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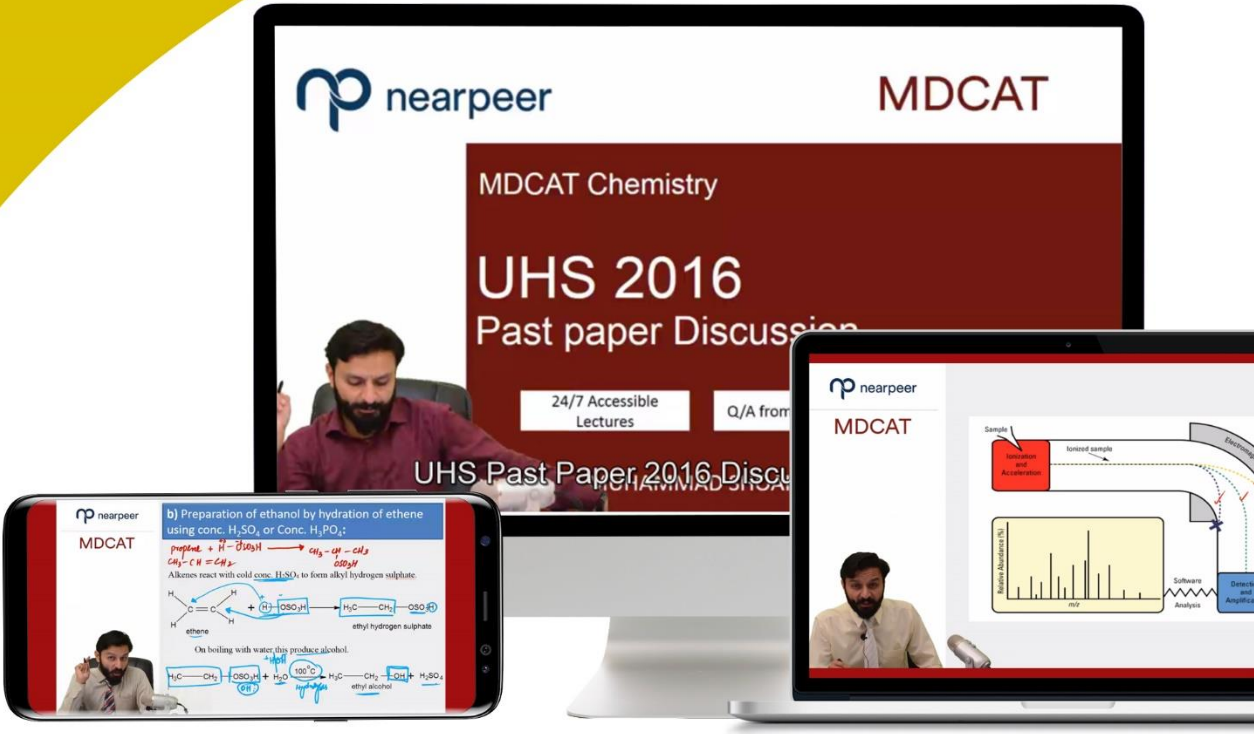
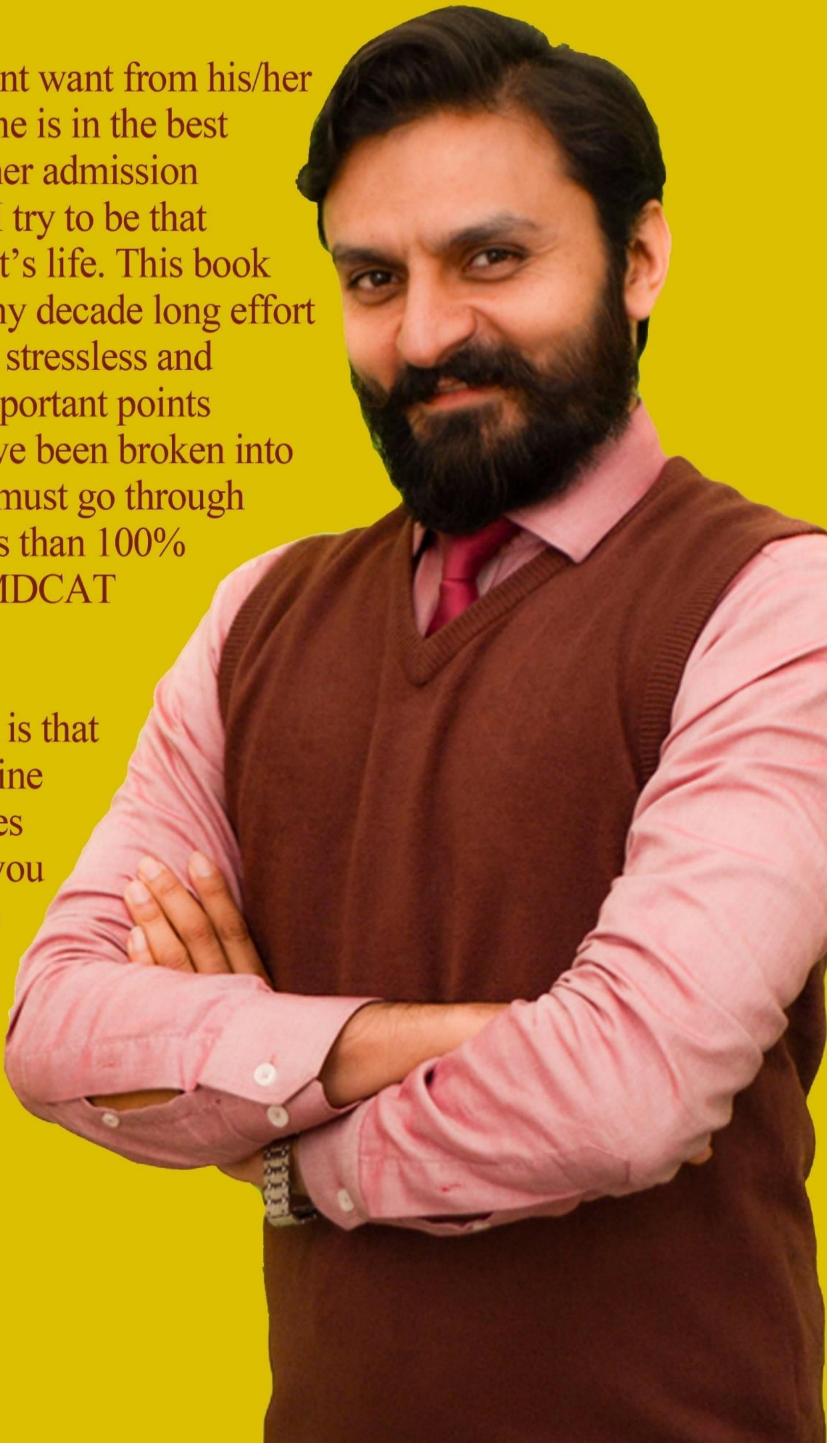


Meet Your Instructor

Prof Shoaib Anwar

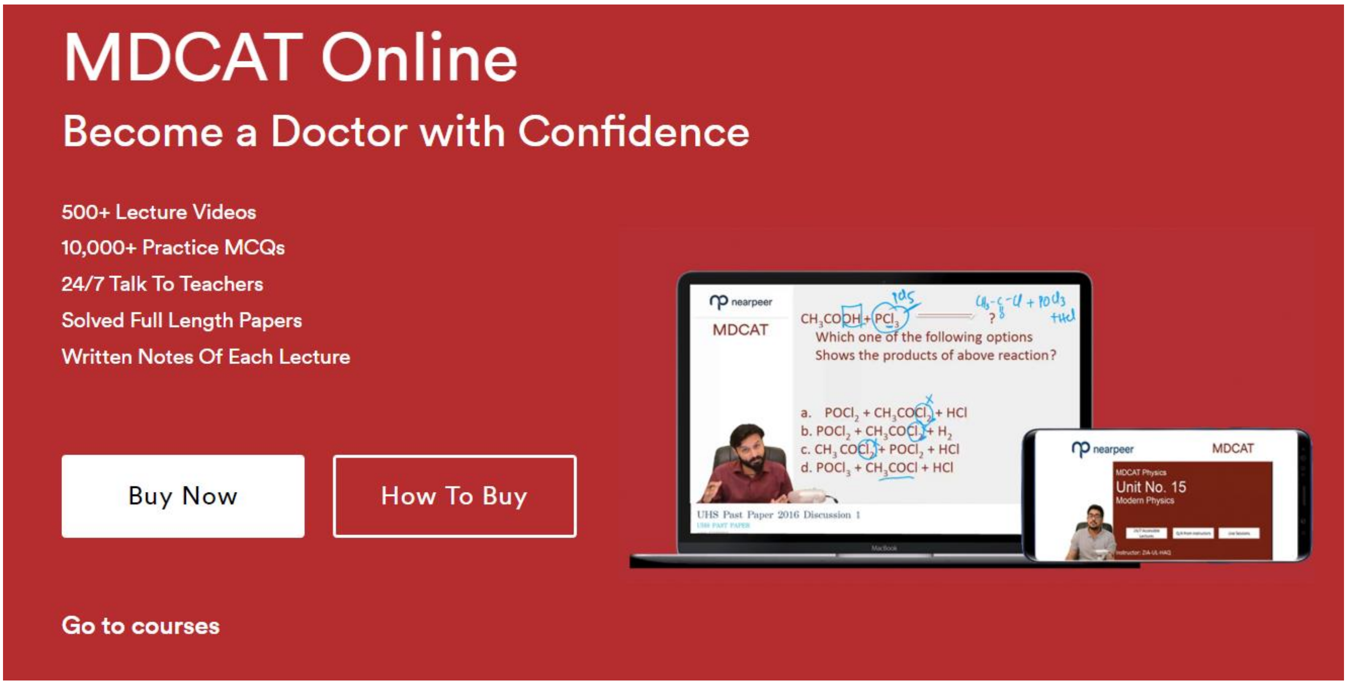


What does an MDCAT Student want from his/her teachers? A comfort that he/she is in the best hands that can guarantee his/her admission in the medical college. Well, I try to be that hand, that comfort in a student's life. This book that you are going to start is my decade long effort to make students' preparation stressless and enjoyable. In this book, all important points from MCQs point of view have been broken into precise bullet points that you must go through to make sure you score no less than 100% on the Chemistry portion in MDCAT exam.

The best way to use this book is that you study it alongside my online MDCAT Lectures and Quizzes on www.nearpeer.org. Once you take my lecture and revise the concept from this book, there is no reason you cannot score FULL Marks in MDCAT Chemistry Portion.

My Prayers with you all.

Shoaib Anwar.



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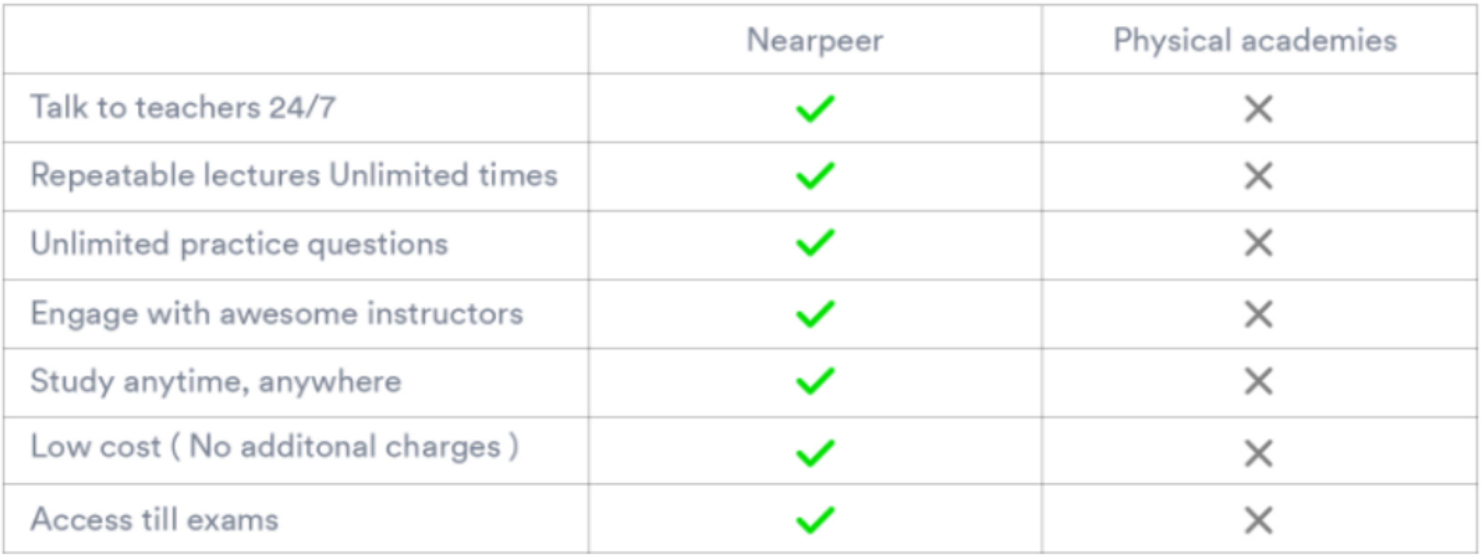
MDCAT
Which one of the following options
Shows the products of above reaction?
UHS Past Paper 2016 Discussion 1
MDCAT Physics
Unit No. 15
Modern Physics



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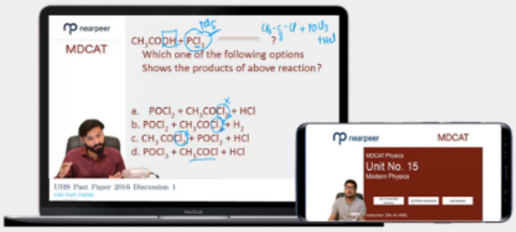
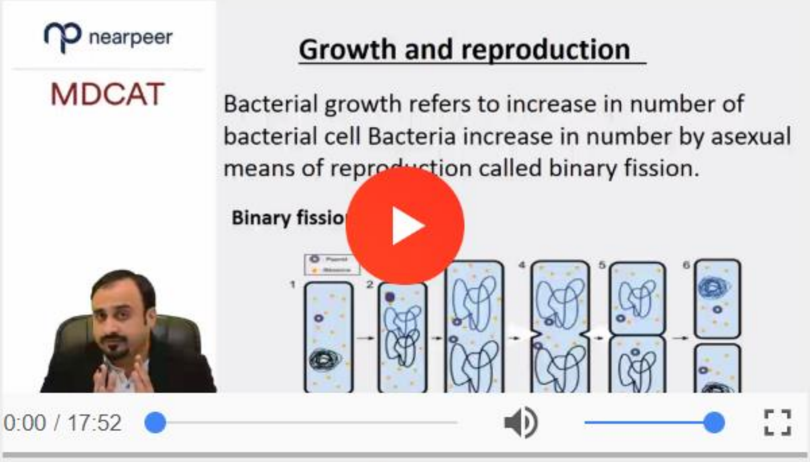


$CH_3COOH + PCl_3 \longrightarrow ?$

Which one of the following options Shows the products of above reaction?

a. $POCl_2 + CH_3COCl_2 + HCl$
b. $POCl_2 + CH_3COCl_2 + H_2$
c. $CH_3COCl_2 + POCl_2 + HCl$
d. $POCl_3 + CH_3COCl + HCl$

All The Lectures In Your Pocket



Growth and reproduction

Bacterial growth refers to increase in number of bacterial cell Bacteria increase in number by asexual means of reproduction called binary fission.

Binary fissio

Biology Demo Quiz

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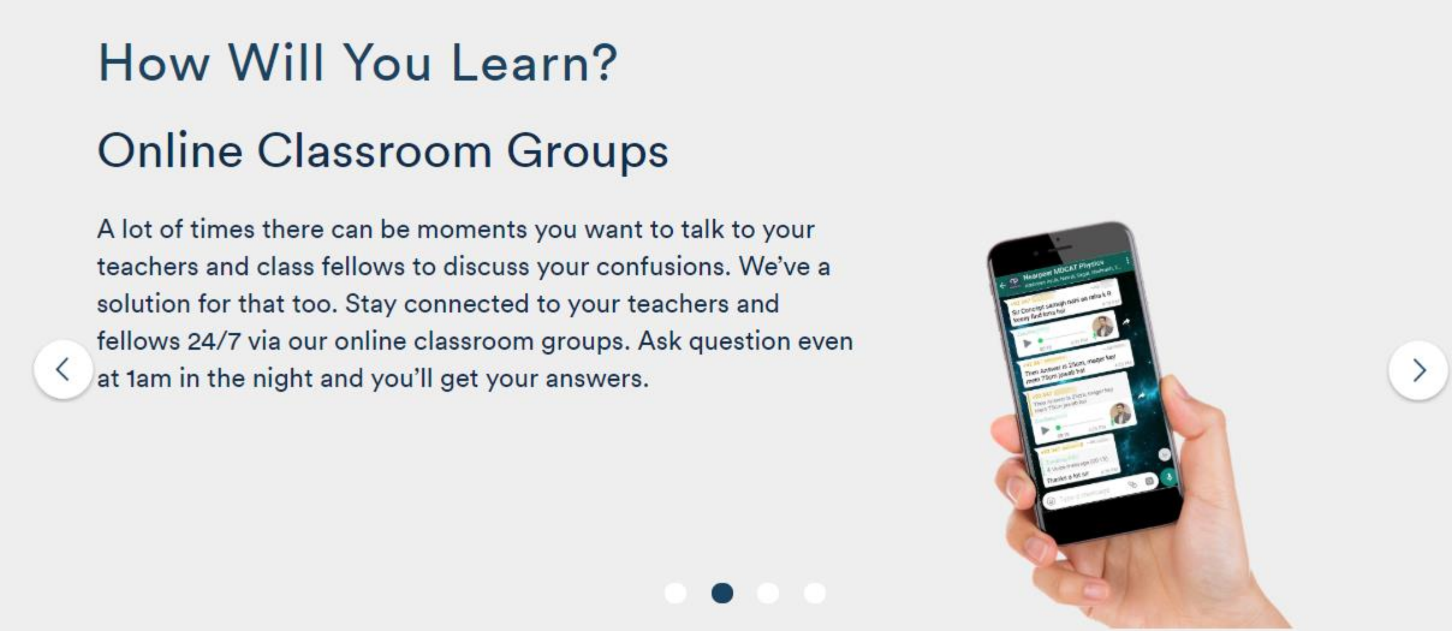

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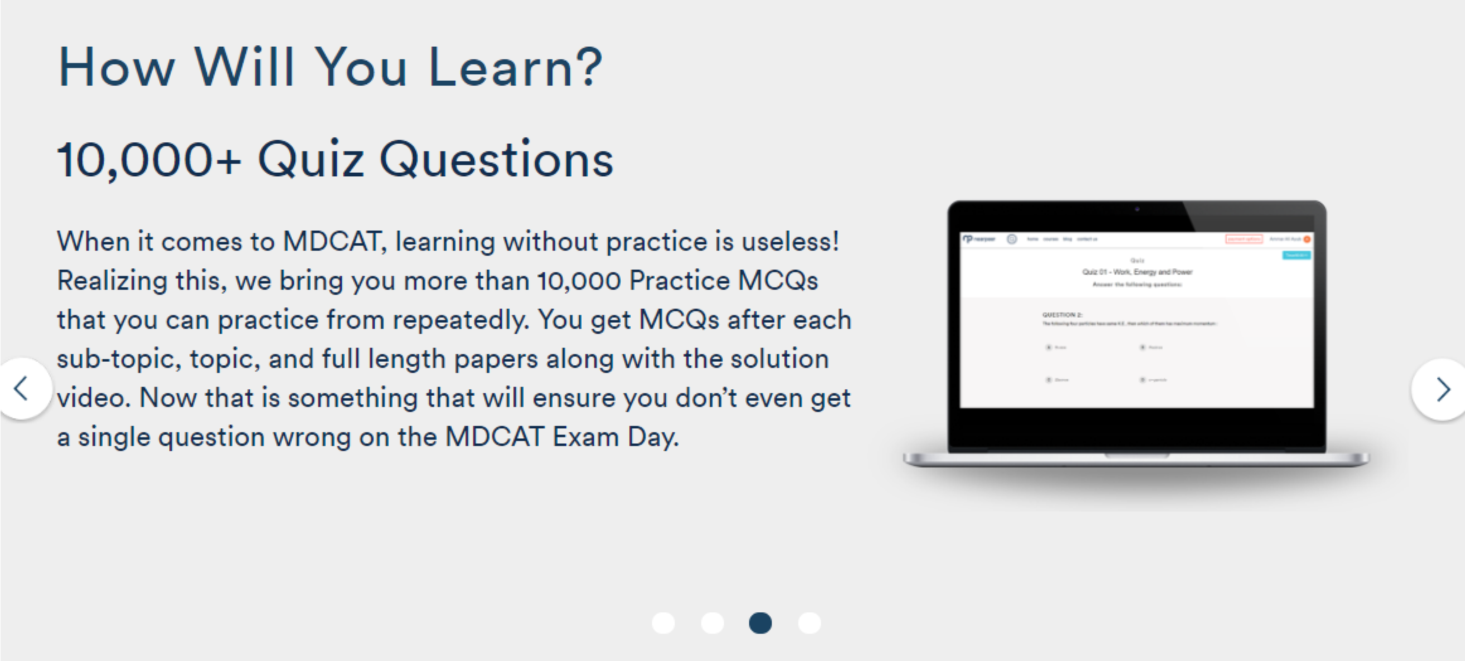
A lot of times there can be moments you want to talk to your teachers and class fellows to discuss your confusions. We've a solution for that too. Stay connected to your teachers and fellows 24/7 via our online classroom groups. Ask question even at 1am in the night and you'll get your answers.



