad \dots (5)$$

Thus, n can be calculated, provided a is known for which C_{XY_n} is maximum.

If the absorbance of the mixture is D , then for a cell of path length, l , we can write,

$$D = l (\epsilon_X C_X + \epsilon_Y C_Y + \epsilon_{XY_n} C_{XY_n}) \quad \dots (6)$$

If there is no reaction between the components X and Y, then the optical density, D' , of the mixture will be given by,

$$D' = l [\epsilon_X M a + \epsilon_Y M (1 - a)] \quad \dots (7)$$

From equations (6) and (7), we have,

$$D - D' = \Delta D = l [\epsilon_X C_X + \epsilon_Y C_Y + \epsilon_{XY_n} C_{XY_n} - \epsilon_X M a - \epsilon_Y M (1 - a)] \quad \dots (8)$$

Substituting the values of C_X and C_Y from equations (1) and (2) in equation (viii), we get,

$$\Delta D = l. C_{XY_n} (\epsilon_{XY_n} - \epsilon_X - n\epsilon_Y)$$

or
$$\frac{d(\Delta D)}{da} = l (\epsilon_{XY_n} - \epsilon_X - n\epsilon_Y) \cdot \frac{dC_{XY_n}}{da} \quad \dots (9)$$

It is thus evident that ΔD will have maximum value when C_{XY_n} is maximum, i.e., $\epsilon_{XY_n} > (\epsilon_X + n\epsilon_Y)$. Similarly, ΔD will have a minimum value when C_{XY_n} is minimum, i.e., $\epsilon_{XY_n} < (\epsilon_X + n\epsilon_Y)$. Thus, the value of n can be obtained from the maximum or minimum position of a curve between ΔD and a .

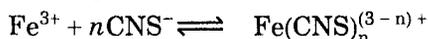
If only one maxima or minima is obtained it means that only one complex is formed. If, however, two or more maxima or minima are obtained, two or more complexes are formed.

EXPERIMENT No. 9

Object : To find the composition of ferric ion-thiocyanate complex by Job's method.

Apparatus : Lomb-Bosch type spectrophotometer, etc.

Theory : The complex between Fe^{3+} and CNS^- ions is formed as follows:



The value of n can be calculated using equation (5). (For details, see earlier pages).

Procedure : Prepare $4 \times 10^{-3} M$ solution of $Fe(NO_3)_3$ in $0.02M HNO_3^*$ having the total ionic strength of 0.04. Similarly, prepare $4 \times 10^{-3}M$ solution of $NaCNS$ in $0.036M HCl^\dagger$ having the same ionic strength 0.04.

Now prepare a number of solutions of mixture, by mixing 9.5, 9.0, 8.5, ... 0.5 ml of $Fe(NO_3)_3$ and 0.5, 1.0, 1.5 ... 9.5 ml of $Fe(NO_3)_3$ and 0.5, 1.0, 1.05 ... 9.5 ml of $NaCNS$, respectively. Now determine the wavelength of maximum absorbance, λ_{max} by measuring the absorbances of each mixture against water as blank, in the range 380—540 m μ . It is found that $\lambda_{max} = 460 m\mu$. Now measure the absorbance of the solutions containing pure components and the mixture against water at this wavelength. In this case, the absorbance of the original solution will be zero, so ΔD will be the absorbance of the mixture.

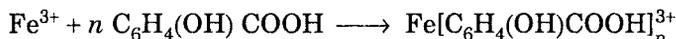
Observations and Calculations : Plot the values of absorbance (ordinate) of the mixture against the composition, a , of the mixture (abscissa) and determine the value of a , corresponding to the maxima and hence calculate the value of n .

EXPERIMENT No. 10

Object : To study the complex formation between *Fe (III) and salicylic acid and to find the formula and stability constant of the complex.*

Apparatus and Chemicals : Filter absorptinmeter with filters or spectrophotometer in the visible range, burettes, labelled stoppered glass tubes, $0.002 M HCl$, $0.001 M$ salicylic acid in $0.002 M HCl$, $0.002 M$ feric ammonium alum in $0.002 M HCl$.

Theory : $Fe(III)$ and salicylic acid form a complex in acid solution in the pH range 2.6–2.8. At this pH, the $-OH$ and $-COOH$ groups remain unionised. Suppose the complex formation occurs according to the following equation :



The stoichiometry of the equation can be determined by Job's method. When equimolecular solutions of the reactants are mixed in varying proportions, the maximum amount of complex at equilibrium is formed when the proportions of the reactants used correspond to the empirical formula of the complex. If x and $(1 - x)$ are respective parts of equimolecular solutions of $Fe(III)$ and salicylic acid in the mixture corresponding to the maximum amount of the complex formed, then

$$n = \frac{(1 - x)}{x}$$

As the complex is coloured, its equilibrium concentration can be followed by measuring the absorbance of the solution.

The stability constant or the equilibrium constant for the formation of the complex is given by,

$$K = \frac{[Fe [C_6 H_4 (OH) COOH]_n^{3+}]}{[Fe^{3+}] [C_6 H_4 (OH) COOH]^n}$$

* HNO_3 is added to suppress the hydrolysis of $Fe(NO_3)_3$.

† HCl is added to make the same total ionic strength in the two solutions.

In order to have maxima in the curve of D_{AB_n} versus x , it is required that the Fe(III)–salicylic acid complex is stable in the pH range 2.6–2.8. This range is obtained by preparing solution of the reactants in 0.002 M HCl.

Procedure : By means of burettes, prepare 10 ml mixtures of Fe(III) and salicylic acid solutions in properly labelled stoppered glass tubes in the following ratios :

Ferric alum solution (ml)	9	8	7	6	5	4	3	2	1
Salicylic acid solution (ml)	1	2	3	4	5	6	7	8	9

Now measure the absorbance or transmittance of one of the solutions (5 : 5 mixture) using successively all the filters against water as blank and select the proper filter giving the maximum absorbance. By using the same filter, measure the absorbance of each mixture.

(In case of a spectrophotometer, plot the absorption spectrum of 5 : 5 mixture against water as blank over the range 480–610 nm and determine λ_{\max} . Then measure the absorbance of each mixture at the same wavelength).

Plot the absorbance or transmittance of each mixture (ordinate) against x (0 to 1) and find the value of x corresponding to the maxima or minima of the curve. Then calculate the value of n and so the formula of the complex can be calculated. (In this case, $n = 1$, so the formula of the complex is $\text{Fe}[\text{C}_6\text{H}_4(\text{OH})\text{COOH}]^{3+}$).

Calculations : For finding the stability constant of the complex, prepare a series of solution of ferric alum with 0.002 M HCl. Saturate each solution with salicylic acid powder so as to convert the ferric ions completely in the complex form. The concentration of the complex ion in each solution will be equal to that of ferric ions. Measure the absorbance of each of these solutions and draw a calibration curve for the complex by plotting absorbance or transmittance (ordinate) against concentration.

S. No.	Initial conc. of Fe^{3+} (a mol dm^{-3})	Initial conc. of salicylic acid (b mol dm^{-3})	Equilibrium conc. of complex (c mol dm^{-3})	Equilibrium conc. of Fe^{3+} [(a - c) mol dm^{-3}]	Equilibrium conc. of salicylic acid [(b - c) mol dm^{-3}]	Stability constant (K_c)
1.						
2.						
3.						
4.						
5.						
						Mean = ...

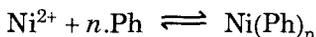
From the calibration curve, we can obtain corresponding to the observed absorbance, the equilibrium concentration of the complex ion in each solution under first experiment. The equilibrium concentrations of Fe^{3+} ions and salicylic acid in each solution can then be calculated by subtracting the concentration of the complex from their respective initial concentrations.

EXPERIMENT No. 11

Object : *To study the formation of complex formed between nickel ion and o-phenanthroline by Job's method.*

Apparatus : Same as in preceding experiment.

Theory : Nickel ion forms three complex ions with o-phenanthroline (Ph) as shown below :



The value of n can be 1, 2 and 3. (For details, see earlier pages).

Procedure : Prepare 100 ml of 0.1M NiSO₄ solution. Now take 10, 9, 8, ... 1 ml of this solution and 0, 1, 2, ... 9 ml of distilled water in 10 bottles numbering 1 to 10. Also prepare 100 ml of 0.1M o-phenanthroline solution and add 1, 2, ... 9 ml of this solution in the bottles from numbers 1 to 10. This gives NiSO₄ and Ph concentration in the molar ratio 9 : 1, 8 : 2, ... 2 : 8, 1 : 9.

Measure the absorbance of three solutions containing the Ni : Ph molar ratios as 1 : 1, 1 : 2 and 1 : 3 against water (blank) in the wavelength range, 500-650 mμ at 10 mμ intervals. Obtain the absorption spectra and find the most suitable wavelengths for the first, second and third complex, which are 620, 580 and 530 mμ, respectively.

Now measure the absorbance, D , of the various solutions at each of the above three wavelengths. Also obtain calibration curves for NiSO₄ and Ph by measuring absorbance of a series of their standard solutions. Determine the absorbance of NiSO₄ and Ph at concentrations equal to those in the mixture and calculate, D' , the absorbance of the mixture assuming that there is no reaction.

Observations and Calculations : Plot ΔD , i.e., $D - D'$ values as ordinate against a at each wavelength and the concentration a corresponding to maxima in the curves is determined. Thus, n can be calculated.

EXPERIMENT No. 12

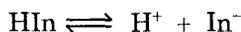
Object : *To determine the dissociation constant of phenolphthalein colorimetrically.*

Apparatus and Chemicals : Absorptionmeter with suitable filters, about seven test tubes, 0.2M NaOH (free from carbonate), 0.2M boric acid (1.237 g/100 ml), saturated solution of sodium carbonate, buffer solutions in the pH range 8.0-10.4 made from NaOH and boric acid (as given in the procedure), freshly prepared solution of phenolphthalein (0.2 g in 100 ml rectified spirit, 10 ml of this solution diluted to 100 ml with water).

Theory : We know that acid-base indicators have different colours in the acidic and alkaline solutions, e.g.,

Indicator	Colour		pK _{in}
	Acidic medium	Alkaline medium	
Phenolphthalein	Colourless	Pink	9.7
Methyl red	Red	Yellow	5.1
Methyl orange	Red	Yellow	3.7

The colour change is due to an exchange of H^+ ions between the two forms. Suppose the acid form of the indicator is represented by HIn , then its dissociation can be taken as



The dissociation constant of the indicator is given by

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

If the concentration of the indicator in a solution is C mole L^{-1} and its degree of dissociation is α , then,

$$[H^+] = C \cdot \alpha$$

$$[In^-] = C \alpha$$

$$[HIn] = (1 - \alpha) C$$

The degree of dissociation can be shifted not only by changing the concentration of the indicator but also by changing the pH, i.e., H^+ ion concentration of the solution. The pH changes are possible by using appropriate buffer solutions.

Another important point in the use of indicators is that changes in colour are perceptible from a 10% dissociation to a 90% dissociation of indicator. This complete range is controlled by a change in pH of solution in the range $pK_{In} \pm 1$. Therefore, for finding the dissociation of an indicator experimentally, we need buffers of pH range $pK_{In} \pm 1$. When H^+ ion concentration is controlled, we can write,

$$K_{In} = \frac{[H^+] \times C\alpha}{(1 - \alpha) C} = \frac{[H^+] \cdot \alpha}{(1 - \alpha)}$$

Taking reciprocals, we have

$$\frac{1}{K_{In}} = \frac{1}{[H^+]} \cdot \frac{(1 - \alpha)}{\alpha}$$

On taking logarithms,

$$pK_{In} = pH - \log \frac{\alpha}{(1 - \alpha)} \quad \left(\because pA = \log \frac{1}{A} \right)$$

or
$$\log \frac{\alpha}{(1 - \alpha)} = pH - pK_{In}$$

The second term on the RHS is constant. As pH of the solution increases, the value of α also increases.

For evaluating K_{In} , known adjustment in $[H^+]$ is involved as well as a measurement of either $[In^-]$ or $[HIn]$ or both of which may be coloured. In case a filter is found which can act as absorbent of light of colour corresponding to only one form of the indicator, study can be performed colorimetrically. It is quite possible for phenolphthalein as well as for other indicators also. Thus, we can estimate the concentration of HIn and In^- colorimetrically.

Procedure : First the following buffer solutions are prepared in test tubes.

Solution no.	1	2	3	4	5	6
0.2 M NaOH (ml)	0	1.0	2.0	3.0	3.5	4.0
0.2 M Boric acid (ml)	10.0	9.0	8.0	7.0	6.5	6.0
pH	6.90	7.95	8.54	8.98	9.12	9.45

In the seventh test tube take 10 ml of saturated sodium carbonate solution. This has high pH value so as to cause almost complete dissociation of phenolphthalein.

Now add 3 drops of indicator solution to each of the seven test tubes. Maximum colour will be developed in test tube no. 7. Use this solution to find the appropriate filter for maximum absorption and lowest optical density. By using this filter, the transmittance and optical density for all the seven solutions are measured.

Calculations : If C is the total concentration of phenolphthalein in each tube, the concentration of ionised phenolphthalein will be $\alpha \cdot C$. For tube no. 7, the value of $\alpha = 1$.

$$\alpha_i C \propto A_i \quad (\text{For each tube})$$

$$C \propto A_7 \quad (\text{For tube no. 7})$$

So, for any tube, $\alpha_i = \frac{A_i}{A_7}$

Moreover, for any tube,

$$A_i = \log \frac{I_0}{I_i} = \epsilon (\alpha_i C) x$$

For tube no. 7, $A_7 = \log \frac{I_0}{I_7} = \epsilon Cx$

$$\therefore \alpha_i = \frac{\log (I_0/I_i)}{\log (I_0/I_7)} = \frac{\log (1/T_i)}{\log (1/T_7)}$$

or $\alpha_i = \frac{-\log T_i}{-\log T_7} = \frac{\log T_i'}{\log T_7'}$

This shows how α can be calculated for each tube. Thus, pK_{In} can be calculated from the equation : $pK_{In} = pH - \log \frac{\alpha}{(1 - \alpha)}$

A calibration curve for phenolphthalein ions can also be drawn. This can be performed by taking 10 ml of saturated sodium carbonate solution in 4 or 5 test tubes and adding 1, 2, 3, 4 and 5 drops of phenolphthalein solution to them in turn. The absorbance value is measured for each test tube and plotted against the concentration (abscissa) of phenolphthalein ions. This graph can be utilised for determining ionised phenolphthalein in the six tubes of the first experiment. These are then used for calculating α and then pH and K_{In} .

EXPERIMENT No. 13

Object : To determine the ionisation constant of bromophenol blue.

Apparatus and Chemicals : Spectrophotometer, pH meter and glass electrode assembly, solid bromophenol blue, 1M sodium acetate, 1M hydrochloric acid, 1M sodium hydroxide solution.

Procedure : Prepare a stock solution of the indicator by moistening 0.1000 g of powdered bromophenol blue with a few drops of ethanol, dissolving in 1.5 cm³ of 0.1M NaOH solution and then making up to 100 cm³ with water. Now prepare the following buffer solutions containing the indicator :

Approximate pH	Vol. of 1M sodium acetate solution (cm ³)	Vol. of M HCl solution (cm ³)	Vol. of indicator solution (cm ³)	Distilled water (cm ³)
2.0	0	0.5	0.4	50
3.3	20	12.0	0.4	50
3.4	20	11.0	0.4	50
3.7	20	10.0	0.4	50
4.2	20	8.0	0.4	50
4.6	20	5.0	0.4	50
5.3	20	2.0	0.4	50
9.0	20	0	0.4	50

Then proceed as in the above experiment Carry out the absorbance measurements in the range 450-600 nm using 10 mm glass cells at intervals of 20 nm; smaller intervals (5nm) are necessary near the wavelength of maximum absorption. Measure the absorbance (D) of each solution at the wavelength of maximum absorption. Also measure the absorbances, D_{HA} and D_{A^-} , of the acidic and alkaline solutions, respectively at the same wavelength of maximum absorption.

Calculations : For each solution, evaluate the expression $\log (D - D_{A^-})$ and plot these values against the corresponding pH (ordinate). The intercept of the linear graph so obtained gives the value of pK_a .

Result : The ionisation constant of bromophenol blue =

PHOTOMETRIC TITRATIONS

These titrations are based on the fact that the optical density of the solution of a coloured substance is directly proportional to its concentration. Therefore, in this titration, the colour intensity either increases or fades away and the end point can be found graphically by plotting optical density against volume of titrant added. If the volume change is appreciable during titration, the necessary correction $(V + v)/V$ should be applied to optical density values.

The end point is obtained as the point of intersection of two straight lines (if the reaction is complete) obtained in the above case. If the reaction is not complete at the end point, the curves will not be linear near the end point. It can then be obtained by extrapolating the straight line portions of the curves.

Photometric titrations can be carried out as shown in figure (5). In the figure, the spectrophotometer is specially adapted to make a titration cell. In case, the spectrophotometer is not adapted, the solution to be titrated is taken in the cuvette which is half filled. The titrant is successively added to the cuvette after taking it out each time after measuring the optical density.

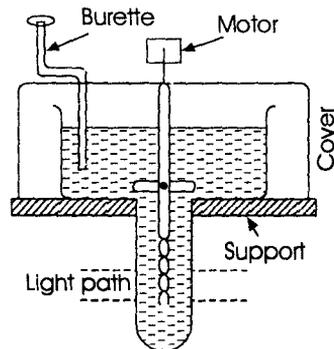


Fig. 5 : Photometric titration apparatus.

EXPERIMENT No. 14

Object : *To titrate a solution of 0.1N NaOH (approximately) against 0.1N HCl, spectrophotometrically.*

Apparatus : Spectrophotometer with a titration cell, burette, magnetic stirrer etc.

Theory : As explained above.

Procedure : Fill the titration cell with 25 ml of 0.1N NaOH and add 4-5 drops of phenolphthalein solution (monitor). Mix the contents thoroughly and obtain the absorption curve from 480 to 600 m μ . From the maxima of absorbance vs. wavelength curve, calculate the wavelength of maximum absorption, λ_{\max} , which in this case will be 545 m μ .

Now wash the cell and pipette out 1 ml of the unknown HCl solution. Add 100 ml of distilled water and 4-5 drops of phenolphthalein. Adjust the cell in its position and fill the burette with 0.1N NaOH and use a stirrer as shown in figure (5).

Now set the spectrophotometer to 100% transmittance or zero optical density at λ_{\max} , i.e., 545 m μ . Add 0.1 N NaOH in 0.05 ml doses from a micro-burette and note the absorbance each time. Continue additions and stop the titration when a large number of readings of absorbance are obtained.

Observations and Calculations : A curve is plotted between absorbance corrected for dilution (ordinate) and volume of titrant (abscissa) and the end point is obtained from the intersection of two straight line portions of the curve. Now calculate the strength of HCl solution using normality equation.

Result : The strength of HCl solution = ... g/litre.

EXPERIMENT No. 15

Object : *To find the strength of a given ferric ammonium sulphate solution (approximate strength 0.05M) by using EDTA solution spectrophotometrically.*

Apparatus : Same as in preceding experiments.

Theory : This titration is based on the fact that Fe^{3+} -salicylic acid complex, which has maximum absorption at 525 m μ is less stable than Fe^{3+} -EDTA complex. Thus, if EDTA is added to Fe^{3+} -salicylic acid complex, the latter will disappear and the optical density will thus decrease as the end point is reached. After the end point, the absorbance will become constant. (For further details see preceding pages).

Procedure : Prepare 100 ml 0.1M EDTA* (Ethylene diaminetetra-acetic acid, mol. wt. = 372), 100 ml 0.1M ferric ammonium sulphate, acetic acid and sodium acetate buffer with pH ~ 2.4 and 6% salicylic acid solution in acetone. Take 5 ml

*EDTA solution may be standardised by using 0.1N ZnSO_4 solution and Eriochrome Black T solution (indicator) During the titration, 2-3 ml of ammonia buffer (7 g of NH_4Cl + 57 ml of 0.88 M NH_3 + 43 ml distilled water) having a pH ~ 10.0 is also added.

of Fe^{3+} solution, 1 ml of salicyclic acid solution, 20 ml of buffer solution and about 65 ml of distilled water in the cell and obtain the absorption spectrum of Fe^{3+} -salicyclic acid complex against the buffer solution as a blank. The wavelength of maximum absorption, λ_{max} is obtained which is $\sim 525 \text{ m}\mu$. EDTA does not absorb light at this wavelength.

Now adjust the wavelength knob to $525 \text{ m}\mu$ and set the transmission to 100% or absorbance to zero. Add 0.5 ml of EDTA solution and note the absorbance of the solution. After 2 ml of titrant, add it in 0.1 – 0.2 ml stages and note the absorbance, till its value becomes constant. The titrant is further added in 2 ml stages.

Observations and Calculations : The absorbance is noted against each addition of titrant and a plot is drawn between absorbance (ordinate) and volume of titrant (abscissa). From the point of intersection of the two straight lines, obtain the end point and the strength of ferric solution.

Result : The strength of ferric ammonium sulphate solution
= ... g/l.

EXPERIMENT No. 16

Object : To find the strength of CuSO_4 solution by titrating it with EDTA spectrophotometrically.

Apparatus : Same as in preceding experiments.

Theory : The Cu-EDTA complex absorbs more strongly at a wavelength $745 \text{ m}\mu$ than copper solution. Thus, the absorbance will increase with the addition of EDTA solution, till after the end point the absorbance becomes constant. (For further details, see earlier pages).

Procedure : Prepare 100 ml 0.04 M CuSO_4 , 100 ml 0.1 M EDTA, 100 ml 0.1M HCl and 100 ml 0.1M CH_3COONa solutions. First find the value of λ_{max} for Cu-EDTA complex ($\lambda_{\text{max}} = 745 \text{ nm}$), as described in experiment no. 10. Now take 10 ml of CuSO_4 solution, 20 ml of buffer solution (10 ml of 0.1M HCl + 10 ml of 0.1M CH_3COONa) and 60 ml of water ($\text{pH} = 2.4 - 2.8$) in the titration cell. Set the spectrophotometer to give zero absorbance at wavelength of 745 nm . Titrate with small aliquots of EDTA, first 0.5 ml and then 0.3 ml portions. Record the absorbance reading every time after thorough stirring. Make 4–5 additions beyond the end point.

Observations and Calculations : Determine the equivalence point and hence the concentration of copper sulphate solution by plotting absorbance (ordinate) corrected for volume change against the titre readings (abscissa).

Result : The strength of CuSO_4 solution = ... g/l.

EXPERIMENT No. 17

Object : To titrate ferrous ammonium sulphate with potassium permanganate solution spectrophotometrically.

Apparatus : Same as in preceding experiments.

Theory : Same as in preceding experiments.

Procedure : Prepare 100 ml 0.02M ferrous ammonium sulphate in 1M H₂SO₄, 100 ml 0.02M KMnO₄ solutions. Take 10 ml of 0.02 M KMnO₄ in the cell and scan the absorption curve in the wavelength range 430-650 mμ at 5 mμ intervals. Find the wavelength of maximum absorption. Two absorption bands at ~ 550 and 525 mμ are absorbed. At these wavelengths, ferrous ammonium sulphate does not absorb light.

Now take 5 ml of ferrous ammonium sulphate solution and 100 ml of 1M H₂SO₄. Set the transmission to 100% or zero absorbance at wavelength 550 or 525 mμ. Continue adding 0.1 ml of KMnO₄ and note the absorbance of the solution after each addition. This is done till absorbance becomes ~ 2.0.

Observations and Calculations : Same as in preceding experiments.

Results : The strength of KMnO₄ solution = ...g/l.

EXPERIMENT No. 18

Object : To determine the concentration of Cu(II) and Fe(III) solutions photometrically by titrating them with EDTA.

Apparatus : Same as in preceding experiments.

Theory : The stability constant of Cu-EDTA complex is sufficiently low as compared to Fe³⁺-EDTA complex. If to a mixture of Cu (II) and Fe (III), EDTA solution is added, the formation of Cu-EDTA complex starts only when all the Fe³⁺ ions are removed in the form of Fe³⁺-EDTA complex. The complex of copper absorbs strongly ~ 745 mμ, whereas that of Fe³⁺ does not do so. The end point of Fe³⁺ is indicated by starting of formation of copper complex, when absorbance begins to increase. The end point of copper is indicated as the absorbance becomes constant after attaining a maximum value as shown in figure (6).

Procedure : Prepare 100 ml each of 0.02M CuSO₄ and 0.02M ferric ammonium sulphate, 0.1M EDTA and a buffer of pH ~ 2.0.

Take the mixture (say 15 ml of Cu and 15 ml Fe) of Cu(II) and Fe(III) in the titration cell and add 30 ml of buffer solution and dilute the contents to 100 ml. Set the wavelength and absorbance to 745 mμ and zero, respectively. Now add 0.1M EDTA solution in aliquots of 0.2 ml, till the absorbance finally becomes constant. Make 4-5 additions after the end point.

Observations and Calculations : Plot the values of absorbance corrected for volume (ordinate) against volume of titrant (abscissa) and find out the strength or concentration of Cu(II) and Fe(III) solutions as explained in the theory.

Result : The concentration of Cu(II) and Fe(III) in the given mixture is ... and

....

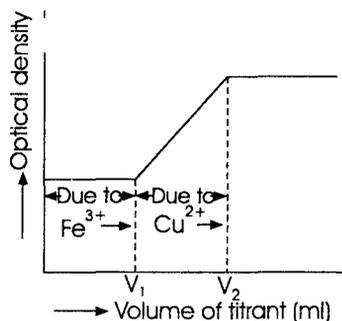


Fig. 6

EXPERIMENT No. 19

Object : *To determine simultaneously arsenic (III) and antimony (IV) in a mixture by spectrophotometric titration.*

Apparatus and Chemicals : Spectrophotometer, potassium bromide, potassium bromate, arsenious oxide, antimony (III) chloride, 6M HCl

Theory : In acid solution, arsenic (III) is oxidised to arsenic (V) and antimony (III) to antimony (V) by potassium bromate and potassium bromide solution. Absorbance of the mixture at 326 nm during the course of titration remains constant till all the arsenic (III) has been oxidised. The absorbance then decreases to a minimum at antimony (III) end point. Afterwards, it increases with the addition of excess titrant.

Procedure : Prepare standard bromate/bromide solution by dissolving 0.6952 g of potassium bromate (mol. wt. 167, A.R. quality) and 2.84 g of potassium bromide in water and making the solution to 250 cm³ with water. This gives 0.0166M (0.1N) potassium bromate/potassium bromide solution.

Prepare a mixture of arsenic (III) and antimony (III) by dissolving 0.1236 g arsenic (III) oxide and 0.3644 g of antimony (III) chloride in about 6M hydrochloric acid, and making the solution to 1 dm³ with the acid solution. This gives 2.5×10^{-3} N arsenic oxide and 5×10^{-3} N antimony chloride solution.

Take 100 cm³ of arsenic/antimony solution in the titration cell of the spectrophotometer. Set the wavelength of 326 nm and measure the absorbance after successive addition of 0.2—0.3 cm³ aliquots of bromate/bromide solution.

Observations and Calculations : Plot a curve between absorbance (ordinate) and volume of titant (abscissa) and obtain the titration curve. First break of the plot corresponds to the equivalence point of arsenic (III) and the second to that of antimony (III). Now calculate the concentrations of arsenic (III) and antimony (III) in the solution.

Result : Concentration of arsenic = g/L

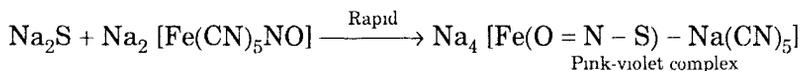
Concentration of antimony = g/L

EXPERIMENT No. 20

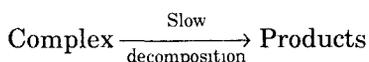
Object : *To study the kinetics of decomposition of the complex formed between sodium sulphide and sodium nitroprusside, spectrophotometrically and also to determine the order and rate constant of the reaction.*

Apparatus and Chemicals : Spectronic-20 colorimeter with 10 mm. glass cells, 0.002 M sodium sulphide solution, 0.002 M nitroprusside solution.

Theory : The test for sulphur in an organic compound is based on the appearance of pink-violet colour on adding a few drops of sodium nitroprusside to the sodium extract of the compound. The appearance of pink violet colour is due to the formation of a complex between sodium sulphide (obtained on fusion of the compound with sodium) and sodium nitroprusside.



The colour, however, fades out due to the decomposition of the complex.



The appearance of the pink colour and hence the success of the test depends upon the concentration of NaOH (pH 9.8 to 11.5) which is formed by the interaction of sodium with water. If too much sodium is taken for fusion, the colour may not appear at all or may be very short lived.

The kinetics of decomposition of the complex may easily be followed spectrophotometrically by measuring the absorbance (optical density) of the reaction mixture with time at the wavelength (525 nm) of maximum absorption of the complex.

Procedure : With the shutter closed, *i.e.*, when no light falls on the photocell, adjust the 'dark current control' to zero. Fill one of the absorption cells (10 mm glass cell) with water and place it in the cell holder of the instrument. Set the wavelength to 525 nm and adjust 'light control' to percentage transmission equal to 100. Take out the cell from the instrument.

Prepare a reaction mixture (at room temperature) by mixing 25 cm³ each of the two solutions. Immediately pour the mixture into another thoroughly cleaned absorption cell, place it in the cell holder and measure the absorbance D , at intervals of 15 seconds. Take at least 10 readings.

Calculations and Result : Plot a curve between absorbance (ordinate) and time (abscissa) and show that half life period, *i.e.*, time required for the absorbance to decrease to its half value is independent of the initial value of absorbance, *i.e.*, initial concentration of the complex, showing thereby first order kinetics of decomposition of the complex.

Plot $\log D$ against time (abscissa). The plot will be linear with slope equal to $-k/2.303$. Hence, calculate the rate constant k .

Plot $\log (D - D')$ against time t as abscissa (D and D' being the absorbances at times t and $t + \Delta t$, where Δt is a constant time interval). The graph will be linear showing thereby the first order kinetics (Guggenheim method). From the slope ($-k/2.303$) of the graph, calculate the value of the rate constant of the reaction.

EXPERIMENT No. 21

Object : To determine colorimetrically the order and the energy of activation for the decomposition of violet coloured complex of ceric ions and *N*-phenylanthranilic acid.

Apparatus and Chemicals : A colorimeter, pure ceric sulphate, *N*-phenyl-anthranilic acid.

Theory : In the titrimetric standardisation of Ce (IV) with Fe (II), *N*-phenylanthranilic acid is used as an indicator which gives violet colour at the end point. The appearance of violet colour is due to the oxidised form of the indicator. However, the violet colour slowly changes to yellow on standing due to the decomposition of the oxidised form of the indicator. The kinetics of decomposition of coloured complex can conveniently be followed colorimetrically.

Procedure and Observations : Dissolve 0.1611 g of ceric sulphate (mol. wt. 322.24) in 1M H_2SO_4 to 50 cm^3 . This gives nearly 1×10^{-2} M solution.