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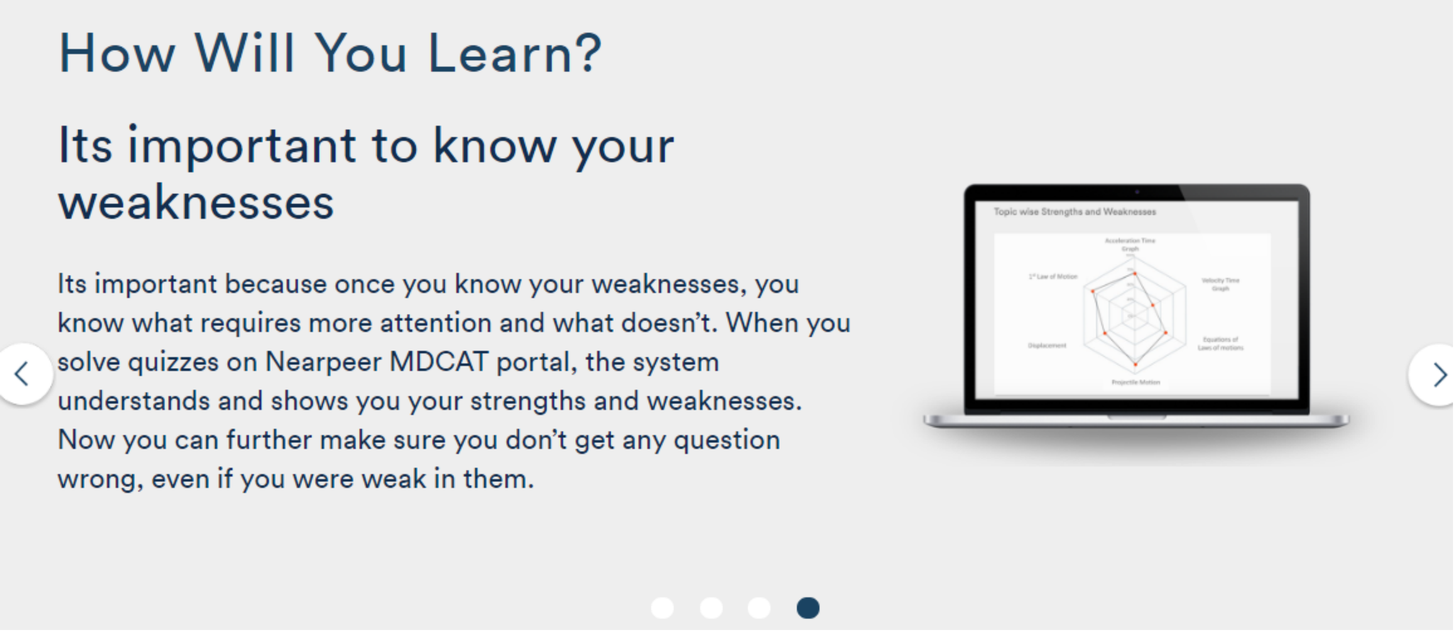


How Will You Learn?

Its important to know your weaknesses

Its important because once you know your weaknesses, you know what requires more attention and what doesn't. When you solve quizzes on Nearpeer MDCAT portal, the system understands and shows you your strengths and weaknesses. Now you can further make sure you don't get any question wrong, even if you were weak in them.

UHS TOPIC IA

FUNDAMENTAL CONCEPTS

LEARNING OUTCOMES

In this topic, student should be able to:

a) Define relative atomic, molecular and formula masses, based on the ^{12}C scale and concept of isotopes.

b) Explain mole in terms of the Avogadro's constant.

c) Apply mass spectrometric technique in determining the relative atomic mass of an element using the mass spectral data provided.

d) Calculate empirical and molecular formulae, using combustion data.

e) Understand stoichiometric calculations using mole concept involving.

  i) Reacting masses

  ii) Volume of gases

  iii) Percentage yield

f) Describe and explain following concentration units of solutions:

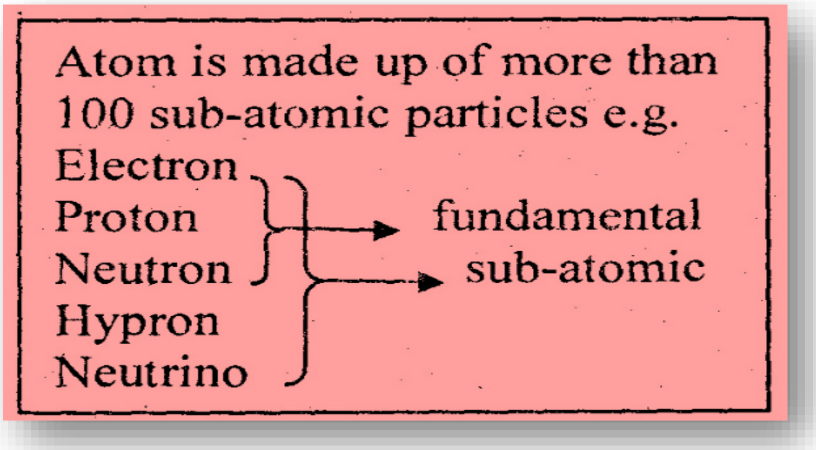
  i) Percentage composition

  ii) Molarity

  iii) Mole fraction

ATOM

The smallest particle of an element which takes part in the chemical reaction is called an atom. May exist independently



Atom is made up of more than
100 sub-atomic particles e.g.
Electron
Proton
Neutron
Hypron
Neutrino

fundamental
sub-atomic

Examples

Monatomic gases:

•	Helium	(He)
•	Neon	(Ne)
•	Neutron	(N)

May not exist independently

Examples:

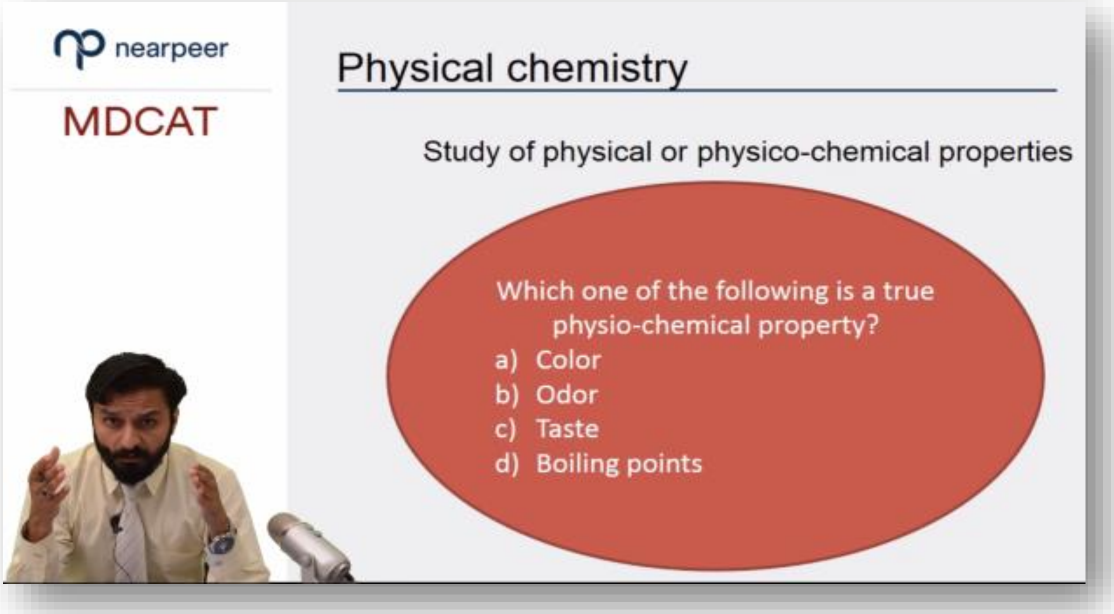
•	Hydrogen	(H)
•	Oxygen	(O)
•	Nitrogen	(N)

A) RELATIVE MASS

Relative mass is the mass of a given substance scaled with carbon-12. C-12 is used as standard in this scale because

1. It is highly stable isotope
2. Its mass is exactly in whole numbers i.e. 12.000
3. It can be handled easily

Note: The mass of an atom of an element as compared to the mass of an atom of carbon-12



Physical chemistry

Study of physical or physico-chemical properties

Which one of the following is a true physio-chemical property?
a) Color
b) Odor
c) Taste
d) Boiling points

Get video solution of the practice questions of this unit at www.nearpeer.org. Visit Module 2 of Chemistry.

ATOMIC MASS UNIT

The unit used to express the relative atomic mass is called atomic mass unit (amu) and it is 1/12 of the mass of one atom of C-l2.

1 amu = 1.661×10^{-27} kg

1 amu = 1.661×10^{-24} g

Examples:

i) Chlorine

Isotopes	$^{35}_{17}\mathrm{Cl}$	$^{37}_{17}\mathrm{Cl}$
Relative abundance	75 %	25 %

(i) Relative isotopic mass $^{35}_{17}\mathrm{Cl}$ = 35 amu

(ii) Relative isotopic mass $^{37}_{17}\mathrm{Cl}$ = 37 amu

(iii) Relative atomic mass

$$= \frac{\text{relative Isotopic mass} \times \text{RA of } ^{37}_{17}\mathrm{Cl} + \text{Relative isotopic mass} \times \text{RA of } ^{37}_{17}\mathrm{Cl}}{100}$$

(iv) Relative atomic mass of Cl = $\frac{35 \times 75 + 37 \times 25}{100}$

(v) Relative atomic mass of Cl = 26.25 + 9.25 = 35.5 amu

ii) Neon

Isotopes	$^{20}_{10}\mathrm{Na}$	$^{21}_{10}\mathrm{Na}$	$^{22}_{10}\mathrm{Na}$
Relative abundance	90.92 %	0.26 %	8.82 %

Relative atomic mass of Neon

$$= \frac{20 \times 90.92 + 21 \times 0.26 + 22 \times 8.82}{100} = 20.18 \text{ amu}$$

RELATIVE ISOTOPIC MASS

Note:The mass of an isotope of an element as compared to the mass of an atom of carbon-l 2

Example:

i) Relative isotopic mass of Chlorine-35 is 35 amu

ii) Relative isotopic mass of Chlorine- 37 is 37 amu

RELATIVE MOLECULAR MASS

Note:The mass of a molecule as compared to the mass of an atom of carbon-12

Example:

i) Relative molecular mass of water is 18 amu

ii) Relative molecular mass of carbon dioxide is 44 amu

RELATIVE FORMULA MASS

Note:The mass of a formula unit as compared to the mass of an atom of carbon-l2

Examples:

i) Relative formula mass of NaCl is 58.5 amu

ii) Relative formula mass of Na_2SO_4 is 142 amu

POINT TO PONDER

The relative formula mass of a compound, with the same symbol M is the sum of the?

B) MOLE

The relative atomic mass of an element, relative molecular mass of covalent compound or relative formula mass of ionic compound or Ionic specie expressed in grams is called mole. It is detonated by 'n' and abbreviated as 'mol'

Examples:

1 mole of Na = 23.0 g of sodium (one gram atom of Na)

1 mole of H_2O = 18.0 g of water (one gram molecule of H_2O)

1 mole of NaCl= 58.5 g of sodium chloride (one gram formula of NaCl)

1 mole of (SO_4^{-2}) = 96 g of sulphate ion (one gram formula unit massor (SO_4^{-2})

DETERMINATION OF MOLE

There are three main methods to determine number of moles of a substance:

(i) When mass of substance is given in grams.

$$\text{Number of moles of substance} = \frac{\textit{mass in grams of given substance}}{\textbf{Relative atomic mass/molecular mass/formula mass}}$$

(ii) For a certain number of particles (atoms, ions or molecules)

$$\text{Number of moles of substance} = \frac{\textbf{Number of particles of the given substance}}{\textbf{6.022 x 1 023 (Avogadro's number of particle's)}}$$

(iii) For volume of a given gas in dm^3 at STP

$$\text{Number of moles of substance} = \frac{\text{Volume of the gas in dm}^3\text{ at STP}}{22.414\text{ dm}^3}$$

one mole	particles	6.022×10^{23} atoms	6.022×10^{23} molecules	6.022×10^{23} formula units	6.022×10^{23} atoms
	mass	gram atom mass of element	gram molecular mass of the molecular substance	gram formula mass of the ionic compound formula unit	gram ionic mass of the ionic specie
	volume	At STP (if gas) = 22.4 dm^3			

AVOGADRO'S NUMBER (NA)

It is the number of particles (atoms, ions or molecules) present in one mole of a substance. It is denoted by NA. Its value is 6.022×10^{23}.

Examples:

(i) 23 g Na = 1 mole = 6.022×10^{23} atoms

(ii) 18.0 g H_2O = 1 mole = 6.022×10^{23} molecules

(iii) 58.5 g NaCl = 1 mole = 6.022×10^{23} formula units

(iv) 96 g SO_4^{-2} = 1 mole = 6.022×10^{23} ions

MASS SPECTROMETER:

An instrument which is used to measure the exact masses of different isotopes of an element together with their relative abundances is called mass spectrometer.

TYPES OF MASS SPECTROMETER

- **Aston's mass spectrometer**

It was designed to identify isotopes of an element on the basis of atomic masses.

• Dempster's mass spectrometer

It was designed to identify isotopes of an element which are in the solid state.

Parts of Modern Mass spectrometer

- Vaporization chamber
- Ionization chamber
- Electric field (acceleration)
- Magnetic field (Deflection)
- Ion collector (Detection)
- Recorder
- Amplifier

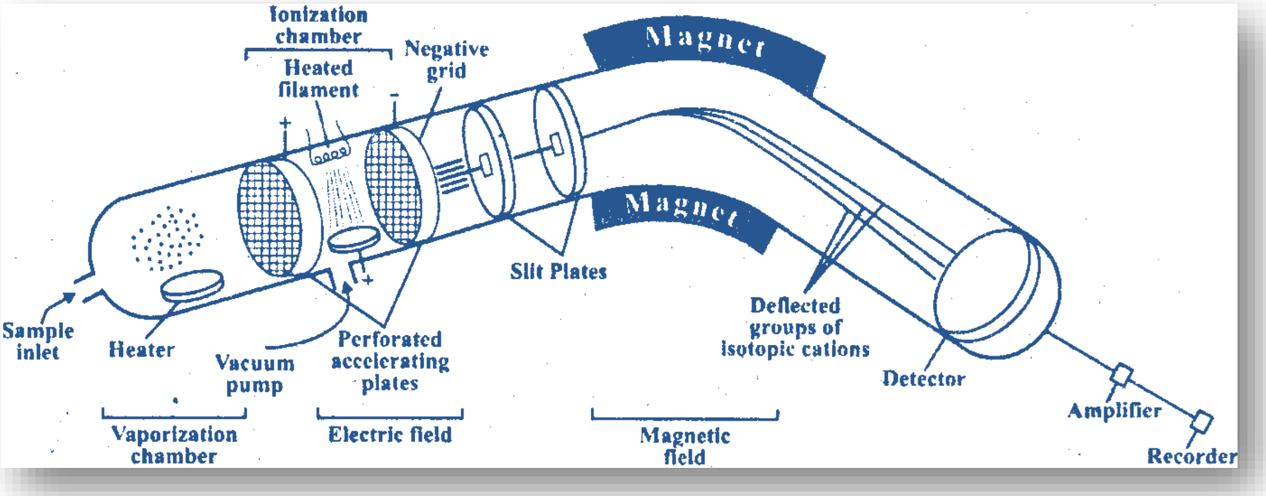
The first five parts are present in Dempster's mass spectrometer while as two parts are present in modern spectrometer.

Instrumentation of Dempster's mass spectrometer:

It has following five main parts:

STAGES	FUNCTION
Vaporization chamber	In this chamber the sample of the element is vaporized and the vapor pressure is reduced to 10^7 to 10^{-6} torr
Ionization Chamber	In this chamber sample of the element is ionized either by electron ionization chamber beam. $e^- + X \rightarrow X^+ + e^- + e^-$
Electric Field	Electric field is applied to accelerate the positive ions. The applied potential difference is of 500-2000 volts
Magnetic Field	On passing through magnetic field deflection of positive ions take place according to their mass/charge ratio. $\frac{m}{e} = \frac{H^2r^2}{2E}$

Electrometer or ion Collector	Ion collector receives positive ions according to their mass/charge ratio related to isotopes. i) The strength of current measured by ion collector gives the relative abundance of ions of a definite m/e value. ii) The same experiment is performed with C-12 isotopes and the current strength is compared.



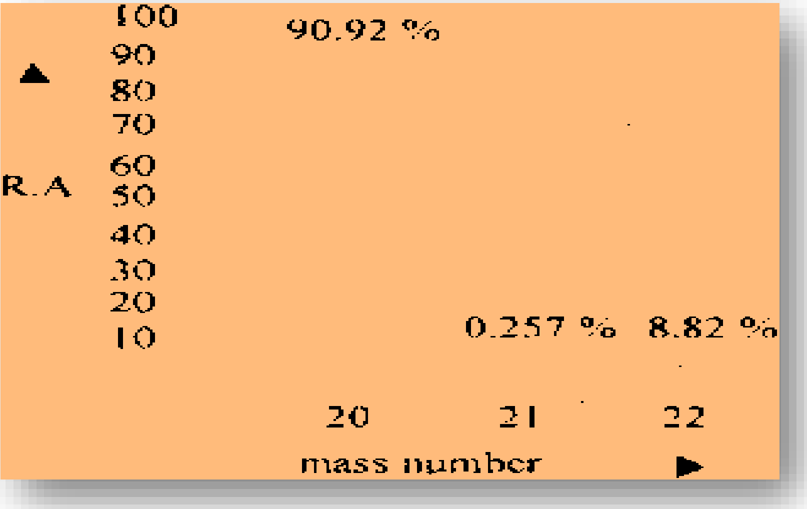
MASS SPECTROMETER

Other techniques for the separation of isotopes:

- Gaseous diffusion
- Thermal diffusion
- Distillation
- Ultra centrifuge
- Electromagnetic separation
- Laser separation

Examples:

(i) The mass spectrum of Neon:

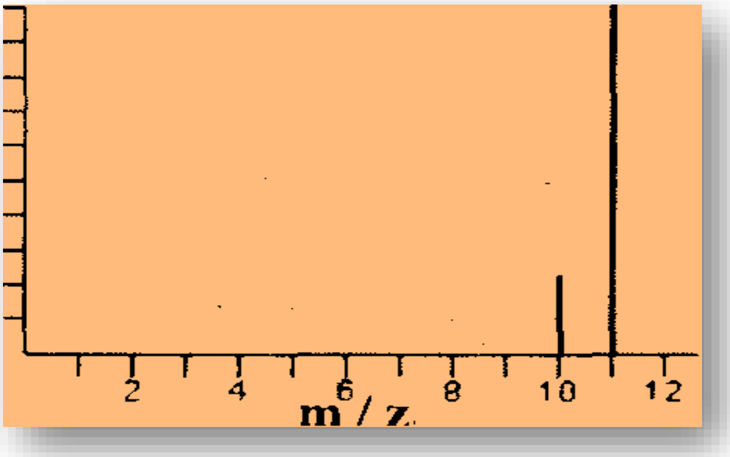


- **The Number of isotopes:** The three peaks in the mass spectrum show that neon contains three isotopes with relative isotopic masses 20, 21 and 22, respectively.
- **The abundance of isotopes:** The relative heights of the peaks give a direct measure of the relative abundance of the isotopes.

(ii) The mass spectrum for boron:

- **The number of isotopes: 100**
- **Relative Abundance**: 50

The two peaks in the mass spectrograph shows that there are 2 isotopes of boron with relative isotopic masses of 10 amu and 11 amu on the ^{12}C scale.



- **The abundance of the ISOTOPES**:

The relative heights of the peaks give a direct measure of the relative abundances of the isotopes.

- **Working out the relative atomic mass:**

Suppose there are 123 typical atoms of boron, 23 of these would be ^{10}B and 100 would be ^{11}B. The total mass of these would be (23 x 10) + (100 x 11) = 1330. The average mass of these 123 atoms would be 1330 / 123 = 10.8 (to 3 significant figures).

- 10.8 is the relative atomic mass of boron. A simple average of 10 and 11 is, of course, 10.5. Our answer of 10.8 allows for the fact that there are a lot more of the heavier isotope of boron and so the "weighted" average ought to be closer to that.

(iii) The mass spectrum of chlorine:

The ions formed from chlorine element are Cl_2^+ in the mass spectrum. These ions won't be particularly stable, and some will fall apart to give a chlorine atom and a Cl^+ ion. This is term as fragmentation.

$Cl^2 \rightarrow Cl + Cl^+$

- If the Cl atom formed isn't then ionized in the ionization chamber, it simply gets lost in the machine neither accelerated nor deflected.
- The Cl^+ ions will pass through the machine and will give lines at 35 and 37, depending on the isotope and you would get exactly the pattern in the last diagram.
- The problem is that we also observe lines for the un-fragmented Cl_2^+ ions.
- The possible combinations of chlorine-35 and chlorine-37 atoms in a Cl_2^+ ion are as:

(i) Both atoms in ion could be ^{35}Cl with relative- mass of 70

(ii) Both atoms could be ^{37}Cl with relative mass of 74

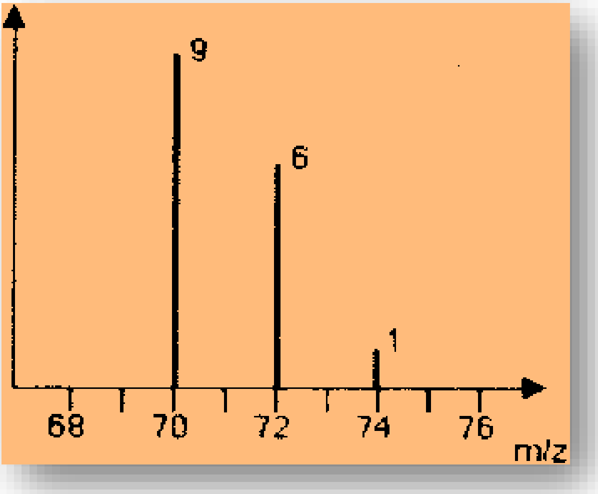
(iii) One atom in ion could be ^{35}Cl and second atom could be ^{37}Cl with relative mass of 72

Total masses of the three possible Cl_2^+ ions could be of:

35 + 35 = 70 Relative

35 + 37 = 72 Abundance

37 + 37 = 74

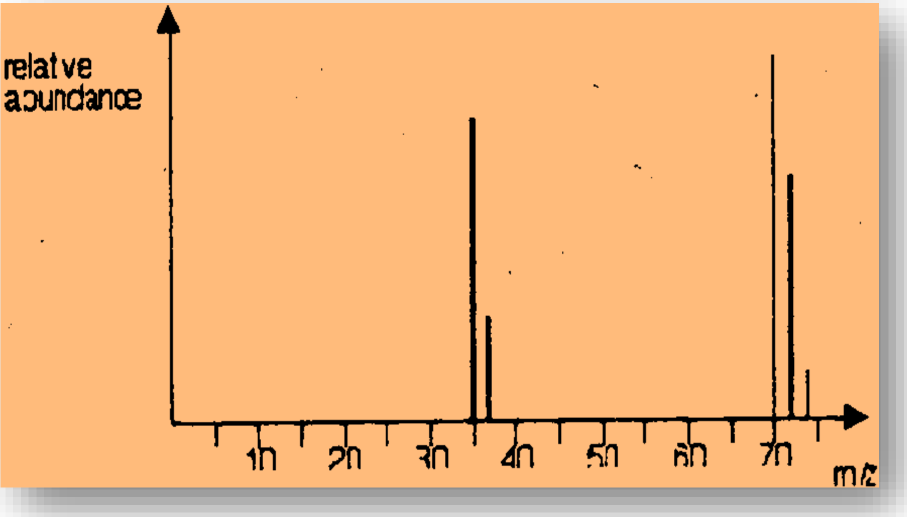


Conclusion: We will have two sets of lines

(i) Two lines for monatomic ions at m/z = 35 and 37, respectively indicating that it has two isotopes. The relative heights of the peaks at m/z = 35 and 37 are in the ratio 3: l

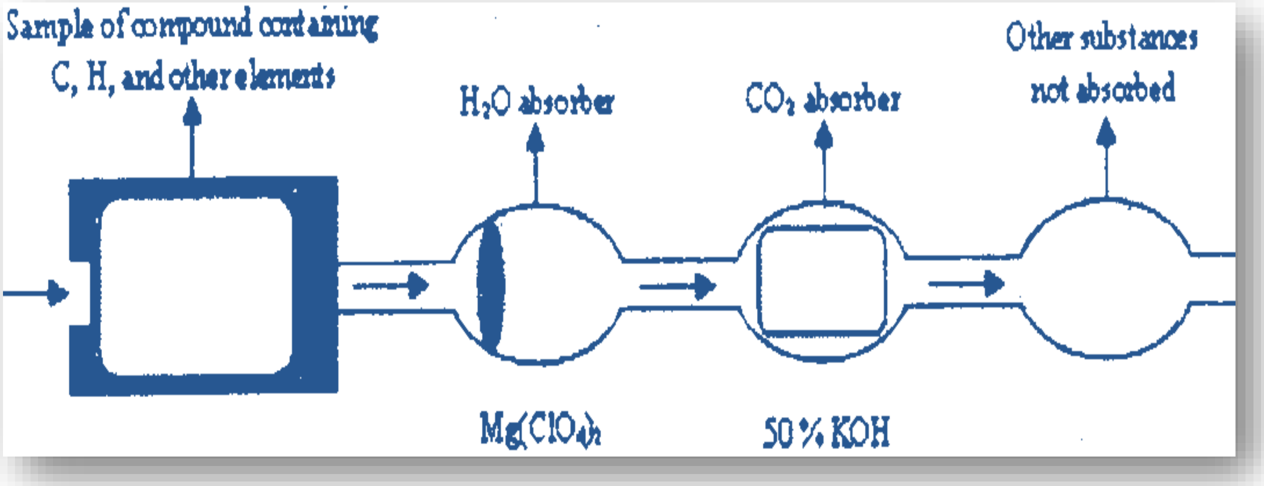
(ii) Three lines for molecular ions at m/z = 70, 72 and 74, respectively. The relative heights of the peaks at m/z = 70, 72 and 74 are in the ratio 9:6: I.

The overall mass spectrum is as follows:



COMBUSTION ANALYSIS

The sequence of combustion analysis is shown in the following diagram.



By combustion analysis only those organic compounds can be analyzed which simply contain carbon, hydrogen and oxygen.

From the masses, percentages are calculated by using the following formulae:

(i) % age of carbon $= \frac{mass\ of\ CO^2\ obtained\ in\ experiment}{\text{mass of organic compound}} \times \frac{12}{44} \times 100$

(ii) % age of hydrogen $= \frac{\text{Mass of } H_2O \text{ obtained in experiment}}{\text{mass of organic compound}} \times \frac{2.0}{18.0} \times 100$

(iii) % age of oxygen = 100 – (% of carbon + % of hydrogen)

Example:

A sample of liquid consisting of carbon, hydrogen and oxygen was subjected to combustion analysis. 0.5439 g of the compound gave 1.039 g of CO_2, 0.6369 g of H_2O. Determine the empirical formula of the compound.

Solution:

Element	%	No. of gram atoms	Atomic ratio	Empirical Formula
C	$\frac{1.039g}{0.5439g} \times \frac{12.00}{44.00} \times 100 =$ 52.108	$\frac{52.108}{12} = 4.34$	$\frac{4.34}{2.17} = 2$	C_2H_6O
H	$\frac{0.6369g}{0.5439g} \times \frac{2.016}{18} \times 100 =$ 13.115	$\frac{13.115}{1.008} = 13.01$	$\frac{13.01}{2.17} = 6$	
O	11 – (52.108 + 13.115) = 34.77	$\frac{34.77}{16.00} = 2.17$	$\frac{2.17}{2.17} = 1$	

DIFFERENCE BETWEEN EMPRIRICAL AND MOLECULAR FORMULA

EMPIRICAL FORMULA	MOLECULAR FORMULA
A formula which represents the simplest whole number ratio of atoms of elements in a compound is called empirical formula	A formula which represents actual number of atoms of each element in a molecular compound is called molecular formula
It is obtained from % age composition of elements i.e. chemical analysis	It is obtained by multiplying 'n' with empirical formula i.e. from empirical formula
This term is used for both molecular and ionic compounds	This term IS used only, for molecular compounds
Examples: NaCl, CH_2O, CH are empirical formula of sodium chloride, glucose and benzene respectively	**Examples:** $C_6H_{12}O_6$ and C_6H_6 are molecular formulae of glucose and benzene respectively

POINT TO PONDER:

The empirical formula shows percentage composition by ……..

Note:

The term empirical formula is used for ionic compounds and giant covalent structures (sand SiO_2, graphite and diamond C) it is also used for covalent compounds as CH_2O for glucose and acetic acid.

Relationship between empirical and molecular formula:

Molecular formula = n × empirical formula

STOICHIOMETRY

:

Stoichiometry is a branch of chemistry, which tells us the quantitative relationship between reactants and products in a balanced chemical equation.

CHEMICAL EQUATION:

Chemical equation in the statement that describes a chemical reaction in term of symbols and chemical formulas.

Limitation of balanced chemical equations:

They do not tell about the,

(i) Conditions (temperature and pressure)

(ii) Rate of reaction

(iii) Physical state of reactants and products

(iv) Mechanism of reaction

We sometime write a chemical equation that never happens

Conditions for stoichiometric calculations:

Stoichiometric calculations are based on the following conditions:

(i) All the reactants must be completely converted into the products.

(ii) The side reaction must not occur

(iii) The law of conservation of mass and the law of definite proportions must be obeyed while doing the calculations.

The following types of relationship can be studied with the help of a balanced chemical equation at STP

$2H_{2(g)}$ +	$O_{2(g)}$ →	$2H_2O_{(g)}$	$\Delta H = -482$ kJ/mol
2-moles	l-mole	2-moles	
4 g	32 g	36 g	
44.828 dm^3	22.414 dm^3	44.828 dm^3	

(i) Mass-mass Relationship:

If we are given the mass of one substance, we-can calculate the mass of the other substance.

(ii) Mass-mole Relationship or Mole-mass Relationship

If we are given the mass of one substance, we can calculate the moles of other substance and vice versa.

(iii) Mass-volume Relationship

If we are given the mass of one substance, we can calculate the volume of the other substances and vice versa.

(iv) Mole-mole Relationship

If we are given the mole of one substance, we can calculate the mole of the other substances and vice versa.

LIMITING REACTANT:

Limiting reactant is a reactant that controls the amount of the products formed in a chemical reaction due to being less than the required amount. It can also be defined as follows:

(i) It is a reactant that produces least number of moles of product

(ii) It is consumed earlier in the reaction

Identification of Limiting Reactant

To identify a limiting reactant, the following three steps are performed:

(i) Calculate the number of moles from the given amount of reactants

(ii) Calculate the number of moles of product formed from the given moles of each reactant

(iii) Identify the reactant as limiting reactant which produces least moles of the product

YIELD

The amount of the product obtained as a result of the chemical reaction is called yield.

Types of Yield:

(a) Theoretical Yield:

The amount of the product calculated from the balanced chemical equation is called the theoretical yield.

(b) Actual Yield:

The amount of the product obtained in a chemical reaction experimentally is called actual yield.

(c) **Percentage Yield**:

$$5\ \text{yield} = \frac{actual\ yield}{Thoeretical\ yield} \times 100$$

POINT TO BE REMEMBERED:

Actual yield is always less than theoretical yield.

REASONS:

(i) A practically inexperienced worker has many shortcomings and cannot get the expected yield.

(ii) The processes like filtration, crystallization etc. if not properly carried out, decrease the actual yield.

(iii) Some of the reactants might take part in a competing side reaction and reduce the amount of the desired product.

CONCENTRATION UNIT OF SOLUTIONS

PARTICULAR	PERCENTAGE COMPOSITION	
Definition		Solute in percent of solvent. Four ways of expression of percentage composition
	1)	$\frac{W}{w}$% It is weight of solute dissolved per 100 g of solution W
	2)	$\frac{W}{w}$% It is volume of solute (cm^3) dissolved per 100 g of solution
	3)	$\frac{W}{w}$% It is a weight of solute (g) dissolved per 100 cm^3 of solution V
	4)	$\frac{W}{w}$% It is volume of solute (cm^3) dissolved per 100 cm^3 of solution V

Expression	Expressed by percentage (%)

POINT TO PONDER:

A solution prepared by dissolved number of moles of solute in 1 dm^3 of solution is called ……….

Example: 1 M NaOH solution means 1 mole (40 g/dm^3 of solution)

MOLARITY

The number of moles of a solute dissolved per dm^3 of a solution is called molarity.

Symbol:

It is denoted by 'M'.

Examples: 0.1 M NaOH solution and 0.02 M $KMnO_4$ solution

Formulae:

(1) Molarity (M) = $\frac{Moles\ of\ solute}{\text{Volume of solution in dm}^3} = \frac{n}{\text{v}}$

(2) Molarity (M) = $\frac{Mass\ of\ solute}{\text{molar mass of solute}} \times \frac{1}{\text{Volume of solution in dm}^3} = \frac{W_2}{M_2} \times \frac{1000}{V(cm^2)}$

Mole Fraction:

(Especially suitable for solution having more than two components)

The ratio of the number of moles of a component to the total number of moles of all the components of solution is called mole fraction.

Symbol:

It is denoted by 'X'

Explanation:

Let us have components A, Band C making a solution and their number of moles is n_A, n_B and n_C respectively.

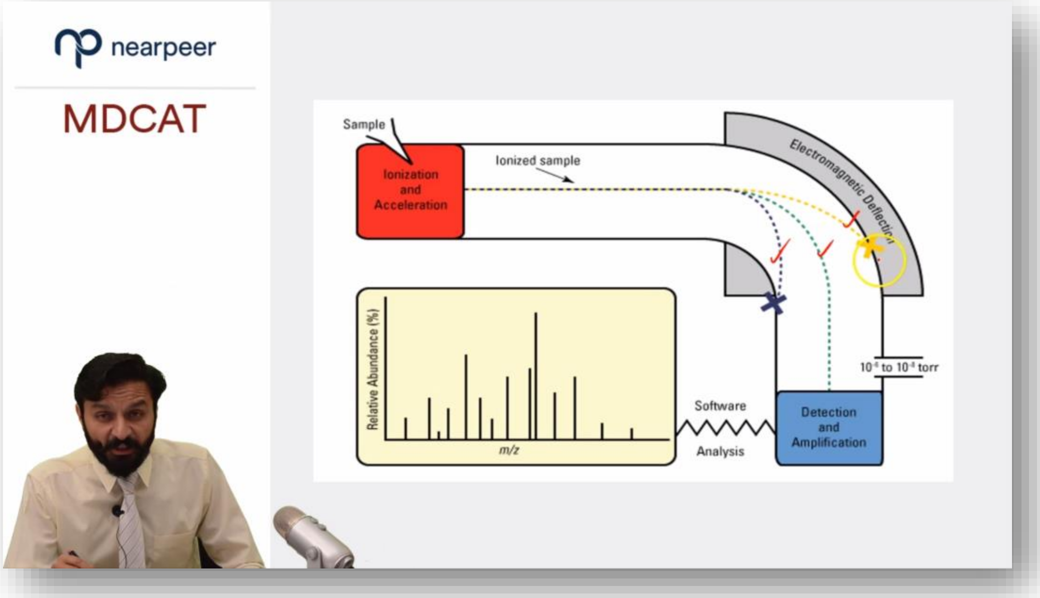
X_A, X_B and X_C are their mole fractions and are given below:

$$X_A = \frac{n_A}{n_A+n_B+n_C}$$

$$X_B = \frac{n_B}{n_A+n_B+n_C}$$

$$X_C = \frac{n_C}{n_A+n_B+n_C}$$

- The sum of the mole fractions of all the components of solution is unity (one)
- To get mole percent, mole fraction is multiplied by 100
- There are no formal units of mole fraction because it is a ratio of same quantity
- Mole fraction of a component in a solution is always less than one



PRACTICE EXERCISE (FOR UHS TOPIC 1 (A)

1. **The separation of positive ions of isotopes of an element on while passing through magnetic field depends upon**

A) m / e ratio C) Strength of magnetic field

B) Electric field D) All of the above

2. **Which isotopes of element in third period of periodic table contain the same number of neutron as in $^{32}_{16}S$**

A) ^{23}Na C) ^{28}Si

B) ^{24}Mg D) ^{31}P

3. **The volume occupied by 1.4g of N_2 at STP is**

A) $2.24dm^3$ C) $1.12dm^3$

B) $22.4dm^3$ D) $112cm^3$

4. **0.36 moles of aluminum and oxygen react to produce alumina, which of the following is limiting reactant and non-limiting reactant?**

A) O_2, Al C) Al_2O_3, O_2

B) Al, O_2 D) Al, Al_2O_3

5. **Which one of the following is equal to one mole H_2O?**

A) 22.414 dm^3 of H_2O

B) 1 dm^3 of H_2O

C) 2 mole H_2 molecule and one mole O_2 molecule

D) One mole steam

6. A collection of 0.55g of electron is equal to

A) 0.1 mole of electron B) 1000 moles of electrons

C) 100 moles of electrons D) None of the above

7. The number of moles of NO_2 which contains 16 g of oxygen:

A) 0.25 C) 0.50

B) 1.0 D) 1.50

8. The volume occupied by 2.0 g of Ne at STP:

A) 2.24 dm^3 C) 22.4 dm^3

B) 1.12 dm^3 D) 112 cm^3

9. Which one of the following pair is not iso-electronic:

A) CO, N_2 C) Na^+, Ne

B) Ca , Ar D) K^+, Ar

10. 180 g of glucose contains number of hydrogen atoms:

A) 3.6×10^{-23} C) 6.0×10^{23}

B) 7.2×10^{23} D) 7.2×10^{24}

11. Which of the following elements has nine isotopes:

A) Ca C) Pd

B) Cd D) Sn

12. Which of the following will form single peak in mass spectrograph:

A) Iodine C) Arsenic

B) Fluorine D) All of these

13. Which one of the following contains maximum no. of molecules:

A) 16.0 g of CH_4 C) 16.0 g of O_2

B) 16.0 g of CO_2 D) 16.0 g of H_2O

14. Mass of sodium in 53 g of Na_2CO_3 is:

A) 23 g

B) 92 g

C) 46 g

D) 106 g

15. 20 moles each of Mg and O_2 react to form MgO. The amount of MgO formed would be:

A) 20 g

B) 800 g

C) 400 g

D) 1600 g

16. The number of peaks obtained in mass spectrometry shows:

A) Charge on isotopes

B) Number of isotopes

C) Mass of isotope

D) Relative abundance of isotopes

17. Percentage of oxygen in calcium carbonate is:

A) 40%

B) 12%

C) 48%

D) 165

18. The water formed in combustion analysis is absorbed by passing through the solution of

A) $Mg(ClO_4)_2$

B) very dilute KOH

C) 50% KOH

D) $Mg(ClO_3)_2$

19. The number of possible molecular ions generated in mass spectrometer for Chlorine is

A) 4

B) 3

C) 2

D) 1

20. A solution used to absorb CO_2 during combustion analysis is

A) Magnesium chlorate

B) Very dilute potassium hydroxide

C) magnesium perchlorate

D) 50% potassium hydroxide

21. In mass spectrograph, the height of peak tells us about:

A) No. of isotopes

C) Nuclei of atoms of an element

B) Sister atoms of element

D) Natural abundance of isotopes

22. Which of the following is always a whole number?

A) Atomic mass

B) Mass number

C) Atomic volume
D) Both A) and B)

23. 2 mole of H_2S and 11.2 dm^3 of SO_2 (at S.T.P) reacts to form moles of sulphur:

$$SO_2 + 2H_2S \longrightarrow 3S\downarrow + 2H_2O$$

A) 1.5
B) 3
C) 11.2
D) 6

24. A compound having empirical formula C_3H_3O and its molecular mass is 110.02. Its molecular formula is:

A) C_3H_3O
B) $C_6H_6O_2$
C) $C_9H_9O_3$
D) $C_3H_6O_2$

25. Which isotope need strongest magnetic field for equal deflection?

A) Ne-20
B) Ne-21
C) Ne-22
D) All need equal

26. 0.5 moles of methane and 0.5 moles of ammonia gas have equal:

A) Volume
B) Molecules
C) Mass
D) Atoms

27. The charge on 1 mol of electrons is:

A) 1 Faraday
B) 2 Faradays
C) 3 Faradays
D) Zero

28. A hydrocarbon contains C = 80%, H = 20%. What is its empirical formula?

A) CH_2
B) CH_3
C) CH_4
D) C_2H_6

29. A mixture of 5 ml of CH_4 and 10 ml of C_2H_6 will produce how much CO_2 on complete combustion:

A) 25 ml
B) 45 ml
C) 15 ml
D) 60 ml

30. What is the ratio of volume of 1 g H_2 to the volume of 16 g CH_4 at S.T.P.?

A) 1 : 1	B) 1 : 2
C) 1 : 8	D) 2 : 1

31. Which of the following is correct sequence of processes involved in modern mass spectrometer?

A) Vaporization, ionization, electric field, amplification, recording, ion collector, magnetic field.

B) Ionization, electric field, ion collector, vaporization ion collector, recording, amplification.

C) Vaporization, -ionization, electric field , magnetic field, ion collector, amplification and recording.

D) all of them

32. One mole of different compounds mostly has:

A) different masses and different number of molecules

B) same masses but different number of molecules

C) different masses but same number of molecules

D) same masses as well as same number of molecules

33. Which of the following compounds has the empirical formula CH_2O ?

A) CH_3COOH	B) CH_3OH
C) C_2H_5OH	D) HCOOH

34. Which of the following contains the greatest number of N-atoms?

A) 22.414 dm^3 of nitrogen gas at STP	B) 500 cm^3 of NH_3 at STP
C) 1.0 mole of NH_4Cl	D) 6.02×10^{23} molecules of NO_2

35. How many moles of oxygen gas can be obtained by the electrolytic decomposition of 90 g of water?

A) 2 moles	B) 2.5 moles
C) 4.5 moles	D) 5 mole

36. The number of moles of CH_4 which contains 3.0 g of carbon:

A) 1.0 B) 0.75

C) 0.5 D) 0.25

37. **A sample in the ionization chamber of mass spectrometer is ionized by:**

A) Electrons B) Proton

C) Neutron D) Nucleus

38. Which of the following sets contains only compounds?

A) Air, water, sodium B) Hydrogen, ammonia, oxygen

C) Carbon monoxide, phosphine, phosgene D) Table salt, glucose, German silver

39. The least number of molecules are present in:

A) 16 g CH_4 B) 16 g O_2

C) 16 g SO_2 D) 16 g H_2O

40. The empirical formula and molecular formula are related by:

A) Simple integers B) Fractions

C) Sum of atoms D) Nature of atoms

41. 10g NaOH has been dissolved in 1dm^3 of solution, molarity of the solution is

A) 10.15 M C) 0.25M

B) 0.20M D) 3.2 M

42. Which of the following concentration unit of solution is independent of temperature

A) Molarity C) Molality

B) Weight / volume D) None of the above

43. Which of the following method is used to express concentration of the solution when the concentration of solution is very low?

A) Composition C) Molarity

B) ppm D) Molality

44. The mass of urea in 100g of water in 0.3 molal solution

A) 1g C) 1.4g

B) 1.2g D) 1.8g

45. A solution has 92g ethyl alcohol, 96g methyl alcohol, 90g H_2O. Mole fraction of water in solution is

A) 0.2 C) 0.5

B) 0.3 D) 0.4

46. A concentration unit that can be used to measure the concentration of solution having more than two components:

A) Molality C) Molarity

B) Mole fraction D) W/W %

47. A solution of glucose is 10% W/V. The volume to which 1g mole of it dissolved will be:

A) 1 dm^3 C) 1.8 dm^3

B) 200 cm^3 D) 900 cm^3

48. The sum of mole fraction of all the components of solution is always:

A) equal to unity C) 100

B) Less than one D) Less than 100

49. Which of the following is affected by temperature change:

A) Molality C) Molarity

B) Mole fraction D) W/W %

50. An aqueous solution of sucrose has been labelled as 1 molal. The mole fraction of sucrose is:

A) $\frac{1}{55.5}$ B) $\frac{1}{56.5}$

C) $\frac{1}{57.5}$ D) $\frac{55.5}{55.6}$

ANSWER KEY

1	**A**	**11**	**B**	**21**	**D**	**31**	**C**	**41**	**C**
2	**D**	**12**	**D**	**22**	**B**	**32**	**A**	**42**	**C**
3	**C**	**13**	**A**	**23**	**A**	**33**	**A**	**43**	**B**
4	**B**	**14**	**A**	**24**	**B**	**34**	**A**	**44**	**D**
5	**D**	**15**	**B**	**25**	**C**	**35**	**B**	**45**	**C**
6	**C**	**16**	**B**	**26**	**B**	**36**	**D**	**46**	**B**
7	**C**	**17**	**C**	**27**	**A**	**37**	**A**	**47**	**C**
8	**A**	**18**	**A**	**28**	**B**	**38**	**C**	**48**	**A**
9	**D**	**19**	**B**	**29**	**A**	**39**	**C**	**49**	**C**
10	**D**	**20**	**D**	**30**	**D**	**40**	**A**	**50**	**B**

Video form solution of all of the practice questions are available for your Chemistry MDCAT course at www.nearpeer.org

UHS TOPIC II A

STATES OF MATTER

LEARNING OUTCOMES

In this topic, student should be able to:

a) Understand gaseous state with reference to:

i) Postulates of kinetic molecular theory

ii) **Gas laws:** Boyle's law, Charles' law, Avogadro's law and gas equation

(PV = nRT) and calculations involving gas laws

iii) Deviation of real gases from ideal behaviour at low temperature and 'high pressure'

iv) Conditions necessary for gasses to approach ideal behavior.

b) Discuss liquid state with reference to:

Evaporation, vapour pressure, boiling and hydrogen bonding in water

Explain the lattice structure of a crystalline solid with special emphasis on:
- i) Giant ionic structure, as in sodium chloride.
- ii) Simple molecular, as in iodine
- iii) Giant molecular, as in diamond; silicon (IV) oxide.
- iv) Hydrogen-bonded, as in ice .

d Outline the importance of hydrogen bonding to the physical properties of substances, including NH_3, H_2O, C_2H_5OH and ice

e) Suggest from quoted physical data the type of structure and bonding present in a substance,

INTRODUCTION

There are four states of matter namely, gas, liquid, solid and plasma. The simplest state is gas and complex one is plasma. Gas, liquid and solid states are considered to be phase transition states because they are inter-convertible into each other at constant temperature, whereas, plasma state is not a phase transition state because it is formed from gaseous state with continuously increasing temperature.