Prepare the indicator solution by dissolving 0.1 g of it in 5 cm^3 of 0.1 M NaOH and diluting to 50 cm^3 with water. This gives 9.39×10^{-3} M solution of the indicator.

Mix 5 cm^3 of ceric sulphate solution and 0.5 cm^3 of the indicator solution, and dilute the mixture to 50 cm^3 with 1 M H_2SO_4 so as to yield a reaction mixture containing 1×10^{-3} M Ce(IV) and 1×10^{-4} M N-phenylanthranilic acid in 1M H_2SO_4 .

Measure the absorbance of the reaction mixture at intervals of 30 s at 580 nm against 10^{-3} M Ce(IV) in 1.0M H_2SO_4 as the blank. Ce(IV) and N-phenylanthranilic acid do not absorb at this wavelength.

Calculations : (a) Plot a curve between log (absorbance) and time (abscissa). The plot would be a straight line showing thereby the first order kinetics of the reaction. Calculate the first order rate constant from the slope ($-k/2.303$) of the straight line graph.

(b) Plot a curve between absorbance (ordinate) and time (abscissa), and from this curve obtain half life period ($t_{1/2}$) and calculate the rate constant ($k = 0.693/t_{1/2}$).

(c) From the absorbance and time graph, obtain the absorbances A_t and A'_t after times t and $t + \Delta t$, respectively, where Δt is time interval and from the linear graph (slope = $-k/2.303$) calculate the rate constant.

Result : The value of rate constant is nearly $2.6 \times 10^{-3} \text{ s}^{-1}$ at 25°C.

PHOTOCHEMICAL REACTIONS

Several reactions, which normally do not occur to an appreciable extent, can be brought about by exposure to radiation, particularly in the ultraviolet region. The radiation is absorbed by the reactant molecules which are then raised to the excited state (higher electronic state). The excited molecule may follow one or more courses. It may (i) emit the radiation of same or different wavelength (ii) return to the normal state, the energy being dissipated as heat (iii) decompose into free radicals or react with another molecule in the reaction (iv) transfer the absorbed energy to other substance, which then undergoes the chemical change.

In the primary photochemical process each molecule is activated by the absorption of one quantum of radiation. Therefore, quantum yield which is defined as

$$\phi = \frac{\text{Number of molecules activated}}{\text{Number of quanta absorbed}}$$

is always unity. However, the resulting activated or even dissociated molecule may involve in thermal or dark reactions, known as *secondary reactions*. Thus, the overall quantum yield which is defined as

$$\phi = \frac{\text{Number of molecules decomposed}}{\text{Number of quanta absorbed}}$$

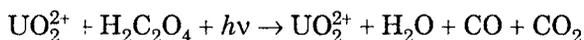
may not be unity. It can vary widely. Its value can be less than unity (due to partial deactivation) or be nearly 10^6 for chain reactions depending upon the nature of the secondary reactions.

EXPERIMENT No. 22

Object : *To study the decomposition of oxalic acid in a solution photosensitized by uranyl sulphate.*

Apparatus and Chemicals : Mercury vapour lamp and a choke, 6 pyrex glass or quartz (15×2.5 cm) tubes, circular shielding box with supporting racks for tubes, 0.01 *M* oxalic acid solution, 0.02*M* uranyl sulphate solution, 0.005 *M* potassium permanganate solution.

Theory : Uranyl ions absorb radiation of wavelength in short wave region but no reaction occurs, the energy being dissipated as heat. However, in presence of oxalic acid (which does not absorb the radiation in this region) the absorption of radiation by uranyl ions is increased. This may be due to the formation of a loose compound between uranyl ions and oxalic acid. This compound decomposes into carbon monoxide and carbon dioxide as follows :



The reaction is readily followed by titrating the residual oxalic acid with standard potassium permanganate solution.

Procedure : Paint the inner side of the box and the supporting racks with optical black. Set the supporting racks for the tubes in circles of 10 and 20 cm from the lamp, placed centrally.

Fill each of the six tubes with 50 cm³ of a 1 : 1 mixture of oxalic acid and uranyl sulphate solutions, and hang them vertically in the supporting rack around the lamp at a distance of 10 cm. Replace the lid and switch on the lamp. Use special goggles when the lid is removed, while the mercury lamp is on.

Remove the tube successively after 5, 10, 20, 30, 40 and 50 minutes, and titrate in duplicate the solution (20 cm³ aliquot) of each tube with standard solution of potassium permanganate after heating it to nearly 70°C in the presence of 10 cm³ of dilute sulphuric acid. Record the titre values. Also titrate the original mixture (20 cm³ aliquot) in duplicate.

Carry out similar experiments using the same six tubes to study the effect of changes in (a) concentration of oxalic acid (b) concentration of uranyl sulphate (c) distance from the lamp. Change only one variable at a time.

Calculations : From titre readings, calculate the amount of oxalic acid decomposed at different times. Plot graphs between the amount of the acid decomposed (ordinate) and time (abscissa). Determine the order of the reaction.

Result : The order of reaction is

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 23

Object : *To determine the composition of a binary mixture of aurine and crystal violet spectrophotometrically.*

Both these dyes absorb light in the visible range 400–650 ml. Use standard solutions in ethanol :

Crystal violet = 0.0056 gL^{-1} (mol wt. = 408)

Aurine = 0.038 gL^{-1} (mol. wt. = 290)

Prepare a mixture by mixing equal volumes of the two solutions and another by mixing them in any other volume ratio. Carry out the measurements and compare the results obtained with those already known. Proceed as in experiment 8.

EXPERIMENT No. 24

Object : To determine the composition of a binary solution containing N-butylacetanilide and benzyl benzoate in 95% ethanol, photometrically.

Proceed as in experiment 8.

EXPERIMENT No. 25

Object : To test the validity of Beer's law for a solution of CuSO_4 and also to determine λ_{max}

Proceed as in experiments 2 and 6.

EXPERIMENT No. 26

Object : To find the concentration of CuSO_4 solution using Duboscq colorimeter.

Proceed as in experiment 1.



POLAROGRAPHY AND AMPEROMETRY

(Current-Potential Relationships)

Polarography is an instrumental technique and consists in the measurement of applied potential versus current flow in solutions and the data so obtained can be interpreted in terms of the nature and behaviour of many substances and systems.

Heyrovsky (1923) devised polarographic method of analysis using dropping mercury electrode. The current-potential curve was obtained by means of an automatic registering apparatus known as **polarograph** and the resulting curve is known as a **polarogram**.

A polarograph essentially consists of two mercury electrodes. One electrode consists of a pool of mercury at the bottom of the cell and the other consists of mercury falling drop-by-drop from a fine bore capillary glass tube (dropping mercury electrode). It can be used both in oxidation and reduction processes, the only difference being that in oxidation process, it is made the anode and the mercury pool in the cell the cathode and vice versa in a reduction reaction. The complete diagrammatic representation of the apparatus is shown in figure (1).

[1] Description of Apparatus

It consists of a flask A containing the experimental solution, which can be saturated with H_2 by passing the gas through a glass tube B. Thus, reservoir C constitutes a part of the dropping mercury cathode, the drops of mercury falling at a rate of 20-30 drops per minute from the end of a capillary tube D. The anode consists of mercury pool at the bottom of the flask H, the connection is made by a sealed in wire. The cathode C and the anode E are connected to the appropriate ends of a battery F. The applied voltage can be varied by means of a sliding contact G along a potentiometer wire HI. The potentiometer consists of a number of turns of wire wound around a rotating drum, the contact G being fixed. The only idea behind this is, that in this manner the applied E.M.F. is varied in a regular known manner. The current strength is indicated by a galvanometer J, across the terminals of which is connected a shunt

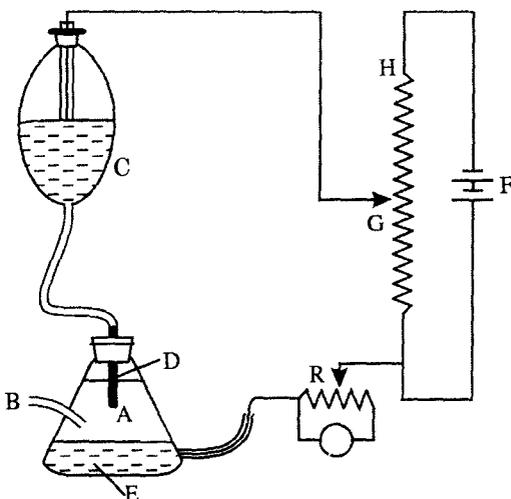


Fig. 1 : Polarographic technique.

K so that the sensitivity of the instrument can be varied when desired. The corresponding current strength is registered photographically by the light reflected from mirror galvanometer on to a sheet of sensitized paper, attached to rotating drum which is synchronized with the one carrying the potentiometer wire.

As the anode has a large area of surface and current is probably of the order of 10^{-6} amp., the polarisation at this electrode is negligible and the potential of anode may, therefore, be regarded as constant. If this potential is measured, by comparison with a standard reference electrode, the potential of cathode can thereby be determined, by measuring the total E.M.F. across the cell.

Though a number of other electrodes, such as streaming, hanging, rotating micro-electrodes, gold, graphite and carbon electrodes have also been used. The dropping mercury electrode has several advantages in comparison with the other electrodes. The dropping mercury electrode, usually abbreviated as d.m.e., is preferred because :

(1) Mercury can be easily purified by first running it through a column of 10% nitric acid several times and then through a column of distilled water and finally the dry metal is distilled under reduced pressure at least three times.

(2) The metal is noble.

(3) Mercury has a high overvoltage, which makes possible the deposition of ions difficult to reduce.

(4) The metal can easily be restored after its successive use.

(5) The diffusion current assumes steady value almost immediately and is reproducible.

(6) Its surface area is reproducible with any given capillary.

[II] Polarographic Cells

A number of polarographic cells have been used commercially. Some of them are as follows :

The first cell (fig. 2) is the original cell devised by Heyrovsky. It is available in several capacities. The second cell (fig. 3) is also similar with the only difference that a conical flask is replaced by a beaker.

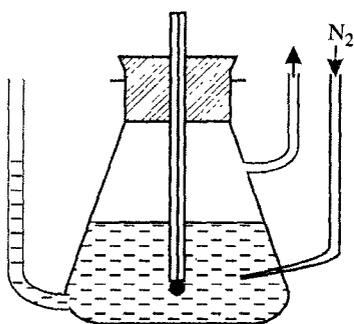


Fig. 2 : Polarographic cell

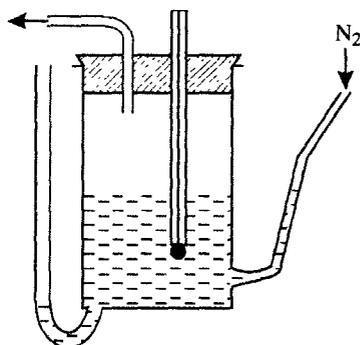


Fig. 3 : Polarographic cell

[III] Theory and Working of the Apparatus

As has been stated earlier, polarography is concerned with the reactions taking place at the dropping mercury electrode or micro-electrode, as it is usually called. When a reaction at the electrode takes place, it is always associated with an

'electron bargain', that is, either an electron is transferred from the electrode to the component of the electrolyte or the component of the electrolytic solution loses the electron to the electrode. If a component accepts electrons, it is called an **oxidant** and when it loses electrons it is called a **reductant**. An oxidant is reduced when it accepts electrons and a reductant is oxidised when it loses electrons. The electrode at which the process of reduction takes place, (e.g., $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$ or $\text{Cu}^+ + e \rightarrow \text{Cu}$) is called cathode and when oxidation takes place at its surface, (e.g., $\text{Cu} \rightarrow \text{Cu}^+ + e$ or $\text{Cu}^+ \rightarrow \text{Cu}^{2+} + e$) it is called an anode. The electrons leave the surface of the electrode and enter the body of the solution when at the cathode the reduction of an oxidant takes place. The electrons pass from the solution to the electrode surface when the oxidation of a reductant takes place at anode. During these processes an equivalent amount of reductant (when an oxidant is reduced) and oxidant (when a reductant is oxidised) are formed. The above discussion may be summarised as follows :



The reaction has been shown reversible because an electron cannot exist freely in the solution, therefore, a reduction process at cathode is always necessarily associated with the simultaneous oxidation at the anode.

Let us now consider the electrolysis of oxygen-free dilute solution of cadmium chloride. If the connections are made as shown in fig. (1) the following are the probabilities due to which the positively charged ions will be attracted towards the cathode.

(1) Mutual force of attraction arising from the opposite electrical charges on electrode and metal ion.

(2) A force of diffusion arising from the difference of concentration produced at the electrode surface.

These two factors govern the total current which passes through the cell and the total current can thus be regarded as the sum of these two factors.

A dilute solution for analysis is placed in the cell and the E.M.F. applied to the cell is increased. In the beginning, a small current passes through the cell. As the E.M.F. applied to the cell is increased and reaches the discharge potential of one of the cations present in the experimental solution, the current flowing through the cell undergoes a steep rise and then levels off. It is seen, therefore, that as the contact *G* is moved along *IH* thus increasing the E.M.F. between the anode and the cathode, the current also increases in a series of different waves, each wave representing the electro-reduction of particular species. The complete voltage current curve is shown in figure (4).

Resulting polarogram is obtained with a solution of calcium chloride (also known as, 'ground solution' and serves to carry the current) containing several cations such as copper, lead, cadmium, zinc, manganese and barium ions, each having a concentration of 0.1 g ion per litre. The waves for the deposition of each ion are shown in fig. (4)

The first steep rise is due to discharge of Cu^{2+} ions. The levelling off that follows the rise, is due to concentration polarisation. The first discharged ions are those, which are in the immediate vicinity of the cathode. As the process continues, the

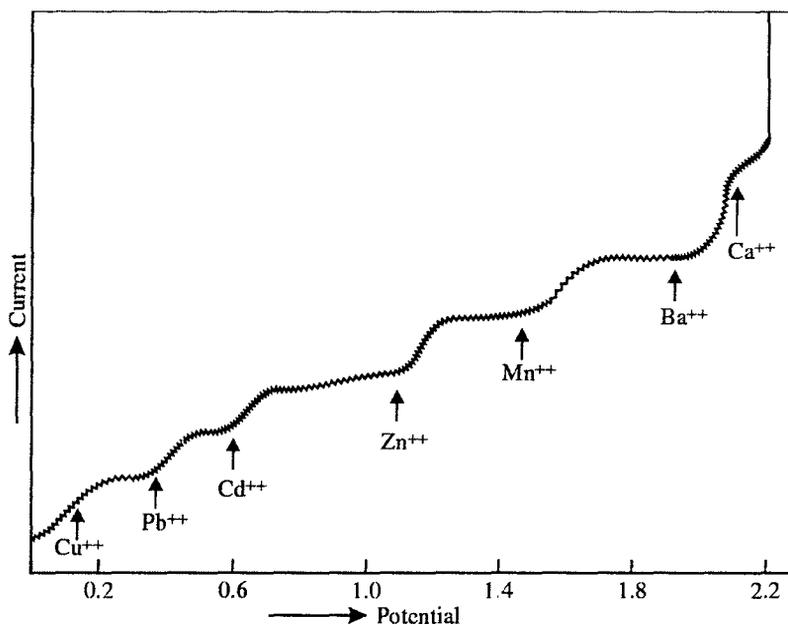


Fig. 4: Polarogram

Cu^{2+} ions from the main bulk of the solution diffuse towards the cathode to take the place of those which have already been discharged. A point is reached when the rate of diffusion of Cu^{2+} ions towards cathode no longer suffices to satisfy the requirement of the current. Hence, a discharge of the next ion, *i.e.* lead in the series of ascending discharge potentials occurs, in addition to the discharge of Cu^{2+} ions. Therefore, a second steep rise and levelling off is noted. Similarly, process is continued for other ions present in the solution.

Each wave consists of a vertical part and a horizontal part. The former represents the increase of current flow during the process of discharge of the ions. The latter represents the increase of potential with almost constant current.

[IV] Factors Affecting Limiting Current

Limiting current can be regarded as the sum of the following contributing factors : (a) *Residual or condenser current* (b) *Migration current*, (c) *Diffusion current*, (d) *Adsorption current* (e) *Kinetic current*.

(a) **Residual or condenser current** : Mercury is unique in remaining electrically uncharged when it is dropping freely into a solution containing an indifferent electrolyte, such as KCl , KNO_3 etc. If a current-voltage curve is determined for a solution containing ions with a strongly negative reduction potential, (*e.g.*, potassium ions), a small current flows before the decomposition of the solution begins. This current increases almost linearly with the applied voltage, and it is observed even when the purest air free solutions are used, so that it cannot be due to the reduction of impurities. It must, therefore, be considered a *nonfaradic* or *condenser current*, made appreciable by the continual charging of new mercury drops to the applied potential. It is known that metals when submerged in an electrolyte, are covered with an electrical double layer with positively and negatively charged ions. The composition of the double layer and hence the charging current varies, depending upon the potential which is imposed upon the metal.

In practice one often finds that the indifferent electrolyte contains traces of impurities, so that small, almost imperceptible currents are super-imposed upon the condenser current. It is customary to include all these currents in the residual current. As will be seen later, in practical polarographic work, the residual current is automatically subtracted from the total observed current by proper extrapolation and placement of tangents to the wave.

(b) Migration current : Electro-active material reaches the surface of the electrode largely by two processes. One is the migration of charged particles in the electric field caused by the difference of potential existing between the surface of the electrode and the solution, the other is concerned with the diffusion of particles, and will be discussed in the succeeding paragraph. Heyrovsky (1934) showed that the migration current can be practically eliminated if an indifferent electrolyte is added to the solution in a concentration so large that its ions carry essentially all the current. (An indifferent electrolyte is one which conducts the current but does not react with the material under investigation, nor with the electrodes within the potential ranges under study). In practice, this means that the concentration of the added electrolyte (supporting electrolyte) must be at least 100-fold that of the electro-active material. An example of this supporting electrolyte will make it clear. Let us imagine an electrolytic solution containing potassium ions $0.10M$ and copper ions $0.005M$. If we assume that the equivalent conductivity of each ion is of approximately equal then it follows that 90% of the current will be transported to the cathode by the potassium ions and only 10% by the copper ions. Both ions will tend to diffuse towards any portion of the solution where a concentration gradient exists, but the rate of diffusion will be slow. If the concentration of the potassium ions be increased until it represents 99% of the total cations present, practically all the current passing through the cell will be transported by the potassium ions. Under such conditions, the electroactive material can reach the electrode surface only by diffusion. It must be emphasised that the supporting electrolyte must be composed of the ions which will discharge at the potentials which will not interfere or react chemically with the ions under investigation.

(c) Diffusion current : The effect of various factors on the diffusion current had been examined by Ilkovic (1948) who derived an equation by regarding the thickness of the cathode layer as small compared to the radius of the drop and thus using a relation for linear diffusion of the ionic species during electrolysis.

Strictly speaking, the linear diffusion of an ionic species during electrolysis will occur in the presence of a plane electrode forming one end of a cylindrical vessel, when the diffusion of the ions will be linear, parallel to the axis of the cylinder. Despite this approximation, the equation applies well to diffusion near spherical mercury drops, though for accurate determination, some correction terms are necessary. The *Ilkovic equation* is given by,

$$I_d = 607n D^{1/2} m^{2/3} t^{1/6} c$$

where I_d = diffusion current in microamperes, n = number of electrons involved in the reduction of one molecule of the reducible substance, D = diffusion coefficient of the substance in $\text{cm}^2/\text{sec.}$, m = weight of mercury in grams flowing through the capillary of the cathode per sec., t = time necessary for the formation of one drop of mercury and c = concentration of the substance in millimole/litre.

The diffusion coefficient, D is dependent upon temperature T , viscosity of the medium η , ionic mobility, u and ionic strength of the solution, μ . The value of t depends upon the pressure of mercury and the interfacial tension at the mercury solution interface. It follows that at constant values of D , t , n and m , the Ilkovic equation becomes :

$$I_d = Kc$$

i.e., diffusion current is directly proportional to the concentration of the reducible substance.

[V] Modification of Ilkovic Equation

Lingane and Loveridge derived an equation on the basis of the spherical diffusion of the ionic species, *viz.*,

$$I_d = 607n D^{1/2} m^{2/3} t^{1/6} (1 + 39D^{1/2} m^{-1/3} t^{1/6})$$

The term in bracket corresponds to the difference between linear and spherical diffusion. This correction term is not large, amounting to about 3-7% of the total current. This equation is taken for accurate work.

In order to obtain the true d.c. of a substance, a correction must be made for the residual current. The most reliable method for making the correction is to evaluate in a separate polarogram, the residual current of the supporting electrolyte alone. The value of the residual current at any particular potential of the dropping electrode is then subtracted from the total current observed, as illustrated in fig. (5). In practice, an adequate correction can be obtained by

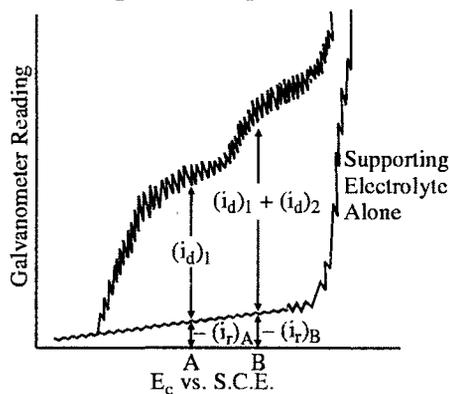


Fig. 5.

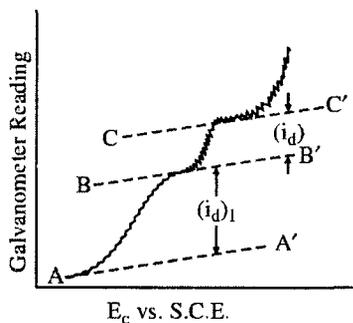


Fig. 6.

extrapolating the residual current portion of the polarogram immediately preceding the rising part of the polarogram, and taking as the diffusion current the difference between the extrapolated line and current-voltage wave. This method is useful when the polarogram consists of several waves. In this case, the diffusion current plateau of a preceding wave may be extrapolated. This method is shown in figure (6).

(d) Adsorption current : Current-voltage curves obtained with d.m.e., frequently exhibit pronounced maxima, which are reproducible and which can be usually eliminated by the addition of certain appropriate *maximum suppressors*. These maxima vary in shape, *e.g.*, from sharp peaks to rounded humps, which gradually decrease to the normal diffusion current curve as the applied voltage is

increased. The maxima may be due to the stirring of the liquid around the mercury drop or to adsorption of electro-active material on the electrode surface, but the exact cause is unknown. To measure the true diffusion current, the maxima must be eliminated. Fortunately, this can be easily affected by adding small quantities of dye and indicator ions, (*e.g.*, sodium methyl red) or colloids, (*e.g.*, gelatin or agar-agar). Gelatin is generally employed in concentrations of 0.002–0.01%, higher concentration will suppress the current.

(e) **Kinetic current** : This current is due to a slow reaction process occurring between adsorbed ions at the surface of the d.m.e. prior to electron exchange. This phenomenon is mostly found in organic fields especially in the study of carboxylic radicals.

[VI] Half-Wave Potential

Consider the reversible reduction of an oxidant to a reductant at a dropping mercury cathode (an oxidant accepts electrons, a reductant loses electrons). The relevant equation for the electrode potential is given by,

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}} \quad \dots (1)$$

where E° = value of electrode potential when a_{ox} and a_{red} are equal, a_{ox} = activity of the oxidant, a_{red} = activity of the reductant.

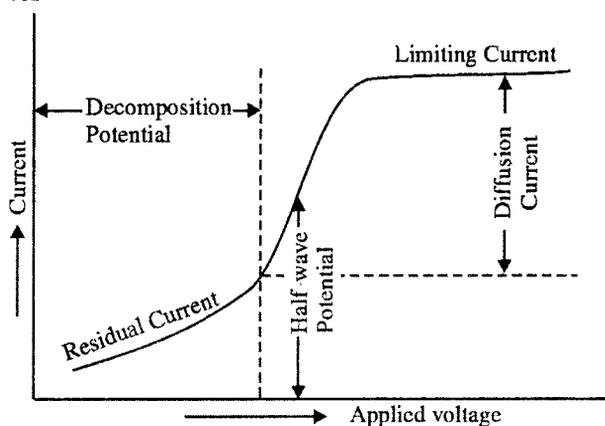


Fig. 7 : A typical current-applied voltage curve (polarogram)

On replacing the activity terms by concentration terms, equation (1) becomes:

$$E \approx E^\circ + \frac{RT}{nF} \log \frac{C_{\text{ox}}}{C_{\text{red}}} \quad \dots (2)$$

At the beginning of the electrolysis, the concentration of the reducible substance must be the same in the bulk of the solution and the electrode-solution interface. As soon as the decomposition potential is exceeded, some of the oxidant at the interface is reduced and is replenished from the bulk of the solution by means of diffusion. The reductant diffuses away from the electrode into the solution. At very high potentials, all the oxidant reaching the electrode is reduced, so that the newly formed reductant is present and the current will thus be the diffusion current.

The current at any point is thus determined by the rate of diffusion of the oxidant from the bulk of the solution to the electrode surface under a concentration gradient ($C_{\text{ox}})_b$ to C_{ox} , where ($C_{\text{ox}})_b$ is the concentration in the bulk of the solution. Thus,

$$I = k \{(C_{\text{ox}})_b - C_{\text{ox}}\} \quad \dots (3)$$

where I = current at any point on the polarographic wave
 k = velocity constant of diffusion

$$\text{When } C_{\text{ox}} = 0, \text{ then, } I = k (C_{\text{ox}})_b = I_d \quad \dots (4)$$

where I_d = diffusion current.

$$\text{From equations (3) and (4), } C_{\text{ox}} = \frac{(I_d - I)}{k} \quad \dots (5)$$

If the reductant is soluble in water and none was originally present with the oxidant, it will diffuse from the interface to the bulk of the solution, therefore, the current (I) will be proportional to the concentration gradient,

$$C_{\text{red}}, \text{ viz., } I = k_1 C_{\text{red}} \quad \dots (6)$$

Equation (6) holds good if the reductant is insoluble in water, but soluble in mercury by forming an amalgam.

Combining equation (2) with (6), we get

$$E = E^\circ - \frac{RT}{nF} \ln \frac{k}{k_1} + \frac{RT}{nF} \ln \frac{I_d - I}{I} \quad \dots (7)$$

When $I = 0.5I_d$, equation (7) reduces to,

$$E = E_{0.5} = E^\circ - \frac{RT}{nF} \ln \frac{k}{k_1} \quad \dots (8)$$

The potential at the point on the polarogram where the current is half the diffusion current is known as the half-wave potential ($E_{0.5}$). The value of half wave potential is independent of the concentration of the oxidant in the bulk of the solution and is a characteristic constant for the reversible redox system.

Combining equations (8) and (7), we get the general equation of the polarographic wave,

$$E = E_{0.5} + \frac{RT}{nF} \ln \frac{I_d - I}{I} \quad \dots (9)$$

It follows from equation (9) that a curve between $\ln \frac{I_d - I}{I}$ and corresponding potential of the micro-electrode is a straight line with a slope of RT/nF for a reversible reaction. The intercept of this straight line on the ordinate will give the value of half-wave potential.

[VII] Derivative Polarogram

It is the trace or curve obtained as the first derivative of direct polarographic waves, (i.e., by plotting $\Delta i/\Delta E$ against E). Such a curve shows a peak, at the half-wave potential and by measuring the height of the peak it is possible to obtain qualitative and quantitative data on the reducible substance. The height of the peak is proportional to the concentration and the minimum represents d.c. plateau. The curve [fig. (8)] is a typical

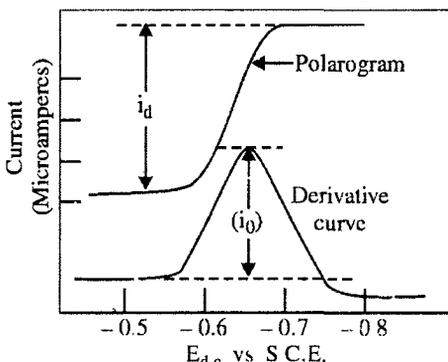


Fig. 8

conventional polarogram for 0.003M CdSO₄ in M-KCl in presence of 0.005% gelatin.

[VIII] Determination of the Formula and Stability Constant of Complex Metalion

The polarographic method can be applied with great precision to the study of the complex metal ion by virtue of the fact that the half-wave potentials of the metal ions are shifted (usually to more negative values) due to complex ion formation. By measuring this shift as a function of the concentration of complexing agent, both the formula and the stability constant can be determined.

Polarographic method has been found to be of immense utility and provides a sound technique for studying both qualitative as well as quantitative aspects of the metal complexes. The quantitative information regarding stability constant of a complex ion can only be obtained when the electrode reaction is taking place reversibly. Therefore, it becomes necessary to establish reversibility of the electrode reaction before a quantitative approach is made.

If the reduction or an oxidation at the d.m.e. is taking place reversibly, then the difference between the half-wave potentials of the simple and the complex ions at 25°C is given as follows :

$$(E_{0.5})_c - (E_{0.5})_s = \frac{0.0591}{n} \log K_c - \frac{0.0591}{n} \log \frac{f_s k_c}{f_c k_s} - \frac{0.0591}{n} p \log C_x \quad \dots (10)$$

where the subscripts *s* and *c* refer to the simple and complex metal ions, respectively, *K_c* is the dissociation constant for complex ion and *C_x* is the ligand concentration.

Direct information about the activity coefficients which appear in the above equation is rarely available and even if the values are worked out with the help of extended Debye-Huckel equation, the method apart from being tedious does not give reliable results. The values of activity coefficients and *k* are, therefore, usually both neglected altogether. When this is done, the above equation takes the following form :

$$(E_{0.5})_c - (E_{0.5})_s = \frac{0.0591}{n} \log K_c - \frac{0.0591}{n} p \log C_x \quad \dots (11)$$

Equation (11) has two important applications. First, it permits the determination of *p* and then the formula of the complex ion from the data on the half-wave potentials of the complex at different concentrations of the complexing agent. This follows from a differentiation which gives,

$$\frac{(E_{0.5})_c}{\log C_x} = 0.0591 \frac{p}{n} \quad \dots (12)$$

The above equations (10), (11) and (12) are applicable to reversible reactions. The irreversible reactions, however, should be approached in a different way.

Irreversible reactions : The reversibility of the electrode reaction is a pre-requisite of the methods due to Lingane (1941), de Ford and Hume (1951). For the complexes which reduce irreversibly at d.m.e., methods with certain limitations are available. Ringborn and Ericksson (1953) developed the methods for the treatment of complexes which are reduced irreversibly. A method due to Subrahmanya (1960) utilises a modification of the method by Tamamushi and Tanaka (1949), for an irreversible process, *i.e.*,

$$\frac{\Delta E}{\Delta \log C_x} = - \frac{j \times 2.303 RT}{\alpha \cdot nF} \quad \dots (13)$$

where ΔE is the shift in the half-wave potential of the complex metal ion, C_x is the concentration of the ligand, j is the number of ligand bound in the complex and α is the fraction of the total applied potential that favours the forward reaction.