KINETIC THEORY OF GASSES (KMT)

NAME OF SCIENTIST	CONTRIBUTION
Bernoulli	Founder of KMT
Clausius	Derived Kinetic equation and deduced all the gas laws from KMT
Maxwell	Presented the law of distribution of velocities
Boltzmann	Studied the distribution of energies among the molecules
Van der Waal	Corrected the pressure and volume factors in ideal gas equation to make it applicable to the real gases.

(i) Every gas consists of large number of very small particles called molecules. Gases like He, Ne, Ar have mono-atomic molecules.

(ii) The molecules of gas move haphazardly, colliding among themselves and with the walls of container changing their directions.

(iii) The pressure exerted by the gas molecules is due to the collision of its molecules with the walls of container. The collisions among the molecules are perfectly elastic.

(iv) The molecules of the gases are widely separated from one another and there are sufficient empty spaces among them.

(v) The molecules of the gases have no forces of attraction for each other

(vi) The actual volume of molecules of a gas is negligible as compared to the volume occupied by the gas

(vii) The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them

(viii) The average kinetic energy of the gas molecules varies directly as the absolute temperature of the gas

CLAUSIUS KINETIC ENERGY EQUATION

$PV = \frac{1}{3} mNc^2$ (C^2 is called mean square velocity)

Relationship between the absolute temperature and velocities of gas molecules

According to Maxwell distribution law of velocities

- Root mean square velocity ($C_{rms} = \sqrt{\frac{3RT}{M}}$)

Conclusions:

Creation: Determine the average speed f a helicon atom at room temp:

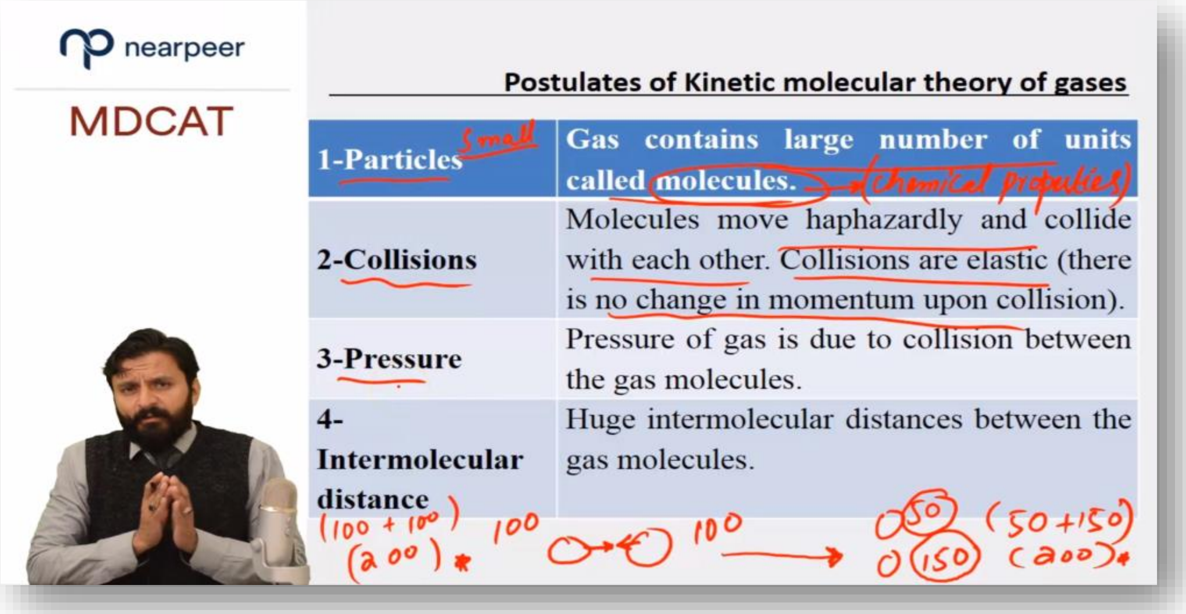
$C_{rms} = \sqrt{\frac{3RT}{M}}$ $M = 4 \times 10^{-3}$ kg /mol

- In gases and liquids, temperature is the measure of average translational kinetic energy of the molecules

- In solids, temperature is the measure of average vibrational kinetic energies of molecules.

- The average translational kinetic energy of gas molecules is directly proportional to the Kelvin temperature of a gas i.e. $E_k \alpha T$

- When heat flows from one body to another, the molecules in the hotter body give up some of their kinetic energy through collisions to the molecules in the colder body.



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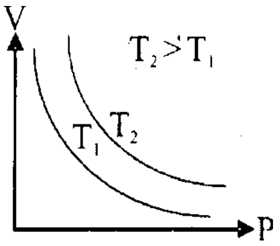
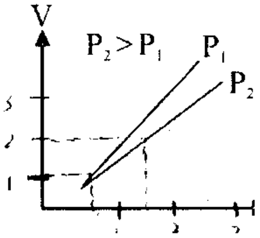
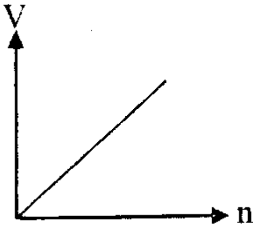
MDCAT

Postulates of Kinetic molecular theory of gases

1-Particles	**Gas contains large number of units called molecules.**
2-Collisions	Molecules move haphazardly and collide with each other. Collisions are elastic (there is no change in momentum upon collision).
3-Pressure	Pressure of gas is due to collision between the gas molecules.
4-Intermolecular distance	Huge intermolecular distances between the gas molecules.

GAS LAWS

PARTICULARS	BOYLE'S LAW	CHARLES'S LAW	AVOGADRO'S LAW
Statement	The volume of a given mass of an ideal gas is inversely proportional to the applied pressure at constant temperature.	The volume of a given mass of an ideal gas is directly proportional to the absolute temperature and constant pressure.	The volume of a given ideal gas is directly proportional to the number of moles at STP
		The volume of given mass of a gas increases or decreases by 1/273 of its original volume at 0° C for every 1° C	Equal volumes of all the ideal gases contain equal number of molecules at

		rise or fall in temperature at constant pressure.	same temperature and pressure.
Mathematical representation	PV = K or $P_1V_1 = P_2V_2$	V/T = K or $P_1/T_1 = P_2/T_2$	V/n = K or $P_1/n_1 = P_2/n_2$
Graphical verification			
	By putting a weight on moveable piston of cylinder filled with gas. The volume of gas decrease.	On heating a cylinder filled with gases having a moveable piston. The volume of gases increases.	On increasing the number of moles of a gas in a closed cylinder. The volume increases.

1 – atm: The pressure of air which can support 760 nm of Hg column at sea level is called one atmospheric pressure. 1-atm: = 6 cm of Hg

= 760 mm of Hg

= 760 torr.

= 14.7 psi

= 101325 pa (Nm^{-2})

= 1.01325 Bar

General Gas Equation:

On combining the Boyle's law, Charles's law and Avogadro's law:

PV = K

V/T = K

V/n = K

we get PV = nRT (R is called general gas constant)

This is called an ideal gas equation or genera gas equation. IS equation is completely obeyed by the ideal gases.

Rearrangement of General Gas Equation:

Boyle's law PV = nRT = K (when "n" and "T" are constant)

Charles's law $\frac{V}{T} = \frac{nR}{P}$ = K (when "n" and "P" are constant)

Avogadro's law $\frac{V}{n} = \frac{RT}{P}$ = K (when "T" and "P" are constant)

Ideal Gas Constant(R):

The value of R depends upon the units chosen for pressure, volume and temperature. It is independent of the nature of gas. The value of "R" can be derived by using general gas equation.

PV = nRT

R = PV/nT

Units of R:

1 m^3	=	1000 dm^3
1 dm^3	=	1000 cm^3
1 dm^3	=	0.001 m^3
1 cm^3	=	0.001 dm^3
1 cm^3	=	10^{-5} m^3
1 Nm	=	I J
1 cal.	=	4.18 J

1 J	=	0.239 cal.
1J	=	10^7 ergs

(a) When P is in atm and V in dm^3

$R = 0.0821\ dm^3 atm\ K^{-1} mol^{-1}$

(b) When P is in mm Hg or torr and V in dm^3 or cm^3

$R = 62.4\ cm^3\ mm\ Hg\ K^{-1}\ mol^{-1}$

$R = 62400\ cm^3\ torr\ K^{-1} mol^{-1}$

(e) When P is in Nin^{-2} and V in m^3 (SI units)

$R = 8.314\ NmK^{-1} mol^{-1}$

$R = 8.314\ JK^{-1} mol^{-1}$

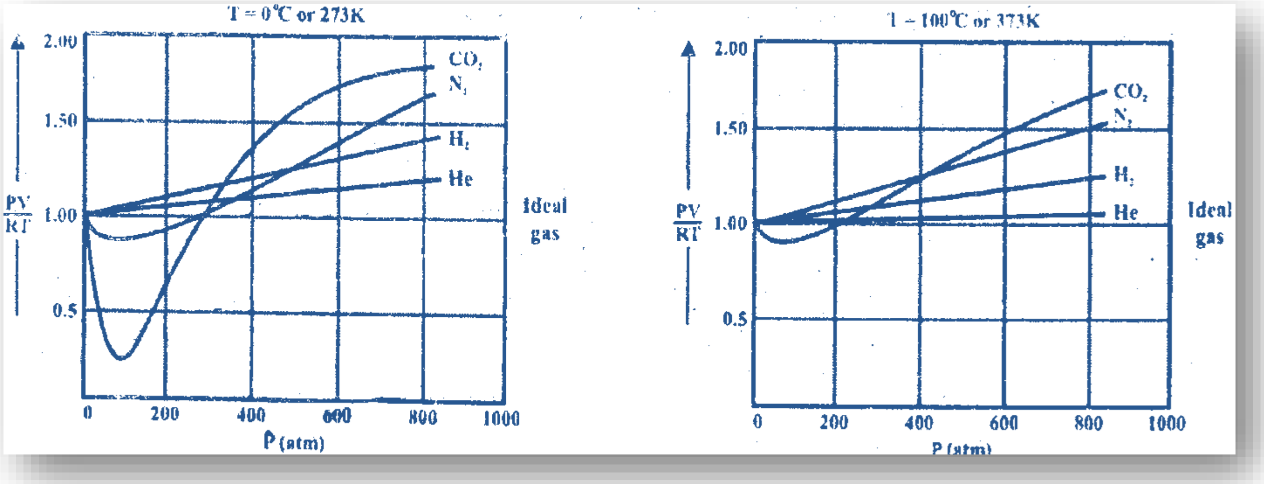
$R = 1.987\ calK^{-1} mol^{-1}$

Note:

Kinetic equation of gases can be employed to justify all the gas laws. In other words it proves the gas laws to get their explanation from kinetic theory of gases.

Non-Ideal Behavior of Gases:

- If a graph is plotted between pressure on x-axis and the PY (compressibility factor or Z) on y-axis for an ideal gas, a straight line parallel to the pressure axis is obtained.
- For real gases (non-ideal gases), the graph is no more parallel to the pressure axis.



At high temperature under low pressure, the graph for real gases come closer to the, expected straight line.

- If Z = 1 then line would be parallel to x-axis.
- If Z < 1 then the line obtained will below the line of ideal gas which means that there is larger decrease in volume of the gas than predicted by general gas equation due to the appearance of attractive forces present among the molecules.
- If Z > 1 then the line obtained will be above the line of an ideal gas which means that there is less decrease in the volume of the gas than predicted by the general gas equation due to appearance of repulsive forces present among the molecules.

Conclusion:

(i) Gases are ideal at low pressure and non-ideal at high pressure.

(ii) Gases are ideal at high temperature and non-ideal at low temperature.

Causes of Deviation of Real Gases From Ideal Behavior:

The real gases deviate from ideal behavior due to two faulty assumptions of KMT of gases. These are:

(i) The volume of the gas molecules themselves is negligible as compared to the total gas volume.

(ii) There are no attractive forces among the molecules of a gas.

Conditions Necessary for Gases to Approach Ideal Behavior:

(i) Gases behave ideally at high temperature, because under these conditions, gases have high kinetic energy. That is the reason why the forces between them are weaker and each gas molecules behave almost independently and hence become ideally.

(ii) Gases behave ideally at low pressure, because under these conditions, gases have great distances between them. That is the reason why the, forces between them are weaker and each gas molecules behave almost independently and hence become ideally.

EVAPORATION

The spontaneous change of a liquid into its vapours is called evaporation and it continues at all temperatures.

Example:

CHARACTERISTICS		FACTORS AFFECTING	
		•	Surface area of the liquid
•	Natural phenomenon	•	Nature of the liquid
•	Cooling process		→ Size of the molecules
•	Continued at all temperature		→ Shape of the molecules
•	Endothermic process		→ Intermolecular forces
•	Surface phenomenon	•	Temperature
		•	External pressure

POINT TO PONDER:

- Molecules with high energy escape from the liquid to the?
- At equilibrium, the rate of evaporation equal the?

The maximum vapour pressure developed by a liquid is its saturated vapour pressure at that temperature

Barometer:

A device for measuring the pressure of the atmosphere.

Monometer:

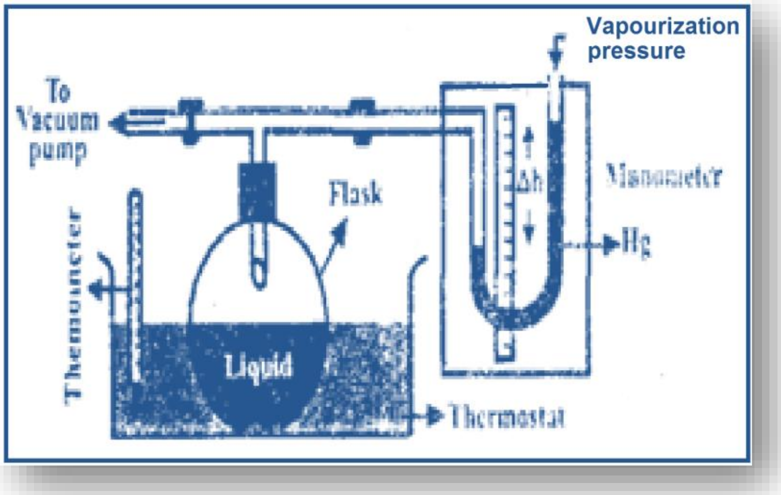
A device for measuring pressure of a gas or a liquid I vessel.

VAPOR PRESSURE

The pressure exerted by the vapors of a liquid in equilibrium with its liquid at a given temperature is called vapor pressure.

Factors Affecting Vapor Pressure:

- Nature of the liquid
- Size of the molecules
- Shape of the molecules
- Intermolecular forces
- Due to weaker intermolecular forces, at 20^{0}C vapor pressure of isopentane is more (580 torr.) than glycerol (0.0016 torr.)
- External Pressure.



POINT TO PONDER: Each time that equilibrium is established between liquid the vapour becomes richer in the?

POINT TO BE REMEMBERED

- Vapour pressure of water, is 4.579 torr at 0^o C.
- The rate of change of a vapour pressure with temperature can be calculated by Clausius equation.

MEASUREMENT OF VAPOR PRESSURE

- Mano-meter is used to measure
- Thermostat is a system whose temperature can be control by means of knob.
- Vacuum is created by vacuum pump
- Liquid is frozen and then melted so that air can be removed $P = Pa + \Delta h$

BOILING POINT

The temperature at which the vapour pressure of the liquid becomes equal to external pressure is called boiling point. Boiling point depends upon external pressure.

Note: The boiling point of decomposition point of glycerin is 290° C

NO.	EXTERNAL PRESSURE	BOILING POINT OF H_2O
1)	1489 torr	120° C
2)	700 torr	98° C (Murree Hills)
3)	323 torr	69° C (Mount Everest)
4)	23.7 torr	25° C

HYDROGEN BONDING IN WATER

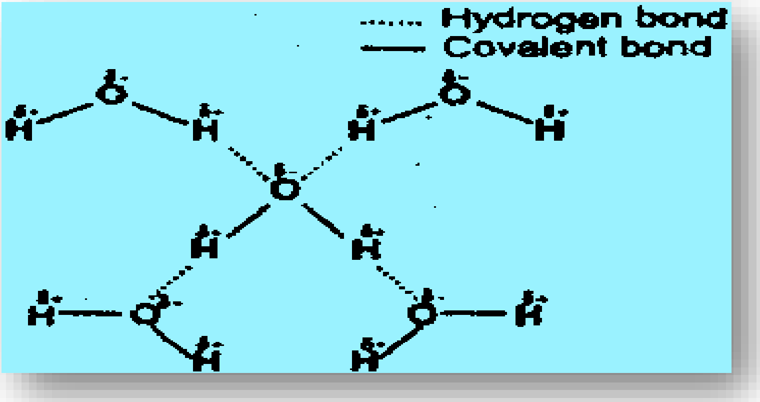
Hydrogen bonding is the electrostatic force of attraction between a highly electronegative atom and partial positively charged hydrogen atom.

POINTS TO BE REMEBERED

- Exceptionally low acidic strength of HF molecule as compared to HCl, HBr and HI is due to strong hydrogen bonding.

- Ammonia and hydrogen fluoride can form only one hydrogen bond due to presence of only one utilizable lone pair of electrons and one utilizable H-atom respectively.
- Water can form two hydrogen bonds as it has two utilizable hydrogen atoms and two utilizable lone pairs on oxygen atom.

Note: The strength bond is generally twenty times less than that of a covalent bond.



HYDROGEN BONDINIG IN WATER

STRUCTURE OF SODIUM CHLORIDE:

Independent molecules of NaCl do not exist in vapour phase as well as in solid state.

That is why NaCl is said formula unitof sodium chloride.

- Number of Formula Units per Unit Cell:

The Unit cells that shares one Cl^- ion at one comer = 8

A unit cell gets a share of one Cl^- ion at one comer = $^{1}/_{8}$

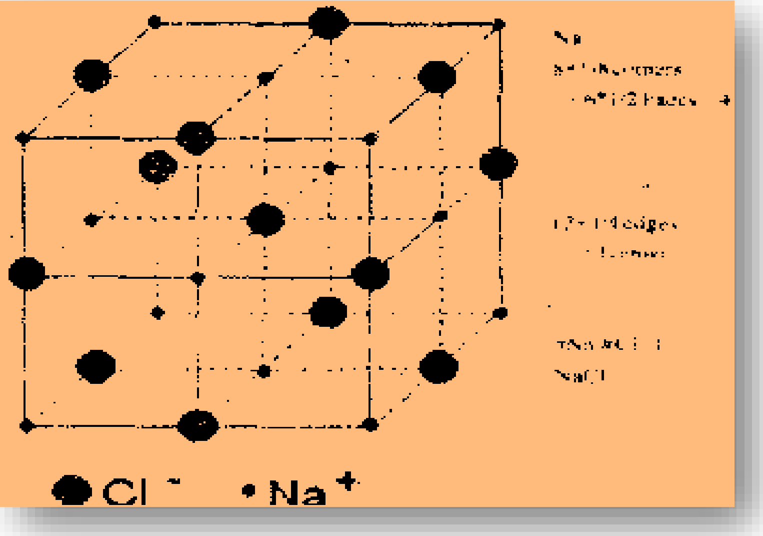
A unit cell gets a total share of Cl^- ion at eight comers = $8x^{1}/_{8}$

A unit cell gets a share of one Cl- ion at one face = $^{1}/_{2}$

A unit cell gets a total share of Cl^- ions at six faces = $6\ x^{1}/_{2} = 3$

So, a unit cell gets a total number of Cl – 1 ions = 4Cl⁻

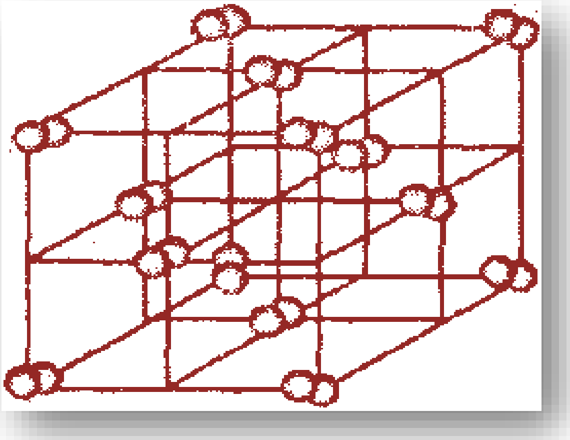
Similarly, there are four Na' ions in a unit cell. Hence, there are four formula units (4NaCl) of NaCl in a unit cell.



POINT TO PONDER: The number of ions that can surround one cation is called the?

STRUCTURE OF IODINE

In the solid state, the molecules of iodine align in the form of layer lattice. I-I bond distance is 271.5 pm and it is appreciably longer than in gaseous iodine (266.6 pm). Iodine is a poor conductor of electricity. Lattice points are occupied by I_2 molecules. It has faced centered cubic structure.

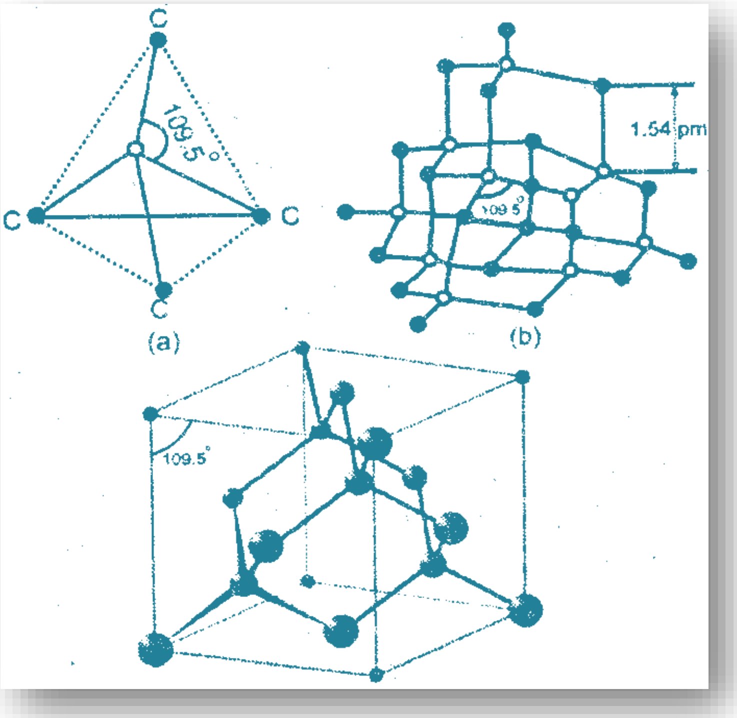


STRUCTURE OF DIAMOND

(i) In the structure of diamond, each carbon atom is linked with four other carbon atoms through covalent bonds which run through the crystals in three dimensions carbon has 4 valence electrons.

(ii) The four atomic orbitals (one 2s and three 2p) undergo Sp^3 hybridization to give four Sp^3 hybridized orbitals.

(iii) All the bond angles are 109.5° and the bond lengths are 154 pm. The whole lattice is the continuous because of C – C covalent bonding.



(iv) The entire diamond crystal behaves as a huge giant three-dimensional carbon molecule. It is also called a macromolecule.

(v) Non-Conductor:

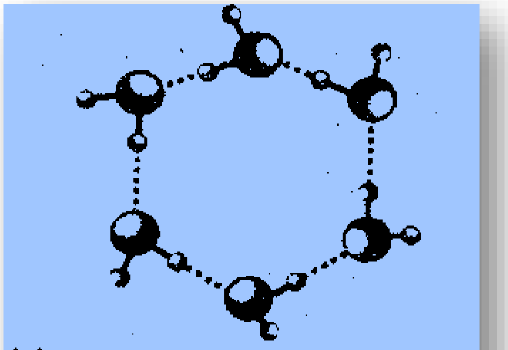
It has no free electrons, so it does not conduct electricity. Each carbon atom in diamond has all the four valence electrons tightly' bound in covalent bonds. Hence, are not available to conduct electricity.

Structure of Silicon (IV) Oxide:

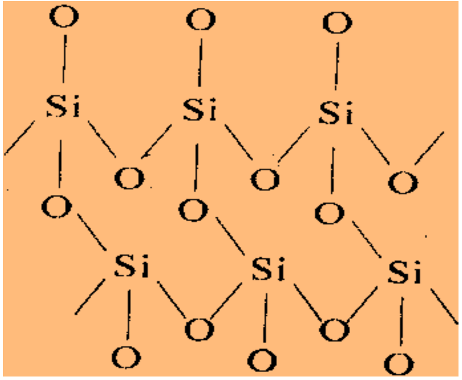
- SiO_2, an empirical formula: In the interior of the silica network, every silicon atomic bonded tetra hardly to four oxygen atoms and every oxygen atom is bonded to two silicon atoms.

The simplest ratio of silicon to oxygen atoms is 1 : 2. SiO_2 is the empirical formula of silica.

- Structure of silicon dioxide considered to be essentially, one molecule.
- High surface activity of Silica: The atoms of silicon and oxygen at the surface of the chunk do not have all their valencies satisfied. That is why, silica shows high surface activity.



A hexagon in the structure of ice



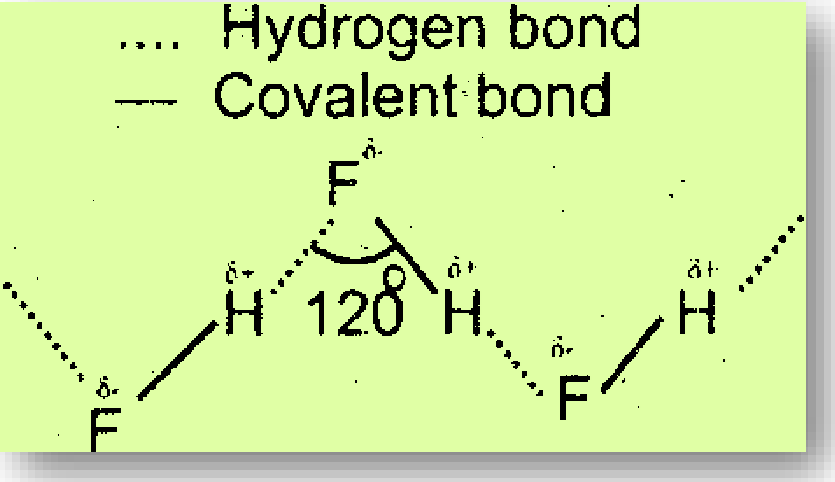
STRUCTURE OF ICE

In Ice, the oxygen atom of water molecule IS, surrounded by four H-atoms. The two H atoms are linked through covalent bond while the other two H-atoms are linked through H-bond. This is extended throughout creating the empty spaces in the structure.

That is why when water freezes it occupies 9 % more space and its density decreases. That's why ice float on the surface of water.

1) Hydrogen bonding in NH_3:

There is only one hydrogen bond per NH_3 molecule. Hydrogen bonding in NH_3 molecules is shown below due to weak hydrogen bonding it exists as a gas and has low boiling point.



2) Hydrogen bonding in HF:

There is only one hydrogen bond per HF molecule. HF molecules join each other in Zigzag manner due to the presence of hydrogen bonding. HF shows exceptionally low acidic strength than HCl, HBr and HI due to:

(i) Hydrogen bonding between its molecules.

(ii) Hydrogen atom being entrapped between two highly electronegative atoms (F). As a result, release of hydrogen atom becomes difficult. This makes it weaker acid. Hydrogen bonding between HF molecules is much stronger due to greater electro-negativity difference between Hydrogen and Fluorine. This is the reason why it exists as a liquid.

POINT TO PONDER: The double helix of DNA is held by?

Substances dissolve in water if they can form H bonds with it.

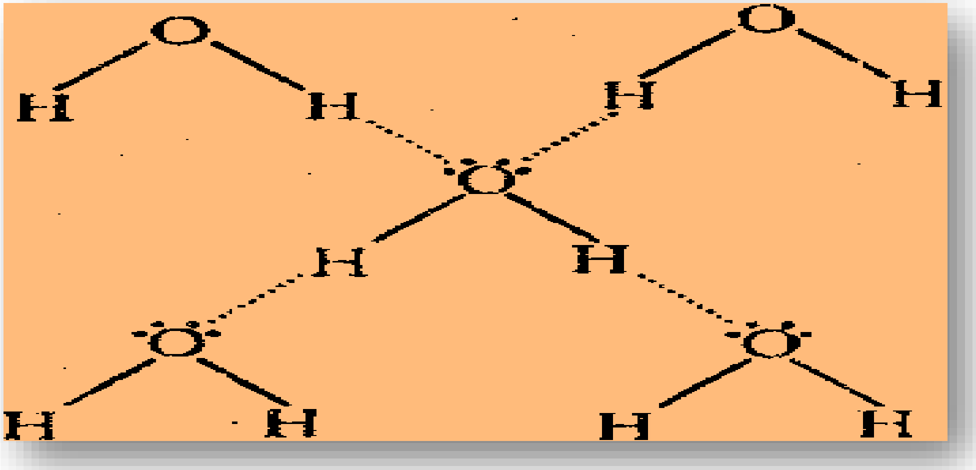
3) Hydrogen bonding in H_2O:

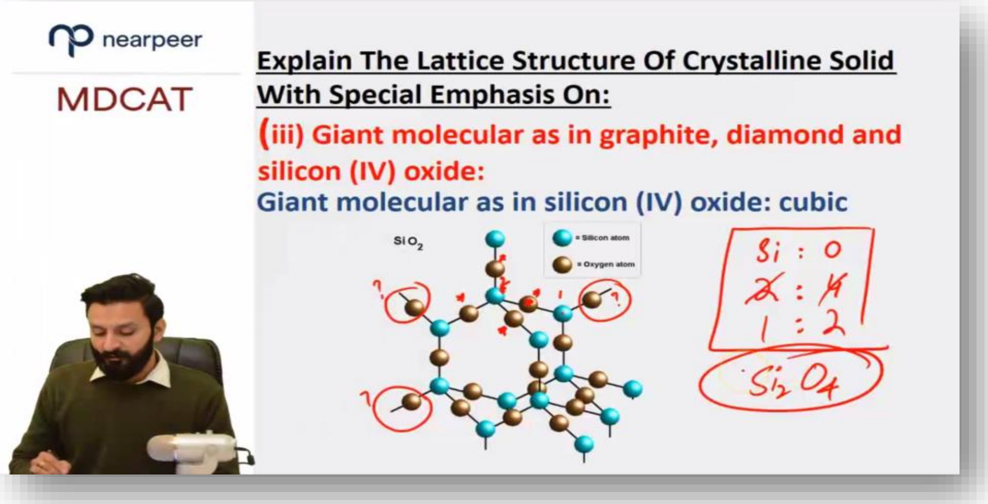
There are two hydrogen bonds per water molecule.

This is the reason, why its intermolecular hydrogen bonding is stronger than that of HF and NH^3. This is responsible for very high boiling point of water.

4) Hydrogen bonding in ethyl alcohol:

Hydrogen bonding in ethyl alcohol is weaker than water. This is the reason why boiling point of alcohol is lower than that of water and is more volatile.

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MDCAT

Explain The Lattice Structure Of Crystalline Solid With Special Emphasis On:

(iii) Giant molecular as in graphite, diamond and silicon (IV) oxide:

Giant molecular as in silicon (IV) oxide: cubic

Si : O

$\cancel{2}$: $\cancel{4}$

1 : 2

Si_2O_4

Get better understanding of the Unit 2A of MDCAT Chemistry by studying from 3D diagrams at www.nearpeer.org

PRACTICE EXERCISE (FOR UHS TOPICS)

1. **With increase of temperature from T1 to T2, isotherm moves away from the axis. This is because of**

A) Increase in pressure C) Increase in volume

B) Increase in mass D) both ‘a’ and ‘b’

2. **Pressure of air that can support 760mm Hg coloumn at sea level is called**

A) 1atm C) 101325Nm^{-2}

B) 114.7 psi pounds inch^{-2} D) All of these

3. **If absolute temperature of gas is reduced to ½ and pressure is doubled, the volume of gas will**

A) Remains unchanged C) Increase four times

B) Reduce to 1/4th D) Be doubled

4. **The value of universal gas constant R depends on**

A) Temperature of gas C) Number of moles of gas

B) Volume of gas D) Units of volume and pressure

5. **Main cause of deviation of real gases form ideal behaviour is**

A) There are no force of attraction among the molecules of gas

B) Actual volume of gas molecule is negligible as compared to total volume of vessel

C) Gases exert pressure when strikes with wall of container

D) Both “a” and “b”

6. **A gas will approach ideal behaviour at**

A) Low temperature C) High temperature, low pressure

B) Low temperature , high pressure

D) High temperature, high pressure

7. The expression for root mean square velocity is:

(A) $C_{rms} = \left(\frac{3RT}{M}\right)^{1/2}$

(C) $C_{rms} = \left(\frac{3PV}{M}\right)^{1/2}$

(B) $C_{rms} = \left(\frac{3P}{d}\right)^{1/2}$

(D) All are correct

8. The kinetic molecular theory of gases was put forward in 1873 by:

(A) Boltzmann

(C) Maxwell

(B) Clausius

(D) Bernouli

9. At constant temperature, the pressure of an ideal gas is doubled, its density becomes:

(A) Half

(C) Double

(B) Same

(D) None

10. Which one has the lowest density at room temperature:

(A) Ne

(C) N_2

(B) NH_3

(D) CO

11. Under what conditions real gases deviate from ideal behaviour:

(A) High temperature

(C) Low temperature

(B) High pressure

(D) Both (B) and (C)

12. Which of the following is the weakest force?

A) Ion dipole force

C) Dipole dipole force

B) Dipole induced dipole force

D) London dispersion force

13. Which of the following molecules has minimum boiling point?

A) Water

C) Acetone

B) Ammonia D) Ethyl alcohol

14. Boiling point of propanone is greater than propane. This is because

A) Propanone has hydrogen bonding C) Propanone has dipole forces

B) Propanone has ion dipole forces D) Propanone has debye forces

15. Which of the following is incorrect about evaporation?

A) It is a continuous process C) It is a surface phenomena

B) It causes cooling D) It is exothermic

16. With the increase of carbon atoms in class of organic compounds, which property decreases?

A) Viscosity C) Density

B) Melting point D) Vapour pressure

17. Which liquid has minimum vapour pressure?

A) Isopentane C) Chloroform

B) Diethyl ether D) Caron tetrachloride

18. A sample of 5.0g of which substance is held together by dipole dipole forces

A) H2 C) HBr

B) NH3 D) CaH2

19. A substance which possess characteristically low vapor pressure can be expected to have

A) Weak intermolecular forces C) Smaller ΔHv

B) Highest boiling point D) All of the above

20. DNA has two spiral chains. They are linked through Hydrogen bonding which is dominant between

A) C and H C) O and H

B) N and H D) N and O

21. Vapour pressure of water at 100oC is:

A) 55 mm Hg

B) 355 mm Hg

C) 760 mm Hg

D) 1489 mm Hg

22. Which one of the following does not show hydrogen bonding:

A) Water

B) Phenol

C) Ethyl alcohol

D) Diethyl ether

23. NaCl shows number of formula units per unit cell

A) 3

B) 4

C) 5

D) 6

24. Which of the following ionic compounds has smaller lattice energy

A) LiCl

B) NaCl

C) KCl

D) RbCl

25. Which of the following substance shows property of covalent crystals?

A) NaI

B) KI

C) CdI_2

D) LiCl

26. Diamond is bad conductor of electricity due to

A) Tight structure

B) Less free electrons is its structure

C) High density

D) Is transparent to light

27. Which is a pseudo solid?

A) CaF_2

B) Glass

C) NaCl

D) All of these

28. Which of the following statements is incorrect

A) Structure of ice is hexagonal

B) Ethanol is more soluble in water than chloromethane

C) Propane has less boiling point than pentane

D) Strength of H-bond is 20 times less than covalent bond

29. Which is the example of crystalline solid

A) Glass

C) Rubber

B) Plastic

D) Quartz

30. Ionic compounds which have maximum ∆Hlattic

A) LiCl

C) KCl

B) NaCl

D) CaCl2

31. For gases obeying Boyle's law, if pressure is quadrupled, the volume becomes:

A) Double

B) One half

C) One fourth

D) Remains constant

32. Gases are good conductor of electricity at:

A) Low temperature

D) Low pressure

C) High pressure

D) Low temperature and high pressure

33. The volume of 2.8g of CO at 27°C and 0.0821 atm. is:

A) 30 dm3

B)3 dm3

C) 0.3 dm3

D) 1.5 dm3

34. At higher temperature isotherm moves away from both the axes because of increase in:

A) Pressure

B)Volume

C) Number of moles

D) All

35. How many balloons of 0.25 dm3 capacity at 1 atmospheric pressure can be filled from a hydrogen gas cylinder of 5 dm3 capacity at 10 atmospheric pressure?

A) 50

B) 90

C) 180

D) 200

36. What will be the ratio of volumes of equal masses of O2, H2 and CH4 kept in same container under same conditions?

A) 2 : 16 : 2

B)1 : 16 : 2

D) 2 : 16 : 1

D) 1 : 2 : 1

37. If V1 = 5 litres, P1 = 2 atm, P2 = 1 atm., T1 = 273°C, T2 = 0°C and V2 = ? in litre.

A) 5

B)80

C) 125

D) 10

38. When a graph is plotted between pressure on x-axis and the PV/RT on y-axis for an ideal gas, then:

A) Hyperbolic curve is obtained

B) A straight line is obtained running in-between x-axis and y-axis

C) A straight line is obtained running parallel to pressure axis

D) A peak is obtained running parallel to compressibility factor axis

39. Which gas is likely to be the most ideal?

A) H2S

B) CH4

C) NH3

D) Ne

40. Which is correct increasing order of boiling points of the hydrides of VI-A group?

A) $H_2Te < H_2S < H_2Se < H_2O$

B) $H_2S < H_2Se < H_2Te < H_2O$

C) $H_2Se < H_2S < H_2O < H_2Te$

D) $H_2Te < H_2Se < H_2S < H_2O$

41. Hydrides of which one of the following group has relatively low boiling points?

A) IV-A

B) VI-A

C) V-A

D) VII-A

42. The overall structure of ice is just like that of a:

A) Graphite

B) Sugar

C) Tin D) Diamond

43. Which one of the following statement is not true about evaporation?

A) Spontaneous process B) Causes cooling

C) Temperature increasing D) Increases with increase in surface area

44. Following properties will decrease with increase in temperature except:

A) Surface tension B) Viscosity

C) Density D) Vapour pressure

45. Which of the following molecules should be more volatile?

A) HF B) HCl

C) HBr D) HI

46. Which of the following has no hydrogen-bonding?

A) Diethyl ether B) Water

C) Ethyl alcohol D) Phenol

47. For the wetting liquids:

A) Force of adhesion exceeds the force of cohesion

B) Force of cohesion exceeds the force of adhesion

C) Force of adhesion becomes equal to force of cohesion

D) All the above statements are incorrect

48. Amorphous substances show:

(i) Short and long range order

ii) Short range order

(iii) Long range order

(iv) have no sharp melting point

A) (i) and (ii) are correct B) (ii) and (iv) are correct

D) (ii), (iii) and (iv) are correct D) (i) and (iv) are correct

49. They hydrogen bonding is absent is:

A) Ice B) $CHCl_3$ & CH_3COCH_3

C) Steam D) DNA

51. Ethylene glycol has less V.P than ethanol because:

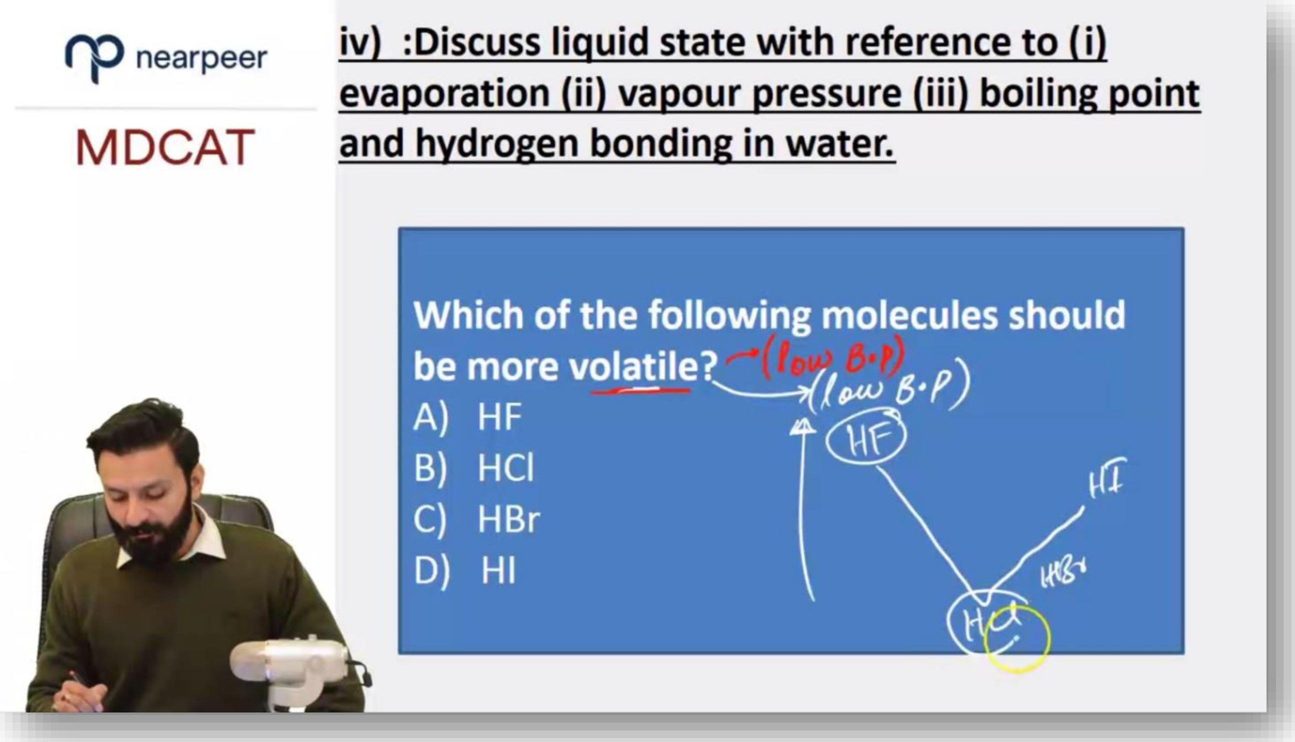
A) Molecular mass B) Size of molecule

C) H-bond D) Ethylene less volatile than C_2H_5OH

ANSWER KEY

1	**C**	**11**	**D**	**21**	**C**	**31**	**C**	**41**	**A**
2	**D**	**12**	**D**	**22**	**D**	**32**	**D**	**42**	**D**
3	**B**	**13**	**C**	**23**	**B**	**33**	**A**	**43**	**C**
4	**D**	**14**	**C**	**24**	**D**	**34**	**B**	**44**	**D**
5	**D**	**15**	**D**	**25**	**D**	**35**	**D**	**45**	**B**
6	**C**	**16**	**D**	**26**	**A**	**36**	**B**	**46**	**A**
7	**D**	**17**	**B**	**27**	**B**	**37**	**A**	**47**	**A**
8	**D**	**18**	**C**	**28**	**A**	**38**	**C**	**48**	**B**
9	**C**	**19**	**B**	**29**	**D**	**39**	**D**	**49**	**C**
10	**B**	**20**	**B**	**30**	**A**	**40**	**B**	**50**	**C**

Video Solution of the Practice Questions and Tips on how to approach the questions. Visit: www.nearpeer.org



iv) :Discuss liquid state with reference to (i) evaporation (ii) vapour pressure (iii) boiling point and hydrogen bonding in water.