By using the modified Heyrovsky-Ilkovic equation for an irreversible reaction, *i.e.*,

$$E_{d.c} = E_{0.5} - \frac{RT}{\alpha \cdot nF} \log \frac{i}{(i_d - 1)} \quad \dots (14)$$

or
$$E_{0.75} - E_{0.25} = \frac{2RT}{\alpha \cdot nF} \log 3 \quad \dots (15)$$

From equation (15),
$$E_{0.75} = E_{0.25} + \frac{2 \times 0.0591}{\alpha n} \log 3 \quad (\text{At } 25^\circ\text{C})$$

or
$$\alpha \cdot n = \frac{n \times 0.0591 \times 0.4771}{E_{0.75} - E_{0.25}} = \frac{0.05630}{E_{0.75} - E_{0.25}} \quad \dots (16)$$

α is thus known from the values of $(E_{0.75} - E_{0.25})$. The values of j were evaluated from equation (13), according to which

$$j = - \frac{\Delta E}{\Delta \log C_x} \cdot \frac{\alpha \cdot n}{0.0591} \quad \dots (17)$$

The dissociation constant, K_c can be evaluated from the expression,

$$(E_{0.5})_c - (E_{0.5})_s = \frac{RT}{\alpha \cdot nF} \log K_c - \frac{jRT}{\alpha \cdot nF} \log C_x \quad \dots (18)$$

provided the reduction of the simple metal ion takes place reversibly.

Subrahmanya applied this method to study the mono-, di- and tri-ethanol amines of iron, cadmium, nickel, cobalt, copper, lead and zinc at 30° in alkaline media. However, the success of the method depends upon the reversibility of the simple ion in equation (15) when evaluating the value of dissociation constants.

EXPERIMENT No. 1

Object : To study the variation of diffusion current with concentration, and also to construct a wave height-concentration curve for cadmium ion.

Apparatus and Chemicals : Polarograph assembly, 0.1 M $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ solution, 1.2% (W/V) gelatin solution, cylinder of hydrogen or nitrogen.

Theory : In presence of an excess of base or supporting electrolyte and a maximum suppressor, the diffusion current alone is responsible for the wave, the height of which forms the basis of quantitative analysis. Diffusion current, I_d , is related to the concentration, C of the reducible ion according to the equation

$$I_d = kn \cdot F \cdot C \cdot D^{1/2} \cdot m^{2/3} \cdot t^{1/6}$$

where n is the number of electrons involved in the reduction of a mole of the ion, D the diffusion coefficient of the reducible substance, m the weight of mercury flowing through the capillary per sec, t (seconds) the time required for the

formation of one drop of mercury and k is a constant. If all other factors, except concentration, are constant, then

$$I_d = KC$$

Thus, a graph of I_d against C will be a straight line passing through the origin; This graph may be used as the calibration curve for quantitative analysis.

Procedure : Set up the polarograph and electrode assembly as explained. Dilute, respectively 0.2, 0.5, 1.0, 2.0, 3.0, 4.0 and 5 cm³ of 0.1 M cadmium sulphate solution to 100 cm³, so as to get 2×10^{-4} , 5×10^{-4} , 1×10^{-3} , 2×10^{-3} , 3×10^{-3} , 4×10^{-3} and 5×10^{-3} M solutions. Before dilution add 10 cm³ 1.0 M KCl and 10 cm³ of gelatin solution to each solution.

Following the technique plot the polarograms at suitable sensitivity for each of the solutions.

From the sensitivity and the chart reading calculate I_d for each concentration and plot the graph between I_d and C . It is, however, more convenient to plot $\log I_d$ against $\log C$ (abscissa).

EXPERIMENT No. 2

Object : To plot a polarogram for a mixture of Cd²⁺, Zn²⁺ and Mn²⁺ ions.

Apparatus and Chemicals : Polarograph assembly, 0.01M solutions of CdSO₄ · 8/3 H₂O, ZnSO₄ · 7H₂O and MnSO₄, 1.0M KCl solution, 0.2% (W/V) gelatin solution, cylinder of hydrogen or nitrogen.

Theory : In a mixture of simple ions (when no complex formation takes place), the half wave potential for the reduction process is independent of the metal ion concentration. It is also unaffected by the presence of other reducible ions. It is, thus, possible to analyse the mixture of reducible ions provided the $E_{1/2}$ values of different ions differ at least by 0.2 V.

Procedure and Observations : Dilute separately 10 cm³ of each metal solution, previously adding 10 cm³ of 1.0 M KCl solution and 10 cm³ of gelatin solution, to 100 cm³ in a volumetric flask. Prepare a mixture of the three metal ions by mixing 10 cm³ each of the metal solution, 10 cm³ of KCl solution and 10 cm³ of gelatin solution and finally diluting it to 100 cm³.

Plot separately the polarograms of each metal solution and their mixture.

Take exact 10 cm³ of the mixture in the cell and plot the polarogram. Add to this solution exactly 0.1 cm³ of one of the metal solutions, deareate, and again plot the polarogram. Make a few more small additions and plot the polarogram each time.

Calculations : Compare $E_{1/2}$ and limiting diffusion current obtained from the polarogram for each metal ion measured separately and in the mixture.

Measuring the increase in the values of I_d by making small additions of a particular metal (the increase in concentration must be calculated taking into account the volume change), calculate the concentration of that metal originally present, using I_d value already measured.

AMPEROMETRIC TITRATIONS

[I] Principle of amperometric titrations : The accuracy of polarographic estimations is of the order of 1%. A better accuracy of the order of 0.1% can be achieved by devising a titration, in which the voltage (polarising voltage) applied across the indicator electrode and reference electrode is kept constant and the diffusion current (= limiting current – residual current) passing through the cell is measured and plotted against the volume of reagent added, because diffusion current is proportional to the concentration of the electroactive material in the solution. The end point is the point of intersection of two lines giving the change of current before and after the equivalence point. Such titrations are known as **amperometric, polarographic** or **polarometric titrations**. The term amperometric is derived from ampere, the unit of current. As the diffusion current is a consequence of polarisation at a micro-electrode, the technique is known as polarometry.

[II] Description of the apparatus : The equipment for conducting amperometric titrations is simple. Although it may be the same as for polarography, yet several simplifications are possible.

A number of suitable reference electrodes that can be used are saturated calomel electrode and Ag/AgCl electrode etc. No thermostat is necessary because the temperature of the solution will seldom vary appreciably during the short time, 10 minutes or less is necessary to conduct the titration.

The indicator electrode may be a dropping mercury electrode (d.m.e.) or a platinum rotating micro-electrode. But the latter is advantageous as (i) it is simple to construct, (ii) it extends the workable range on the positive voltage side upto 0.9 V and (iii) the rotation of the electrode makes the diffusion layer thinner, thereby increasing the value of d.c. as much as 20 times the value in polarography, hence the technique becomes more sensitive.

Platinum-rotating micro-electrode consists of a short length of platinum wire, protruding 5 to 10 mm from the wall of a piece of glass tubing. The latter is bent at right angles at a short distance from the end of the stem so as to sweep an area of the solution with the wire. The electrode is mounted in the shaft of a motor and rotated at a constant speed of 600 r.p.m.

Removal of O_2 is done as in conventional polarography by bubbling H_2 or purified N_2 before the commencement of titration, and for 1 minute after each addition of the titrant. The voltage applied between the indicator electrode and the reference electrode is kept constant and a sensitive galvanometer or micro-ammeter is made to indicate the value of d.c. after each increment of the titrant has been added.

[III] Calculations : The values of d.c. are plotted against c.c. of the titrant added. The technique can be described by taking the titration of a reducible substance, lead ion, with a non-reducible reagent SO_4^{2-} ion. A polarogram of a solution containing lead ions is represented by a curve 'A' in fig. (9). If the voltage is held at any value of d.c. plateau, the limiting current will be represented by i_0' where the initial concentration of lead ions is C_0 . The titrant exhibits no d.c. at the applied E.M.F. Increments

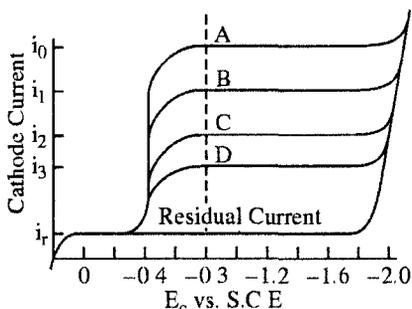


Fig. 9 : Current-voltage curve of Pb^{2+} ions after each addition of SO_4^{2-} ions

of titrant remove some of the electro-active Pb^{2+} ions. As their concentration decreases, the current also decreases with it to i_1, i_2, i_3 and finally i_r , where the Pb^{2+} ions have completely reacted and the only current flowing is a residual characteristic of the supporting electrolyte.

If successive values of d.c. are plotted against volume of titrant added, the result is a straight line which levels off at the end point. The intersection of the extrapolated branches of the titration curve gives the end point. Usually four points may be enough for an estimation, points corresponding to 0, 50, 150, 200 percent equivalent of titrant. When the titrated ion is reducible and the titrant is non-reducible, *i.e.*, only the titrated ion gives d.c., as in the case of Pb^{2+} ions with sulphate, the form of the curve will be as shown in fig. (10). When the titrated ion is not reducible, but the titrant is reducible, (*i.e.*, it gives d.c.) as in the case of SO_4^{2-} ions with Pb^{2+} ions, the amperometric curve will be of the shape as shown in fig. (11).

When the titrated ion and titrant both are reducible, *i.e.*, give d.c. at the applied voltage chosen, the current will drop to the end point, then increases again to give a V-shaped amperometric titration curve as shown in fig. (12). Alyward (1955) titrated Mo against $\text{Pb}(\text{NO}_3)_2$ at a constant potential of -0.8v at which both Mo and Pb gave cathodic d.c., and obtained curve of the type as shown in figure (12). Similar curves are obtained in the titration of Pb^{2+} ion with $\text{Cr}_2\text{O}_7^{2-}$ or Pb^{2+} with Br^- .

In a redox system, where both the oxidant and the reductant give d.c., the former by reduction at the cathode and the latter by oxidation at the anode, the shape of the curve will be given by figures (13) and (14). Taking the example of Fe^{3+} ion with Ti (ous) ion, the current decreases linearly with the addition of Ti (ous) ion to the ferric until it attains the zero value at the end point. On passing the end point, a new d.c. is caused by the oxidation of the Ti (ous) ion. Generally, there will be a

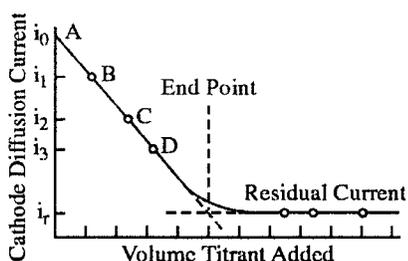


Fig. 10 : Amperometric titration curve for Pb^{2+} and SO_4^{2-} ions, performed at $E_0 = 0.7$ volt vs S.C.E.

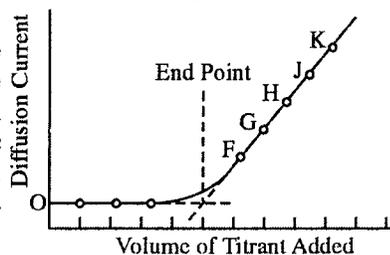


Fig. 11

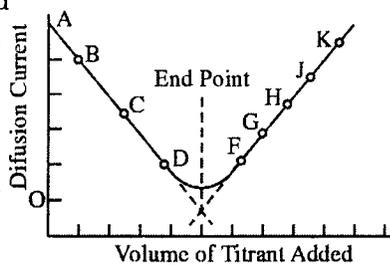


Fig. 12

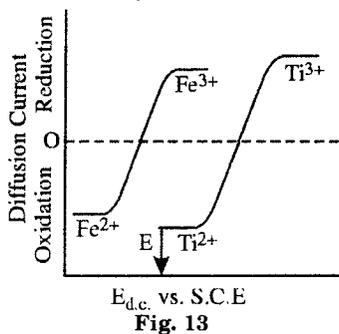


Fig. 13

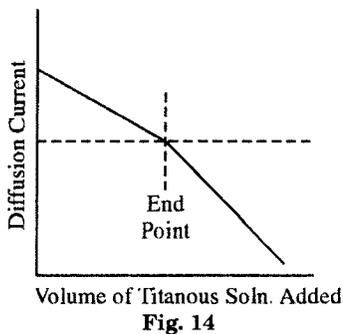


Fig. 14

change in the slope of the curves caused by the difference in the diffusion coefficients. In ideal cases, the extrapolated portions of the two curves will meet at zero value of current. Dilution of solution consequent on addition of the titrant affects the current value and the limiting current variations no longer remain linear with the increments of the titrant. If the titrant is 10 fold stronger than the titrated solution, the influence of dilution will be negligible. However, a correction may be applied by multiplying the current value with $\frac{V+v}{V}$, where V = original volume, v = small increase in volume after titration.

The technique of amperometric titration was further developed by Neuberger (1939), who extended it to precipitation reactions using organic reagents like oxine salicyldioxime. A mixture of I^- , Br^- and Cl^- has also been titrated with Ag^+ ions. Micromolar solutions of Cd have been titrated against EDTA amperometrically under controlled pH, for which a special type of titration cell is used. A mixture of Bi, Pb, Co, Fe and Mn has been titrated amperometrically under controlled pH conditions using EDTA.

[IV] Titration with two indicator electrodes or dead stop end point method : Two-electrode technique is a modification of the single micro-electrode amperometry. Two similar platinum micro-electrodes are immersed in the titration cell. A small constant directed voltage of magnitude 0.1 to 0.01 V is applied to the pair by selection of suitable contact point on a potentiometer.

A minute electrolysis takes place under these conditions. The amount of oxidation of the reduced form of the ion at the anode is exactly equal to the amount of reduction of the oxidised form of the ion at the cathode. Therefore, both anode and cathode are equally depolarised as long as both the oxidised and reduced forms of the ions co-exist.

At the end point, when one of the forms has been completely exhausted by titration, only one electrode remains depolarised, whereas the other one is completely polarised. Since the applied voltage is very small under these conditions of polarisation, the current attains a value equal to very close to zero. Therefore, this method is also known as **dead stop end point method**. Foulk (1926-27) suggested that **polarisation end point method** will be a more appropriate term.

At the equivalence point with one electrode polarised and the other depolarised, the system resembles the conventional polarometry with one polarised micro-electrode combined with the non-polarised reference cell. When both the solutions to be titrated and the titrant undergo reaction at the electrode as in the titration of Fe^{3+} ion with Ti^{3+} ion, the current first attains a zero value at the end point, and then shoots up.

An electrometric titration with two electrodes but without external potential source has been reported by Foulk and Bowden (1915-27). Here the two electrodes are not dipped in the same vessel, but in two different vessels linked together through a salt bridge. The supporting solutions of KI in the case of I_2 and hypo titration in the two vessels have different strengths, one being 15 times stronger than the other. The vessel containing weaker solution is used as the titration cell. The other electrode in stronger solution is depolarised anode, while in the weaker solution, the electrode is depolarised cathode. The concentration cell formed by two iodide solutions is seen to give sufficient potential for this dead stop titration method. Other titrations are $KMnO_4$ against $H_2C_2O_4$ and $KMnO_4$ against $Na_2S_2O_3$. Attempts have also been made to conduct amperometric titrations with superposed alternating voltage in which the indicator electrode was vibrating

platinum electrode and the potentials were measured with a vacuum tube voltmeter.

[V] Advantages of amperometric titrations

(1) Amperometric titrations are quicker since the end point is found graphically. A few measurements at constant applied voltage before and after the end point suffice.

(2) The equipment used is simple.

(3) The method is, however, a relative one. So, influence of variables can be discounted, which is not so in polarography. Electrode characteristics are un-important.

(4) The results of the titration are independent of the characteristics of the capillary.

(5) The temperature need not be known, provided it is kept constant during titration.

(6) Although a polarograph is convenient as a means of applying the voltage to the cell, its use is not essential in amperometric titrations. The constant applied voltage may be obtained with a simple potentiometric device.

(7) The range and the sensitivity of this technique are higher than conductometric, potentiometric or polarographic method.

(8) Each branch of amperometric titration curve is the average of several recorded points and, therefore, the error is smaller than that in polarography

(9) Foreign salts may be present without interference and are indeed, usually added as the supporting electrolyte in order to eliminate migration current.

(10) Amperometric titrations can be carried out in cases where potentiometric or visual indicator methods are unsatisfactory, e.g., when the reaction product is markedly soluble or appreciably hydrolysed.

Maximum suppressors should be used at minimum required concentrations. Use of any additional quantity lowers the value of the limiting diffusion current.

Important precaution : *After a polarographic experiment recover all the mercury from the remaining solution. In no case mercury should be allowed to go into the sink.*

EXPERIMENT No. 3

Object : *To plot current-voltage curves for 0.05M and 0.01M solutions of copper sulphate and sulphuric acid using bright platinum electrodes.*

Apparatus and Chemicals : A four volt potential divider or a rheostat (100 ohm, 1.5 amp), a voltmeter, a milliammeter, a 100 ml beaker. 0.05M solutions of copper sulphate and sulphuric acid. Two bright platinum electrodes about 1 cm × 1 cm each cleaned with chromic acid and set about 2 cm apart.

Procedure : Set up the apparatus as shown in fig. (15). The electrodes should be held in fixed positions and should have a clearance of at least 1 cm from each side and should be 1 cm below the surface of the solution in the beaker. Set the beaker in a bath of water for maintaining constant temperature. Increase applied potential in steps of 0.1 volt. Allow time for the current to stabilize and record readings of voltmeter (V) and milliammeter (mA).

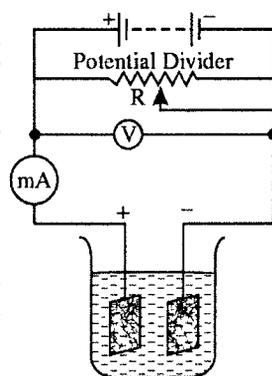


Fig. 15. Decomposition potential set up

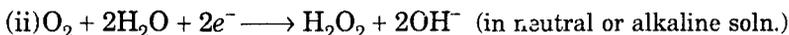
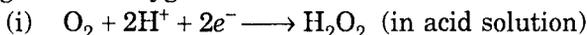
Plot the current-voltage curve for 0.05M copper sulphate solution. Clean the electrodes by dipping in dilute HNO_3 . Repeat with 0.01 M copper sulphate and 0.05M and 0.01 M sulphuric acid solutions separately. Report the information drawn from the curves and discuss their shapes as explained earlier.

EXPERIMENT No. 4

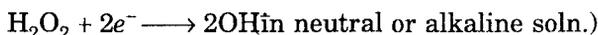
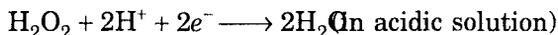
Object : To study the polarogram of the solution of supporting electrolyte with and without elimination of dissolved oxygen.

Apparatus and Chemicals : A polarographic assembly, 0.1M KCl or KNO_3 solution, nitrogen or hydrogen supply, 0.2% gelatin or methyl red solution in water.

Theory : All aqueous solutions exposed to atmosphere have some dissolved oxygen. This oxygen is reducible at the d.m.e. in two steps, viz.,



This gives the first wave at an applied potential of about - 0.1 volt. The second wave is due to the reduction of H_2O_2 and occurs as a drawn out wave from - 0.6 to - 1.3 volt.



Dissolved oxygen may be eliminated by bubbling an inert gas like oxygen free hydrogen or nitrogen for nearly 10 to 15 minutes. Alkaline and neutral solutions and not the acidic solutions can be deoxygenated by adding sodium sulphite (1 g/100 ml of solution) and allowing to stand for nearly 15 minutes.

Procedure : Standardize the polarograph assembly according to directions given by the manufacturer. Adjust mercury height in the dme until the drop time in water is 3-6 second. Plot the polarogram from 0 to -1.9 volt. Adjust the galvanometer sensitivity (if necessary) as current values increase. Repeat after eliminating dissolved oxygen. If an inert gas is used for removing oxygen, it should be passed through some water for saturation with water vapours before passing into the cell. Bubbling should be slow and continued for nearly 15 minutes. Now stop the flow of gas. Then plot the polarogram on the same paper on which the first polarogram has been plotted.

If a current maxima is observed, replot the polarogram after adding 3 ml of gelatin solution or 4 drops of methyl red solution per 100 ml of supporting electrolyte.

Note : If time allows, add maximum suppressor in small fractions to find the minimum quantity required for suppressing the maximum.

EXPERIMENT No. 5

Object : To plot a polarogram for a mixed solution of Cd^{2+} , Zn^{2+} and Mn^{2+} ions in 0.1M KCl.

Apparatus and Chemicals : Polarograph assembly, nitrogen or hydrogen supply, 0.1M KCl, 0.2% gelatin solution and 0.001 M solutions of sulphates of Cd^{2+} , Zn^{2+} and Mn^{2+} .

Procedure : Measure 50 ml of 0.1 M KCl and 5 ml of gelatin solution into the cell. Deoxygenate it for 15 minutes. Add 0.5 ml of cadmium solution. Deoxygenate for 5 minutes and plot the polarogram. Next add 0.5 ml of zinc solution and plot the polarogram again. Further add 0.5 ml of manganese solution and plot the polarogram again. A new wave step will appear with the addition of each new ionic species.

For precision, volume correction may be applied to measure current value to get value for an unchanged volume of 50 ml.

EXPERIMENT No. 6

Object : To determine the half wave potential of Zn^{2+} and Cd^{2+} ion in 0.1 M KCl solution.

Apparatus and Chemicals : Polarograph assembly, 1 M KCl, 0.1 M $\text{CdSO}_4 \cdot \frac{4}{3} \text{H}_2\text{O}$, 0.1 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solutions, 0.2% gelatin solution, hydrogen or nitrogen supply.

Theory : Half wave potential of an ion for a reversible reduction at the dme is independent of the concentration of the ionic species but it depends slightly on the concentration of the supporting electrolyte. So, by keeping the supporting electrolyte concentration constant, polarograms can be plotted for increasing concentrations of the reducible ions.

$$E = E_{0.5} + \frac{2.303RT}{n} \log \frac{I_d - I}{I}$$

$$= E_{0.5} + \frac{0.0591}{n} \log \frac{I_d - I}{I}, \text{ at } 25^\circ\text{C}.$$

A plot of E versus $\log \frac{I_d - I}{I}$ gives a straight line, the slope of which is equal to $0.0591/n$ and the intercept on E axis gives the value of $E_{0.5}$.

Procedure : Set up and calibrate the polarograph assembly. Adjust drop rate for the dme in 0.1 M KCl solution of 3 to 6 seconds per drop. Plot a polarogram for the blank supporting electrolyte.

Reduce the concentration of stock solutions of Cd^{2+} and Zn^{2+} ions to $2.5 \times 10^{-2} \text{ M}$. For preparing a solution for the polarograms, take separately 4, 6, 8 and 10 ml of this diluted solution in a 100 ml graduated flask. Each time add 10 ml of 1.0M KCl solution and 10 ml of gelatin solution and make the solution up to the mark. Transfer a part of the prepared solution to the polarographic cell. Deoxygenate for nearly 15 minutes and plot polarograms over the potential range 0 to -1.5 volt. Adjust the galvanometer sensitivity

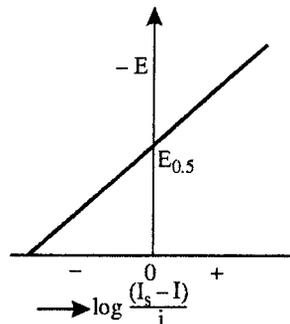


Fig. 16. Determination of $E_{0.5}$

according to requirement. If peak deflections are read on the galvanometer these will be close to the average values of I during the drop-life. Repeat polarograms should be taken in the same solutions.

Plot all polarograms for one ionic species on the same graph paper. Report the $E_{0.5}$ values with reference to the SCE. $E_{0.5}$ values may be obtained from the polarograms and the E vs $\log(I_d - I)/I$ plot.

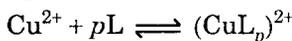
From the data obtained above, prepare a concentration vs. I_d graph. It should be a straight line as required by Ilkovic equation. For this plot, it is not necessary to plot complete polarograms for all solutions. The values of I_d can be directly measured at applied potentials in the range of the *current plateau*.

EXPERIMENT No. 7

Object : To find the formation constant of copper glycinate complex polarographically.

Apparatus : As in preceding experiment.

Theory : The complex formation can be written as



As stated earlier,

$$\begin{aligned} E_{0.5}(\text{simple ions}) - E_{0.5}(\text{complex ions}) \\ = \frac{0.0591}{n} \log K_{\text{complex}} + p \frac{0.0591}{n} \log [\text{L}] \end{aligned}$$

The experiment is conducted by measuring the $E_{0.5}$ value in absence of complexing agent and then in presence of varying concentrations of L, *all high enough to completely form complex with the ions to be complexed*.

Procedure : Prepare the following solutions for plotting polarograms. All of them are made with an ionic strength of unity by using potassium nitrate.

Solution	Potassium glycinate (mole/litre)	Cu(NO ₃) ₂ (mole/litre)	KNO ₃ (mole/litre)	Methyl red (Percent)
1	0.00	5×10^{-4}	5×10^{-1}	0.003
2	0.01	↓	4.8×10^{-1}	↓
3	0.02		4.6×10^{-1}	
4	0.04		4.0×10^{-1}	
5	0.06		3.8×10^{-1}	
6	0.08		3.4×10^{-1}	
7	0.10		3.0×10^{-1}	

Potassium glycinate solutions should be made by combining the required amount of glycine with less than equivalent amount of KOH as some salt formation will also be induced by the amino group in glycine. For 0.05 mole of glycine, 0.04

mole of KOH will be sufficient. The cell temperature should be kept constant at 25°C.

If current values are obtained by measuring potential drop across a series resistance, potential across the polarographic cell will be the applied potential less the potential drop across the series resistance.

Obtain $E_{0.5}$ values for Cu^{2+} ions and the complex ions at different ligand concentrations.

Determine the values of p and K_{complex} .

EXPERIMENT No. 8

Object : To carry out the following amperometric titrations :

(a) A solution of lead nitrate in potassium nitrate against potassium dichromate solution

(b) A solution of potassium sulphate against lead nitrate.

(c) A solution of $\text{Ba}(\text{NO}_3)_2$ in KNO_3 against $\text{K}_2\text{Cr}_2\text{O}_7$.

Apparatus : Polarograph assembly with N_2 supply etc.

Theory : The diffusion currents observed in polarography are proportional to the concentration of electro-reducible ions. If the potential of the dme is kept constant at a value in the plateau of the limiting current of an ion, the observed current will be proportional to the concentration of this ionic species. During the titration, the concentration of ionic species changes. This can be followed by measuring the current on a microammeter or a galvanometer of moderate sensitivity.

The following general situations are observed in amperometric titrations.

(i) Only the solute is electro-reducible at the selected applied potential and the titrant is not reducible at this potential.

(ii) Only the titrant is reducible at the applied potential.

(iii) The solute as well as the titrant are reducible at the applied potential. The corresponding polarograms and current-titrant volume curves are shown in fig. (17).

If volume correction is not applied and precipitate formed during titration is not so insoluble, the experimental titration curve may have curved lines instead of straight lines. The titrant is used as a concentrated solution. This reduces the need for volume correction and introduces less error due to presence of dissolved oxygen. It is safer to bubble inert gas for a short time after every addition of titrant before taking a reading for diffusion current. Solubilities of most of the insoluble substances are appreciably reduced by adding alcohol to the solution.

Procedure : (a) Set up a polarograph. Fix the applied potential first at 0.0 volt and in a repeat titration at -1.0 volt vs SCE. In the titration cell take 25 ml of 0.001 M lead nitrate, 25 ml of supporting electrolyte (0.1M KNO_3 , 0.17M CH_3COOH , 0.06 M CH_3COONa , pH ~ 4.2) and 2.5 ml of 0.2% gelatin solution. Connect the cell to a SCE using a salt bridge of KNO_3 . Set the dme in position. Remove oxygen by bubbling nitrogen for nearly 20 minutes. Take current readings after each addition (0.4 ml) of 0.005M dichromate solution and deoxygenation for

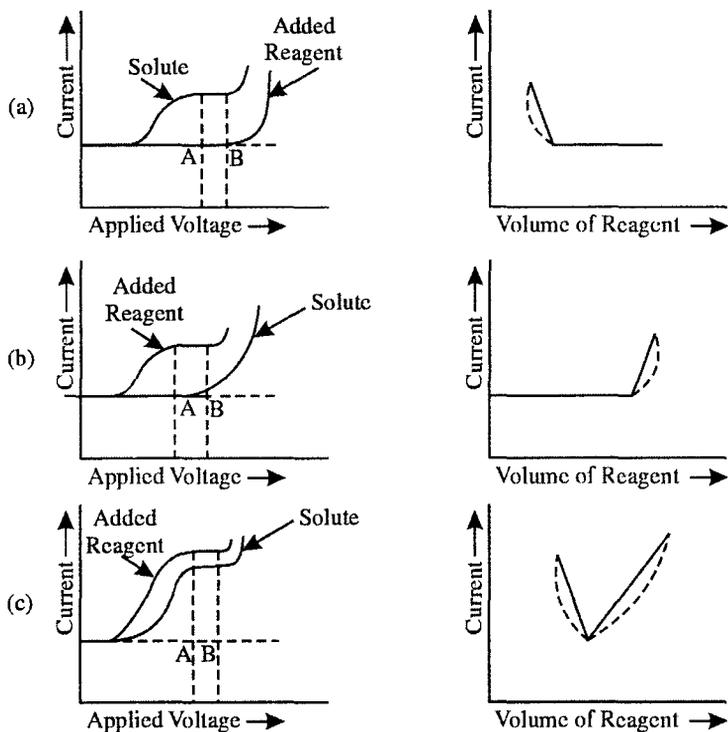


Fig. 17 : Typical amperometric titration curves.

2 minutes. Note the current-volume data. Then plot a graph. Reversed L and V shaped graphs are obtained from which the end point can be easily identified.

Calculate the expected titre value and compare it with the value from the graph.

(b) Titration of sulphate solution (0.01M) can be carried out without a supporting electrolyte as neither sulphate ions nor potassium ions, are reducible near -1.0 volt *vs* SCE. Set the polarograph to -1.2 volt *vs* SCE. Use $0.1 M$ lead nitrate as titrant. Remove dissolved oxygen as usual from the mixture of 25 ml of K_2SO_4 solution, a few drops of conc. HNO_3 and 25 ml of ethanol solution.

In the beginning, the current value will be low and it will start increasing when all the sulphate is precipitated. Now the titration curve will be a reversed L-shaped one.

(c) Repeat as above.

EXPERIMENT No. 9

Object : To determine nickel in solution by amperometric titration with dimethyl glyoxime.

Apparatus and Chemicals : Polarograph assembly, $0.02M$ dimethyl glyoxime in 95% ethanol (0.6 g of the solid in 95% ethanol, diluted to 250 cm^3), supporting electrolyte : $0.1 M$ in NH_4Cl and $0.5M$ in ammonia (1.34 g of NH_4Cl and 2.5 cm^3 of 0.880 ammonia to 250 cm^3 of 0.02% gelatin in water), $0.02 M$ nickel chloride solution (1g $NiCl_2 \cdot 6H_2O/250\text{ cm}^3$).

Theory : At an applied potential of -1.7 V , both nickel and complexing agent are reducible at dme. The titration can be carried out in ammonia/ammonium chloride solution as supporting electrolyte. The titration curve will be V-shaped.

Procedure and Calculations : Set up the polarograph. Take 10 cm^3 of the supporting electrolyte solution and 1 cm^3 of nickel solution in the cell. Deaerate, apply a potential of -1.7 V and measure the diffusion current in the usual manner. Make successive additions of 0.2 cm^3 of dimethyl glyoxime solution to the cell and measure the diffusion current, after deaerating the solution each time.

Correct the readings for dilution by the titrant, and plot the corrected I_d values against volume of titrant. So, find the end point.

EXPERIMENT No. 10

Object : To titrate amperometrically bismuth, lead and calcium in solution with EDTA.

Apparatus and Chemicals : Polarograph assembly, 0.05 M bismuth nitrate, 0.05 M lead nitrate, 0.05 M calcium nitrate and 0.1 M EDTA, 0.2% (W/V) gelatin solution.

Theory : Bismuth forms stable complex at pH 2, whereas lead and calcium do not form complex under these conditions. Lead forms a complex at pH 4 and calcium at pH 8. Thus, simultaneous titration of the three metals with EDTA can be carried out by careful control of pH of the solution.

Procedure : Prepare nearly 0.05 M bismuth nitrate solution by dissolving 2.5 g of the salt in 2 N HNO_3 and diluting it to 100 cm^3 . For lead nitrate solution, dissolve 1.6 g of the salt in 50 cm^3 of 2 N HNO_3 . Dissolve 0.5 g calcium carbonate (A.R.) in minimum quantity of 2 N HNO_3 and dilute to 100 cm^3 . This gives approximately 0.05 M calcium nitrate.

Place 5 cm^3 of each of the metal nitrate solutions into the polarographic cell and adjust the pH to 2.0 (check by means of a pHmeter) by adding solid monochloroacetic acid. Add a few drops of gelatin solution and de-gas the solution with nitrogen for nearly 15-20 minutes. Measure the diffusion current due to Bi^{3+} ions at -0.25 V .

Measure the diffusion current after successive additions of 0.4 cm^3 of EDTA, each time deaerating the solution for 1 minute. Continue the titration till the end point is obtained.

Now adjust the pH of the solution to 4 by adding solid sodium acetate and 1 : 1 ammonia. Deaerate the solution and measure the diffusion current at -0.55 V . Carry out the titration by making successive additions of 0.4 cm^3 of the titrant, each time deaerating the solution and measuring the diffusion current till the end point of Pb^{2+} ions is obtained.

After the end point of lead, adjust the pH to 8 by the addition of more 1 : 1 ammonia and carry out titration in the usual manner at an applied voltage of $+0.05\text{ V}$. After the completion of complexation of calcium, *i.e.*, after the end point the anodic wave of EDTA itself will appear.

Plot diffusion current readings corrected for dilution against the volume of titrant (abscissa) added for the three steps of titration. The first end point gives the volume of EDTA equivalent to bismuth, difference of second and first end points gives the volume equivalent to lead, and the difference of third and second end points gives the volume equivalent to calcium.

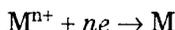
EXPERIMENT No. 11

Object : To determine the formula and the stability constant of a metal ion complex (lead oxalate complex).

Apparatus and Chemicals : Polarograph assembly, 1.0M potassium oxalate solution (Dissolve 46.05 g of A.R. $K_2C_2O_4 \cdot H_2O$ in about 200 cm^3 of water in a 250 cm^3 measuring flask, add a drop of phenolphthalein indicator and then about 0.1 M KOH until pink colour is obtained. Finally make the solution to 250 cm^3), 0.02 M lead nitrate solution (1.10 g of A.R. $Pb(NO_3)_2/250 cm^3$), 1.0 M potassium nitrate solution (25.28 g of A.R. $KNO_3/250cm^3$) and 0.2% gelatin solution.

Theory : The half wave potential, $E_{0.5}$, of a simple metal ion is shifted when it undergoes complex ion formation. The extent of the change in its value depends upon the concentration of the complexing agent. If the change in half wave potential is measured as a function of concentration of the complexing agent, both the coordination numbers, i.e., the formula and the stability constant of the complex ion may be evaluated.

The reduction of a metal ion can be represented as :

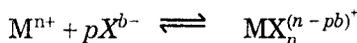


The metal will form an amalgam with the dropping mercury electrode.

The Nernst equation for the electrode potential at 25°C involving the above reaction may be given as :

$$E = E^\circ + \frac{0.0591}{n} \log \frac{M^{n+}}{[M]} \quad \dots (1)$$

Suppose p ions of the complexing agent combine with the metal ion to form the complex ion.



The stability constant, K , of the complex ion can be expressed as :

$$K = \frac{MX_p^{(n-pb)+}}{[M^{n+}] [X^{b-}]^p} \quad \dots (2)$$

Substituting the value of $[M]^{n+}$ from equation (2) in equation (1), we have

$$E = E^\circ + \frac{0.0591}{n} \log \frac{[MX_p^{(n-pb)+}]}{K[X^{b-}]^p [M]} \quad \dots (3)$$

The half wave potential is the potential at which one half of all the oxidized form reaching the surface of the electrode is reduced, i.e., $[Oxidised] = [Reduced]$. Hence, for reduction of simple metal ion, we have

$$E_{0.5} = E^\circ \quad \dots (4)$$

At the half wave potential of the complex ion, $[MX_p^{(n-pb)+}] = [M]$, so equation (3) reduces to

$$\begin{aligned} E_{0.5}' &= E^\circ + \frac{0.0591}{n} \log \frac{1}{K [X^{b-}]^p} \\ &= E^\circ - \frac{0.0591}{n} \log K - p \cdot \frac{0.0591}{n} \log [X^{b-}] \quad \dots (5) \end{aligned}$$

Combining equations (4) and (5), we get

$$E_{0.5} - E_{0.5}' = \frac{0.0591}{n} \log K + p \cdot \frac{0.0591}{n} \log [X^{b-}] \quad \dots (6)$$

The half wave potentials of a series of solutions containing a known concentration of metal and various known concentrations of the complexing agent (25 fold or more so that its concentration is practically the same at the surface of the dropping electrode as in the bulk of the solution). It is evident from equation(5) that a plot of $E_{0.5}^1$ versus $\log [X^{b-}]$ (abscissa) will be a straight line with slope equal to $-0.0591 p/n$. So, the co-ordination number p or the formula of the complex can be determined.

If the half wave potential, $E_{0.5}$, of the simple metal ion is also determined, then equation (6) enables us to evaluate the value of the stability constant K .

Procedure : Place the following solutions in seven 100 cm³ measuring flasks numbered as 1 to 7 :

- (1) 2.00 cm³ of 0.02M Pb(NO₃)₂ and 10.00 cm³ of 1.0 M KNO₃.
- (2) 2.00 cm³ of 0.02 M Pb(NO₃)₂ and 10.00 cm³ of 1.0 M K₂C₂O₄.
- (3) 2.00 cm³ of a 0.02 M Pb(NO₃)₂ and 20.00 cm³ of 1.0 M K₂C₂O₄.
- (4) 2.00 cm³ of 0.02 M Pb(NO₃)₂ and 30.00 cm³ of 1.0 M K₂C₂O₄.
- (5) 2.00 cm³ of 0.02 M Pb(NO₃)₂ and 40.00 cm³ of 1.0 M K₂C₂O₄.
- (6) 2.00 cm³ of 0.02 M Pb(NO₃)₂ and 60.00 cm³ of 1.0 M K₂C₂O₄.
- (7) 2.00 cm³ of 0.02 M Pb(NO₃)₂ and 80.00 cm³ of 1.0 M K₂C₂O₄.

Add to each solution 5 cm³ of 0.2% (W/V) gelatin solution and dilute them to 100 cm³.

Take 20 cm³ of solution 1 into the polarographic cell, deaerate it for nearly 15-20 minutes and measure the diffusion current at applied potentials from -0.20 to -1 volt using saturated calomel electrode as the reference electrode. Carry out similar measurements for the other solutions also.

Plot the polarograms and obtain the half wave potential ($\bar{E}_{0.5}$) for each of the solutions.

Calculations : Plot $E_{0.5}$ (ordinate) versus $\log [C_2O_4^{2-}]$, and from the slope of the straight line, *i.e.*, $-0.0591 p/n$ so obtained, calculate the value of p ($= 2$), which gives the number of oxalate ions combined with each lead atom in the complex ion.

Extrapolate the graph to $[\text{C}_2\text{O}_4^{2-}]$ of 1.0 M, *i.e.*, to $\log [\text{C}_2\text{O}_4^{2-}]$ equal to zero, and obtain the value of $E_{0.5}$ at this concentration. From this value of $E_{0.5}$ and that of simple lead ion in 1 M KNO_3 , calculate the value of stability constant, K , of the complex ion (about 5×10^6) from equation (6). The reciprocal of K gives the instability constant of the complex ion.

Result : The formula of the complex is

The stability constant of the complex is



CHROMATOGRAPHY

Chromatography is a technique devised by Tswett (1903) and is used for separation of complex mixtures of chemically similar substances. In the original technique Tswett used to separate the pigments of green plant leaves, the solution of green colours from leaves in petroleum ether was passed down a vertical glass tube packed with powdered chalk. When excess of petroleum ether was percolated down the column, the different pigments separated into different zones. The column of packing materials was pushed out of the tube and different bands were cut out. Each component was, then extracted by using a suitable solvent. It can also be used for qualitative and quantitative analysis of small quantities of mixtures and also for the preparation of some substances. It consists of two main branches :

1. Adsorption Chromatography

This branch depends on the components of a mixture having different adsorbing capacities on an adsorbent. The more adsorbable components are adsorbed faster than the others. They can be desorbed or eluted by a suitable solvent more slowly and they can displace the less adsorbable components from the surface of the adsorbent. The adsorbent is powdered solid or may be taken as a sheet. It is further classified into two types, *e.g.*,

- (a) *Column chromatography and*
- (b) *Thin layer chromatography.*

(a) Column chromatography : This technique consists in using a column of a suitable substance as the stationary phase or support. However, the separation of the components of the mixture may involve any physical principle, *viz.*, adsorption, partition or ion exchange. The procedure involves the following steps :

(i) Preparation of Column

The column is 25–100 cm long and 1 to 4 cm in diameter. The lower end of the column is narrowed down and it has a wide bore stop-cock. A porous glass disc or a packing of cotton or glass wool serves as a support for the adsorbent column. In the preparation of the column, the lower end is closed and 1/3 rd of the tube is filled with the solvent. A slurry of the powder in the solvent is made which is then allowed to settle down. The excess solvent is removed by draining out. More solvent is allowed to run through the column to wash it. In this way, the powder gets

packed up. Put a filter paper circle equal to the diameter of the tube over the top of the column, in order to prevent the disturbance of the top surface when the column is used for adsorption. The packed column must have the solvent passing through it and covering its surface and it should never be allowed to dry up. A number of adsorbent powders are used, some of them are :

(i) Charcoal (ii) Silica gel (iii) Magnesium silicate (iv) Al_2O_3 (v) Sugar (vi) Starch (vii) Cellulose etc.

[II] Application of the Mixture and the Development of Column

The selection of a solvent is rather difficult. Its selection depends on the solubility characteristics of the components of the mixture. A more polar solvent decreases the adsorbability of an adsorbent-adsorbate pair. The elution solvent may be the same or different from the solvent used for dissolving the mixture. The solvent flow rate should be 50-100 ml per hour. The following solvents are used in order of their decreasing polarities :

Water > Alcohols > Acetone > Ether > CHCl_3 > C_6H_6 > CCl_4 > Cyclohexane > Hexane.

To a prepared column [Fig. (1)], a solution (10-25 ml) of the mixture of components is added. As the solution gradually runs down, the solutes get adsorbed near the top of the column. However, initial adsorption does not separate the components of the column. It is done by flowing the original solvent or a new solvent known as **eluent**. This process desorbs the various components one-by-one. They move down the column as bands by adsorption on fresh parts of the column. The distance between the bands goes on increasing. The band of the component which is least adsorbable is nearest to the lower end of the column. Thus, if the flow of eluent is followed, the least adsorbable component is eluted first which can be collected separately. Similarly, other components of the mixture can be separated.

For a 1-5 cm diameter column, the rate of flow can be adjusted for a particular packing by applying a negative or positive pressure to the column (usually a positive pressure is preferred). For ordinary purposes, suction can be applied to the column by connecting it to the Buchner flask, the latter is connected to a filter pump. A typical arrangement of column chromatography is shown in figure. (1).

(b) Thin layer chromatography (TLC) : In this technique, a thin layer of uniform thickness of the adsorbent is taken on a glass plate. Microscopic slides or larger glass plates are used as supports. The adsorbent layer about 0.25–1.0 mm thick is held with the help of a binder, *e.g.*, plaster of Paris. The adsorbents commonly used are silica gel, cellulose, alumina etc. These are uniformly spread

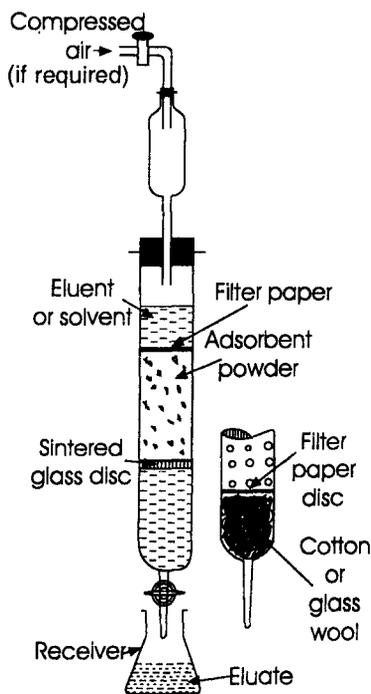


Fig. 1 : Column chromatography apparatus

over a glass plate by an applicator. An applicator usually consists of a block of metal which can hold one or more plates on a groove deep enough to take on the thickness of the plate as well as the adsorbent layer. A slurry of suitable consistency of adsorbents is made in water which is then dropped on dry glass plates. It is then smoothed with a sharp glass edge. These plates are taken on the block and dried over $\sim 50-70^{\circ}\text{C}$ or even higher. When the binder gets set, the glass plates become ready for use which, in turn, are kept in a desiccator or refrigerator to protect them from dust.

The method consists in putting a small spot of the solution containing mixture of components about 1 cm from one end of the glass plate, held flat. The spot is conveniently put by a fine melting point capillary tube. After drying the spot, the end of the plate with the spot is allowed to stand in a vessel containing the eluent and covered. The eluent should rise at the rate of 1 cm in about 4—5 minutes. The components in the solution rise with the eluent at different rates and separate out as spots. The plate is then taken out and dried. The plate is then put in a development chamber which is prepared by covering a beaker tightly with aluminium foil. A filter paper touching the bottom of the chamber is placed against the inner wall to attain the equilibrium between liquid and vapour quickly. The development solvent is now added in sufficient amount so that the filter paper gets saturated and leaves a layer of 5-6 mm in depth at the bottom. The chamber is then allowed to stand for a few minutes till the atmosphere within it is saturated with solvent vapours. The thin layer plate is now placed in the chamber with its spotted end down. The solvent level must be below the sample spots.

Cover the chamber immediately and leave it undisturbed till the solvent has moved $3/4$ of the way up the plate. The plate is now removed and the position of the solvent front is marked with a pencil. If the appropriate spots are not visible, they can be made so by spraying suitable reagent solutions.

The R_F value which is characteristic of a compound under specific conditions is defined as,

$$R_F = \frac{\text{Distance travelled by sample (cm)}}{\text{Distance travelled by solvent (cm)}}$$

TLC has a number of advantages such as :

- (i) Rapid equilibration and development
- (ii) Study at higher temperatures
- (iii) Spots can be scratched for further study.

2. Paper Chromatography

This technique, also known as *partition chromatography*, depends on the distribution of one or more solutes between two immiscible solvents. The partition or distribution coefficient, K is given by,

$$K = \frac{\text{Concentration of solute in solvent A}}{\text{Concentration of solute in solvent B}}$$

Different solutes in a solution of mixture of solutes will have different values of K for the same solvents A and B.

Suppose A is the original solvent and B is the extracting solvent and let the solute be X. The solvent A is held stationary either by its density difference or by its occlusion in the pores of an inert solid packing. The high boiling point liquid is A, while B can be another liquid or gas.

When A and B both are liquids, the technique is known as *liquid-liquid partition chromatography*. When A is a liquid and B is a gas, the technique is called *gas-liquid* or *vapour-liquid chromatography*. If a gas is used for adsorption on a solid, we have *gas-solid chromatography*.

In laboratory, liquid-liquid chromatography is generally used paper chromatography or column partition chromatography. In this technique, a strip or sheet of uniform good quality filter paper, usually Whatman filter paper no. 1, serves as a support for one liquid phase, usually water. The other immiscible liquid is first run over it either by capillary action spread from bottom or by gravity flow from an overhead vessel. For running several samples side-by-side it is convenient to use slotted paper.

In column partition chromatography, water is held stationary on a packing of silica gel and the solution in some other solvent is run through it. However, in paper chromatography, adsorbed water is fixed phase on a paper saturated by suspension in water vapour over a vessel of water.

When the flow of the second liquid is only in one direction, paper chromatography is said to be *one-dimensional*. If on the contrary, the liquid flow is arranged over the filter paper in two directions at right angles to each other, paper chromatography becomes *two-dimensional*.

[I] One Dimensional Paper Chromatography

Depending upon the direction of flow of the mobile phase, three main experimental procedures for one dimensional chromatography are in practice.

(1) **Ascending method** : In this method the solvent contained in a tray in the bottom of the tank moves up the papers due to capillary action. For the simplest form of ascending paper chromatography, a strip of filter paper (nearly 30×5 cm) is cut out and a pencil line is drawn along the width of the paper, about 5 cm from one end. The mixture in the form of solution is applied in the middle of the line in as compact form as possible. The strip is then suspended in a glass tank, above the developing solvent so that the pencil line end dips in the solvent to a depth of 1-2 cm.

Due to the capillary action the solvent moves upwards, the movement of the solvent is fast in the beginning but becomes gradually slower. After a few hours, the movement stops completely when force due to capillary is counter-balanced by the downward force due to gravity. When the solvent front has reached a suitable height or the top, the paper is removed from the tank, the solvent front is marked with a pencil and the paper is allowed to dry. After the solvent front reaches the top, it is not

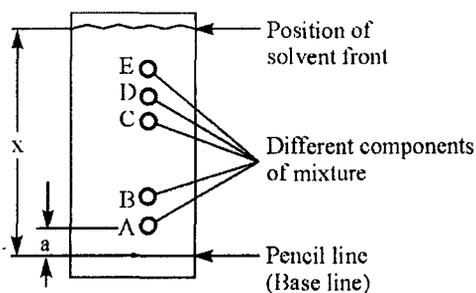


Fig. 2. Ascending paper chromatography

advisable to leave the paper strip in the tank dipped in the solvent for any interval of time, because the diffusion of components of the paper causes the spots to diffuse on the developed chromatogram.

If in place of strip of paper, a complete sheet is used, then multiple separations may be run, side-by-side, under the same conditions of solvent and temperature [Fig. 3(a)].

The substances A and B in the test mixture (X) can be recognised, without determining their R_f values, by running separations of standard samples side-by-side. [Fig. 3(a)].

A typical multi-sheet frame of four rods capable of handling several paper squares is shown in fig. (4). In this process of mounting, the paper remains rigid during development and can be handled easily even while it is wet.

In order to prevent diffusion of the components in multiple separations, a slotted paper, that may be obtained commercially (Whatmann CRL/1 paper), is used [(Fig. 3 (b))]. The paper is rolled into the form of a cylinder and tied with white cotton (not paper clips). The paper roll is then allowed to stand in a Petri dish, containing the solvent, suitably covered with a tall beaker (600 cm³) [Fig. (5)]

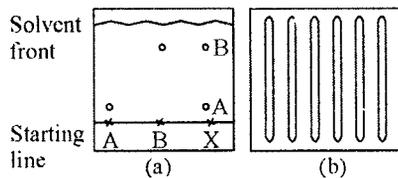


Fig. 3. Two dimensional paper chromatography

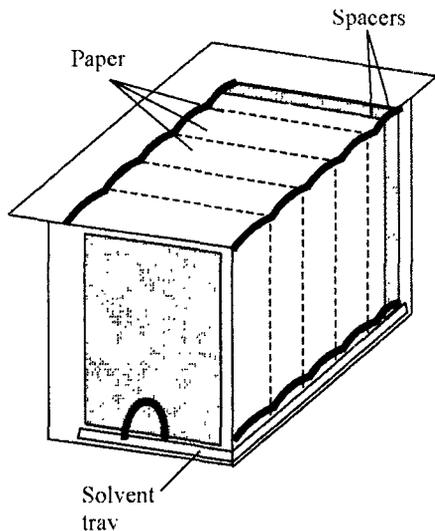


Fig. 4. Multisheet frame for ascending chromatography

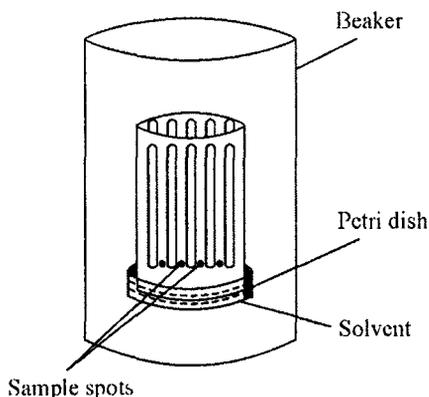


Fig. 5. Whatman CRL/1 paper and assembly

The main advantage of multiple chromatograms lies in that (i) a number of separations can be carried out at a time and (ii) when the reproducibility of R_f value is doubtful, the components in test sample can be recognised by running standard samples simultaneously.

(2) Descending method : Although the ascending method is the most suitable and convenient method but it has a limitation that the distance travelled by the solvent front and so the ascending separation is limited. Therefore, the ascending method is of little use for the separation of slow moving components, *i.e.*, with low R_f values. In descending method, the solvent flows downwards and it is allowed to drip off the end of the paper, which increases its effective length.

In descending chromatography, the paper dips into the solvent contained in a trough near the top of the tank and a heavy glass rod keeps it in position by weighing it down. The paper then hangs over another glass rod placed horizontally parallel to the trough. The mixture to be separated is applied to the paper at a point external to the trough such that the solvent forms an evenly moving front before it reaches the spot. Both strips or sheets of paper can be used for carrying out the separation. In order to get even dripping and uniform flow, the bottom of the paper is cut into the form of serrated edge.

Clearly, the measurement of R_f value is not possible in the descending method, so standards are run simultaneously, and the distances moved by different components of the mixture are compared with those of standards.

(3) Radial or horizontal method : This is a convenient method for rapid separation of mixtures. The method consists in applying the spot of the mixture near the centre of a circular paper held in the horizontal plane and feeding with the solvent at the centre. As the solvent spreads by the usual capillary action it separates the components of the mixture by radial development in the form of concentric arcs of the circle. [Fig. 6 (b)]

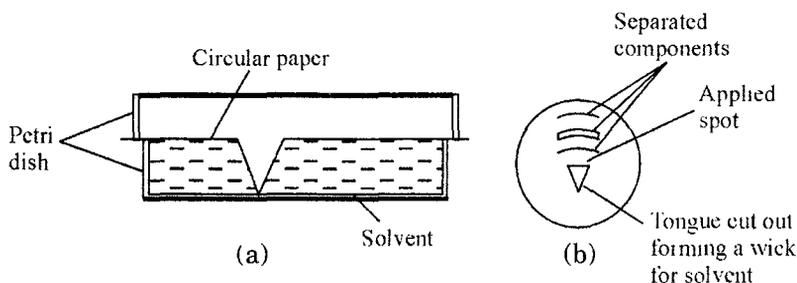


Fig. 6. Horizontal circular paper chromatography

In the simplest form of practical procedure a small tongue or a tag is cut from the centre of a circular filter paper. This is bent at right angles and allowed to dip into solvent contained in the bottom half of Petri dish, the top half then acting as a cover for the paper to prevent evaporation of the solvent. [Fig. 6 (a)].

In another technique, the mixture is applied to the centre of the paper which is then sandwiched between two circular glass plates placed horizontally. The upper plate has a small hole at its centre and the solvent is added drop-by-drop through this hole. The different components will then separate into a series of bands in the form of concentric circles.

Multiple separations may, simultaneously, be run by slotting the paper to give different segments, on each of which a separate spot may be applied [Fig. (7)]

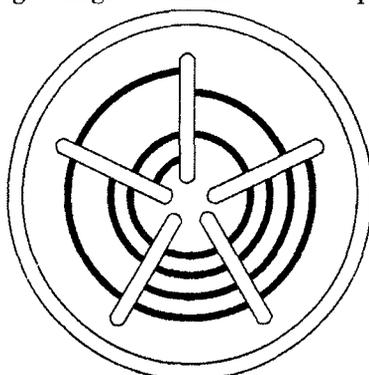


Fig. 7. Chromatogram for 5 samples slotted filter paper circle

[II] Two Dimensional Paper Chromatography

In one dimensional chromatography, it is difficult to differentiate between spots of similar R_f values. The resolution of closely separated (or even overlapping) spots may, however, be improved considerably by using two dimensional chromatography. The technique consists in re-chromatographing of the separated mixture at right angles to the first direction of development, using a different solvent for the second development.

In this method, the spot is applied near one corner of a square sheet of chromatographic paper, about one inch from each corner edge of the paper. Ascending chromatography is performed in one direction with a solvent in the usual way, the mixture separates in the vertical plane.

As evident from fig. 8(a) in the one-dimensional chromatography the components A and B are not well separated. The paper is then dried to remove all the solvent and turned through at right angle such that the developed components of the chromatogram lie in a horizontal plane at the lower end of the paper. [See fig 8(b)]. The chromatography is then carried out in the second direction with a different solvent in which the components of the mixture have different R_f values from those shown in the first solvent. The line of spots produced in the first solvent act as a number of new origins for the second solvent. If the R_f values are appreciably different, the second development causes the overlapping spots to separate [Fig. 8 (c)].

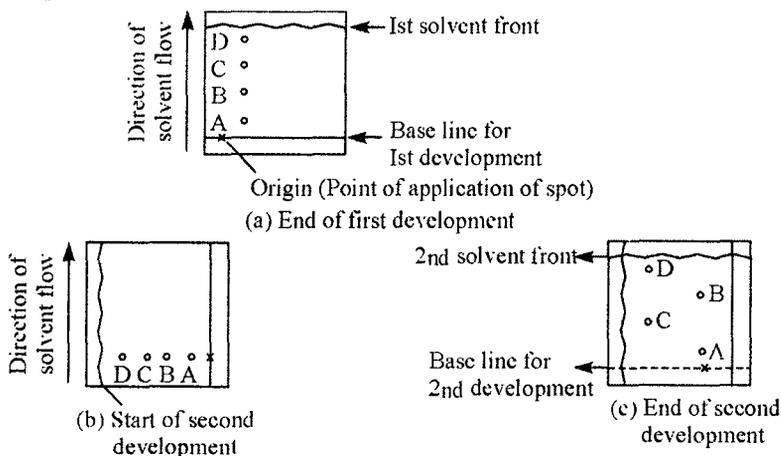


Fig. 8. Two dimensional paper chromatography

In order to measure the R_f value in the two different solvents, the position of the solvent front is marked after each development. The base line for the first development is drawn through the point (x) before applying the mixture, and the base line for the second development may be drawn through the point (x) at right angles to the first base line at the end of the first development.

The apparatus for carrying out two dimensional paper chromatography is shown in fig. (9). Once the papers are mounted on the frame, the correct alignment for the second development can automatically be obtained simply by rotating the frame through 90° .

In a simplified process the square sheet is rolled into a cylinder [Fig. (10)] such that the vertical edges do not overlap. The two edges are held together by means of clips or with tape. The paper cylinder is then allowed to stand in solvent in a closed vessel and development is carried out in the usual way. After development, the paper is opened out and refolded into the form of a cylinder at right angles to the previous fold. The second development is then carried out in the usual manner.

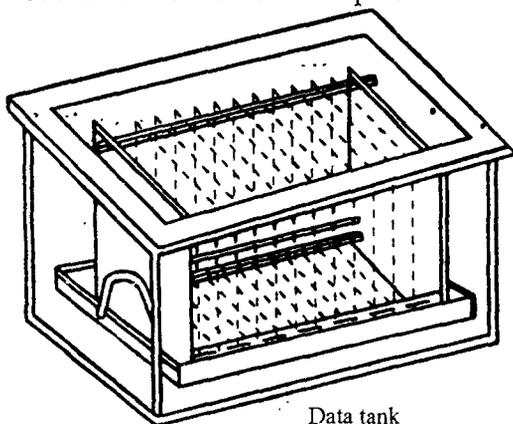


Fig. 9.

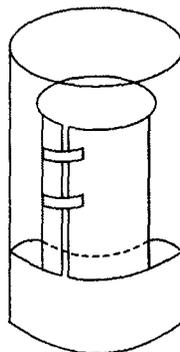


Fig. 10.

[III] Technique of Paper Chromatography

Although different experimental methods are available for paper chromatographic separations yet the basic technique is common to all of these. A brief discussion of the same is mentioned as follows :

(1) Application of the sample to paper : The mixture to be separated is applied to the filter paper in the form of solution in as compact form as possible. So, the mixture must be dissolved in minimum amount of a readily volatile solvent. The smaller the sample applied, the greater will be the resolution of the components. However, the lowest size of the sample is limited by the sensitivity of the method for detecting the separated components. Nearly 0.01 g of material will be capable of separation.

The correct aliquot ($0.5-5 \text{ cm}^3$) of solution may be applied, (a) with a platinum loop (2-3 mm diameter; it has the advantage that it can be easily cleaned by heating to redness in a flame); (b) with a capillary tube such as a melting point tube, using a fresh tube for each solution; (c) with a calibrated micropipette; (d) with a micrometer syringe.

In order to obtain a compact spot with a large volume of the solution to be applied, it is advisable to apply the solution in small amounts at a time. If the solvent is highly volatile, the time interval between two applications should be sufficient to get the spot dried. If it is not so, a warm air blower should be used to dry the spot quickly before next drop is added.