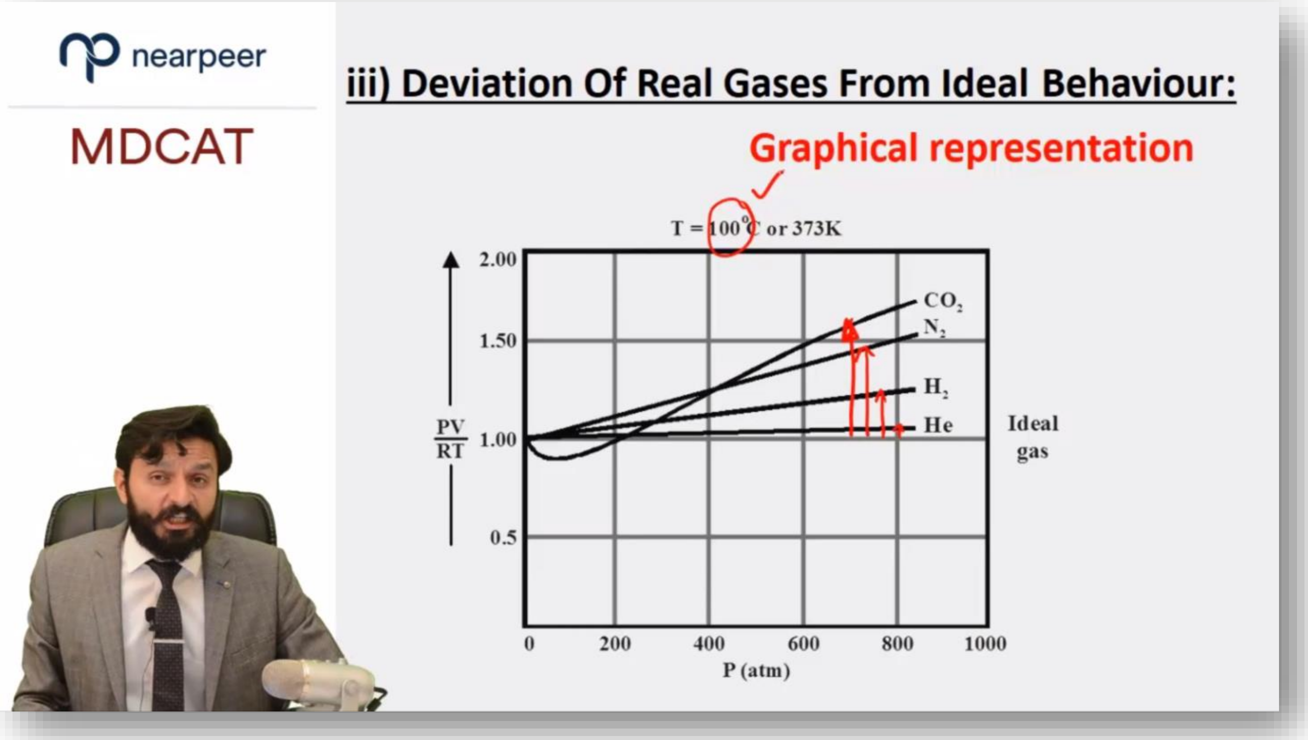
Which of the following molecules should be more volatile? (low B.P) (low B.P)

A) HF

B) HCl

C) HBr

D) HI



iii) Deviation Of Real Gases From Ideal Behaviour:

Graphical representation

T = 100°C or 373K

UHS TOPIC III A

ATOMIC STRUCTURE

LEARNING OUTCOMES

In this topic, student should be able to:

a) Identify and describe the proton, neutron and electron in terms of their relative charges and relative masses.

b) Discuss the behaviour of beams of protons, neutrons and electrons in electric fields.

c) Calculate the distribution of mass and charges within an atom from the given data.

d) Deduce the number of protons, neutrons and electrons present in both atoms and ions for a given proton and nucleon numbers/charge.

e) i) Describe the contribution of protons and neutrons to atomic nuclei in terms of proton number and nucleon number.

ii) Distinguish between isotopes on the basis of different numbers of neutrons present.

f) Describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1,2 and 3 and also the 4s and 4p orbitals.

g) Describe the shapes of s, p and d-orbitals.

h) State the electronic configuration of atoms and ions given, the proton number/charge for period 1, 2, 3 and 4 (hydrogen to Krypton).

i) Explain:

- i) Ionization energy.
- ii) The factors influencing the ionization energies of elements.
- iii) The trends in ionization energies across a period and down a group of the periodic table.

j) Explain and use the term Electron Affinity.

INTRODUCTION

An atom may consist of more than 100 subatomic particles. Out of these, three are called fundamental particles namely, electron, proton and neutron. Number of protons in an atom is called proton number or atomic number (Z). The sum of number of protons and neutrons in an atom is called mass number or nucleon number (A). The mass of the element expressed in grams is called atomic mass (which is not a whole number usually).

Comparative study of electron, proton, and neutron in terms of their masses and charges:

No.	Quantity		Electron	Proton	Neutron
1)	Charge		-1.6022×10^{-19} C	$+1.6022 \times 10^{19}$ C	Neutron
2)	Mass	kg	9.1095×10^{-31}	1.6726×10^{-27}	1.6750×10^{-27}
		amu	5.4858×10^{-4}	1.0073	1.0087
3)	Relative Mass		1	1836 times	1840 times

BEHAVIOR OF BEAM OF ELECTRONS, PROTONS AND NEUTRONS IN AN ELECTRIC FIELD

(i) Electrons:

When electrons are passed through the applied electric field, they undergo deflection towards positive plate showing that they are negatively charged.

(ii) Protons:

When protons are passed through the applied electric field, they undergo deflection towards negative plate showing that they are positively charged.

(iii) Neutrons:

When neutrons are passed through the applied electric field, they remain un-deflected showing that they are neutral particles.

DISTRIBUTION OF MASS AND CHARGES WITHIN AN FROM THE GIVEN DATA

Atomic Number (Z):

The atomic number is the number of protons found in the nucleus of an atom and therefore, identical to the charge number of the nucleus. It is conventionally represented by the symbol *Z.* The atomic number uniquely identifies a chemical element. In an atom of neutral charge, the atomic number is also equal to the number of electrons.

Mass Number (A):

The mass number (A), also called atomic mass number or nucleon number, is the total number of protons and neutrons (together known as nucleons) in an atomic nucleus
(A = Z + N).

- The mass number is different for each different isotope of a chemical element.

- Mass number is not the same as the atomic number (Z) which denotes the number of protons in a nucleus, and thus uniquely identifies an element.

- The difference between the mass number and the atomic number gives the number of neutrons (N) in a given nucleus: N=A – Z. N is known as the neutron number of the atom.

- Since, protons and neutrons have approximately the same mass (and the mass of the electrons is negligible for many purposes), the atomic mass of an atom is roughly equal to A.

Atomic masses are measured in amu (atomic mass unit)

1 amu = 1.66×10^{-27} kg

- Atomic nucleus is represented as $_ZX^A$ where Z, the charge number = number of protons.

A, the mass number = number of protons + number of neutrons.

Number of protons, neutrons and electrons present in both atoms and ions for a given proton and nucleon numbers/charge.

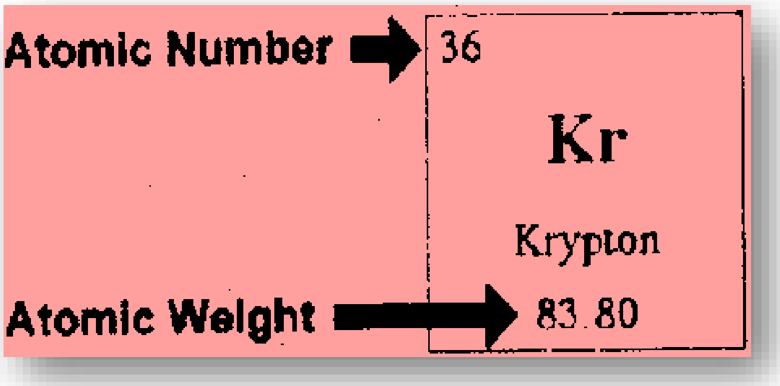
For any element:

Number of Protons = Atomic Number

Number of Electrons = Number of Protons = Atomic Number

Number of Neutrons = Mass Number – Atomic Number

Example:



For Krypton:

- Number of Protons = Atomic Number = 36
- Number of Electrons = Number of Protons = Atomic Number = 36
- Number of Neutrons = Mass Number = Atomic Number = 84 – 36 = 48

Proton Number (Atomic Number):

The proton number is equal to the number of protons in the nucleus of an atom.

The proton number is also equal to the number of electrons in orbit around a neutral atom.

Nucleon Number (Mass Number):

The nucleon number is equal to the total number of nucleons (protons and neutrons) in the nucleus of an atom.

Distinguish between isotopes on the basis of different numbers of neutrons present:

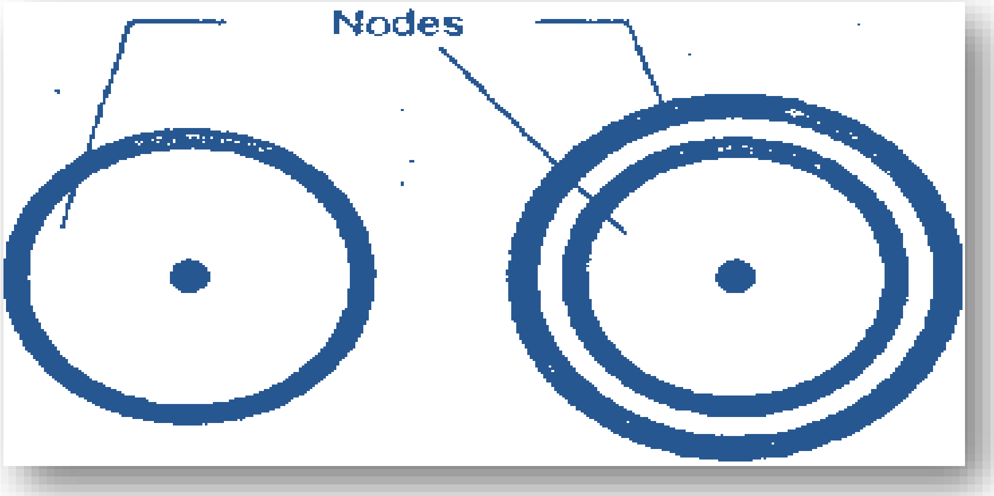
Isotopes are atoms of the same element which differ in mass and in number of neutrons. The number of protons (the atomic number) is equal for all isotopes of one element, because this number defines the elemental type of the atom.

- The number of neutrons differ between different isotopes of the same element, as does the total number of nucleons (or protons + neutrons) known as the mass number. This determines the physical properties of an element.

- The number of electrons is equal to the number of protons in a neutral atom (of net electric charge zero), and this number of electrons determines the chemical properties of the atom.

For example:

Carbon-12, carbon-13 and carbon -14 are three isotopes of the element carbon with mass numbers 12, 13 and 14 respectively.



- The atomic number of carbon is 6 (every neutral atom of carbon has exactly 6 protons and 6 electrons).
- The neutron numbers in these isotopes of carbon are therefore

(i) C-12 = 12 – 6 = 6

(ii) C-13 = 13 – 6 = 7

(iii) C-14 = 14 – 6 = 8

Describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the 4s and 4p orbitals:

•Number of subshells is equal to given principal quantum number and their relative energies are:

s < p < d < f

Principal quantum number (n)	Number of subshells	Relative energies of sub-shell	Number of orbitals
n = 1	1-subshell (s)	s	1-orbital
n = 2	1-subshell (s, p)	s < p	4-orbitals
n = 3	1-subshell (s, p ,d)	s < p < d	9-orbitals
n = 4	1-subshell (s, p, d, f)	s < p < d < f	16-orbitals

POINT TO PONDER: The volume of space in which there is a 95 % chance of finding the electron is called?

SHAPES OF S AND P ORBITALS

(i) Shapes of s-orbitals:

s-orbital is spherical in shape and is represented by a circle (cut of sphere)higher the value of 'n' for s-subshell, greater will be its size.

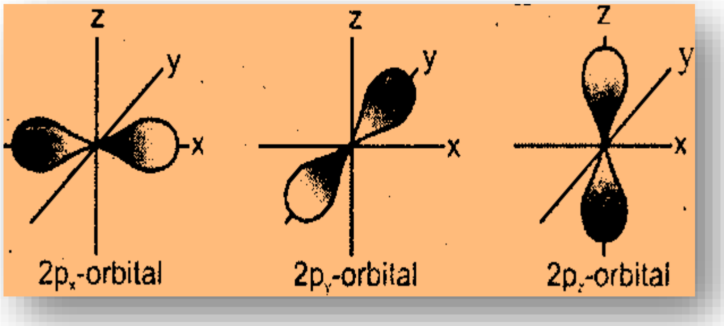
Example: 2s is larger in size than 1s.

Nodal Surface or Nodal Plane:

The probability of finding the electron is zero between two orbitals. This plane is called Nodal plane or Nodal surface.

(ii) Shapes of p-orbitals:

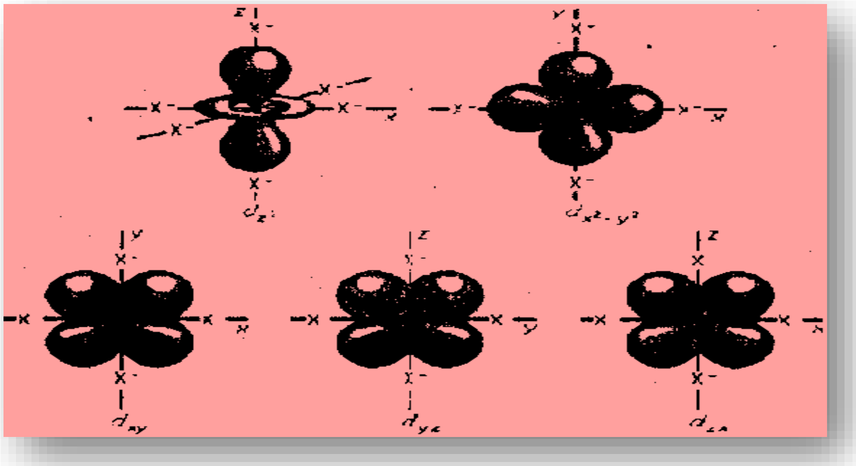
Each p-orbital has two lobes in dumbbell shape. These lobes are either oriented along x-axis (p_x), y-axis (p_y) or z-axis (p_z). The size of p-orbital increases with increase in its 'n' value.



Example:3p_x orbital is larger in size than 2p_x but both have same shape.

(iii) Shapes of d-orbitals:

Each d-orbital has four lobes or two dumbbell in sausage shape. These lobes are oriented along x-axis, y-axis and z-axis. The size of d-orbital increases with increase in its 'n' value.



ELECTRONIC DISTRIBUTION

It is distribution of electrons in shells, sub-shells and orbitals of an atom according to definite rules. The following rules are adopted in order to distribute the electrons in the orbitals of sub-shells of shells in an atom.

AUFBAU PRINCIPLE:

The electrons should be filled in energy sub-shells in order of increasing energy values. The electrons are first placed in

Is, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s and so on

POINT TO PONDER: It is impossible for two electrons reading is the same orbital of a poly electron atom to have the same values of four quantum numbers?

Pauli's Exclusion Principle:

Two electrons in the same orbital must have opposite spins.

Hund's Rule:

If degenerate orbitals are available and more than one electron are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins.

NOTE: Half-filled and completely filled sub-shells, are more stable e.g. Cr and Cu.

ELECTRONIC CONFIGURATION OF SOME ELEMENTS

ELEMENT	ATOMIC NUMBER	ELECTRON CONFIGURATION NOTATION
Hydrogen	1	$1s^1$
Helium	2	$1s^2$

Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$Is^2\ 2s^2\ 2p_x^1\ 2p_y^0\ 2p_x^0$
Carbon	6	$Is^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_x^0$
Nitrogen	7	$Is^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_x^1$
Oxygen	8	$Is^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_x^1$
Fluorine	9	$Is^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_x^1$
Neon	10	$Is^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_x^2$
Sodium	11	$[Ne]3s^1$
Magnesium	12	$[Ne]3s^2$
Aluminum	13	$[Ne]\ 3s^2\ 3p_x^1\ 3p_y^0\ 3p_z^0$
Silicon	14	$[Ne]\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
Phosphorus	15	$[Ne]\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
Sulphur	16	$[Ne]\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$
Chlorine	17	$[Ne]\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$
Argon	18	$[Ne]\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$
Potassium	19	$[Ar]4s^1$
Calcium	20	$[Ar]4s^2$
Scandium	21	$[Ar]4s^2\ 3d_{xy}^1\ 3d_{yz}^0\ 3d_{xz}^0 3d_{xz}^0\ 3d_{x^2-y^2}^0\ 3d_{x^2}^0$
Titanium	22	$[Ar]4s^2\ 3d_{xy}^1\ 3d_{yz}^1\ 3d_{xz}^0 3d_{x^2-y^2}^0\ 3d_{-x^2}^0$
Vanadium	23	$[Ar]\ 4s^2\ 3d_{xy}^1\ 3d_{yz}^0 d_{xz}^0 3d_{x^2-y^2}^0\ 3d_{x^2}^0$
Chromium	24	$[ArJ4s^1\ 3d_{xy}^1\ 3d_{yz}^1 d_{xz}^1 3d_{x^2-y^2}^1\ 3d_{x^2}^1$
Manganese	25	$[Ar]\ 4s^2\ 3d_{xy}^1\ 3d_{yz}^1\ 3d_{xz}^1 3d_{x^2-y^2}^1\ 3d_{x^2}^1$

Iron	26	$[Ar]4s^2\ 3d_{xy}^2\ 3d_{yz}^1\ 3d_{xz}^1 3d_{x^2-y^2}^1\ 3d_{x^2}^1$
Cobalt	27	$[Ar]4s^2\ 3d_{xy}^2\ 3d_{yz}^2\ 3d_{xz}^2 3d_{x^2-y^2}^1\ 3d_{x^2}^1$
Nickel	28	$[Ar]4s^1\ 3d_{xy}^2\ 3d_{yz}^2\ 3d_{xz}^2 3d_{x^2-y^2}^1\ 3d_{x^2}^1$
Cooper	29	$[Ar]4s^2\ 3d_{xy}^2\ 3d_{yz}^2\ 3d_{xz}^2 3d_{x^2-y^2}^2\ 3d_{x^2}^2$
Zinc	30	$[Ar14s^2\ 3d_{xy}^2\ 3d_{yz}^2\ 3d_{xz}^2 3d_{x^2-y^2}^2\ 3d_{x^2}^2$
Gallium	31	$[Ar]4s^2\ 3d^{10}4p_x^1 4p_y^0 4d_z^0$
Germanium	32	$[Ar]4s^2\ 3d^{10}4p_x^1 4p_y^0 4d_z^0$
Arsenic	33	$[Ar]4s^2\ 3d^{10}4p_x^1 4p_y^1 4d_z^1$
Selenium	34	$[Ar]4s^2\ 3d^{10}4p_x^2 4p_y^1 4d_z^1$
Bromine	35	$[Ar]4s^2\ 3d^{10}4p_x^2 4p_y^1 4d_z^1$
Krypton	36	$[Ar]4s^2\ 3d^{10}4p_x^2 4p_y^2 4d_z^2$

IONIZATION ENERGY

The minimum amount of energy required to remove an electron from the outer most shell of an isolated gaseous atom is called ionization energy.

Example:

$H_{(g)}$ + heat energy → $H^{+}_{(g)}$ + le^{-}ΔH = 1313.315 kJ/mole

POINT TO PONDER: Measurement of successive ionization energies supports the idea?

Factors Affecting the Ionization Energy:

(i) Atomic radius is inversely related to ionization energy

(ii) Effective nuclear charge is directly related to ionization energy.

(iii) Shielding effect is inversely related to ionization energy

(iv) Nature of orbital (order of ionization energy s > p > d > f

TRENDS IN PERIODIC TABLE

(i) Down the group:

The ionization energy decreases down the group due to decreasing nuclear force which is due to:

(a) Successive addition of shells:

As a result of this, valence electrons are placed away from nucleus and are easily removable.

(b) Shielding effect:

It increases with increasing number of shells.

(ii) Along the Period:

The ionization energy generally increases along the period with increasing nuclear force/charge which is due to.

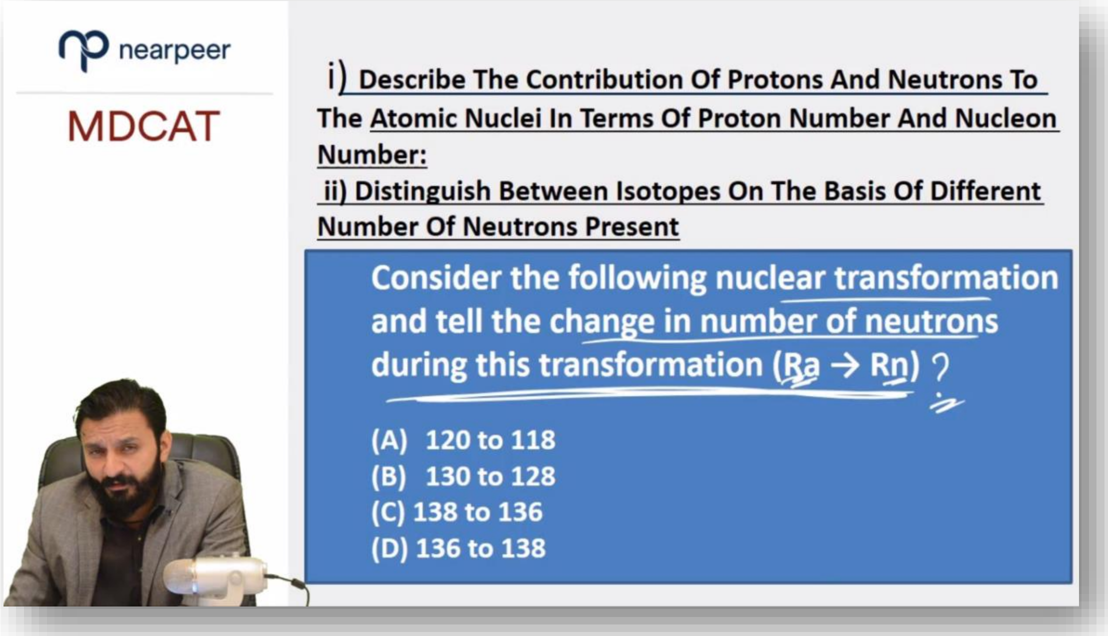
(a) Increasing Proton number:

The nuclear charge on the nucleus and negative charge (electrons) in the valence shell increases with increasing proton number along the period. As a result, attraction increases and electrons become more tightly bound.