It is important that the point of application of mixture should be marked. The origin is marked by a pencilled \times on a pencilled base line drawn 4-5 cm from the edge of the paper. For multiple separations, the marks must be 2-3 cm apart to prevent interference by overlapping and further every spot should be numbered.

(ii) Drying the paper chromatogram : After the development of chromatogram, the paper is removed from the tank and the position of the solvent front is marked with a pencil. If the solvent is sufficiently volatile, the paper can be dried simply by suspending it for a short time by means of a clip, in a fume

cup-board. In case of less volatile solvents, hot air blower or drying oven should be used to dry the chromatogram.

(iii) **Location of the separated spots :** In case of coloured compounds, the separated spots can readily be detected on a paper chromatogram. However spots of colourless compounds are to be detected by some suitable technique. Observation of the paper under U.V. light is a useful device to detect the position of the final spots.

The most widely used method of locating the colourless spots is the production of coloured compounds with a suitable reagent. Either the paper is dipped in the locating reagent or the latter is sprayed from an atomizer (in case the separated components are soluble in the reagent).

Amino acids can be made visible by (i) *ninhydrin* : 20% (W/V) in acetone; (ii) *isatin* : 0.2% (W/V) in acetone; (iii) Ehrlich's reagent - 1 g *p*-dimethyl-aminobenzaldehyde in 90 cm³ acetone and 10 cm³ concentrated hydrochloric acid.

Table 1. Commonly used solvents and indicators for paper chromatographic separation of some organic compounds.

Compound	Solvent system	Indicators for locating spots
Amines	1-butanol-acetic acid.	Ninhydrin solution, iodine solution.
Amino acids	Phenols : phenol-ammonia, tert. butyl alcohol, 1-butanol.	Ninhydrin solution (0.1 to 0.2% in ethanol).
Organic acids	Mixtures of formic acid with ethanol, 2-propanol, 1-butanol and other alcohols.	Bromocresol green or bromophenol blue solution in ethanol.
Sugars	1-butanol; acetic acid; ethyl acetate; pyridine, water.	<i>p</i> -Amino dimethylaniline; silver nitrate, 2 : 5-dinitro salicylic acid solution (0.3%).

Table 2. Some common solvent mixtures employed in chromatographic separations.

<i>Solvent mixture 1.</i>	Ethanol (7 volumes) + Distilled water (3 volumes).
<i>Solvent mixture 2.</i>	Butanol (6 volumes) + Glacial acetic acid (1 volume).
<i>Solvent mixture 3.</i>	Acetone (17 volumes) + Distilled water (1 volume) + concentrated hydrochloric acid (2 volumes).
<i>Solvent mixture 4.</i>	<i>n</i> -Butanol (3 volumes) + Ethanol (1 volume) + 2M aqueous ammonia solution (1 volume).

Table 3. Specific spray reagents for functional groups.

Compound class	Reagent	Procedure	Result
1. Acids	Bromocresol green	Dissolve 0.4 g in 100 ml ethanol, add 0.1N NaOH until colour just appears.	Yellow spot.
	2,6-Dichlorophenol, indophenol (sodium salt)	Dissolve 0.1g in 100 cm ethanol	Red spots on the blue background.
2. Alcohols	Ceric ammonium nitrate	Dissolve 6g in 100 ml 4N HNO ₃ .	Brown spots on yellow back ground.
	Vanadium oxinate	Dissolve 0.1g in 100 ml alcohol free chloroform.	Red spots on green background.

3. Amines	Cobalt thiocyanate	Dissolve 3g ammonium thiocyanate and 1g cobalt chloride in 20 ml water.	Primary, secondary and tertiary aliphatic amines give blue spots on white background.
	Salicylic acid	Dissolve 1 g in 100 ml toluene.	Primary, aliphatic and aromatic amines give yellow spots on white background.
4. Anti-oxidants	Dichloroquinone-4-chloroimine	Dissolve 1 g in 100 ml ethanol, respray after 15 minutes with 2% borax in 4% ethanol.	Various colours on white background.
5. Phenols	4-Amino antipyrène	(a) Dissolve 3 g in 100 ml ethanol (b) Dissolve 8g of potassium ferricyanide in 100 ml H ₂ O. Spray with (a) then (b) and then expose to ammonia vapours.	Red, orange or pink spots on pale background.
6. Phosphate esters	Ammonium molybdate perchloric acid	Dissolve 0.5g ammonium molybdate in 5 ml water and 1 ml conc. HCl; add 2.5 ml perchloric acid and cool, dilute to 50 ml with acetone and allow to stand for 24 hrs. After spraying expose for two minutes to an IR lamp, then for 7 minutes to longwave UV light.	Blue spots on white background.
7. Polynuclear aromatic hydrocarbons	Formaldehyde-sulphuric acid	Dissolve 2 ml 37% HCHO solution in 100ml conc. H ₂ SO ₄ .	Various colours on white background.

EXPERIMENT No. 1

Object : To separate a mixture of sudan red and sudan yellow by adsorption on silica gel column.

Apparatus : Column of silica gel, conical flask etc.

Theory : See preceding pages.

Procedure : Weigh about 0.1 – 0.3 gram of each component and dissolve it in 40 ml C₆H₆. Add this solution to the top of the column. The components will be

completely adsorbed. Develop the chromatogram by running benzene. The washings are continued till both the bands are eluted out separately one after the other and collected separately. Crystallise the two components by evaporating benzene. The residues thus obtained are weighed and percentage recoveries calculated.

EXPERIMENT No. 2

Object : *To separate a mixture of methylene blue and fluorescein (sodium salt) on an alumina column.*

Apparatus : Chromatography tube (about 25 cm × 1.7 cm diameter), alumina (chromatographic grade 100-200 mesh), rectified spirit, sodium salt of fluorescein, methylene blue.

Theory : The separation can be done in two ways, viz., (i) the mixture is dissolved in alcohol (rectified spirit) and elution is carried out with alcohol and we get methylene blue as eluate. Fluorescein can be eluted using water as the eluent afterwards. (ii) the solution of the mixture is prepared in water and the elution is carried out first with water and then with alcohol.

Procedure : (i) Prepare a column of alumina of about 20 cm length by pouring a slurry of 25 g alumina in alcohol into the chromatographic tube (See figure (1)). Place a filter paper or polyethylene disc on the top of the column to prevent subsequent disturbance of the packing.

Weigh out nearly 5 mg each of methylene blue and sodium salt of fluorescein, and dissolve them in about 5 cm³ of rectified spirit contained in a test tube.

Allow the solvent in the tube to drain by opening the tap of the exit. When the surface is about to become dry, *i.e.*, the float has fallen nearly to the top of the column, add the dye solution quickly.

Attach a tap funnel to the chromatographic tube by means of a rubber bung and fill it with alcohol. When the last drop of the solution passes through the column, allow the alcohol to drip.

The blue colour of methylene blue soon starts to pass down the column, while the fluorescein remains adsorbed strongly at the top. Continue washing till all the methylene blue has passed into the receiving flask and the filtrate is colourless.

Now replace the alcohol in tap funnel by water and allow it to run. Very soon the fluorescein band starts widening and passes down the column. Continue the elution till all the fluorescein has passed into the receiver.

(b) Prepare the adsorbent column in water. Also prepare the solution of the dyes in water. Repeat the experiment as above, eluting the column first with water and then with alcohol. This time fluorescein will be washed first, whereas methylene blue will remain adsorbed at the top.

EXPERIMENT No. 3

Object : *To separate a mixture of 2 : 4-dinitrophenyl hydrazones by adsorption chromatographic technique.*

Apparatus and Chemicals : Chromatography tube (about 25 cm long and 1.7 cm diameter), bentonite, kiesselguhr (acid washed) chloroform, ethanol, 2 : 4 dinitrophenyl hydrazones of acetone and methyl ethyl ketone and *n*-butyraldehyde.

Procedure : Prepare 2 : 4-DNP derivatives of the carbonyl compounds. Weigh nearly 0.005 g each of the two DNP derivatives and dissolve the mixture in minimum amount of chloroform, say 10 cm³

Prepare a slurry of the adsorbent by shaking about 16 g bentonite and 4 g of kiesselguhr with 32 cm³ of chloroform. Place a small plug of glass wool in the constricted end of the tube and with the lower end stoppered, add about 16 cm³ of chloroform. Pour the slurry of the adsorbent into the tube, allow it to settle and run off the excess solvent. Again add a small amount of solvent and float a filter paper or polyethylene disc on the solvent.

Open the stopper and allow the solvent to run off. When the solvent has fallen to within 1-2 mm of the top of the column, pour the solution of the mixture quickly into one portion. Insert a tap funnel by means of a rubber bung into the upper end of the tube and fill it with chloroform.

When the last drop of the solution passes into the column, allow the solvent to drip.

Very soon the two dinitrophenylhydrazones will start to separate into two bands which will travel down the column. Continue washing with chloroform, till the lower band is completely dissolved off. Collect the eluate in a clean conical flask. Allow about 80 cm³ more of the solvent to percolate.

Now replace the chloroform in the tap funnel by ethanol-chloroform mixture (1 : 50) and continue the elution. Collect the second band in a second receiver.

Evaporate the solutions under reduced pressure and determine the yield by weighing the solid obtained.

EXPERIMENT No. 4

Object : *To separate a mixture of o-and p-nitroanilines on an alumina column.*

Apparatus and Chemicals : Chromatography tube (about 30 cm long and 3 cm diameter), alumina, benzene, o-and p-nitroanilines.

Procedure : First, prepare a slurry of alumina in benzene. Place a small plug of glass wool in the lower end of the tube and add about 10 cm³ benzene. Pour the slurry into the tube to give a column about 20 cm long, and cover the packing with a filter paper or polyethylene disc to prevent the disturbance of the column when the solution or the solvent is added.

Weigh out nearly 0.25 g each of o-and p-nitroanilines and dissolve the mixture in about 30 cm³ benzene.

Allow the solvent in the tube to drain by opening the tap. When the surface of the column is about to dry, add the solution of the mixture quickly in one portion.

Immediately fit up a tap funnel, by means of a rubber bung, into the upper end of the tube and fill it with benzene. When the solution has fallen almost to the surface of the column, allow benzene to run.

The two nitroanilines will now start separating into two yellow bands which then move down the column. Continue the elution and collect the two bands in separate vessels.

Concentrate the two solutions, crystallize and identify the compounds. Also, weigh the pure compounds to measure the yield.

EXPERIMENT No. 5

Object : *To study the isolation of ions of inorganic substances by paper chromatography.*

Apparatus : Same as explained in paper chromatography.

Theory : See preceding pages.

Procedure : Set up the ascending method of paper chromatography.

(a) **For Fe^{2+} , Cu, Co and Ni :** Dry a Whatman no. 41 filter paper and spray rubeanic acid (0.1 g dissolved in 60 ml ethanol and 40 ml water mixture). The solvent used is a mixture of acetone (87 parts), conc. HCl (8 parts) and water (5 parts). Proceed as explained before.

Dry and expose the sheet to ammonia vapours. The respective colours for Fe^{2+} , Cu, Co and Ni will be grey, deep grey, orange and blue.

(b) **For Fe^{3+} , Co, Ni, Mn :** Proceed as explained above. However, use Whatman no. 1 filter paper and a mixture of acetone (90 parts) and 6M HCl (10 parts) as solvent. The developed paper is dried and dipped in an ammonical solution of dimethyl glyoxime. The respective colours for Fe^{3+} , Co, Ni, Mn will be brown, dark brown, red and reddish brown.

(c) **For Cl^- , Br^- and I^- :** Proceed as explained above. Use Whatman no. 1 filter paper and a mixture of *n*-butanol (40 parts), 1.5M NH_3 solution (40 parts) and pyridine (20 parts) as solvent. The developed paper is dried and dipped in ammonical $AgNO_3$ solution. The R_F values are calculated. These values will be in the order $Cl^- > Br^- > I^-$.

EXPERIMENT No. 6

Object : *To study the separation of organic acids by one dimensional paper chromatography.*

Apparatus and Chemicals : Multisheet frame and tank, sheets of chromatography paper (Whatman No. 1), organic acids (tartaric, citric, oxalic, malonic, malic, succinic, fumaric and adipic acids), bromophenol, *n*-butyl formate, formic acid (98%), iso-propanol and sodium formate.

Procedure : Prepare solutions (about 1%) of individual organic acid in 10% iso-propanol-water. This gives 100 μg ($100 \times 10^{-4}g$) of acid in a 10 μl solution.

Prepare the developing solvent by mixing *n*-butyl formate, formic acid and water in the ratio 1 : 1 : 4 by volume.

Draw a pencil line about 3-4 cm from one end and mark \times (origin) on it at an interval of 2-3 cm. Apply 1 cm^3 of each acid solution, in minute amounts at a time,

separately on marks \times . The spots must be as compact as possible. Use hot air blower to allow the solution to dry after each application.

Also, apply the mixture on another mark \times .

Put sufficient solvent in the tray of chromatographic tank and suspend the sheets of the paper, with the pencilled end dipped into the solvent to a depth of about 0.5 cm. The development of the chromatogram in the enclosed tank is allowed to continue till the solvent front rises to a sufficient distance (about 4 hours will be sufficient time).

Remove the paper chromatograms from the tank and mark the position of the solvent front in each sheet. Suspend the sheets, upside down, and allow them to dry overnight. The various acids will be detected as yellow spots on a blue-black background.

Measure the distance of the centre of each spot and that of the solvent front from the origin. Then calculate the R_f value of each spot. Also, calculate the R_f values of the various spots of the mixture. The different acids in the mixture can be recognised by comparing the separated spots directly with standards which have been run in identical conditions.

EXPERIMENT No. 7

Object : To study the separation of amino acids by one-and-two dimensional paper chromatography.

Apparatus and Chemicals : Multisheet frame and tank for two dimensional ascending chromatography [Fig. (9)]. If such apparatus is not available, use cylindrical method, 20 or 10 cm square sheets of Whatman No. 1 paper, ethanol, *tert*-butanol, *iso*-propanol, phenol, ammonia (sp. gr. 0.88), ninhydrin, amino acids (e.g., glycine, arganine, aspartic acid, phenylalanine, histidine, tryosine).

Procedure : Prepare solutions of each acid (2.5 mg/cm^3) in 10% aqueous isopropanol with the addition of 1 drop of concentrated hydrochloric acid to aid solution. (This gives $25 \mu\text{g}$ of acid in a $10 \mu\text{l}$ aliquot of solution. Now prepare mixture of the acids containing a similar quantity of each of the constituent acids.)

Prepare a 0.05% solution of ninhydrin (location reagent) in absolute alcohol.

Prepare the following development solvents :

Solvent-1 : ethanol (60 vol), *tert*-butanol (20 vol), water (15 vol), ammonia solution (5 vol);

Solvent-2 : phenol (80 parts by weight), water (20 parts by weight), or the following pairs of solvent may be used;

Solvent-1 : ethanol, water and ammonia solution in the ratio 80/10/10 by volume;

Solvent-2 : *n*-butanol, acetic acid (glacial) and water in the ratio 60/15/25 by volume.

Draw a pencilled base line, on each square paper, about 3-4 cm from, and parallel to, one of the edges of the paper. Mark \times (origin) on each line, about 4 cm apart from the left hand edge. Apply $10 \mu\text{l}$ of the solution of each acid and of the mixture individually on these marks. In order to obtain compact spots, add the solution in small amount at a time and evaporate the solvent each time by hot air blower.

It is important to note that the paper must be handled only at the edges, otherwise contamination of spots of amino acids may be picked up from the hands.

Mount the papers in the frame, base line downward. Put the solvent-1 in the tray of the tank and lower the frame so that the papers dip in the solvent to a depth of about 1 cm. Close the tank and ensure that it is air tight. Allow the development to proceed till the solvent has risen nearly to the top of the paper. Remove the frame from the tray, and mark the position of the solvent front with a pencil on each paper. Dry the papers (in the frame) by a jet of hot air.

In another tank, put second solvent-2* (if another tank is not available use the first tank after thorough cleaning). Turn the frame through right angle so that the line of the first development is now at the bottom of the paper. As before, allow the development to proceed till the solvent front has reached near the top of the paper. Remove the frame from the tank and mark the solvent front with a pencil. Dry the papers by means of hot air blower, and ensure that all the phenol has been removed. In no case, the paper should be heated above 40°C as phenol attacks some amino acids. Any residual phenol can be removed by rolling the papers into the form of cylinders and dipping in a measuring cylinder containing acetone. Then, hang the papers in air to dry.

Spray the papers lightly and evenly with ninhydrin reagent, and warm the papers with hot air from the blower. All amino acids will be detected by purple spots on a white background.

Measure the distance of each spot and solvent front from the base line. Calculate the R_f value of each acid in each of the two solvent, calculate the R_f value of each of the separated components in each of the solvents, and by comparison recognise the individual spots.

EXPERIMENT No. 8

Object : *To differentiate common sugars by paper chromatography and to analyse their mixture.*

Apparatus : Sets for ascending, descending and horizontal paper chromatography etc.

Theory : See preceding pages.

Procedure : The following solutions of indicators are prepared:

(a) **Phloroglucinol solution :** Dissolve 0.1 g of phloroglucinol in 40 ml of 90% ethanol and 10 ml of 25% (W/V) trichloroacetic acid. It gives brown, faint brown and grey-green colour with fructose, galactose and pentoses.

(b) **Aniline phthalate solution :** Dissolve 1.5 ml of aniline (A.R.) and 1.6 g of phthalic acid in 95 ml of acetone and 5 ml of water. Hexoses, pentoses and rhamnose salmon give brown, red and pink colour, respectively.

Apply spots of 1% (W/V) aqueous solution of individual sugars on filter paper and develop chromatograms. Similarly, develop chromatogram of honey or sugar mixture. Develop by flow of each solvent separately and dry the wet sheets in air. When dry, dip in the indicator solution and determine R_f value.

* If the second solvent is phenol-water, a beaker containing a few drops of ammonia solution (sp. gr. 0.88) should be placed in a corner of the tank so as to produce an atmosphere of ammonia.

EXPERIMENT No. 9

Object : *To demonstrate the separation of inorganic ions by paper chromatography.*

Apparatus : Tank for ascending chromatography, 25 cm square Whatman No. 1 paper or CRL/1 slotted paper, 5% (W/V) aqueous solutions of nitrates of metals, sodium or potassium salts of anions. Solvent and locating reagents are given under the heading of procedure.

Theory : The separation of inorganic compounds is based upon their different solubilities in the organic solvent. In some cases, the solubility is due to the formation of soluble complex between the compound and the solvent, whereas in other cases complex forming reagent is added deliberately.

Procedure :

(a) Separation of Co, Ni, Mn and Zn

Location reagents : Prepare solutions (i) 50 mg tri-sodium pentacyanoamine ferroate in 20 cm³ water and (ii) 10 mg rubeanic acid in 10 cm³ ethanol. Mix the two solutions, shake for a few minutes and filter. The reagent must always be freshly prepared.

Solvent : Prepare the developing solvent by mixing acetone (87 vols), concentrated hydrochloric acid (8 vols) and water (5 vols).

Mark five origins (×) numbered 1 to 5, on the pencilled line drawn near the bottom edge of the paper. Apply 10 μl of each Co, Ni, Mn, Zn solutions on 1, 2, 3, and 4th origin, respectively and of mixture of the four (2 μl each) on the 5th origin. Dry the spots with hot air blower.

By observing the usual precautions, develop the chromatogram (dipping the paper in the solvent contained in the tray of the tank) until the solvent front reaches nearly the top of the paper. This will require about 3-4 hours. Remove the paper from the tank, mark the position of the solvent front with a pencil and allow it to dry.

Expose the dried chromatogram to ammonia vapour (from density 0.88 ammonia) to neutralize any residual acid and dip the paper in the location reagent. In order to remove undesirable background purple colour, wash the chromatogram with 2M acetic acid till background colour is negligible.

Identify the components of the mixture by comparing the separated spots with four standards.

(b) Separation of Fe, Cu, Co and Ni

(i) *Location reagents :* Solutions of rubeanic acid (0.1 g dissolved in 60 cm³ ethanol and 40 cm³ water).

(ii) *Solvent :* Same as in (a).

Apply the mixture spot on the paper as described in (a), and develop the chromatogram until the solvent reaches nearly the top of the paper. Dry the paper with warm air, spray with locating reagent, dry and fume with ammonia vapour

(from 0.88 ammonia). The four metals Fe, Cu, Co and Ni can now be detected by grey, deep gray, orange and blue colour, respectively.

(c) Separation of Cu, Co, Ni, Zn, Fe, Mn and Mo

(i) *Location reagents* : (1) Same as in (a). (2) 1% (W/V) aqueous solution of potassium thiocyanate.

(ii) *Developing solvent* : The different developing solvents are required for this experiment. Solvent-1 [methyl ethyl ketone, concentrated hydrochloric acid and water in the ratio of (75/15/10)]. Solvent-2 (Methyl ethyl ketone and concentrated hydrochloric acid in the ratio of 92/8)

Solvent-1 is suitable for the separation of all metal ions mentioned above except Mn and Ni which appear as mixed spot. The separation of Mn and Ni can, however, be achieved by solvent-2.

Perform the experiment with two duplicate papers separately in solvent 1 and 2 as described in (a).

In order to identify Mo in presence of Fe, spray the chromatogram with location reagent (2) (potassium thiocyanate). Iron and molybdenum will give red and orange thiocyanate complex, respectively.

(d) Separation of Fe, Mn, Co and Ni

(i) *Location reagent* : Ammoniacal solution of dimethylglyoxime.

(ii) *Developing solvents* : Acetone (90 vols), 1 M hydrochloric acid (10 vols).

After drying the developed chromatogram, dip the paper in the location reagent. The separated spots of iron, manganese, cobalt and nickel will give brown, red brown, dark brown and red colour, respectively with the location reagent.

(e) Separation of Al and Zn (Whatman No. 1 paper)

(i) *Location reagent* : 20% (W/V) alcoholic solution of alizarin.

(ii) *Developing solvents* : Tert-butanol (40 vols), acetone (40 vols), 3M hydrochloric acid (20 vols).

After development of the chromatogram, dry and dip the paper in the location reagents. Colours : aluminium-red, zinc-violet.

(f) Separation of Na, K and Li (Whatman No. 1 paper)

(i) *Location reagent* : 20% (W/V) alcoholic solution of violuric acid.

(ii) *Developing solvent* : Absolute methanol.

Colours of the separated spots with the location reagent : sodium and potassium-yellow and brown, lithium-violet.

(g) Separation of chloride, bromide and iodide (Whatman No. 1 paper)

(i) *Location reagent* : Ammoniacal silver nitrate solution.

(ii) *Developing solvent* : *n*-Butanol (40 vols), pyridine (20 vols) and 1.5 M ammoniacal solution (40 vols).

After the development of the chromatogram, pass the paper through ammoniacal silver nitrate solution (location reagent).

THIN LAYER CHROMATOGRAPHY

Thin layer chromatography (TLC) is a special example of chromatography in which the stationary phase is coated on to a glass plate in the form of a thin and uniform layer. The chromatographic separations are then carried out in much the same way as in ascending paper chromatography. Since the basic principles of TLC and column adsorption chromatography are the same, the coated plate is regarded as an open column. However, thin layer chromatographic separation have the following advantages over both the column and paper chromatographic techniques.

(i) The choice of stationary phase is wide, and any of the materials alumina, silica gel, kiesselguhr, cellulose, acetylated cellulose, ion exchange cellulose powders, etc. may be used for preparing thin layers.

(ii) Due to the finely powdered state of the stationary phase, the solvent is drawn up at a fast rate, *i.e.*, development is more rapid. A development time of 30 minutes is sufficient as compared to a few hours required in paper chromatography.

(iii) The separated components can be recovered with greater ease, scrapping the layer with a knife and dissolving the substance into a suitable solvent.

(iv) TLC separations are extremely sharp, and therefore, much smaller quantities can be separated, 1 μg of each compound in the mixture to be applied is sufficient for separation.

(v) The thickness of the adsorbent layer coated on the glass can be changed according to will.

(vi) There is more scope for the choice of identifying reagents. Detection of fluorescent compounds under ultraviolet light is easier than on paper because the inorganic background does not fluoresce.

[I] Technique

The experimental procedure of thin layer chromatography involves the following steps :

(i) The glass plates (10-20 cm long and 5-10 cm wide, or 10 cm square for two dimensional chromatography) are thoroughly cleaned, first with caustic alkali and then with distilled water.

(ii) The finely powdered adsorbent is made into a moderately thick slurry with water or organic solvent. The slurry should be uniform and may be prepared by thorough mixing or stirring. The adsorbent layer, (0.25 to 1 mm thick) is held firmly on the glass plate with binders, *e.g.*, plaster of Paris, which is added to the slurry. Uniform layer of the slurry is spread on the plate with the help of an applicator available commercially.

A simple applicator, suitable for microscopic slides is shown in fig. (11), On the top surface of a block of aluminium or brass (10 \times 25 \times 2 cm high) a depression, about 0.3 mm deeper than the thickness of the slide is cut and machined to take about 10 microscopic slides. Dry and clean glass plates are put in the position on the block, and the block is placed on a level surface. Adsorbent slurry is then poured over the plates, and smoothed by a glass straight edge or a smooth roller. The whole system is dried at nearly 50-70°C. The dried slides with adsorbent layer are then removed from the block and stored in a dessicator to protect from dust till required.

(iii) With the help of a melting point capillary, micropipette or micrometer syringe, a small spot of the mixture to be separated is applied about 1 cm from one end of the plate, exactly in the same way as for the paper chromatography. The spots are then dried.

(iv) The plate, with spot end downward, is allowed to rest on the bottom of the development tank. The developing solvent in the bottom of the tank must be sufficient to dip the plate to a depth of about 1 cm. For about 10 cm movement of the solvent, a development time of nearly 20 to 40 minutes will be required.

(v) At the end of development, the plates are removed from the tank and dried. The separated spots may then be seen under ultraviolet light or may be sprayed with suitable location reagent. In another method, the chromatogram may be sprayed with concentrated sulphuric acid and subsequently heated. The separated spots of organic compounds will become visible due to highly sensitive charring effect.

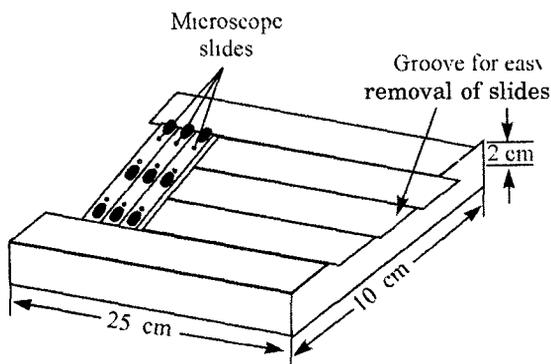


Fig. 11. Application block for preparation of microscopic slides for TLC

EXPERIMENT No. 10

Object : To demonstrate the separation of dyes (azobenzenes) by thin layer chromatography.

Apparatus and Chemicals : Silica gel (preferably "silica gel G" containing gypsum), thin layer spreading device, glass plates (15 × 10 cm), screw topped bottles or covered jars, benzene and the dyes (azobenzene, *p*-methoxy azobenzene, Sudan yellow, Sudan red, *p*-amino azobezene, *p*-dimethylamino azobenzene, *p*-hydroxy azobenzene).

Procedure : Take about 15 g of "silica gel G" in dry beaker or china dish, and gradually add to it about 10 cm³ distilled water with constant stirring by a glass rod. Continue to stir till a uniform paste free from air bubbles is formed. Add about 10 cm³ more of distilled water to it and obtain the slurry of suitable consistency.

Pour the slurry on to the clean and dry plates set in the spreading device and apply a thin layer (0.25 mm thick) of the adsorbent to them. It should be noted that the duration of time from wetting the silica gel to the application of thin layer should not be more than 4 minutes which is the setting time of the binder (calcium sulphate).

Allow the layer to dry for 5-10 minutes and then heat the plates in an oven at 100–120°C for about half an hour.

Prepare solutions of each of the dyes in benzene (20 mg in 10 cm³) and suitable mixed solutions of two or three of the dyes, at a concentration of 0.1% each.

Make pencilled base line about 2 cm from the bottom edge of the plate. At about 1 cm from the end of the plate make three or four equally spaced marks (×) on the base line and apply small samples (about 4-5 μl of the mixture and reference solutions on each of these marks separately. Precaution must be taken that the spot must be as small as possible. Use a current of hot air if necessary. Similarly, prepare other plates with other solutions and mixture.

Put the solvent (benzene) in a jar or screw topped bottle to a depth of about 1 cm, and allow the prepared plate to rest on the bottom of the jar (bottle) and lean it up against the side. Close the jar (bottle) with a plate (cap), and allow the solvent to flow up until the solvent front nearly reaches the top. Remove the plate from the bottle, mark the position of the solvent front and allow the solvent to evaporate. The dyes should have separated as compact spots. Similarly, develop the chromatogram of other plates.

Calculate the R_f values of the components in the single solutions and in the mixtures.

EXPERIMENT No. 11

Object : *To analyse a mixture of components, say ortho- and para-nitroanilines by TLC technique.*

Apparatus : Alumina, TLC plates, covering jar, dish etc.

Theory : See preceding pages.

Procedure : Prepare solution of both the components separately in benzene (0.2 g in 10 ml) and some mixture of these components. Take a TLC plate and put three pencil marks from its one edge. Now place a small spot of the mixture on the central mark and similar spots of the pure component's solution on the outer marks. Allow to dry in hot air. Now take a layer of 0.5 mm of C_6H_6 in a flat dish and put it in a jar. Now place the TLC plate vertically in the dish and close the jar with a plate. When the solvent front rises to about 1 cm from the top edge, remove the TLC plate and mark the solvent front. Also mark the spots on the plates.

Calculate R_f values of the components from single solution and from the mixture.

ION EXCHANGE OR DISPLACEMENT CHROMATOGRAPHY

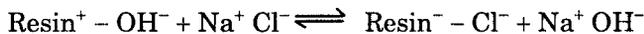
Displacement chromatography is a modified form of adsorption chromatographic technique. In this technique, substances to be separated are first adsorbed by an adsorbent and then released by eluting or washing the column with a solution containing a solute which is more tightly held by the adsorbent than the substances under test. Ion exchange columns are of special use in this type of chromatographic separations, a technique called as ion exchange chromatography.

Ion exchangers are usually classified into two main groups, *anion exchangers* and *cation exchangers*, depending upon the type of the ion that can be exchanged on the resin. These two types are also known as *base* and *acid resins*, respectively. Other than natural clays and zeolites, the inorganic exchangers, synthetic organic resins with acidic or basic groups have been prepared. The cation exchange resins, containing SO_3H or $-\text{COOH}$ groups (known as strong and weak acid cation), are

the high molecular weight insoluble substances. The cation exchange reaction of the resin can be represented by the following equation.