(b) Constant number of shells:

Along a period the number of shells

(Principal quantum number = n) remains same, so there is no shielding effect.



i) Describe The Contribution Of Protons And Neutrons To The Atomic Nuclei In Terms Of Proton Number And Nucleon Number:

ii) Distinguish Between Isotopes On The Basis Of Different Number Of Neutrons Present

Consider the following nuclear transformation and tell the change in number of neutrons during this transformation (Ra → Rn) ?

(A) 120 to 118

(B) 130 to 128

(C) 138 to 136

(D) 136 to 138

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PRACTICE EXERCISE

1. **Which of the following formula is used to determine number of sub-shells in a shell?**

A) $2n^2$ C) $m = 2\ell + 1$

B) $\ell = n - 1$ D) 2(2l+1)

2. **Ionization energy does not depend upon one of the following factor**

A) atomic number C) shielding effect

B) nuclear force D) mass number

3. The maximum number of electrons in a sub-shell with l = 3 is:

(A) 6

(C) 10

(B) 14

(D) 18

4. Quantum number values for 2p orbitals are:

(A) n = 2, l = 1

(C) n = 1, l = 2

(B) n = 1, l = 0

(D) n = 2, l = 0

5. When 6d orbital is complete, entering electron goes into:

(A) 7f

(C) 7s

(B) 7p

(D) 7d

6. Total number of d-electrons in an atom of atomic number 26 is:

(A) 4

(C) 5

(B) 6

(D) 7

7. The ionization energy value of hydrogen

(A) -1313 kJ/mol

(C) 1313 kJ/mol

(B) -1313 kJ/mol/n^2

(D) 496 kJ/mol

8. Which of the following species has greatest number of electrons in the valence shell

(A) H^{1-}

(C) F^{1-}

(B) B

(D) N

9. Which of the following species has fundamental particles in order e > n > p

Compare the lightest isotopes

(A) N^{3-}

(C) Cl^{1-}

(B) O^{2-}

(D) P^{3-}

10. The highest ionization energy is shown by a group elements

(A) Alkali metals

(C) Alkaline earth metals

(B) Halogens

(D) Noble gases

11. The iso-electronic species amongst the followings are

(A) Ne, K^{1+}, F^{1-}

(C) Ar, K^{1+}, Cl^{1-}

(B) Ar, K^{1+}, F^{1-}

(D) He, H^{1-}, Li

12. For particular subshell, the maximum value of ionization energy is shown when electron is present in

(A) s

(C) p

(B) d

(D) f

13. The ionization energy is maximum for

(A) O

(C) B

(B) C

(D) N

14. The particle that shows minimum response in the applied electric field

(A) Electron

(C) Proton

(B) Neutron

(D) positron

15. The order of subshells with respect to the relative energies

(A) $s > p > d > f$

(C) $s < p < d < f$

(B) s > f > p > d (D) s < p < f < d

16. Which of the following is correct with respect to the application of principle?

(A) Hund's rule = electron in subshells

(B) Auf-bau principle = electrons in orbital

(C) Pauli's exclusion principle = spin of electrons in one orbital

(D) n + *l* = electrons in orbitals

17. Electron is lighter than a neutron by how many times

(A) 1836 (C) 1840

(B) 1700 (D) 1800

18. Consider the following nuclear transformation and tell the change in number of neutrons during this transformation (Ra → Rn)

$$^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

(A) 120 to 118 (C) 130 to 128

(B) 138 to 136 (D) 136 to 138

19. The electronic configuration of an element in trivalent state is [$_{18}$Ar], 4s^2, 3d^4. This electronic configuration of represents an element

(A) Cr (C) A*l*

(B) Mn (D) Co

20. By comparing the lightest isotopes, indicate one which is odd with respect to neutrons

(A) N (C) C

(B) O (D) H

21. The orbital which is farthest to the nucleus is:

(A) f (C) p

(B) d (D) s

22. Which statement is incorrect?

(A) Second ionization energy is higher than first ionization energy

(B) Third ionization energy is lower than fourth ionization energy

(C) First ionization energy is lower than third ionization energy

(D) Fourth ionization energy is greater than fifth ionization energy

23. Which one of the following has the same number of electrons as an alpha particle?

(A) H (C) H_2

(B) H^+ (D)He

24. Which one of the following electronic configurations represents an element that forms a simple ion with a charge of -3?

(A) $1s^2\ 2s^2\ 2p^6 3s^2\ 3p^1$

(B) $1s^2\ 2s^2\ 2p^6 3s^2\ 3p^3$

(C) $1s^2\ 2s^2\ 2p^6 3s^2\ 3p^6\ 3d^1\ 4s^2$

(D)$1s^2\ 2s^2\ 2p^6 3s^2\ 3p^6\ 3d^3\ 4s^2$

25. Which of the following formulae represents a particle with the composition 1 proton, 1 neutron and 2 electrons? (D represents deuterium, ^{2}H)

(A) D

(B) D^-

(C) H^-

(D)He

26. Which of the following particles would, on losing an electron, have a half-filled set of p orbitals?

(A) C^-

(B) N

(C) N^-

(D) O^+

27. The electronic configurations of four elements are given. Which of these elements has the highest first ionization energy?

(A) $1s^2\ 2s^2\ 2p^3$

(B) $1s^2\ 2s^2\ 2p^4$

(C) $1s^2\ 2s^2\ 2p^6 3s^1$

(D) $1s^2\ 2s^2\ 2p^6 3s^2\ 3p^3$

28. Which equation is used to define the first ionization of bromine?

(A) $\mathrm{Br(g)} \rightarrow Br^-(g)$ -e^-

(B) $\mathrm{Br(g)} \rightarrow Br^+(g)+e^-$

(C) $\frac{1}{2}Br_2\mathrm{(g)} \rightarrow Br^-(g)$ -e^-

(D) $\frac{1}{2}Br_2\mathrm{(g)} \rightarrow Br^+(g) + e^-$

29. The set of orbitals having n + *l* = 5 are:

(A) 2p, 3d, 3s

(B) 3s, 4p, 4d

(C) 3p, 3d, 5s

(D) 5s, 4p, 3d

30. The values of quantum numbers for the valence electrons of an atom are given by n = 2, *l* = 1, m = 0, +1, –1, s = +$\frac{1}{2}$. The given atom is:

(A) Lithium

(C) Carbon

(B) Berylium

(D) Boron

31. The ratio of e/m values of a proton and an α-particle is:

(A) 2 : 1

(C) 1 : 2

(B) 1 : 1

(D) 1 : 4

32. If the value of principal quantum number is 3, the maximum number of value of magnetic quantum number:

(A) 1

(C) 5

(B) 4

(D) 9

33. If the value of n = 4, the number of possible values of "*l*"?

(A) 2

(C) 4

(B) 3

(D) 5

34. In chromium (Cr – 24) the number of electrons with azimuthal quantum numbers, *l* = 1 and 2 are respectively:

(A) 12 and 4

(C) 16 and 4

(B) 12 and 5

(D) 16 and 5

35. The set of quantum numbers which represents the highest energy of an electron?

(A) $n = 3, l = 1, m = 1, s = +\frac{1}{2}$

(C) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

(B) $n = 3, l = 2, m = 1, s = +\frac{1}{2}$

(D) $n = 3, l = 0, m = 0, s = +\frac{1}{2}$

36. Which of the following sets of the quantum numbers is permitted?

(A) $n = 4, l = 2, m = +3, s = +\frac{1}{2}$

(B) $n = 3, l = 3, m = +3, s = +\frac{1}{2}$

(C) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

(D) $n = 4, l = 3, m = +1, s = 0$

37. The electronic configuration of H^{-} is:

(A) $1s^0$

(B) $1s^1$

(C) $1s^2$

(D)$1s^2\ 2s^1$

38. The electronic configuration of $_{29}Cu$ is:

(A) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$

(B) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$

(C) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^9$

(D) $1s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$

39. How many electrons can be accommodated in subshell for which n = 3, l = 1?

(A) 6

(B) 32

(C) 10

(D) 18

40. Consider the following nuclear reaction $^{27}_{13}Al + ^{4}_{2}H \longrightarrow ^{30}_{15}P + \ldots\ldots\ldots$

(A) Neutron

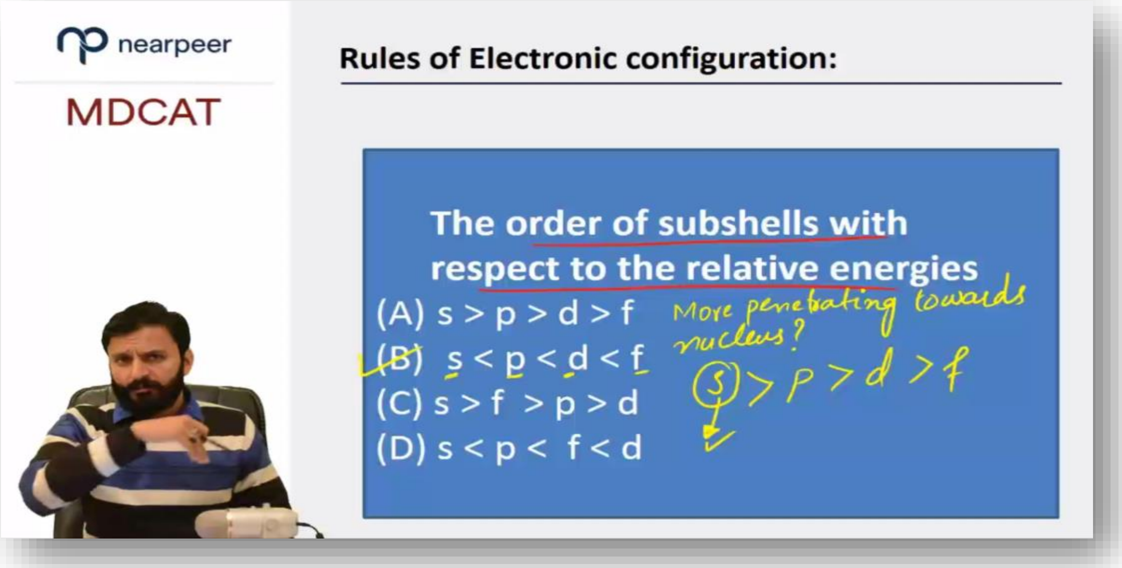
(B) Proton

(C) Positron

(D) Antineutrino

ANSWER KEY

1	**B**	**11**	**C**	**21**	**A**	**31**	**A**
2	**D**	**12**	**A**	**22**	**D**	**32**	**D**
3	**B**	**13**	**D**	**23**	**B**	**33**	**C**
4	**A**	**14**	**B**	**24**	**B**	**34**	**B**
5	**B**	**15**	**C**	**25**	**B**	**35**	**B**
6	**B**	**16**	**C**	**26**	**C**	**36**	**C**
7	**C**	**17**	**C**	**27**	**A**	**37**	**C**
8	**C**	**18**	**B**	**28**	**B**	**38**	**B**
9	**D**	**19**	**D**	**29**	**D**	**39**	**A**
10	**D**	**20**	**D**	**30**	**D**	**40**	**A**



Rules of Electronic configuration:

The order of subshells with respect to the relative energies

(A) $s > p > d > f$

(B) $s < p < d < f$

(C) $s > f > p > d$

(D) $s < p < f < d$

More penetrating towards nucleus?

$s > p > d > f$

UHS TOPIC IV A

CHEMICAL BONDING

LEARNING OUTCOMES

In this topic, student should be able to:

a) Characterize electrovalent (ionic) bond as in sodium chloride and calcium oxide

b) Use the 'dot-and-cross' diagrams to explain:

i) Covalent bonding, as in hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), hydrogen chloride, carbon dioxide, methane and ethane.

ii) Co-ordinate (dative covalent) bonding, as in the formation of the ammonium ionin: $H_3N^+–{}^-BF_3$ and H_3O^+

c) Describe the shapes and bond angles in molecules by using the qualitative model of Valence Shell Electron-Pair Repulsion (VSEPR) theory up to 4 pairs of electron including bonded electron pair and lone pair around central atom.

d) Describe covalent bonding in terms of orbital overlap, giving σ and π bonds.

e) Explain the shape of and bond angles in ethane, ethene and benzene molecules in terms of σ and π bonds

f) Describe hydrogen bonding, using ammonia and water as simple examples of molecules containing N-H and O-H groups.

g) Explain the terms bond energy, bond length and bond polarity (electronegativity difference) and use them to compare the nature of covalent bonds i.e. polar and non-polar.

h) Describe, intermolecular forces (Van der Waal's forces), based on permanent and induced dipoles, as in HCl, $CHCl_3$, Halogens and in liquid noble gases.

i) Describe metallic bonding in terms of positive ions surrounded by mobile electrons (sea of electrons).

j) Describe, interpret and/or predict the effect of different types of bonding (ionic bonding; covalent bonding; hydrogen bonding; Van der Waal's forces and metallic bonding) on the physical properties of substances.

k) Deduce the type of bonding present in a substance from the given information.

CHEMICAL BOND:

The force which holds two ro more atoms or ions to form a large variety of compounds is called chemical bond.

Causes of Chemical Combination:

Atoms of elements combine with each other to stabilize themselves. Two factors are 'necessary for their satisfaction:

(a) Every atom tries to attain electronic configuration near to a noble gas (wants to follow octet rule). The tendency of atoms to attain a maximum of eight electrons in the valence shell is called octet rule.

(b) Each atom tries to attain lowest energy state because it is a stable state.

IONIC BOND OR ELECTROVALENT BOND

The electrostatic force of attraction between oppositely charged ions is called ionic bond or electrovalent bond.

Ionic bond is formed' by the complete transfer of electrons from more electropositive elements to more electronegative elements.

Conditions necessary for ionic bond formation:

(1) Electropositive elements with low ionization like VI-A and VII-A, that lose electron and form cation.

(2) Electronegative elements with high electron affinity like VI-A and VII-A that gain electron and form

anion.

Note: Ionic bond is non-rigid and non-directional.

Examples:

(1) Formation of NaCl:

(i) $Na_{(g)} \rightarrow Na^+_{(g)} + 1e^-$ ΔH = 496 kJ/mole

2, 8, 1 2, 8

(ii) $Cl_{(g)} + le^- \rightarrow CI^-_{(g)}$ ΔH = – 349 kJ/mole

2, 8, 7 2, 8, 8

Then sodium and chloride ions combine to form NaCl.

$Na^+_{(g)} + CI^-_{(g)} \rightarrow NaCl_{(g)}$

POINT TO PONDER: In some ionic compounds there is a degree of sharing of electron clouds between cations and anions.

(2) Formation of CaO:

(i) $Ca_{(g)} \rightarrow Ca^{+2}_{(g)} + 2e^-$

2,8, 8,2 2,8, 8

(ii) $O_{(g)} + 2e^- \rightarrow O^{-2}_{(g)}$

2, 6 2,8

Then $Ca^{+2}_{(g)}$ combine to form CaO

$Ca^{+2}_{(g)} + O^{+2}_{(g)} \rightarrow CaO_{(5)}$

DOT CROSS DIAGRAM:

(i) Covalent Bond:

A bond formed by mutual sharing of electron between the two atoms is called covalent bond.

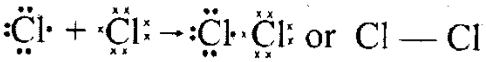
(a) Hydrogen molecule:

When two hydrogen atoms share their valence electrons, a covalent bond is formed.

Hx+•H → Hx•H or H – H

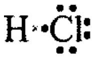
(b) Chlorine molecules:

When two chlorine atoms share their valence electrons, a covalent bond is formed.

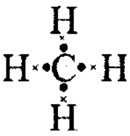


POINT TO PONDER: There is no sharp distinction between an ionic bond and a covalent bond?

(c) Hydrogen chloride molecule:

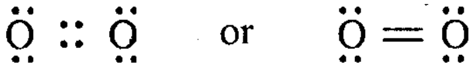


(d) Methane molecule:



(e) Oxygen molecules:

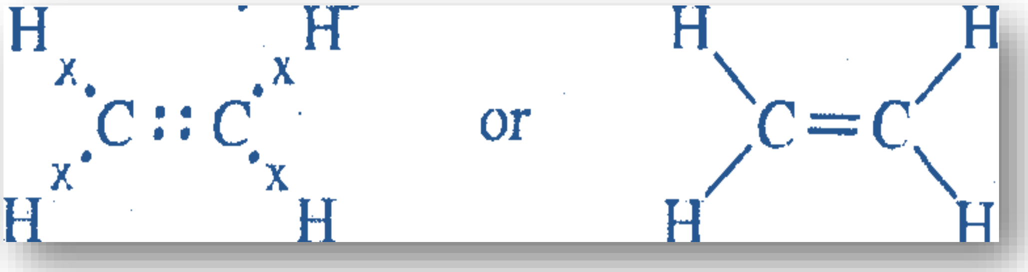
When two oxygen atoms share their valence electrons, a double covalent bond is formed



POINT TO PONDER: Fajan's rule predict the ionic and covalent character of bonds?

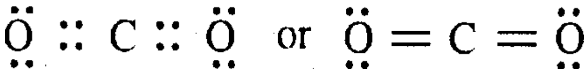
(f) **Ethene**:

When two carbon atoms share their valence electrons, a double covalent bond is formed. Each carbon atom makes two bonds separately with two hydrogen atoms.



(g) **Carbon dioxide**:

Two carbon atoms two bonds with each of the oxygen atoms separately.

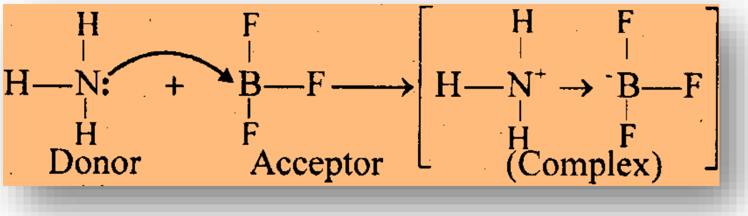


(ii) Co-ordinate Covalent Bond (Dative bond):

A covalent bond formed by the donation of an electron-pair by one of the bonded atoms to other is called co-ordinate covalent bond or dative or Danor-accepmr, bond. This bond is formed by over lapping of one completely filled orbital with one empty orbital. An atom that donates a pair is called acceptor (Lewis acid) this bond is re produced by an arrow pointing from donor to accepter.

Dative bonding between NH_3 and BF_3:

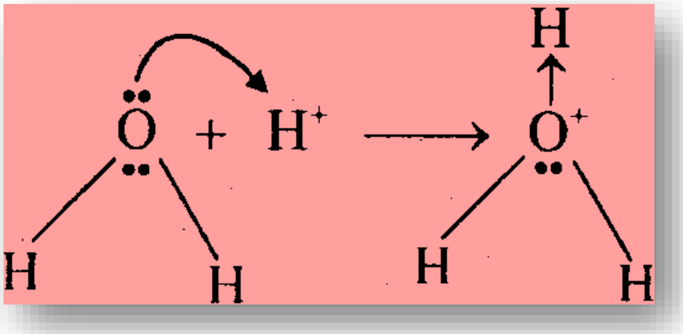
Nitrogen atom in $\ddot{N}H_3$ have lone pair and it donates it to Boron in BF_3 (which is electron deficient of octet) to form a co-ordinate covalent bond.



Note: In this case donor develops a positive charge and acceptor gets negative charge.

(1) **Hydronium ion formation**:

Oxygen in water donates a lone pair to form co-ordinate covalent bond to give H_3O^+. After this bond formation, distinction between covalent and Co-ordinate covalent bond vanishes i.e. all the bonds behave alike with 33 % co-ordinate covalent and 66 % covalent character.

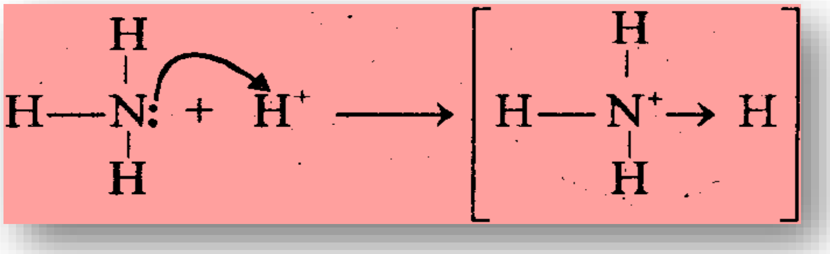


Hydronium Ion

(2) Compounds of nitrogen and its family members.

(i) Ammonium ion formation

Nitrogen in NH_3 donates its lone pair to H^+ to form Co-ordinate covalent bond and to give $^+NH_4$ (Ammonium ion).

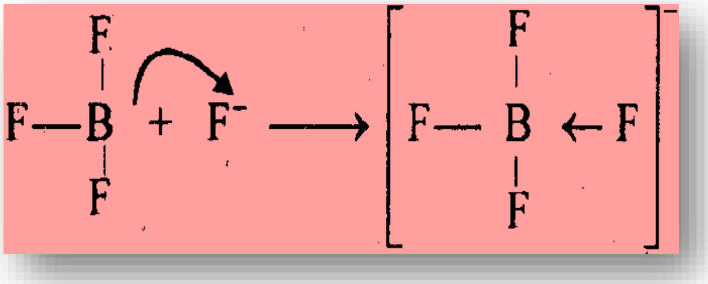


Ammonium ion

Similarly, Nitrogen in primary (RNH_2) secondary (R_2NH) and tertiary amines (R_3N) form this bond with H^+.