Anion exchange resins contain quaternary ammonium or amino groups, and are known as *strong* and *weak base amino exchangers*, respectively. The reaction on anion resin can be represented as follows :



It should be noted that the adsorbed component cannot be desorbed simply by washing the column with the solvent. The adsorbed cation by cation exchanger (acid resin) can be released by washing the column with acid (usually 10% HCl), and the resin is regenerated in the H^+ form. On the other hand, an anion exchanger is regenerated with alkali.

The principle of ion exchange chromatography is that when two or more substances are adsorbed, elution of the column will make different substances to be released one by one, which depends on the strength of electrostatic linkages,

[I] Technique of Ion Exchange Chromatography

The apparatus and the technique used in ion exchange chromatographic separations are the same as for column chromatography. The main difference of this technique from adsorption or partition chromatography lies in that in the former the adsorbent used can be re-used after regeneration, while in the latter techniques the adsorbent used has to be discarded.

The ion exchange resin with small particles (100-200 mesh) is packed in chromatographic tube in a manner which is similar to that mentioned in column chromatography. A positive or negative pressure is applied to the column in order to control the flow rate (approx. $100 \text{ cm}^3/\text{hr.}$).

EXPERIMENT No. 12

Object : *To prepare free acid or base from the salt of an organic acid (say sodium citrate) or base (say aniline hydrochloride) using cation and anion exchange resins.*

Apparatus and Chemicals : Chromatography tube ($20 \times 1.5 \text{ cm}$) with a sintered glass disc and tap, cation exchanger in acid form (*e.g.*, Zeo-karb 225, Dowex 50 or Amberlite IR-120), anion exchanger in hydroxide form (*e.g.*, De Acidite FF, Dowex 1 or Amberlite IR-400), 3M hydrochloric acid and 0.5 M sodium carbonate solution, sodium citrate and aniline hydrochloride.

Theory : When an organic acid is highly soluble in water, it cannot be obtained easily by treating its salt with dilute hydrochloric acid. This can, however, be achieved using cation exchange resins.

Procedure : (A) *Preparation of acid*

Place some ion-free water in the chromatography tube and pour a slurry of the cation exchange resin, in sufficient quantity to get a column about 15 cm long. Allow most of the water to run off, pass about 100 cm^3 of 3M hydrochloric acid through the column to get the resin regenerated (H^+ form), and finally wash the column with excess of ion-free water till the effluent is neutral to methyl red. Do not allow the column to become dry.

Now pour about 50 cm³ solution of sodium salt of the acid (sodium citrate) containing 0.1 g of the salt on to the column, and allow it to percolate at the rate of nearly 2-3 cm³ per minute, by adjusting the tap. Wash the column with about 100 cm³ distilled water and collect the effluent and the washings in a conical flask. Evaporate the solution of the acid (citric acid) so obtained to get the acid in crystallized form.

Leave the column regenerated by passing HCl solution and subsequently washing thoroughly with distilled water.

(B) *Preparation of base from its salt*

Fill another chromatography tube, with anion exchanger and regenerate by passing 100 cm³ of 0.5 M sodium carbonate solution through it. Wash the column thoroughly with distilled water till the washings do not turn pink with phenolphthalein.

Pass about 50 cm³ of solution of the salt of base (containing about 0.1 g of the salt) through the column at the rate of 2-3 cm³ per minute. Collect the eluate and subsequent washings with distilled water.

Regenerate the resin with sodium carbonate solution and wash thoroughly with ion-free water.

EXPERIMENT No. 13

Object : *To determine the concentration of a salt solution by ion exchange chromatography.*

Apparatus and Chemicals : Chromatography tube (30 × 1.5 cm), strong acid cation exchange resin in the hydrogen form (Zeo-Karb 225 or Dowex 50), sodium sulphate, standard alkali (approx. 0.1 M).

Theory : When a dilute solution of a salt, say sodium sulphate, is passed down a column of strong cation exchanger in H⁺ form the following reaction takes place :



The reaction occurs quantitatively, *i.e.*, hydrogen ions (free acid) are formed in equivalent amounts of sodium ions. The concentration of sodium ions may, therefore, be determined simply by titrating the eluate of the column with standard alkali solution.

Strong anion exchange resins also cause the quantitative salt splitting, but their use is limited owing to the reason that the last traces of alkali regenerant are difficult to be removed.

Procedure : Fill the tube with a slurry of the resin in distilled water as described in previous experiment. Pass ion-free water through the column and ensure that the effluent is neutral.

Prepare a standard solution of sodium sulphate (nearly 0.02 M) and allow 50 cm³ of it to pass down the column at a rate of 2 cm³ of distilled water and add the washings to the eluate.

Titrate the eluate (acid released) against the standard alkali solution using phenolphthalein as an indicator and calculate the concentration of the original solution. Compare this value with the known concentration.

EXPERIMENT No. 14

Object : To determine the composition of a solution containing an acid and its salt (acetic acid and sodium acetate).

Procedure : Pass a known volume (say 100 cm³) of the solution through a strong cation exchanger in hydrogen form and collect the eluate and washings with distilled water. Titrate the eluate with a standard alkali and calculate the total acid (acid already present + that released) concentration. The concentration of the acid already present can be determined by titrating a known volume of the original solution against standard alkali solution. The difference of the two values gives the concentration of the acid released and so the concentration of the salt can be calculated.

PAPER ELECTROPHORESIS OR ZONE ELECTROPHORESIS

(I) Principle

The principle of paper electrophoresis is based on the migration of charged particles like ions or colloidal particles in an electrical field. In this technique, the migration is stabilised using a filter paper strip as the supporting medium and cannot be influenced by convection currents in the same manner as in the free boundary method. This technique is also known as *zone electrophoresis*, because the complete separation of various components leads to the formation of zones.

A potential difference is applied to the ends of strip of a filter paper impregnated with a suitable buffer solution, near the centre of the strip a drop of the sample is applied. The different charged components move with different velocities and form discrete zones. These zones can be located by suitable methods such as *staining*.

(II) Factors Affecting Migration of Charged Particles

(1) Properties of the ion involved, such as sign and net charge, colloidal, molecular or ionic nature.

(2) Properties of buffer solution such as, pH, ionic strength and viscosity.

(a) Regulation of pH of the buffer promotes suitable ionisation of the molecules undergoing separation.

(b) The effect of ionic strength lies in that higher the ionic strength the less the diffusion.

(c) Ionic mobility is decreased and heat produced is increased due to higher conductivity.

(3) Field strength

(4) Current density

(5) Temperature

(6) Quality of paper used.

(III) Apparatus

The apparatus consists of an air tight chamber in which wet paper strips can be supported under slight tension between the electrode chambers and a D.C. supply. The apparatus for horizontal paper electrophoresis is shown in figure (2). Generally, platinum wire or carbon rod electrodes are used.

In order to prevent the diffusion of the products of electrolysis on to the paper, the chambers containing the electrodes are separated from chambers into which the paper dips. On both sides, the adjacent chambers are connected by wicks or glass tubes packed with cotton, glass or asbestos wool. So, the pH of the inner chamber remains unchanged and, therefore, the pH gradient along the paper is avoided. The siphoning of the solution during electrolysis must be checked by keeping the level of the buffer solution in the four chambers at the same height. The solution in the adjacent chambers quickly acquires the same level due to the diffusion through the wicks. The levelling between the electrode chambers can be carried out by a Y-piece siphon and suction tube.

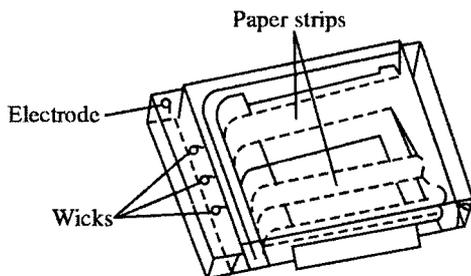


Fig. 2 : Apparatus for horizontal paper electrophoresis

(IV) Experimental Method

Dry filter strips of suitable length and 3 cm width are taken and a pencil line is drawn on each of the strips to mark the origin. The strips are loaded on the horizontal frame. Pour the buffer solution into the four chambers to a constant level, whereby the paper becomes completely wet immediately due to capillary action. By means of a micro-pipette, about 5–10 μl (microlitre) of the sample is put to the origin point in the centre of the width of the wet paper strip. The tank is immediately covered with a heavy glass strip. A known potential difference is applied and the polarity of electrodes is noted.

After sufficient time has elapsed for good separation, the current is switched off. The strips are immediately removed and dried to fix the separated components. The strip of filter paper containing the separated zones of mixture is known as *electrophoregram* or *electrophoretogram*. In case the components are colourless, the individual zones are located by dipping the paper in a staining bath of a suitable location reagent.

EXPERIMENT No. 15

Object : To study the separation of inorganic cations by paper electrophoresis.

Apparatus and Chemicals : Paper electrophoresis apparatus, 100–200 D.C. power supply, Whatman no. 1 filter paper strips of 3 cm width, micro-pipette (or melting point tube), 0.1M solutions of silver cadmium and copper nitrates, 0.05M KNO_3 solution (as conducting medium).

Procedure : Set up the paper strips with origin marked by a pencil line in the apparatus [See figure (2)] for horizontal electrophoresis and pour 0.05M KNO_3 solution into the four chambers to a constant level.

By means of a micro-pipette apply separately about 5–10 μl samples of individual metal solutions and a mixture thereof (0.05M with respect to each) across the marked origins of the papers. Apply a constant potential of 100–200 volts D.C. for nearly 3–4 hours.

Now remove the paper strips from the apparatus, dry them and locate the position of the metals (Ag, Cd and Cu) by exposing the strips to hydrogen sulphide.

EXPERIMENT No. 16

Object : *To study the separation of amino acids in a mixture by paper electrophoresis.*

Apparatus and Chemicals : Paper electrophoresis apparatus, 120–150 volts D.C. power supply, Whatmann no. 1 filter paper strips of about 3 cm width, micro-pipette (or melting point tube), 0.01M solutions of lysine, valine and glutamic acid and a mixture thereof (0.1M with respect to each), 0.1M phosphate buffer (pH = 7.0; 70 cm³ M/15 Na₂HPO₄.12H₂O + 4.0 cm³ M/15 KH₂PO₄), 0.2% (w/v) ninhydrin in acetone.

Procedure : Set up the filter paper strips in the horizontal paper electrophoresis apparatus. Pour the buffer solution in the four chambers of the apparatus. Now apply about 5–10 μl samples of individual amino acid solution and the mixture thereof (by means of a micro-pipette). Apply a potential of nearly 150 volts D.C. power supply for nearly 2–3 hours. Switch off the current, remove the strips of filter paper and dry them at 100°C. Finally, locate the amino acids by dipping them in a solution of ninhydrin in acetone.

EXPERIMENT No. 17

Object : *To determine the iso-electric point of glutamic acid by paper electrophoresis.*

Apparatus and Chemicals : Paper electrophoresis apparatus, 100–200 volt D.C. power supply, Whatmann no. 1 filter paper of 3 cm width, 0.01M solution of glutamic acid (mol. wt. = 147), buffer solution in pH range 2.4 (CH₃COONa + HCl buffers), 0.2% (w/v) ninhydrin in acetone, alkaline ninhydrin for very acidic buffer solutions (0.2 g of ninhydrin in 100 cm³ ethanol + 0.5 cm³ of 1M KOH, having pH ≈ 2).

Theory : An amino acid is said to be at its iso-electric point when the concentration of negative ions (RH⁻) is equal to that of positive ions (RH₂⁺). As these ions are large, they possess nearly the same equivalent conductivity and so equal amounts will migrate in an electric field. So, at the iso-electric point, an ampholyte appears to be stationary in an electric field, even though the solutions may have appreciable conductivity. Usually, an ampholyte is not at its iso-electric point in the pure solution. So, by controlled pH the iso-electric point of an ampholyte can be achieved.

Procedure : Set up three filter paper strips with pencil marks in horizontal electrophoresis apparatus, filled with one of the buffer solutions. By means of a micro-pipette, apply nearly 5 μl of glutamic acid solution to the marked origin of each paper.

Apply a constant potential of 120 volts for nearly 3 hours. Switch off the current and remove one strip. Carry out the electrophoresis for further 3 hours and remove the second strip. Carry out the electrophoresis for further 3 hours and remove the third strip. Dry the papers and locate the position of the amino acid by dipping them in a solution of ninhydrin in acetone. Dry the papers and heat them at 100°C for nearly 1–2 minutes.

Repeat the experiment with other buffer solutions, each time keeping the applied voltage constant and removing the papers at exactly the same time intervals.

Determine the distance moved by the acid from the origin and note the direction. Plot a graph between pH (ordinate) and distance (abscissa) removed (positive or negative) in a given time interval. The point at which the graph cuts the ordinate axis gives the pH (3.1) at the iso-electric point. Plot different graphs for different time intervals.

SUGGESTIONS FOR FURTHER WORK

EXPERIMENT No. 18

Object : *To check up by column or TLC technique whether the following inks consist of single or multiple mixtures of dyes :*

(a) Royal blue (b) Red (c) Blue black (d) Black.

Proceed as in experiment no. 11.

EXPERIMENT No. 19

Object : *To separate components of chlorophyll by ascending paper chromatography.*

Proceed as in experiment no. 8.



DIPOLE MOMENT AND MAGNETIC SUSCEPTIBILITY

Dipole moment is a property of molecules in which the distribution of charge is un-symmetrical. For non-polar molecules, its value is zero, but for polar molecules, dipole moment has certain value. It is given by the product of charge (e) on one atom and the bond length (l). Therefore,

$$\mu = e \times l$$

The unit of dipole moment is esu-cm. or debye (d).

Dipole moment can be obtained by different methods. The easiest way is to calculate its value from dielectric constants of substances. For measuring the latter, the substance is filled between the plates of a capacitor and the capacity of the condenser so formed is measured. **Dielectric constant (D) of a substance** is defined as *the ratio of the capacitance of a condenser with the substance between the plates (C) and the capacitance of the same condenser with the space between the plates being evacuated (C_0)*. So, $D = C/C_0$. The observed dielectric constant of the substance depends upon the following factors:

- (a) Permanent dipole moment of molecules.
- (b) Polarisability of molecules in an applied field.
- (c) Concentration (or density) of the substance when used as a solution between the condenser plates. Gases and vapours will have lower dielectric constant than the liquid form of the same substance.

Clausius and Mosotti gave the following relation between polarisability (α) and dielectric constant (D) of a medium between the charged plates.

$$\frac{4}{\pi} \pi N \alpha = \frac{D-1}{D+2} \cdot \frac{M}{\rho} \quad \dots (1)$$

where M = molar mass (g mol^{-1}), ρ = density (g ml^{-1}), N = Avogadro number, α = polarisability, which is the moment induced by unit field.

The R.H.S. of equation (1) is called the **molar polarisation**. In a non-polar molecule the polarisation is all induced and so the induced molar polarisation (P_i) is given by,

$$P_i = \frac{4}{3} \pi N \alpha = \frac{D-1}{D+2} \cdot \frac{M}{\rho} \quad \dots (2)$$

Molar polarisation has units of molar volume, as D is a dimensionless quantity.

In polar molecules, the total molar polarisation (P_t) which is measured from dielectric constant, $\left[\frac{D-1}{D+2} \cdot \frac{M}{\rho} \right]$ is the sum of two effects, *viz.* induced and orientation polarisations. Thus

$$P_r = P_i + P_0$$

where $P_0 =$ Orientation polarisation.

$$P_t = \frac{D-1}{D+2} \cdot \frac{M}{\rho}$$

$$\therefore \frac{D-1}{D+2} \cdot \frac{M}{\rho} = P_i + P_0 = \frac{4}{3} \pi N \alpha + P_0$$

The molar orientation polarisation (P_0) of a substance having a dipole moment (μ) was shown by Debye to be expressed as,

$$P_0 = \frac{4}{3} \pi N \left(\frac{\mu^2}{3kT} \right)$$

where $k =$ Boltzmann's constant

$$\therefore P_t = \frac{D-1}{D+2} \cdot \frac{M}{\rho} = \frac{4}{3} \pi N \alpha + \frac{4}{3} \pi N \left(\frac{\mu^2}{3kT} \right) \quad \dots (3)$$

The first term on RHS of equation (3) is a constant and μ is also constant for a given substance, therefore,

$$P_t = \frac{D-1}{D+2} \cdot \frac{M}{\rho} = A + \frac{B}{T}$$

where $A = \frac{4}{3} \pi N \alpha$ and $B = \frac{4\pi N}{9k} \cdot \mu^2$

This shows that total molar polarisation varies linearly with $1/T$.

The induced polarisation may be calculated and subtracted from molar polarisation. So, light is considered as an electromagnetic radiation of very high frequency such that it induces dipoles in molecules on its way but does not orient them. The interaction between molecules and light is calculated in terms of molar refraction (R) as :

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho}$$

where $n =$ refractive index.

When the substance does not exhibit absorption in the visible range, then

$$R_D = R_\infty.$$

$$\therefore R_D = R_\infty = \frac{4}{3} \pi N \alpha$$

We thus have,

$$P_t - R_D = \frac{4\pi N}{9kT} \cdot \mu^2$$

where $R_D =$ molar refraction for D -line of sodium.

While using polar liquids, the dipoles distort adjacent molecules and induce additional dipoles. This increases the measured polarisation. This difficulty can, however, be removed by dissolving a polar substance (solid or liquid) in non-polar solvents, *e.g.*, C_6H_6 , CCl_4 etc. The total molar polarisation of a solution ($P_{1,2}$) in a non-polar solvent follows the additivity rule. This rule is given by,

$$P_{1,2} = \frac{D-1}{D+2} \cdot \frac{(x_1 M_1 + x_2 M_2)}{\rho}$$

where M_1 and M_2 = molar masses

x_1, x_2 = mole fractions of the components.

ρ = density of the solution

1 and 2 = These numbers refer to solvent and solute, respectively.

$$\Sigma x_i M_i = \frac{\Sigma n_i M_i}{\Sigma n_i} = \text{Number average molar mass}$$

$$P_{1,2} = x_1 P_1 + x_2 P_2$$

For dilute solutions of 2 in 1, P_1 can be taken to be equal P_1^0 , i.e., molar polarisation of pure solvent.

$$P_2 = \frac{P_{1,2} - P_1^0 x_1}{x_2}$$

The value of P_2 for each solution can be calculated from molar polarisation of solution and pure solvent. A graph of P_2 against x_2 is plotted and extrapolated to obtain the value of P_2 , with molar refraction of pure solute.

$$P_2^0 = R_2 = \frac{n_2^2 - 1}{n_1^2 + 2} \cdot \frac{M_2}{\rho_2}$$

or
$$P - R_2 = \frac{4}{3} \pi N \cdot \left(\frac{\mu^2}{3kT} \right)$$

or
$$\mu = 0.128 \times 10^{-18} \times (P_2^0 T)^{1/2} \text{ debye.}$$

EXPERIMENT No. 1

Object : To determine the dipole moment of the given liquid.

Apparatus : Capacitance cell, impedance or capacitance bridge, Abbe's refractometer, pycnometer.

Theory : As explained in the beginning of this chapter.

Procedure : Suppose the experimental liquid is chlorobenzene. The density and refractive index of chlorobenzene (solute) are determined along with the temperature. Then the density and dielectric constant of benzene (solvent) and solutions of polar liquid in benzene at mole fractions of solute ranging from 0.003 to 0.1 are measured.

Calculations : The molar polarisation of solvent in each solution is calculated. The polarisation of solute in each solution is also calculated. A graph is plotted between P_2 and x_2 and it is extrapolated to $x_2 = 0$. The dipole moment of the solute

is then calculated by using molar polarisation and molar refraction at infinite dilution.*

Result : The dipole moment of the given substance = ... debye.

Precautions : The experiment should be performed very carefully as chlorinated solvents, e.g., nitrobenzene, chlorobenzene produce toxic vapours and have skin irritation.

MAGNETIC SUSCEPTIBILITY

We see that when a substance is placed in a magnetic field, a magnetic moment is induced in it. If the induced moment is parallel to the external field, the substance is called **paramagnetic** or **ferromagnetic**. When the magnetic field due to the induced moment is antiparallel to the external field, the substance is called **diamagnetic**, and the moment in this case is always small.

The intensity, I , of induced magnetisation (magnetic moment per unit volume) in an external magnetic field, H , is given by

$$I = \kappa H \quad \dots (1)$$

where κ (kappa) is known as the **volume susceptibility**. It is the magnetisation induced by unit field, and is a dimensionless quantity.

The susceptibility per g of the material, known as **mass susceptibility** or **specific susceptibility**, χ , is obtained by dividing κ by the density, ρ , of the material, i.e.,

$$\chi = \kappa / \rho \quad \dots (2)$$

where χ has the dimensions of $\text{cm}^3 \text{g}^{-1}$

The molar magnetic susceptibility, χ_M , is obtained by multiplying specific susceptibility by molecular weight of the substance, i.e.,

$$\chi_M = \chi \times M = \frac{\kappa}{\rho} \cdot M \quad \dots (3)$$

A substance is classified as diamagnetic, paramagnetic and ferromagnetic according to the sign and magnitude of its χ value. For diamagnetic substances, χ is negative and is of the order of 10^{-6} c.g.s. units. For paramagnetic and ferromagnetic substances, χ is positive and is of the order of 10^{-3} and 10^2 units, respectively.

[I] DIAMAGNETISM

Nearly all known substances are diamagnetic. The diamagnetic effect in a substance arises from the orbital motion of the electrons around the nucleus. Application of magnetic field causes the precession of the electronic orbits, and the induced magnetic field opposes the external field. The diamagnetic effect is independent of temperature and is practically the same for a substance in the gas or liquid phase. It was observed by Langevin that for a monoatomic molecule or any spherically symmetrical molecule, the diamagnetic susceptibility can be expressed as,

$$\chi_M = \frac{Ne^2}{6mc^2} \Sigma r^2 = -2.84 \times 10^{10} \Sigma r^2 \quad \dots (4)$$

where e and m are the electronic charge and mass, respectively, N is the Avogadro's number and r^2 is the mean square of the orbital radii.

The molar susceptibility in a diamagnetic substance has been seen to be an additive and constitutive property. It is thus possible to ascribe susceptibility contributions to various atoms, ions and to structural factors. The diamagnetic susceptibility of a molecule may be calculated by the contribution of atoms, groups and bonds.

[II] PARAMAGNETISM

The most important source of paramagnetism is the magnetic moment associated with the spin of the electron or electrons. The molecules (or atoms or ions) of a paramagnetic substance possess a permanent magnetic moment which is due to the presence of one or more unpaired electrons in the orbits. These electrons may be regarded as bar magnets. If coupled, these give rise to permanent magnetism (ferromagnetism or anti-ferromagnetism); If it is independent, then there will be no permanent magnetism. These tiny magnets tend to orient themselves parallel to the external field (paramagnetism). However, this alignment is opposed by the thermal motion of the molecules, and hence the paramagnetism depends on temperature.

In fact, the applied field has both diamagnetic and orientation effects on the paramagnetic molecules. On the basis of statistical considerations Langevin showed that the paramagnetic contribution to the molar susceptibility is $N^2\mu^2/3kT$, where N is the Avogadro's number, k the Boltzmann constant, T the absolute temperature and μ the magnetic moment of each molecule. Therefore,

$$\chi_M = a_M + \frac{N\mu}{3kT} \quad \dots (5)$$

where a_M is the diamagnetic contribution to the molar susceptibility.

Except a few cases, a_M is usually very small; and so it is either ignored or evaluated from atomic susceptibilities. Thus, the determination of χ_M at one or more temperatures helps us to calculate the value of μ . Equation (5) can be written in the form :

$$\chi_M = \alpha_M + \frac{C}{T} \quad \dots (6)$$

where C is called the Curie constant for the given substance

A modified form of this law is known as Curie-Weiss law and is given by :

$$\chi_M (\text{corrected}) = \frac{C}{T - \theta} \quad \dots (7)$$

where θ is known as Weiss constant. The constant is computed from the equation :

$$\mu_{eff} = 2.84 \sqrt{\chi_M (\text{corrected}), (T = \theta)} \quad \dots (8)$$

where μ_{eff} is the effective magnetic moment and χ_M (corrected) is the molar susceptibility corrected for the diamagnetic effect. The susceptibility corrections (DC) of some atoms, ions and linkages are given in table -1

Table -1. Diamagnetic corrections (D.C.) ($\times 10^{-8}$ g atom)

Atoms	DC	Atoms	DC	Ions	DC	Ions	DC
H	2.93	Sc	23.0	Li ⁺	1.0	F ⁻	9.1
C	6.00	Te	37.3	Na ⁺	6.8	Cl ⁻	23.4
N (ring)	4.61	P	26.3	K ⁺	14.9	Br ⁻	34.6
N (open chain)	5.57	As(V)	43.0	Rb ⁺	22.5	I ⁻	50.6
N (monoamide)	1.54	As(III)	20.9	Cs ⁺	35.0	NO ₃ ⁻	18.9
N (diamide and imide)	2.11	Sb(III)	74.0	NH ₄ ⁺	13.3	ClO ₃ ⁻	30.2
O (ether and alcohol)	4.61	Na	9.2	Hg ²⁺	40.0	ClO ₄ ⁻	32.0
O (ketone and aldehyde)	- 1.73	K	18.5	Mg ²⁺	5.0	BrO ₃ ⁻	38.8
O (carboxyl)	3.36	Mg	10.0	Zn ²⁺	15.0	IO ₄ ⁻	51.9
F	6.3	Al	13.0	Pb ²⁺	32.0	IO ₃ ⁻	51.4
Cl	20.1	Zn	13.5	Ca ²⁺	10.4	CN ⁻	13.0
Br	30.6	Hg(II)	33.0	Fe ²⁺	12.8	SCN ⁻	31.0
I	15.0	Si	20.0	Cu ²⁺	12.8	SO ₄ ²⁻	40.1
S	15.0	Sn(IV)	30.0	Co ²⁺	12.8	CO ₃ ²⁻	29.5
		Pb	46.0	Ni ²⁺	12.8	OH ⁻	12.0

Linkage corrections :

C = C	- 5.5	C in benzene ring	- 0.24
C \equiv C	- 0.8	C - Cl	- 3.1
C = C - C = C	- 10.6	C - Br	- 4.1
		C - I	- 4.1
C = N - R	- 8.2	H ₂ O	13

The effective magnetic moment at any temperature T can be calculated using the following relationship, whether the substances follow the Curie law or Curie-Weiss law.

$$\begin{aligned} \mu_{eff} &= \sqrt{\frac{3k}{N}} \chi_M \text{ (corrected)} T \\ &= 2.84 \sqrt{\chi_M \text{ (corrected)}} T.B.M. \end{aligned} \quad \dots (9)$$

The magnetic moment μ is expressed in units of erg gauss⁻¹. More conveniently, it is expressed in Bohr Magneton (B.M.) which is given by,

$$1\text{B.M.} = \frac{eh}{4\pi mc} = 9.272 \times 10^{-21} \text{ erg gauss}^{-1} \quad \dots (10)$$

where e and m are the electronic charge and mass, respectively, h is the Planck's constant and c the velocity of light.

The spinning as well as the orbital motion of the electron contribute to the magnetic moment of the molecule, atom or ion. In a polyatomic molecule, orbital motions are so rigidly fixed in respect of the nuclei that the applied field cannot alter the same in any way. Even in the case of monoatomic substances in liquid or solid states, the mutual cohesion or the influence of solvent molecules prevent any change in the orbital motion due to applied field. In most cases (except the rare earth ions) the orbital motion does not contribute to the total moment. Therefore, magnetic moment of an atom, molecule or ion having unpaired electrons, n is given by.

$$\begin{aligned} \mu &= \mu_s = 2\sqrt{s(s+1)} \text{ B.M.} \\ &= \sqrt{n(n+1)} \text{ B.M.} \end{aligned} \quad \dots (11)$$

where s is the spin quantum number having values $\frac{1}{2}$, 1 , $\frac{3}{2}$, 2 , etc. Each unpaired electron contributes $\frac{1}{2}$ towards the value of s .

The magnetic moment for a system having orbital contributions may be given as :

$$\mu = \mu_{S+L} = \sqrt{4s(s+1) + l(l+1)} \text{ B.M.} \quad \dots (12)$$

where l is the total angular quantum number. Calculated and experimental values of magnetic moment of some transition metal ions are given in table-2.

Table-2. Magnetic moments of some transition metal ions in B.M.

Ion	s	l	Spectroscopic symbol	μ_s	μ_{s-l}	μ (experimental)
V ⁴⁺	1/2	2	³ D	1.73	3.00	1.7-1.8
Cu ²⁺	1/2	2	³ D	1.73	3.00	1.76-2.2
V ³⁺	1	3	³ F	2.83	4.47	2.6-2.8
Ni ²⁺	1	3	³ F	2.83	4.47	2.8-4.0
Cr ³⁺	3/2	3	⁴ F	3.87	5.20	~ 3.8
Co ³⁺	3/2	3	⁴ F	3.87	5.20	4.1-5.2
Fe ²⁺	2	2	⁵ D	4.90	5.48	5.1-5.5
Co ³⁺	2	2	⁵ D	4.90	5.48	~ 5.4
Mn ²⁺	5/2	0	⁶ S	5.92	5.92	~ 5.9
Fe ³⁺	5/2	0	⁶ S	5.92	5.92	~ 9.9

[III] Magnetic Susceptibility Measurement

Following are the three main methods for the measurement of magnetic susceptibility.

(1) **Faraday's method** : In this method, the specimen is suspended between the poles of an electromagnet by means of a quartz fibre. The latter is connected to quartz fibre micro-balance. The instrumentation is difficult and delicate but the advantage of the method lies in that a very small amount of specimen is required.

(2) **Gouy's method** : It is the most convenient laboratory method for determining susceptibility. An apparatus used for the purpose known as Gouy's balance, consists of essentially three parts, *viz.*,

- (i) specimen tube, usually called Gouy tube
- (ii) a powerful horse-shoe magnet and
- (iii) a sensitive balance.

The specimen tube, a long tube of pyrex glass or perspex, is divided into two regions by a septum, and is suspended from the pan of a sensitive balance so as to hang vertically between the poles of a magnet [Fig. (1)]. The axis of the tube lies at right angles to the lines of force. The septum lies in the strongest part of the field strength.

The part of the tube above the septum is filled with material under experiment upto a mark and the part below is kept empty. The internal diameter of the tube is about 3 mm for solid samples and about 10 mm for liquid ones. The length of the tube may vary from 3 to 10 cm. The Gouy tube is hung in an outer tube which protects it from air currents.

The magnet should give a field of 5,000 to 10,000 gauss. The field should be reasonably homogeneous over a region larger than the diameter of the tube. The diameter of the poles and the gap between them should be of the order of 4 to 7 cm and 1.5 to 2.5 cm. The gap may be increased to 3 to 4 cm if other accessories are to be used, particularly for the study at low temperatures. Liquid nitrogen (-195.8°C) or solid carbon dioxide in acetone (-78.5°C) is used as low temperature bath. The temperature is measured by means of a thermo-couple-potentiometer arrangement. An electromagnet with a regulated power supply is most convenient for obtaining the weights of the specimen in the presence and absence of the field. However, a permanent magnet is less expensive but special arrangements have to be made for making the no field measurements.

A conventional analytical balance or semi-micro Mettler balance is most suitable for measuring the weight change of the specimen in the field off and on. The balance is mounted on a sturdy table over the magnet. The Gouy tube is suspended by a non-magnetic wire, *e.g.*, quartz fibre. Provision should be made for moving a thermometer near the specimen tube.

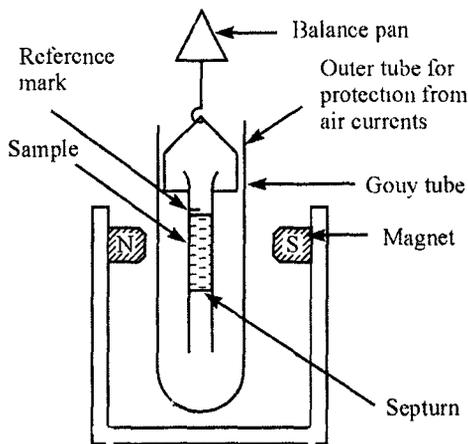


Fig. 1

When the specimen in the Gouy tube is suspended between the poles of the magnet, it experiences a force in the vertical direction with the magnetic field, in addition to the downward gravitational force. This downward force on the tube is given by,

$$F = \frac{1}{2} (\kappa_1 - \kappa_2) (H_x^2 - H_y^2) A + \delta \quad \dots (13)$$

where κ_1 and κ_2 are the volume susceptibilities of the specimen and air respectively, H_x and H_y are the field strengths at the lower end (septum) and the upper end (fixed mark) of the sample, and A is the cross-sectional area of the specimen. The Gouy tube itself acts as a hollow specimen and since it is made of diamagnetic material, a negative force is always acted upon it. A correction term, δ accounts for this small force acting in upward direction, κ_2 is a constant (0.029×10^{-6} c.g.s units cm^{-3}) and the factor $(H_x^2 - H_y^2) A$ is also a constant for a specimen of constant length and cross-section.

The density of the specimen is expressed as w/v (w and v being the mass and volume of the specimen), equation (13) can be written in the form

$$10^6 \chi = \frac{\alpha + \beta F'}{w} \quad \dots (14)$$

where α and β are constants, characteristic of the Gouy tube used; α is equal to $0.029 \times$ volume of the specimen. F' denotes the net force due to the magnetic field on the specimen of mass w and is equal to the difference in the mass of the specimen in the presence and absence of the magnetic field less δ . The correction term δ is equal to the difference of the masses of the empty Gouy tube in the presence and absence of the field.

The calibration term is determined using a material of known susceptibility. Once the constants α and β are known, the value of χ for the paramagnetic substance under examination can be calculated using equation (14). The most commonly used standard in the solid state is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ which has the susceptibility of 5.92×10^6 c.g.s. units at 293.15K. An aqueous solution of nickel chloride (about 30% NiCl_2 by weight) is a convenient reference sample for measuring the susceptibility of solution. The weight susceptibility of an aqueous nickel chloride solution is given by the equation,

$$10^6 \chi = \frac{10030}{T} \cdot \frac{p}{100} - 9.72 \left(1 - \frac{p}{100} \right) \quad \dots (15)$$

where p is the weight percent of nickel chloride in solution.

(3) Quincke's method : The principle of this method is the same as that of Gouy's method. This method is used in the case of liquids. The liquid substance is contained in a U-shaped tube, one limb being wide and the other narrow. The latter is placed between the poles of an electromagnet with the surface of the liquid in the uniform portion of the field, and the change in the level h with the field is determined. It can be shown that the hydrostatic pressure developed is given by,

$$h\rho g = \frac{1}{2} (\kappa_1 - \kappa_2) H^2 \quad \dots (16)$$

where κ_1 and κ_2 are the volume susceptibilities of the liquid and the gas above it.

EXPERIMENT No. 2

Object : *To determine the magnetic susceptibility of Mohr's salt at room temperature and also calculate its magnetic moment.*

Apparatus and Chemicals : Gouy balance with accessories, Gouy tube meant for solid samples (a flat bottom tube with no septum is useful), copper sulphate (A.R. grade) as a standard and Mohr's salt.

Theory : Ferrous salts have four $3d$ -unpaired electrons and, therefore, possess high magnetic susceptibility and moment. The effective magnetic moment of Fe. (II) salts varies between 5.1–5.55 BM. This shows that there is some orbital contribution to spin only value of 4.90 BM.

Procedure : Clean thoroughly the Gouy tube, dry and suspend it from the pan of the balance between the poles of the electromagnet as already described. Determine the weight of the tube both in the absence and presence of magnetic field, *i.e.*, when the electromagnet is off and on.

Grind some A.R. grade copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in a mortar to a fine powder. Transfer a small amount, about 20 mg of the powder to the Gouy tube and tap its bottom firmly against a wooden surface several times so as to shake the powder down. Go on adding the powder in small amounts and tapping in the same way to fill the tube upto the mark. The amount added and the number of tappings must be fixed. The packing technique is very important, for in the Gouy's method the specimen column is treated as a rod of uniform cross-section and density. When the tube is filled upto the mark, determine the weight both in the absence and presence of the magnetic field.

Remove the contents from the tube by careful scrapping with a steel pin, wash it thoroughly with distilled water and dry. Fill it upto the mark with finely powdered Mohr's salt in the same way as done with the standard, and determine its weight both in the absence and presence of the magnetic field.

Again empty the tube, wash thoroughly with distilled water and dry. Fill it upto the mark with air free distilled water (previously boiled and cooled), and take the weight in the absence of the magnetic field. The difference of this weight and that of the Gouy tube in the absence of the field gives the weight of water filled in upto the mark. Dividing this weight with the density of water at the temperature of the experiment, we can calculate the volume of the specimen.

Observations :

- | | |
|--|-----------|
| (1) Weight of empty Gouy tube, field off | = w_1 g |
| (2) Weight of empty Gouy tube, field on | = w_2 g |
| (3) Weight of Gouy tube + copper sulphate, field off | = w_3 g |
| (4) Weight of Gouy tube + copper sulphate, field on | = w_4 g |
| (5) Weight of Gouy tube + Mohr's salt, field off | = w_5 g |
| (6) Weight of Gouy tube + Mohr's salt, field on | = w_6 g |
| (7) Weight of Gouy tube filled with water | = w_7 g |
| (8) Temperature of experiment | = TK |
| (9) Radius of Gouy tube | = r cm |

Calculations :

Specific volume, $V =$ Volume of water in Gouy tube upto the mark $-$ Volume of water in the meniscus.

$$= (w_7 - w_1) \times \rho - \frac{1}{3} \pi r^3$$

where ρ is the density of water at the temperature of experiment.

For the calculation of the calibration constants α and β of the Gouy tube, we proceed as follows :

$$\delta = (w_2 - w_1) \times 10^2 \text{ mg}$$

$$\begin{aligned} F' \text{ with copper sulphate} &= (w_4 - w_3) \times 10^3 - \delta \\ &= \{(w_4 - w_3) - (w_2 - w_1)\} \times 10^3 \text{ mg} \\ &= (w_1 + w_4 - w_2 - w_3) \times 10^3 \text{ mg} \end{aligned}$$

$$w \text{ for copper sulphate} = (w_3 - w_1) \text{ g}$$

$$\alpha \text{ for copper sulphate} = 0.029V = 0.029 \left\{ (w_7 - w_1) \rho - \frac{1}{3} \pi r^3 \right\}$$

$$10^6 \chi \text{ for } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 5.92 \text{ cgs units}$$

From equation (14) calculate the constant β as follows :

$$\begin{aligned} 10^6 \chi &= 5.92 = \frac{\alpha + \beta F'}{w} \\ &= \frac{0.029 \left\{ (w_7 - w_1) \rho - \frac{1}{3} \pi r^3 \right\} + \beta (w_1 + w_4 - w_2 - w_3) \times 10^3}{w_3 - w_1} \end{aligned}$$

It should be noted that by convention α , F' and δ are expressed in mg and w in g.

Evaluating the values of the constant α and β for the Gouy's tube, the magnetic susceptibility for the Mohr's salt can be calculated as follows :

$$\begin{aligned} F' \text{ with Mohr's salt} &= (w_6 - w_5) \times 10^3 - \delta \text{ mg} \\ &= \{(w_6 - w_5) - (w_2 - w_1)\} \times 10^3 \text{ mg} \\ &= (w_1 + w_6 - w_2 - w_5) \times 10^3 \text{ mg} \end{aligned}$$

$$w \text{ for Mohr's salt} = (w_5 - w_1) \text{ g}$$

From equation (14), we have

$$\begin{aligned} 10^6 \chi &= \frac{\alpha + \beta F'}{w} \\ &= \frac{0.029 \left\{ (w_7 - w_1) \rho - \frac{1}{3} \pi r^3 \right\} + \beta (w_1 + w_6 - w_2 - w_5) \times 10^3}{w_5 - w_1} \end{aligned}$$

Thus χ for Mohr's salt can be calculated.

Then, $\chi_M = 392.14 \chi$, where 392.14 is the molecular weight of Mohr's salt.

From equation (9) the effective magnetic moment of the salt is calculated as,

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M} \text{ T B.M.}$$

Precautions : (i) Remove your watch while working near the magnet

(ii) Keep the steel and tools away from the magnet.

= ...



EQUILIBRIUM AND DISSOCIATION CONSTANTS

[I] REVERSIBLE REACTIONS

Several reactions do not go to completion. The reactants do not transform completely into the products even if taken in stoichiometric proportions and the reaction comes to a standstill. In such reactions, called *reversible reactions*, the products too tend to react to give back the reactants. In a state of chemical equilibrium, the rates of forward and reverse reactions are equal.

Consider the following reversible reaction :



The rate of forward reaction = $k_f [A]^a [B]^b$

and Rate of backward reaction = $k_b [C]^c [D]^d$

where k_f and k_b are the velocity constants of the forward and backward reactions, and species in square brackets are the respective active masses, referred to the equilibrium state. At equilibrium (when the reaction reaches standstill) the two rates are equal. Therefore,

$$\frac{k_f}{k_b} = K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots (1)$$

where K , the ratio of rate constants of the forward and backward reactions, is called the **equilibrium constant** of the reversible reaction. The value of K gives the extent of the reaction. Thus, if K is known, the position of equilibrium and so the amounts of the products, may be calculated for any initial concentration of the reactants.

For gaseous reactions the active masses may be expressed in several ways : (i) Partial pressures (atm) giving K_p , (ii) molar concentrations ($c \text{ mol dm}^{-3}$) giving K_c and (iii) activities (a) giving K_{therm}

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \quad \dots (2)$$

$$K_c = \frac{C_C^c C_D^d}{C_A^a C_B^b} \quad \dots (3)$$

$$K_{therm} = \frac{a_C^c a_D^d}{a_A^a a_B^b} = \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \cdot \frac{C_C^c C_D^d}{C_A^a C_B^b} = K_c \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \quad \dots (4)$$

where γ represents the activity coefficients of various species involved in the reaction.

[II] EQUILIBRIUM CONSTANT AND STANDARD FREE ENERGY CHANGE

van't Hoff reaction isotherm gives the relation between the free energy change (ΔG) and the equilibrium constant as :

$$\Delta G = -RT \ln K + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad \dots (5)$$

where a 's are the arbitrary activities of various species. If all the substances are present in their standard states. (i.e. activities are unity), then equation (5) becomes :

$$\Delta G^\circ = -RT \ln K = -2.303 RT \log K$$

Processes occurring at constant temperature and pressure will be spontaneous if $(\Delta G)_{T,P}$ is negative. In a reversible reaction, small changes in both forward and reverse directions are possible. If $(dG)_{T,P}$ is negative in the forward direction, it will be positive for the reverse reaction. However, for the chemical equilibrium to reach, we have the only condition :

$$(dG)_{T,P} = 0 \quad \dots (7)$$

[III] EQUILIBRIUM CONSTANT AND ENTHALPY CHANGE (ΔH) OF THE REACTION

The change of equilibrium constant with temperature is given by the van't Hoff isochore, which is as follows :

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad \dots (8)$$

Separating the variables and integrating equation (8) and assuming ΔH to be independent of temperature over a small temperature range, we obtain.

$$\ln K = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \text{constant}$$

or

$$\log K = -\frac{\Delta H}{2.303R} \cdot \frac{1}{T} + \text{constant} \quad \dots (9)$$

If K_1 and K_2 are the values of equilibrium constants at two temperatures T_1 and T_2 , then we have

$$\log \frac{K_2}{K_1} = -\frac{\Delta H}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad \dots (10)$$

So, from the knowledge of variation of K with temperature, enthalpy change of the reaction (ΔH) can be calculated. A few other important applications of equilibrium constants may be mentioned as follows :

(i) The pK (or $-\log K$) values of weak acids and bases determine the pH range of buffer solutions.

(ii) The correct choice of an indicator in acid-base titration depends on the knowledge of ionization constant of the indicator.

(iii) The value of equilibrium constant of the reaction in redox titrations permits the correct choice of a titrating reagent for a given oxidising or reducing agent.

[IV] DETERMINATION OF EQUILIBRIUM CONSTANTS

Four different types of methods are used for the determination of equilibrium constants. These are : (1) chemical, (2) conductometric, (3) potentiometric and (4)

optical methods. The choice of a method depends upon the particular system to be studied. In this chapter we have described only the chemical methods. Other methods have been discussed in chapters dealing with conductance, optical and potentiometric measurements.

Amongst the chemical methods, the reactants are first mixed and after the equilibrium is established, the resulting system is analysed. Analysis of the equilibrium mixture may be carried out using two different techniques *viz.*, (a) a straight chemical reaction and (b) partition or distribution between two immiscible liquids.

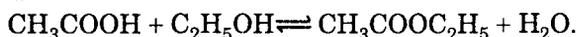
EXPERIMENT No. 1

Object : *To determine the equilibrium constant of the esterification reaction between acetic acid and ethanol.*

Apparatus and Chemicals : 5 Glass stoppered bottles, graduated pipettes (or 1, 2, and 5 cm³ pipettes), 1 dm³ standard 0.5 M sodium hydroxide solution, 100 cm³ of 3 M hydrochloric acid solution, glacial acetic acid, absolute ethanol, ethyl acetate and phenolphthalein indicator.

Theory : An acid and alcohol react to form ester and water, whereas the ester hydrolyses to give back the acid and alcohol. At equilibrium, the two reactions proceed with equal rate. As the equilibrium state is reached very slowly, hydrochloric acid is used to catalyse the reaction and hastens the equilibrium state to be attained.

The equilibrium constant of the reaction



is given by,

$$K = \frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acid}} \times C_{\text{alcohol}}} \quad \dots (1)$$

where *C* terms are the molar concentrations referred to the equilibrium state.

Procedure : Prepare the following mixtures in glass stoppered bottles numbering 1 to 5.

Bottle No.	Volume of 3M HCl (cm ³)	Volume of ethyl acetate (cm ³)	Volume of water (cm ³)	Volume of ethanol (cm ³)	Volume of acetic acid (cm ³)
1	5	0	5	0	0
2	5	5	0	0	0
3	5	4	1	0	0
4	5	4	0	1	0
5	5	4	0	0	1

Stopper the bottles, shake and allow them to stand for a couple of days on the working bench so that equilibrium is established.

Titrate the contents of each bottle with the standard sodium hydroxide solution using phenolphthalein as an indicator.

By means of a pipette take 5 cm^3 of $3M$ hydrochloric acid solution, 5 and 4 cm^3 of ethyl acetate, 1 and 5 cm^3 of water and 1 cm^3 of each of ethanol and acetic acid in separate accurately weighed stoppered small bottles. Weigh the bottles again and determine the weights of each substance mixed in each of the bottles.

Calculations : The initial weights of ester in bottles 2 to 5, water in bottle 3, absolute ethanol in bottle 4 and acetic acid in bottle 5 are known from the direct weighings. Calculate the weight of HCl in each bottle from the titre of sodium hydroxide solution with the contents of bottle 1. If $V_1 \text{ cm}^3$ is the titre for bottle 1, then weight of HCl present in 5 cm^3 of $3 M$ solution = $0.5 V_1 \times 36.5 \times 10^{-3} \text{ g}$

Weight of water in 5 cm^3 of M HCl solution = Weight of solution -- Weight of HCl

So, weight of water initially present in each bottle

= Weight of water placed + Weight of water in 5 cm^3 of $3 M$ HCl

Subtract the titre of NaOH solution for bottle 1 from those for bottles 2 to 5 and calculate the amount of acetic acid in these bottles. If V_2, V_3 and $V_4 \text{ cm}^3$ are the titres of NaOH solution for bottles 2 to 4, then weight of acetic acid formed due to hydrolysis of the ester in respective bottles is :

$$\frac{(V_2 - V_1) \times 0.5 \times 60}{1000}, \frac{(V_3 - V_1) \times 0.5 \times 60}{1000} \quad \text{and} \quad \frac{(V_4 - V_1) \times 0.5 \times 60}{1000} \text{ g}$$

The weight of acetic acid present in bottle 5

$$= \frac{(V_5 - V_1) \times 0.5 \times 60}{1000} \text{ g}$$

where V_5 is the titre of NaOH solution for bottle 5.

Therefore, the weight of acetic acid formed in bottle 5

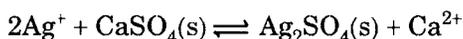
$$= \frac{(V_5 - V_1) \times 0.5 \times 60}{1000} - \text{weight of } 1 \text{ cm}^3 \text{ of } \text{CH}_3\text{COOH}$$

For each mole of acetic acid, 1 mole of ethanol is produced and 1 mole each of water and ester disappears. Calculate the number of moles of each substance in the initial mixture and then the final number at the equilibrium in bottles 2 to 5. Assuming the final volume of the resulting mixture to be 10 cm^3 (which is not strictly true), calculate the concentration (mol dm^{-3}) of each substance at equilibrium. Then, calculate K for the systems in bottles 2 to 5 with the help of equation (1) and take the mean value.

Result : The mean value of equilibrium constant = ...

EXPERIMENT No. 2

Object : To determine the equilibrium constant of the following reversible reaction :



Apparatus and Chemicals : 5 Glass stoppered bottles, sintered glass crucible, Thermostat, standard 0.3 M silver nitrate, 0.1 M ammonium oxalate, 0.1 M ammonium thiocyanate, 0.02 M potassium permanganate, about 0.25 M solution of each of calcium nitrate and potassium sulphate, saturated solution of ferric ammonium sulphate as indicator.

Theory : The equilibrium constant of the reaction is given by

$$K = \frac{C_{\text{Ca}^{2+}}^2}{C_{\text{Ag}^+}^2} \dots (1)$$

The active masses of solid CaSO_4 and Ag_2SO_4 are each unity.

Different equilibrium mixtures are prepared by mixing solutions of silver and calcium nitrate and then partially precipitating the Ag^+ and Ca^{2+} ions as sulphates. At equilibrium, Ag^+ ion concentration is determined by titration with a standard ammonium thiocyanate solution. The total concentration of Ag^+ and Ca^{2+} ions is determined by adding an excess of standard ammonium oxalate solution (whereby both Ag^+ and Ca^{2+} ions get precipitated as oxalates) and back titrating with a standard potassium permanganate solution. Subtraction of the concentration of Ag^+ from the total of Ag^+ and Ca^{2+} ions gives the concentration of Ca^{2+} ions.

Procedure : Prepare the following mixtures in four glass stoppered bottles numbered as 1 to 4.

Bottle No.	Volume of AgNO_3 (cm^3)	Volume of $\text{Ca}(\text{NO}_3)_2$ (cm^3)	Volume of K_2SO_4 (cm^3)
1	25	25	20
2	25	25	25
3	25	25	30
4	25	25	35

Add a very small amount of a mixture of silver and calcium sulphate to each of these solutions so as to initiate the precipitation of silver and calcium sulphates.

Stopper the bottles, shake the mixtures vigorously for nearly 10-15 min and suspend them in a thermostat at 25°C (or simply allow them to stand on the working table). Shake the mixtures periodically for nearly 2-3 hours.

Filter the contents of each bottle through a sintered glass crucible (No. 3) in separate bottles.

Transfer 20 cm^3 of the filtrate from each bottle into a conical flask and titrate with the standard ammonium thiocyanate solution using ferric ammonium sulphate solution as an indicator. The end point is indicated by the appearance of light brown colour of the solution which does not disappear on vigorous shaking. Repeat the determination. This gives the concentration of Ag^+ ions.

Place another 20 cm^3 of the filtrate in a beaker, dilute it with about equal volume of water and heat the contents to about $70-80^\circ\text{C}$. Slowly add 20 cm^3 of ammonium oxalate solution with constant stirring. Both Ag^+ and Ca^{2+} ions get

precipitated as oxalates. Cool the contents and filter through the sintered crucible; wash the precipitate with a little cold water and collect the washings along with the filtrate. Titrate this filtrate with the standard potassium permanganate solution in acidic medium till a light purple colour is obtained. This gives the end point.

Calculations : Let $V \text{ cm}^3$ be the titre of ammonium thiocyanate solution for 20 cm^3 of the filtrate.

$$\therefore \text{Moles of } \text{Ag}^+ \text{ ions in } 20 \text{ cm}^3 \text{ of filtrate} = 0.1 \times V \times 10^{-3}$$

If $V' \text{ cm}^3$ is the titre of potassium permanganate solution ($0.02M = 0.02 \times 5 = 0.1 N$) for back titration, then moles of ammonium oxalate used up for precipitation of Ag^+ and Ca^{2+} ions

$$\begin{aligned} &= 20 \times 0.1 \times 10^{-3} - \frac{1}{2} \times 0.02 \times 5 \times V' \times 10^{-3} \\ &= 2 \times 10^{-3} - 0.05 V' \times 10^{-3} \end{aligned}$$

Moles of ammonium oxalate reacted with Ag^+

$$\begin{aligned} &= \frac{1}{2} \times 0.1 V \times 10^{-3} \\ &= 0.05 V \times 10^{-3} \end{aligned}$$

Moles of ammonium oxalate reacted with Ca^{2+} ions

$$\begin{aligned} &= 2 \times 10^{-3} - 0.05 V' \times 10^{-3} - 0.05 V \times 10^{-3} \\ &= (2 - 0.05 V' - 0.05 V) \times 10^{-3} \end{aligned}$$

\therefore Moles of Ca^{2+} ions in 20 cm^3 of filtrate

$$= (2 - 0.05 V - 0.05 V') \times 10^{-3}$$

Concentration of Ag^+ ions

$$= \frac{0.1 \times V \times 10^{-3}}{20} \times 10^3 = 0.005 V \text{ mol dm}^{-3}$$

Concentration of Ca^{2+} ions

$$\begin{aligned} &= \frac{(2 - 0.05 V' - 0.05 V)}{20} \times 10^{-3} \times 10^3 \\ &= \frac{2 - 0.05 V' - 0.05 V}{20} \text{ mol dm}^{-3} \end{aligned}$$

Substitute the values of molar concentration of Ag^+ and Ca^{2+} ions in each of the mixtures in equation (1) and calculate the equilibrium constant. Report the mean value.

Result : The equilibrium constant for the given reaction = ...

EXPERIMENT No. 3

Object : To determine the equilibrium constant of the keto-enol tautomerism of ethyl acetoacetate.

changed into enol form and the latter is brominated. Then, add about 10 cm³ β-naphthol solution and 50 cm³ of potassium iodide solution, and allow the solution to stand for nearly 15 min. Titrate the liberated iodine with the standard sodium thiosulphate solution till the reddish-brown colour of iodine just disappears. Repeat the determination. From the titration values calculate the exact concentration of stock solution of ethyl acetoacetate.

By means of quantitative dilution of the stock solution, prepare 0.3, 0.2 and 0.1 M solution of the ester in methanol. Transfer 200 cm³ each of 0.4, 0.3, 0.2 and 0.1 M solutions of the ester in four glass stoppered bottles numbered as 1 to 4 and suspend them in a thermostat at 25°C (for room temperature, the bottles can be placed on the working table) for about 1 hr, and shake them periodically.

Transfer 50 cm³ of the solution from bottle 1 into a conical flask (500 cm³) and 50 cm³ of 0.1 M bromine solution, shake and immediately add 10 cm³ of β-naphthol solution. For making the additions quick, use measuring cylinders. Then, add 50 cm³ of potassium iodide solution and dilute hydrochloric acid, shake and allow to stand for nearly 15 min. Titrate the liberated iodine with a standard sodium thiosulphate solution till a colourless end point is obtained. Starch cannot be used as an end indicator as the high concentration of methanol prevents development of blue colour. Repeat the determination.

Similarly, make the determinations (in duplicate) transferring 50 cm³ of aliquot of the solutions from other bottles. For bromination of the enol form, add 50 cm³ of 0.1 M bromine solution to 0.3 and 0.2 M ester solution, and 25 cm³ to 0.1 M ester solution.

Calculations : Chemistry of various reactions reveals that

2 moles of Na₂S₂O₃ ≡ 1 mole of iodine ≡ 1 mole of ester (enol form)

From titres of sodium thiosulphate, calculate the concentration of the enol form of ester in each mixture. Subtract this concentration from the total concentration of ester to obtain the concentration of the keto form. Then, calculate for each solution and take the mean.

$$K = C_{enol}/C_{keto}$$

Result : The mean value of equilibrium constant =

EXPERIMENT No. 4

Object : *To determine the dissociation constant of picric acid by studying its distribution between benzene and water.*

Apparatus and Chemicals : 4 Glass stoppered bottles, thermostat, picric acid, benzene, standard 0.02 M sodium hydroxide solution, phenolphthalein indicator.

Theory : Picric acid (a weak acid) undergoes ionization in its aqueous solution as :



(For the sake of brevity, picric acid is represented as HP and picrate ion as P⁻)

The dissociation constant of picric acid is given by

$$K_c = [\text{H}_3\text{O}^+][\text{P}^-]/[\text{HP}]_W = [\text{P}^-]^2/[\text{HP}]_W \quad \dots (1)$$

Although the acid is weak but it is strong enough to neglect H_3O^+ ions given by ionization of water.

Picric acid exists in the normal form (unionized or unassociated) in benzene and in both the normal and ionized forms in water. The distribution law is applicable to the normal form (common to both the liquids). So, the distribution coefficient of the acid between benzene and water is given by,

$$D = [\text{HP}]_B/[\text{HP}]_W \quad \dots (2)$$

where the subscripts B and W refer to the benzene and water phases, respectively.

Procedure : Prepare about 250 cm³ of saturated solution of picric acid in water. Then, prepare the following mixtures in glass stoppered bottles.

Bottle No.	Volume of saturated solution of picric acid (cm ³)	Volume of water (cm ³)	Volume of benzene (cm ³)
1	100	0	50
2	50	0	50
3	50	25	50
4	50	50	50

All volumes can be measured by measuring cylinders.

Stopper the bottles and suspend them in a thermostat at 25°C for nearly 20 minutes, shake periodically.

By means of a pipette, remove 20 cm³ of aqueous layer (lower layer) from each bottle, avoiding contamination of benzene layer and transfer it to a conical flask. Titrate the solution with a standard sodium hydroxide solution using phenolphthalein as an indicator. A colour change from greenish yellow to orange yellow shows the end point. Make duplicate determination for each bottle.

Similarly, withdraw 10 cm³ of benzene layer from each bottle and titrate the acid with the standard alkali solution to the same end point. The contents should be vigorously shaken during the titration so as to extract the acid into the aqueous solution. Repeat the determination.

Calculations : Suppose C_B and C_W are the concentrations of picric acid in benzene and water layers. In aqueous layer the total concentration of the acid is made up of undissociated molecules (HP) and the dissociated ones (Picrate ions, P^-) Therefore,

$$C_W = [\text{HP}]_W + [\text{P}^-] \quad \dots (3)$$

or,
$$[\text{P}^-] = C_W - [\text{HP}]_W \quad \dots (4)$$

From equation (2)

$$[\text{HP}]_W = [\text{HP}]_B/D = C_B/D \quad \dots (5)$$

Combining equations (4) and (5)

$$[P^-] = (C_W - C_B)/D \quad \dots (6)$$

Equations (1) and (6) give,

$$K_c = \frac{[(C_W - C_B)/D]^2}{C_B/D} = \frac{[(C_W' - C_B')/D]^2}{C_B'/D} \quad \dots (7)$$

Using C_W' and C_B' as the molar concentrations of the acid in water and benzene layers, respectively in bottle 2.

From equation (7), we have

$$(C_W - C_B)/D = \sqrt{\frac{C_B}{C_B'}} \cdot [(C_W' - C_B')/D] \quad \dots (8)$$

Using C_B 's and C_W 's for pairs of the mixtures, calculate the values of distribution coefficient, D and take the mean value. Then, calculate K_a for each set of concentration from different bottles using equation (8) and take the average value.

Result : The average value of distribution coefficient = ...



In factories and other places, gas mixtures used as fuels or flue or chimney gases obtained as products of combustion, are required to be analysed. Orsat apparatus, most commonly used in such analysis, is described in the following experiment.

EXPERIMENT No. 1

Object : *To determine carbon dioxide, carbon monoxide, oxygen and nitrogen in the sample of flue gas provided to you, using a simple Orsat set up.*

Theory : The different gases present in the gas mixture can be separately absorbed in different absorbers. For quantitative estimation, a known volume of the gas mixture is taken. Its volume at the surrounding temperature and atmospheric pressure is measured. After each absorption of a component, the volume of the residual gas is measured again. The following absorbers are used :

- (i) Concentrated solution of KOH for CO_2 .
- (ii) Ammonical solution of cuprous chloride for CO.
- (iii) Alkaline pyrogallol solution for O_2 .

Nitrogen is left behind as an inert constituent as it does not react with any of the absorbing solutions.

Preparation of Solutions

(1) Concentrated KOH solution* : 50% KOH solution is used. Dissolve 125 g of KOH sticks or drops in sufficient water to make 250 ml of the solution. Use hot distilled water and cool the solution before making up the volume. Cork and keep the solution air tight. 1 ml of this solution can absorb about 40 ml of CO_2 at room temperature.

(2) Alkaline pyrogallol solution : Dissolve 50 g of KOH in 100 ml of distilled water. Dissolve 15 g of pyrogallol (pyrogallic acid) in 30 ml of distilled water. Mix the two solutions just before use. (As this alkaline solution quickly absorbs O_2 from air, the solution is not prepared and kept). For keeping, all precautions are to be taken to avoid its contact with air.

*KOH is preferred to NaOH due to its greater solubility and greater solubility of K_2CO_3 than Na_2CO_3 .

(3) **Ammonical cuprous chloride solution** : Dissolve 32 g of NH_4Cl in 100 ml of distilled water. Add about 32 g of cuprous chloride and then add 35 ml of ammonia solution (density = 0.9). Shake thoroughly to dissolve cuprous chloride. A few copper turnings are kept in the solution to avoid oxidation by air. Keep the solution in a well corked bottle.

Orsat Apparatus. The apparatus is shown in fig. (1). The important parts of the apparatus are as follows :

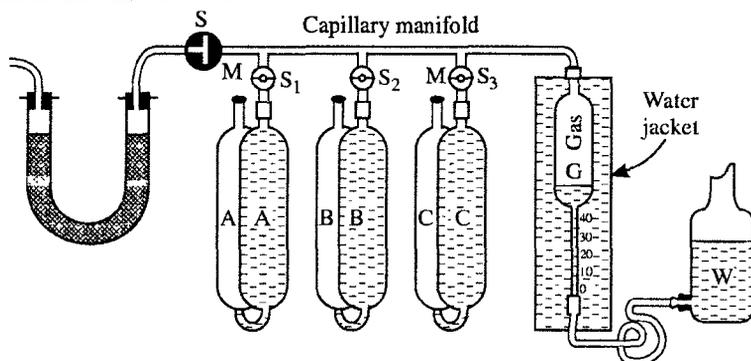


Fig. 1 : Orsat apparatus

(1) **Water cooled gas reservoir or gas burette G** : It is a graduated bulb of 50 to 100 ml capacity. On one side it is connected to a water reservoir bottle W, using a flexible rubber or polythene tube and on the other side to a manifold MM of gas pipettes A, B, C, etc. These are joined separately to a common capillary bore tube.

(2) **Water bottle W** : It contains enough water to push out the complete gas in G. The water is coloured with some dye like methyl orange or methyl red to make its level visible.

(3) **Capillary manifold MM** : The capillary tube carries a number of gas pipettes joined to it through independent stop-cocks. At the end of the capillary tube there is a three-way stop-cock S. It can connect the manifold to atmosphere or to the source of gas through a U-tube filled with glass wool for filtering the gas to be free of solid particles.

(4) **Gas pipettes A, B and C etc.** : Each pipette consists of two bulbs of equal volume connected by a U-bend tube at the bottom. One of these bulbs is fitted with glass tubes to provide better contact of gas with absorbing solution. The absorbing solution is kept in the other bulb. The free ends of pipettes are closed with rubber stoppers.

Procedure : First grease all stop cocks. Now circulate water at constant temperature in the water jacket of gas burette. Fill the water bottle W upto two-thirds with coloured water. Open stop-cock S to air. Open stop cock S_1 and remove the rubber cork on the back bulb of pipette A. Pour KOH solution into it to fill both bulbs to slightly more than half level. Now insert the rubber cork and close stop-cock S_1 . In a similar way, fill the alkaline pyrogallol solution into pipette B and ammonical cuprous chloride solution into C. Close the stop cock S.

Removal of air from the apparatus : Open the stop-cock S to air. Lift water bottle W so that water flows into the gas burette G to fill it completely. Close S

and place the bottle W on the table. Open S_1 slowly. Water flows from the gas burette G into bottle W. Air in pipette A is sucked into G and KOH solution rises in the front bulb carrying glass tubes. As soon as the solution reaches stop-cock S_1 , it is closed. Air from G is expelled to atmosphere as in the first step. In similar steps remove air from pipettes B and C also.

(a) *Checking of air-tightness of apparatus.* Remove the air from the gas burette by opening S to air and filling it with water from W. Close S and place bottle W on the table. Mark the level of water in the gas burette. This level should not fall in five to ten minutes.

(b) *Filling of gas sample into gas burette G.* Connect the source of gas to U-tube. Connect the U-tube to air by stopcock S, and run the gas for a few minutes. This expels air from the U-tube. Turn stopcock S to connect U-tube to gas burette and at the same time lift water bottle up to keep the level of water in G and W equal. Lower W slowly and allow the gas to fill into the gas burette. Close S when sufficient gas has been drawn into the gas burette. Wait for nearly 15 minutes. During this time the gas acquires the temperature of water in the jacket. Make level of water in W and G equal and read and note the volume (V_1) of the gas. Record the temperature of water in the jacket as well as the barometric pressure.

If greater precision is required, the first filling of gas in the gas burette may be expelled to air and a second filling may be used for analysis.

(c) *Analysis of gas.* Open stop-cock S_1 , lift the water bottle to move the gas from G to A. When front bulb of A is filled with gas, start lowering the bottle W to take the gas back into G. To and fro slow movement of gas between G and A should be repeated five times or more. This helps in the absorption of CO_2 . In the end, allow the solution in A to rise back to its initial level or upto stop-cock S_1 and take all the residual gas into G.

Allow the gas in G to have the temperature of water in the jacket (about five minutes). Equalise the water level in G and W and read and note the gas volume.

Transfer gas to A and back several times again. Take the gas back into G and measure the gas volume as before after allowing the temperature to become constant. If this volume reading is less than in the previous case, more gas has been absorbed by KOH solution. Repeat transfer of gas between G and A till no more gas is absorbed. Record the final volume of residual gas, V_2 .

Observations and Calculations : Suppose :

Initial volume of gas = V_1 ml

Volume of gas after absorption in KOH solution = V_2 ml

Volume of CO_2 = $(V_1 - V_2)$ ml

Repeat the experiment for absorption of O_2 in alkaline pyrogallol solution in gas pipette B. Let the final volume of residual gas be V_3 ml.

Volume of oxygen = $(V_2 - V_3)$ ml

Repeat for absorption of CO gas in ammonical cuprous chloride solution in gas pipette C and record the final volume of residual gas, V_4 .

$$\text{Volume of CO} = (V_2 - V_4) \text{ ml}$$

Report analysis as :

$$\text{Initial volume of gas} = V_1 \text{ ml}$$

$$\text{Volume of CO}_2 = (V_1 - V_2) \text{ ml}$$

$$\text{Volume of O}_2 = (V_2 - V_3) \text{ ml}$$

$$\text{Volume of CO} = (V_3 - V_4) \text{ ml}$$

$$\text{Residual gas} = V_4 \text{ ml}$$

As all gas volumes are measured at the same temperature and pressure, percentage of each gas can be easily calculated.

Percentages of :

$$(i) \quad \text{CO}_2 = \frac{V_1 - V_2}{V_1} \times 100$$

$$(ii) \quad \text{O}_2 = \frac{V_2 - V_3}{V_1} \times 100$$

$$(iii) \quad \text{CO} = \frac{V_3 - V_4}{V_1} \times 100$$

$$(iv) \quad \text{Residual gas} = \frac{V_4}{V_1} \times 100.$$

Residual gas in a flue gas is mostly nitrogen.



APPENDIX

Table 1. Concentration of Acids

Acid	Specific Gravity	Percent by Weight	Approximate Normality
HCl (conc.)	1.19	37.89	11 N
HCl (dil.)	—	—	5 N
H ₂ SO ₄ (conc.)	1.84	96.01	36 N
H ₂ SO ₄ (dil.)	—	—	5 N
HNO ₃ (conc.)	1.41	69.80	16 N
HNO ₃ (dil.)	—	—	5 N
CH ₃ COOH (conc.)	1.06	99.51	17 N
CH ₃ COOH (dil.)	—	—	5 N

Table 2. Atomic Number and Atomic Weight of Elements

Atomic Number	Element	Symbol	Atomic Weight (C = 12.000)
1	Hydrogen	H	1.008
2	Helium	He	4.003
3	Lithium	Li	6.940
4	Beryllium	Be	9.013
5	Boron	B	10.82
6	Carbon	C	12.0000
7	Nitrogen	N	14.008
8	Oxygen	O	15.998
9	Fluorine	F	19.000
10	Neon	Ne	20.183
11	Sodium	Na	22.991
12	Magnesium	Mg	24.32
13	Aluminium	Al	26.98
14	Silicon	Si	28.09
15	Phosphorous	P	30.975

Atomic Number	Element	Symbol	Atomic Weight (C = 12.000)
16	Sulphur	S	32.066
17	Chlorine	Cl	35.457
18	Argon	A	39.944
19	Potassium	K	39.100
20	Calcium	Ca	30.08
21	Scandium	Sc	44.96
22	Titanium	Ti	47.90
23	Vanadium	V	50.94
24	Chromium	Cr	52.01
25	Manganese	Mn	54.93
26	Iron	Fe	55.85
27	Cobalt	Co	58.71
28	Nickel	Ni	58.71
29	Copper	Cu	63.54
30	Zinc	Zn	65.38
31	Gallium	Ga	69.72
32	Germanium	Ge	72.60
33	Arsenic	As	74.91
34	Selenium	Se	78.96
35	Bromine	Br	79.916
36	Krypton	Kr	83.80
37	Rubidium	Rb	85.48
38	Strontium	Sr	87.63
39	Yttrium	Y	88.63
40	Zirconium	Zr	91.22
41	Columbium	Cb	—
	Niobium	Nb	92.91
42	Molybdenum	Mo	95.95
43	Technetium	Tc	[99]
44	Ruthenium	Ru	101.7
45	Rhodium	Rh	102.91
46	Palladium	Pd	106.4
47	Silver	Ag	107.880
48	Cadmium	Cd	112.41
49	Indium	In	114.82
50	Tin	Sn	118.70
51	Antimony	Sb	121.76

52	Tellurium	Te	127.61
53	Iodine	I	126.91
54	Xenon	Xe	131.3
55	Caesium	Cs	132.91
56	Barium	Ba	137.36
57	Lanthanum	La	138.92
58	Cerium	Ce	140.13
59	Praseodymium	Pr	140.92
60	Neodymium	Nd	144.27
61	Promethium	Pm	[147]
62	Samarium	Sm	150.35
63	Europium	Eu	152.0
64	Gadolinium	Gd	157.26
65	Terbium	Tb	158.93
66	Dysprosium	Dy	162.51
67	Holmium	Ho	164.94
68	Erbium	Er	167.27
69	Thulium	Tm	168.94
70	Ytterbium	Yb	173.04
71	Lutecium	Lu	174.99
72	Hafnium	Hf	178.5
73	Tantalum	Ta	180.95
74	Wolfran (Tungsten)	W	183.86
75	Rhenium	Re	186.22
76	Osmium	Os	190.2
77	Iridium	Ir	192.2
78	Platinum	Pt	195.09
79	Gold	Au	197.0
80	Mercury	Hg	200.61
81	Thallium	Tl	204.39
82	Lead	Pb	207.21
83	Bismuth	Bi	209.00
84	Polonium	Po	[210]
85	Astatine	At	[210]
86	Radon	Rn	[222]
87	Francium	Fr	[223]
88	Radium	Ra	229.05
89	Actinium	Ac	227

90	Thorium	Th	232.05
91	Proactinium	Pa	231
92	Uranium	U	238.07
93	Neptunium	Np	[237]
94	Plutonium	Pu	[239]
95	Americium	Am	[241]
96	Curium	Cm	[242]
97	Berkelium	Bk	[243]
98	Californium	Cf	[244]
99	Einsteinium	E	[255]
100	Fermium	Fm	[255]
101	Mendelevium	Mv	[256]
102	Nobelium	No	[253]
103	Lawrencium	Lw	[257]
104	Kurchatovium	Kw	[258]

Note : Where no stable isotope is known the mass number of longest lived isotope has been bracketed in the column of atomic weight.

Table 3. Physical Constants of Liquids at 20°C

Liquid	Molecular Weight	Index of Refraction for D - Solution Line	Density (g/ml)
Acetic acid	60.05	1.3721	1.040
Aniline	93.12	1.5863	1.622
Acetone	58.08	1.3588	0.792
Benzene	78.11	1.5011	0.879
Carbon tetrachloride	153.84	1.4620 (15°)	1.595
Chloroform	119.39	1.4465 (18°)	1.4984 (15°)
Ethyl alcohol	46.07	1.3611	0.785 (25°)
<i>n</i> -Heptane	100.20	1.3876	0.6837
<i>n</i> -Hexane	86.19	1.3749	0.6603
Methyl alcohol	32.04	1.3288	0.7917
Toluene	92.13	1.4969	0.8669

Table 4. Transition Temperatures of Hydrates

Substance	Temperature (C°)
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$	32.10
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4$	32.40
$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$	19.73
$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CrO}_4 \cdot 7\text{H}_2\text{O}$	19.52
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O} \rightleftharpoons \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$	58.35
$\text{NaBr} \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{NaBr}$	50.69
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot 2\text{H}_2\text{O}$	61.37

Table 5. Dissociation Constants of Acids in Aqueous Solution at 25°C

Acid	Formula	Dissociation Constant
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2$	1.75×10^{-5}
Arsenic acid	H_3AsO_4	I 5.0×10^{-3}
		II 4.0×10^{-5}
		III 6.0×10^{-10}
Benzoic acid	$\text{C}_7\text{H}_6\text{O}_3$	6.3×10^{-6}
Boric acid	H_3BO_3	6.4×10^{-10}
Citric acid	$\text{C}_6\text{H}_8\text{O}_7$	I 8.4×10^{-4}
		II 1.8×10^{-5}
		III 4.0×10^{-6}
Formic acid	CH_2O_2	1.76×10^{-4}
Lactic acid	$\text{C}_3\text{H}_6\text{O}_3$	1.38×10^{-4}
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	I 6.5×10^{-2}
		II 6.1×10^{-5}
Phenol	$\text{C}_6\text{H}_6\text{O}$	1.3×10^{-10}
Salicylic acid	$\text{C}_7\text{H}_6\text{O}_3$	I 1.06×10^{-3}
		II 1.00×10^{-13}
Succinic acid	$\text{C}_4\text{H}_6\text{O}_4$	I 6.6×10^{-5}
		II 2.8×10^{-6}
Sulphuric acid	H_2SO_4	II 2×10^{-2} (18°)
Tartaric acid	$\text{C}_4\text{H}_6\text{O}_6$	I 1.1×10^{-3}
		II 6.9×10^{-5}
Chloroacetic acid	$\text{C}_2\text{H}_3\text{O}_2\text{Cl}$	1.5×10^{-8}
Dichloroacetic acid	$\text{C}_2\text{H}_2\text{O}_2\text{Cl}_2$	5×10^{-2}

Table 6. Solubility Product

Substance	Solubility product at given temperature	Substance	Solubility product at given temperature
Barium carbonate	7.0×10^{-9} (16°) 8.1×10^{-9} (25°)	Lithium carbonate	1.7×10^{-3} (25°)
Barium chromate	1.6×10^{10} (18°) 2.4×10^{-10} (28°)	Magnesium carbonate	2.6×10^{-5} (12°)
Barium oxalate (BaC ₂ O ₄ .2H ₂ O)	1.2×10^{-7} (18°)	Magnesium oxalate	8.57×10^{-5} (18°)
Barium sulphate	0.87×10^{-10} (18°)	Mercuric sulphide	4×10^{-53} to 2×10^{-49} (18°)
	1.08×10^{-10} (25°)	Mercurous chloride	2×10^{-18} (25°)
	1.98×10^{-10} (50°)		
Cadium sulphide	3.6×10^{-29} (18°)	Silver bromide	4.1×10^{-13} (18°) 7.7×10^{-13} (25°)
Calcium sulphate	6.11×10^{-5} (10°)	Silver chloride	1.50×10^{-10} (25°) 13.2×10^{-10} (50°)
Cuprous chloride	1.02×10^{-6} (18°)	Silver chromate	1.2×10^{-16} (15°) 9×10^{-12} (25°)
Lead carbonate	3.3×10^{-14} (18°)	Silver iodide	1.5×10^{-16} (15°)
Lead chromate	1.77×10^{-14} (18°)	Strontium carbonate	1.6×10^{-8} (25°)
Lead iodide	7.47×10^{-9} (15°) 1.39×10^{-8} (25°)	Zinc oxalate	1.35×10^{-9} (18°)

Table 7. Degree of Ionisation in Normal Solution at 18°C, Unless Indicated

Substance	Degree of ionisation	Substance	Degree of ionisation
Nitric acid	0.82	Tartaric acid (M/10)	0.082
Sulphuric acid	0.51	Acetic acid	0.004
Hydrochloric acid (N/2)	0.876 (25°)	Sodium hydroxide	0.73
Boric acid (M/10)	0.0001	Potassium hydroxide	0.77
Oxalic acid (M/10)	0.50	Ammonium hydroxide	0.004

Approximate degree of ionisation for active salts in 0.1N solution :

Type R^+R^- (e.g., NaNO_3) 0.86Type $(R^+)_2R^{2-}$ (e.g., K_2SO_4) 0.72Type $R^{2+}(R^-)_2$ (e.g., BaCl_2) 0.72Type $R^{2+}R^{2-}$ (e.g., CuSO_4) 0.45**Table 8. Ionic Conductance at Infinite Dilution**

Ion	0°	18°	25°	50°	100°
K	40.4	64.6	74.5	115	206
Na	26.1	43.5	50.9	82	155
NH_4	40.2	64.5	74.5	115	207
Ag	32.9	54.3	63.5	101	188
Cl	41.1	65.5	75.5	116	207
NO_3	40.4	61.7	70.6	104	178
H	240	314	250	465	644
OH	105	172	192	284	439
$\text{C}_2\text{H}_3\text{O}_2$	20.3	34.6	40.8	67	130
$\frac{1}{2}\text{Ba}$	33	55	65	104	200
$\frac{1}{2}\text{Ca}$	30	51	60	98	191
$\frac{1}{2}\text{SO}_4$	41	68	79	125	234
$\frac{1}{2}\text{C}_2\text{O}_4$	39	63	73	115	213
$\frac{1}{3}\text{La}$	35	61	72	119	235

Table 9. Specific Conductivity of KCl Solution

Temperature (°C)	N solution	N/10 solution	N/100 solution
0	0.06541	0.00715	0.000776
5	0.07414	0.00822	0.000896
10	0.08319	0.00933	0.001020
15	0.09252	0.01048	0.001447
20	0.10207	0.01167	0.001278
21	0.10400	0.01191	0.001305
22	0.10594	0.01215	0.001332
23	0.10789	0.01239	0.001359
24	0.10984	0.01264	0.001386
25	0.11180	0.01288	0.001413
26	0.11377	0.01315	0.001819
27	0.11574	0.01337	0.002873
28	0.01362	0.002927
29	0.01387	0.002981
30	0.01412	0.003036
35	0.01539

Table 10. Surface Tension of Liquids

Substance	°C	Surface tension	°C	Surface tension
Acetic acid	20	27.6	50	24.7
Acetone	20	23.7	50	18.6
Benzene	20	28.88	50	25.6
Carbon tetrachloride	20	26.8	50	23.1
Chlorobenzene	20	33.2	50	29.6
Chloroform	20	27.1	60	21.7
Cyclohexane	20	25.3
Ethyl acetate	20	23.9	50	20.2
Ethyl alcohol	20	22.3	50	19.8
Formic acid	20	18.4	40	16.3
<i>n</i> -Hexane	20	22.6	50	20.1
Methyl alcohol	20	28.4	50	25.0
Toluene	20	37.6	50	35.1

Table 11. Interfacial Tension at 20°C

Liquid	γ	Liquid	γ
Benzene-mercury	357	Water— <i>n</i> -Hexane	51.1
Ether-mercury	379	Water—Mercury	375
Water-Benzene	35	Water— <i>n</i> -Octane	50.8
Water—Carbon tetrachloride	45	Water—Ether	10.7

Table 12. Surface Tension of Water at Different Temperatures

Temperature (°C)	Surface tension (dyne/cm)	Temperature (°C)	Surface tension (dyne/cm)
0	75.6	30	71.18
5	74.9	40	69.56
10	74.22	50	67.91
15	73.49	60	66.18
18	73.05	70	64.4
20	72.75	80	62.6
25	71.97	100	58.9

Table 13. Viscosity of Liquids

Liquid	Viscosity (centipoise)	Liquid	Viscosity (centipoise)
Acetaldehyde	0.255 (10°) 0.22 (20°)	Chlorobenzene	0.719 (20°) 0.631 (40°)
Acetic acid	1.31 (5°) 1.155 (25°) 1.04 (30°)	Chloroform	0.58 (20°) 0.542 (25°) 0.514 (30°)
Acetone	0.337 (15°) 0.316 (25°) 0.295 (30°)	Cyclohexane	1.02 (17°)
Aniline	3.71 (25°) 3.16 (30°)	Ethyl acetate	0.455 (20°) 0.441 (25°) 0.400 (30°)
Benzene	0.652 (20°) 0.564 (30°) 0.503 (40°)	Ethyl alcohol	1.200 (20°) 1.003 (30°) 0.834 (40°)
Benzaldehyde	1.39 (25°)	Ethylene glycol	19.9 (20°) 9.13 (40°)
<i>n</i> -Butyl alcohol	2.948 (20°) 2.30 (30°) 1.782 (40°)	Formic acid	1.804 (20°) 1.465 (30°) 1.219 (40°)
Carbon tetrachloride	0.969 (20°) 0.843 (30°) 0.739 (40°)	Glycerine	1490 (20°) 954 (25°) 692 (30°)
Heptane	0.409 (20°) 0.386 (25°) 0.341 (40°)	Methyl acetate	0.381 (20°) 0.320 (40°)
Hexane	0.326 (20°) 0.294 (25°)	Nitrobenzene	2.03 (20°)
<i>iso</i> -Butyl alcohol	4.703 (15°)	Toluene	0.590 (20°) 0.526 (30°) 0.471 (40°)
<i>iso</i> -Propyl alcohol	2.86 (15°) 1.77 (30°)	Turpentine	1.487 (20°) 1.272 (30°) 1.070 (40°)
Methyl alcohol	0.597 (20°) 0.547 (25°) 0.510 (30°) 0.456 (40°)		

Table 14. Viscosity of Water at Different Temperatures

Temperature (°C)	Viscosity (cp)	Temperature (°C)	Viscosity (cp)
0	1.7921	31	0.7840
5	1.5188	32	0.7679
10	1.3077	33	0.7523
15	1.1404	34	0.7371

18	1.0559	35	0.7225
19	1.0299	36	0.7085
20	1.0050	37	0.6947
20.2	1.0000	38	0.6814
21	0.9810	39	0.6685
22	0.9597	40	0.6560
23	0.9358	45	0.5988
24	0.9142	50	0.5494
25	0.8937	60	0.4688
26	0.8737	70	0.4061
27	0.8545	80	0.3565
28	0.8360	90	0.3165
29	0.8180	100	0.2838
30	0.8007		

Table 15. Vapour Pressure and Density of Water at Different Temperatures

Temp. (°C)	Vapour pressure (mm)	Density (g/ml)	Temp. (°C)	Vapour pressure (mm)	Density (g/ml)
0	4.579	0.99987	28	28.349	0.99626
5	6.543	0.99999	29	30.043	0.99597
10	9.209	0.99973	30	31.824	0.99567
15	12.788	0.99913	31	33.695	0.99537
18	15.477	0.99862	32	35.663	0.99505
20	17.535	0.99823	33	37.729	0.99473
21	18.650	0.99802	34	39.898	0.99440
22	19.827	0.99780	35	42.175	0.99406
23	21.068	0.99756	37	47.067	0.99336
24	22.377	0.99732	39	52.442	0.99262
25	23.756	0.99707	40	55.324	0.99224
26	25.209	0.99681	45	71.88	0.99025
27	46.739	0.99654			

Table 16. Critical Solution Temperature

System	Temp. (°C)	Comp.	System	Temp. (°C)	Comp.
Water-Phenol	65.9	66%	Glycerol- <i>m</i> -Toluidine	6.7 120	...
CH ₃ OH-Cyclohexane	49.2	29%			...
Methyl ethyl ketone-Water	- 6 + 33	Nicotine-water	60.8 208	...

Table 17. Parachors and Refractivities

Element	Parachor	Refractivity	Group or linkage	Parachor	Refractivity
Carbon	4.8	2.591	Double bond	23.2	1.575
Hydrogen	17.1	1.028	Triple bond	46.6	1.977
Oxygen	20.0	1.764	3-membered ring	17.0	...
Oxygen (in esters)	60.0	4.601	5-membered ring	8.5	- 0.10
Sulphur	48.5	—	6-membered ring	6.1	0.15
Chlorine	54.3	5.844	Semipolar bond	- 1.6	...
Bromine	68.0	8.741			
Iodine	91.0	13.954			
Nitrogen	12.5	...			

Table 18. Approximate pH Values

Substance	pH	Substance	pH	Substance	pH
Hydrochloric acid, N	0.1	Citric acid, 0.1N	2.2	Sodium hydroxide, 0.01N	12.0
Hydrochloric acid, 0.1N	1.1	Acetic acid, N	2.4	Sodium carbonate, 0.1 N	11.6
Hydrochloric acid, 0.01 N	2.0	Acetic acid, 0.1N	2.9	Ammonia, N	11.6
Sulphuric acid, N	0.3	Acetic acid, 0.01N	3.4	Ammonia, 0.1N	11.1
Sulphuric acid, 0.01N	1.2	Benzoic acid, 0.01 N	3.1	Ammonia, 0.01N	10.6
Sulphuric acid, 0.01 N	2.1	Boric acid, 0.1N	3.1	Borax, 0.1 N	9.2
Oxalic acid, 0.1N	1.6	Sodium hydroxide, N	14.0	Sodium bicarbonate, 0.1N	8.4
Tartaric acid, 0.1N	2.2	Sodium hydroxide, 0.1 N	13.0		

Table 19. Molecular Weights and Equivalent Weights

Substance	Mol. wt.	Eq. wt.	Substance	Mol. wt.	Eq. wt.
Sodium carbonate	106.00	53.00	Iodine	253.82	126.91
Sodium oxalate	134.00	67.00	Potassium hydroxide	56.00	56.00
Silver nitrate	169.89	169.89	Potassium nitrate	101.10	101.10
Oxalic acid	126.06	63.03	Sodium chloride	58.52	58.52
Benzoic acid	122.13	122.13	Copper sulphate	249.71	249.71
Ferrous ammonium sulphate	392.16	392.16	Sodium thiosulphate	248.2	248.2

Potassium ferrocyanide	422.41	422.41	Lead sulphate	303.27	303.27
Potassium dichromate	294.92	49.03			
Potassium permanganate	158.03	31.60	Sodium bicarbonate	84.00	84.00
Potassiumchlorid	74.56	74.56	Borax	381.44	190.72

Table 20. Solubility Chart

Substance	10°	20°	30°	40°	50°	60°	80°	100°
AgCl	8.9 $\times 10^{-4}$	8.9 $\times 10^{-4}$	—	—	5.23 $\times 10^{-4}$	—	—	2.1 $\times 10^{-3}$
AgI	—	—	3.0 $\times 10^{-7}$	—	—	3.0 $\times 10^{-6}$	—	—
AgNO ₃	170	222	300	376	455	526	669	952
BaCl ₂	33.3	35.7	38.2	40.7	43.6	46.4	52.4	58.8
Ba(NO ₃) ₂	7.0	9.2	11.6	14.2	17.1	20.3	27.0	34.2
Ca(NO ₃) ₂ .4H ₂ O	53.55	56.39	60.41	66.21	—	—	—	—
CaCl ₂ .6H ₂ O	65.0	74.5	102	—	—	—	—	—
CoSO ₄	30.55	36.21	46.26	48.85	55.2	60.4	70.0	83.0
CuSO ₄ .5H ₂ O	17.4	20.7	25.0	28.5	33.3	40.0	55.0	75.4
CuCl ₂	42.45	43.5	44.55	45.6	46.65	47.7	49.8	51.9
HgCl ₂	4.6	6.1	7.7	9.3	—	14	23.1	38
I ₂	—	2.9 $\times 10^{-2}$	4.0 $\times 10^{-2}$	5.6 $\times 10^{-2}$	7.8 $\times 10^{-2}$	—	—	—
KBr	59.5	65.2	70.6	75.5	80.2	85.5	95.0	105.0
KCl	31.0	34.0	37.0	40.0	42.6	45.5	51.1	56.7
K ₂ Cr ₂ O ₇	8.5	13.1	—	29.2	—	50.5	73.0	102.0
K ₂ CrO ₄	60.0	61.7	63.4	65.2	66.8	68.6	72.1	75.61
KI	136	144	152	160	168	176	192	208
KMnO ₄	4.4	6.4	9.0	12.56	16.89	22.2	—	—
KNO ₃	20.9	31.6	45.8	63.9	85.5	110.0	169	246
KOH.2H ₂ O	112	126	—	—	—	—	—	—
K ₂ SO ₄	9.22	11.11	12.97	14.76	16.50	18.17	21.4	24.1
K ₂ SO ₄ .Al ₂ (SO ₄) ₃ .24H ₂ O	4.0	5.9	8.39	11.70	17.0	24.75	71.0	—
MgSO ₄ .7H ₂ O	23.6	26.2	29.0	31.3	—	—	—	—
MnCl ₂ .4H ₂ O	68.1	73.9	80.71	88.59	98.15	—	—	—

NH ₄ Cl	33.3	37.2	41.4	45.8	50.4	55.2	65.6	77.3
NaBr.2H ₂ O	—	47.5	49.4	51.4	53.7	—	—	—
NaCl	35.8	36.0	36.3	36.6	37.0	37.3	38.4	39.8
Na ₂ B ₄ O ₇ .10H ₂ O	1.6	2.7	3.9	—	10.5	20.3	—	—
Na ₂ CO ₃ .10H ₂ O	12.5	21.5	38.8	—	—	—	—	—
NaHCO ₃	8.15	9.6	11.1	12.7	14.45	16.4	—	—
NaOH.H ₂ O	—	109	119	129	145	174	—	—
NaI.2H ₂ O	168.65	178.7	190.3	205.0	227.8	256.8	—	—
NaNO ₃	80	88	96	104	114	124	148	180
Pb(C ₂ H ₃ O ₂) ₂	—	55.04	—	—	—	—	—	—
Pb(NO ₃) ₂	48.3	56.5	66	75	85	95	115	138.8
SrCl ₂ .6H ₂ O	47.7	52.9	58.7	65.3	72.4	81.8	—	—
ZnSO ₄ .7H ₂ O	47	54.4	—	—	—	—	—	—

Table 21. Buffer Solutions.(a) *Acetic acid – Sodium Acetate Buffer (0.2M acetic acid ; 0.2M sodium acetate)*

pH	Acetic acid (ml)	Sodium acetate (ml)	pH	Acetic acid (ml)	Sodium acetate (ml)
3.5	94	6	5.2	20	80
4.0	82	18	5.5	12	88
4.5	56	44	5.6	10	90
5.0	30	70

(b) *Phosphate Buffer*

(M/15 potassium dihydrogen phosphate; M/15 disodium hydrogen phosphate).

pH	KH ₂ PO ₄ (ml)	Na ₂ HPO ₄ (ml)	pH	KH ₂ PO ₄ (ml)	Na ₂ HPO ₄ (ml)
5.5	96	4	6.8	50	50
6.0	88	12	7.0	38	62
6.4	72	28	7.5	15	85
6.5	69	31	7.9	7	93
6.6	63	37	8.0	6	94

(c) *Borate Buffer*(d) *0.05M borax ; 0.2 M boric acid*

pH	Borax (ml)	Boric acid (ml)
7.0	6.0	94.0
8.0	27.5	72.5
9.0	80.0	20.0
10.0	97.5	2.5
11.0	98.4	1.6

pH of 0.1M borax solution is 9.2.