(3) BF_4^- Formation:

In BF_3, Boron contains total six bonding electrons. It has incomplete octet that is why one fluoride ion (F^-) donates its one electrons pair to boron and make coordinate covalent bond to complete octet of boron in BF_4^-.



POINT TO PONDER: In Co-ordinate covalent formation:

(i) If both donor and acceptor are neutral, before the bond formation, then donor will get positive charge and acceptor will get negative charge after the bond formation.

(ii) If donor is negatively charged and acceptor is positively charged before bond formation, then both will become neutral after bond formation.

Valence shell electron pair repulsion theory (VESPR theory):

"The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsion at a minimum;"

Note: Lone Pair is not involved in determining the shape of the molecule.

The acronym "VESPR" is pronounced "vesper".

POINT TO PONDER: Lone pairs are closer to the nucleus than bonding pain and exert a greater ____________ force.

Postulates:

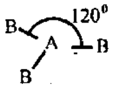
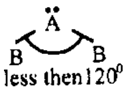
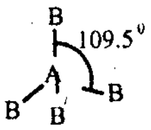
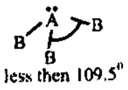
- Both lone pair and bond pair determine the geometry of the molecules.
- Lone pair occupies more space than a bond pair

- The magnitude of repulsion is in the following order
- Lone pair – Lone pair > Lone pair – Bond pair > Bond pair - Bond pair
- Double bond and triple bond behaves like a single bond in determining the geometry of the molecule.

NOTE: CFT and LFT are applied to describe the geometry of complexes.

Limitations:

- VSEPR theory predicts and explains the shapes of molecules but does not give reasons for the formation of bonds.
- It is not applicable for single bond pair system means di-atomic molecules.
- Complexes do not follow this theory.

Type	Electron pairs			Arrangement of pairs	Molecular geometry	Shape	Examples
	Total	Bonding	Lone				
AB_2	2	2	0	Linear	Linear	B – A – B	$BeCl_2$ $HgCl_2$
AB_3	3	3	0	Triagonal planar	Trogonal planar		BH_3BF_3 $AlCl_3$
		2	1		Bent (or angular)		$SnCl_2$,SO_2
AB_4	4	4	0	Tetrahedral	Tetrahedral		CH_4, $SiCl_4$ CCl_4, BF_4^- NH_4^+ , SO_4^{-2}
		3	1		Trigonal pyramidal		NH_3, NF_3, PH_3

		2	2		Bent (or angular)		H_2O, H_2S

Orbital Overlapping Giving σ and π Bonds:

(i) Sigma (σ) bond:

A bond formed by head to head (end to end) overlapping where the probability of finding the shared pair around the line joining the two nuclei is maximum is called as sigma bond.

(ii) Pi (π) bond:

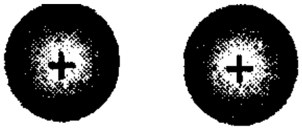
A bond formed by the parallel overlapping where the probability of finding shared pair above and below the line joining the two nuclei is maximum is called pi bond.

Note: π-bond is a weaker bond than sigma bond.

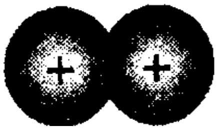
Examples:

(1) **H_2-molecule:**

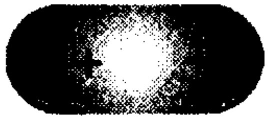
When two hydrogen atoms approach each other, their half-filled Is orbital undergo overlapping to form a sigma bond. One electron from each of 1 s form a pair called shared l bond pair.



Separated H atoms



Overlapping of orbitals



Covalent bond in H_2

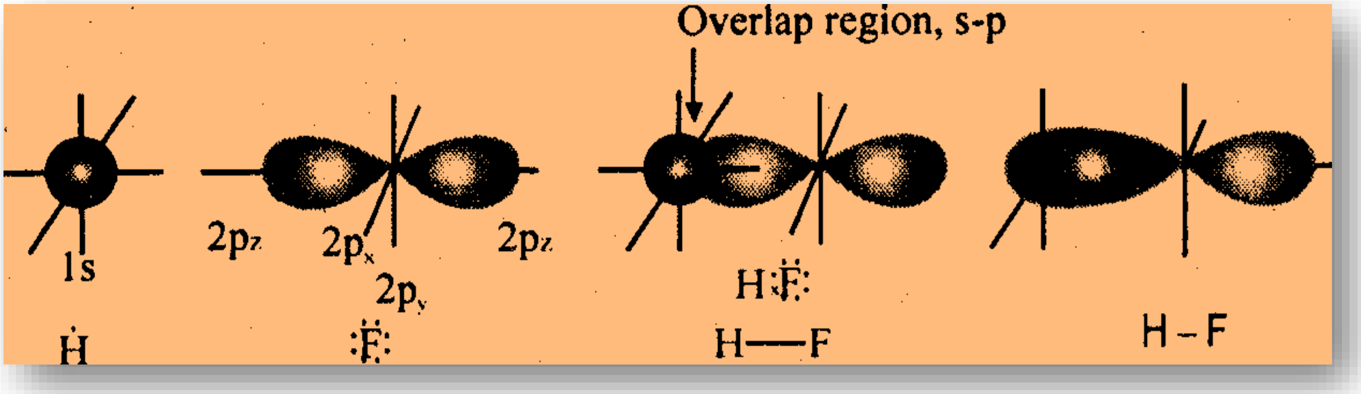
(2) **HF molecule:**

The electronic configuration of both atoms is:

$H_1 = 1s^1$

$F_9 = 1s^2, 2s^2, 2p^2_x, 2p^2_y, 2p^1_z,$

The two half filled orbitals (1s from H-atom and $2p_2$ from F-atom) undergo linear overlap and form a sigma bond. The two unpaired electrons with opposite spin paired up.

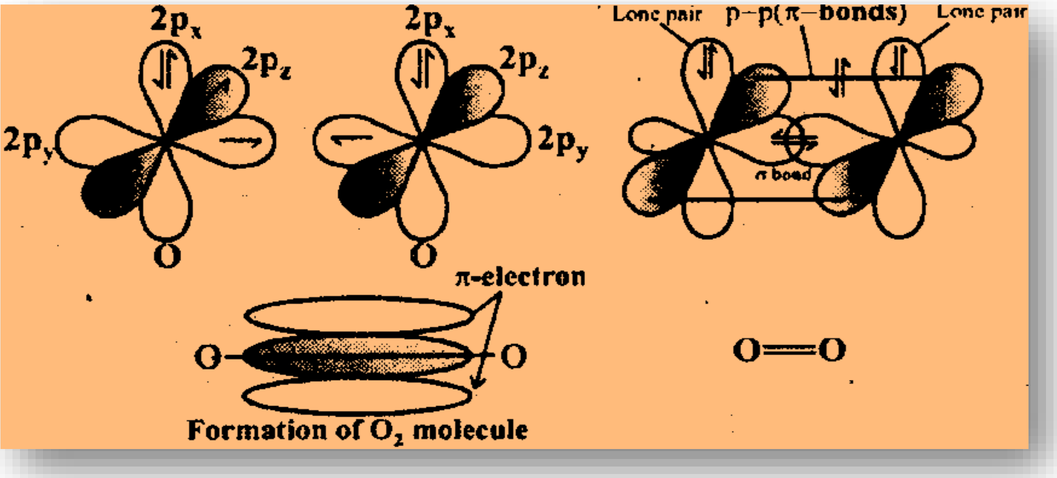


(3) **O_2 molecule**:

The electronic configuration of oxygen atoms is

$O_8 = ls^2, 2s^2, 2p^2_x, 2p^2_y, 2p^1_z,$

Each oxygen atom has two partially filled p-orbitals i.e. p_y and p_z. One of orbital from each of the two oxygen atoms undergo linear overlapping to form a sigma bond. Whereas, two p_z orbitals from each oxygen atom undergo parallel overlapping to form a pi-bond.



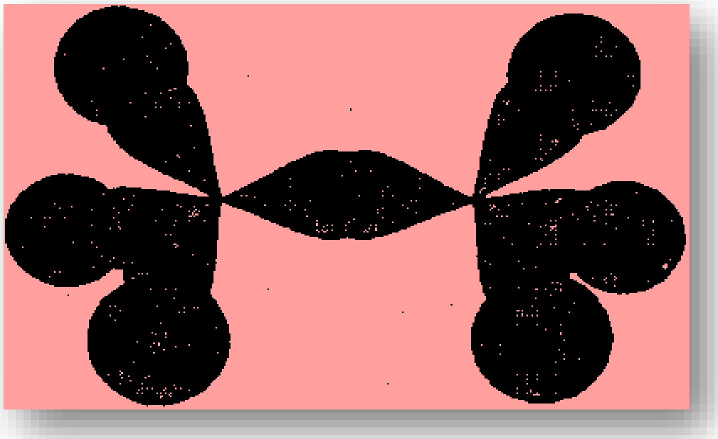
Formation of O_2 molecule

Shapes and bond angles in terms of sigma and pi bonding:

(i) Formation of Ethane molecule:

In ethane ($H_3C - CH_3$), both Carbon atoms are sp^3 hybridized.

- Six (C-H)σ-bonds (three for each carbon atom) are formed by the linear overlapping of six sp^3 hybrid orbitals (three from each carbon atom) with six 1 s orbitals of six hydrogen atoms, separately.
- One (C-C) σ-bond is formed by the overlapping of one sp^3 hybrid orbital of one carbon atom with one sp^3 hybrid orbital of second carbon atom.



Shape:

The shape of the molecule is indicated by arrangement of hybrid orbitals which is tetrahedral. Actually, the whole molecule is a combination of two tetrahedrons.

Geometry:

The bond angle in C_2H_6 molecule is 109.5°.

(iii) Formation of C_2H_4 (Ethene) molecule:

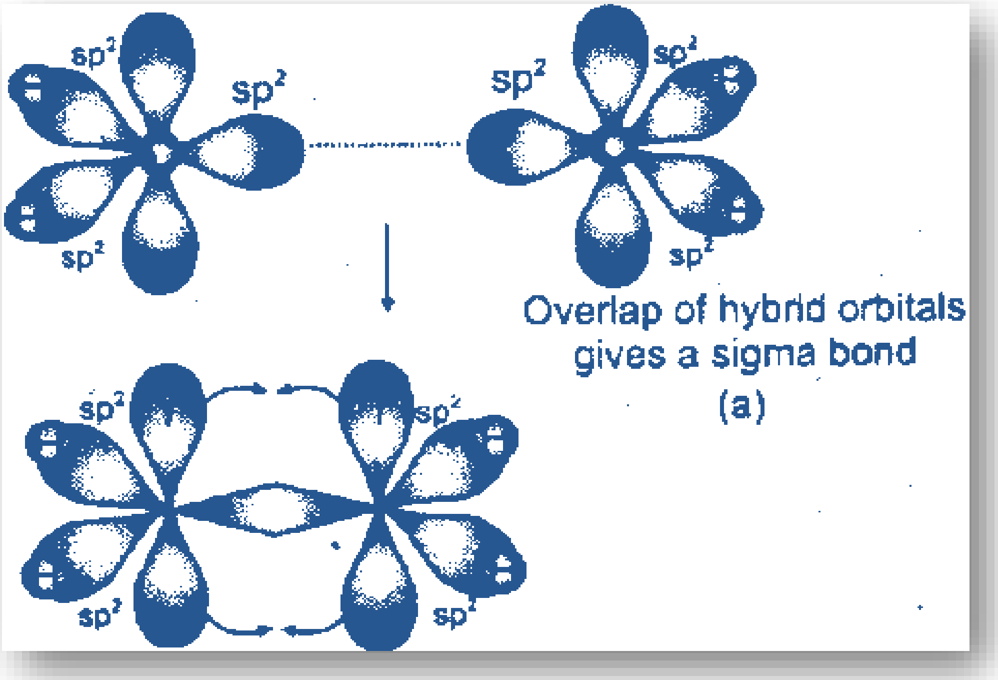
($CH_2 = CH_2$) The electronic configuration of carbon with atomic no. 6 is:

$_6C = 1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^0_z,$ (Ground state configuration)

$_6C = 1s_2, 2s^l, 2p^l_x, 2p^1_y, 2p^l_z,$ (Excited state configuration)

Hybridization

$_6C = 1s^2, (sp^2)^1, (sp^2)^1, (sp^2)^1, 2p^l_z$ (hybridized state)

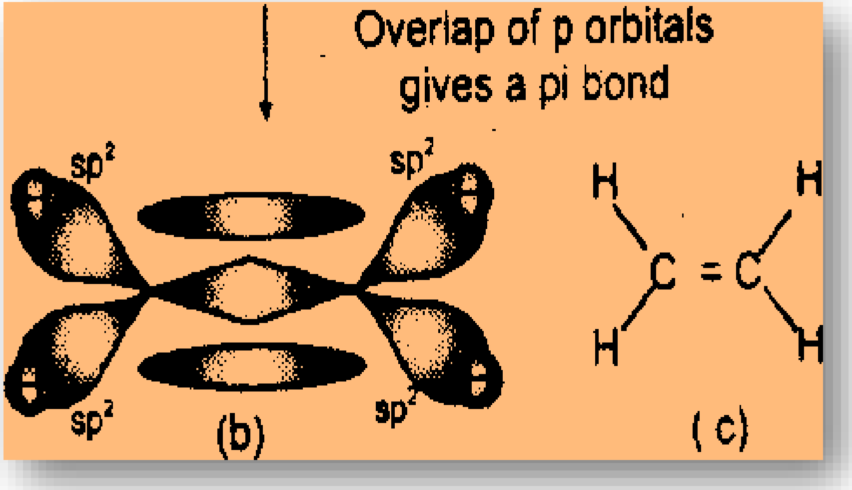


Overlap of hybrid orbitals gives a sigma bond

(a)

(i) **Five sigma bonds**:

- One sigma bond between two carbon atoms by sp^2- sp^2 linear overlapping.
- Two sigma bonds between one carbon atom and two hydrogen atoms separately by sp^2 is gives a sigma bond linear overlapping.
- Two sigma bonds between second carbon atom and two hydrogen atoms separately by sp^2 is linear overlapping.



(ii) **One pi-bond**:

One pi-bond is formed between two carbon atoms by $P_2 - P_2$ parallel overlapping.

Shape:

The shape of the molecule .is indicated by arrangement of pi-bond orbitals which is triangular planar. Actually, the whole molecule is a combination of two triangles.

POINT TO PONDER: For π-bonds to be formed the atoms in $H_2C = CH_2$ be …..

π-bond formation is restricted to …………. atoms

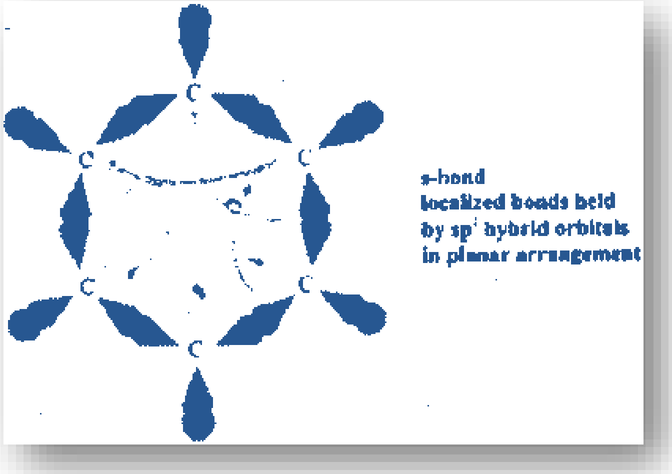
Geometry:

The bond angle In C_2H_4 molecule is 120°.

(iii) Formation of Benzene molecule:

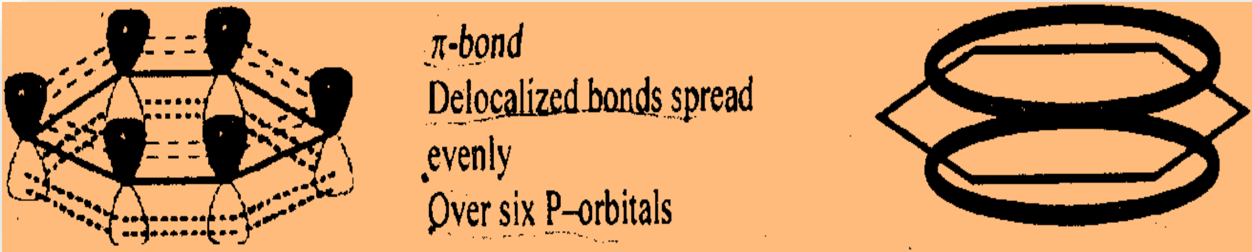
a) sp^2 Orbital Hybridization:

In benzene each carbon atom is sp^2 hybridized. These sp^2-hybrid orbitals on each carbon are utilized to form three sigma bonds, two with adjacent carbon atoms and one with hydrogen atom. As a result, the benzene molecule gets a planar cyclic regular hexagonal structure in which all C-C bond distances are uniform and C-C-C bond angle is 120°.



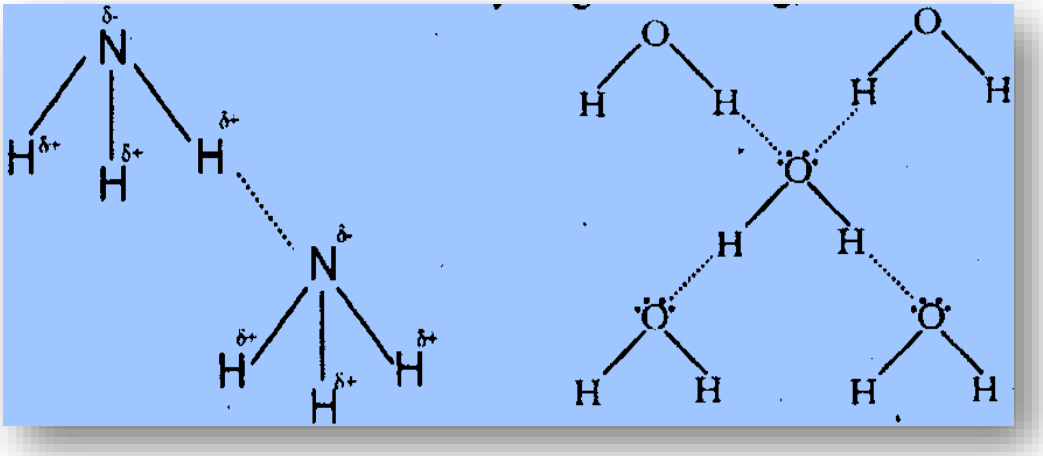
b) Un-hybrid 2p Orbital:

Six un-hybrid p-orbital lying perpendicular to the plane of the molecule and axes parallel to each other, these p-orbitals partially overlap to form a continuous sheath of electron cloud which surrounds the benzene ring from above and below which is shown as follows:



(1) <u>Hydrogen bonding in NH_3:</u>

There is only one hydrogen bond per NH_3 molecule. Hydrogen bonding in NH_3 molecules is shown below. Due to weak hydrogen bonding, it exists as a gas and low boiling point.



(2) Hydrogen bonding in H_2O:

There are two hydrogen bonds per water molecule. This is the reason, why its intermolecular hydrogen bonding is stronger than that of HF and NH_3. This is responsible very high boiling point of water.

BOND ENERGY

The average amount of energy required to break all bonds of a particular type in one mole of the substance is called bond energy.

- Unit of bond energy is kJ mole.

Factors Effecting Bond Energy:

The bond energy is the measure of the strength of bond. The strength of a bond depends upon the following factors.

(i) Electronegativity difference of bonded atoms

(ii) Sizes of the atoms

(iii) Bond length

(iv) Nature of orbital

Applications of bond energy:

- Relative strength of bonds
- % of ionic character in bond
- Estimation of ΔH (Difference of bond breaking and bond forming energies)

BOND LENGTH

The distance between the nuclei of two atoms forming a covalent bond is called bond length.

- Techniques used to determine bond length are electron diffraction, X-ray diffraction or spectral studies.
- Greater the E.N difference between bonded atoms, shorter will be bond length.
- Ionic character shortens bond length.
- Greater the atomic radii of the bonded atoms larger will be the bond length.
- Involvement of π-bond reduces bond length.
- Greater s-character in the hybrid orbital lower will be the bond length of bond length.
- Along the period, bond length decreases.
- **Down the group, bond length increase.**

COMPOUND	BOND	BOND LENGTH (PM)
BF_3 (sp^2 hybridized)	B – F	130
BCl_3 (sp^2 hybridized)	B – Cl	175
SiH_4 (sp^3 hybridized)	Si – H	148
SiF_4 (sp^3 hybridized)	Si – F	155
C_2H_6 (sp^3 hybridized)	C – C	154
C_2H_4 (sp^2 hybridized)	C=C	133

C_2H_2 (sp hybridized)	C=C	120
$(CH_3)_2$ C = O (sp^2 hybridized)	C=Q	122

DIPOLE MOMENT (Degree of Polarity in a Molecule)

The product of the electric charge and the distance between the positive and negative centers is called dipole moment. Dipole moment is a vector quantity.

Mathematically, it can be written as: $\pi = qxr$

Units:

(i) Coulomb metre (Cm)

(ii) Debye (D): ID = 3.336×10^{-30} Cm

Applications:

- % of ionic character
- Geometry of molecules

RELATION BETWEEN MOLECULAR GEOMETRY AND DIPOLE MOMENT

:

FORMULA	DIPOLE MOMENT	MOLECULAR GEOMETRY
AX	Can be non zero	Linear
AX_2	Zero Can be non zero	Linear Bent
AX_3	Zero Can he non zero Can he non zero	Trigonal planar Trigonal pyramidal T-shaped

AX_4	Zero	Tetrahedral
	Zero	Square planar
	Can he non zero	See saw
AX_5	Zero	Trigonal bipyramidal
	Can he non zero	Square pyramidal
AX_6	Zero	Octahedral

INTERMOLECULAR FORCES

Intermolecular forces (Van der Waal's forces), based on permanent and induced dipoles, as in $CHCl_3$, Br_2 and in liquid noble gases,

(i) **CHCh molecule**:

The force of attraction between $CHCl_3$ molecules is permanent dipole due to being permanently polar (due to having greater electro negativity difference), This is the reason why it exists as a liquid.

(ii) **Bromine molecule**:

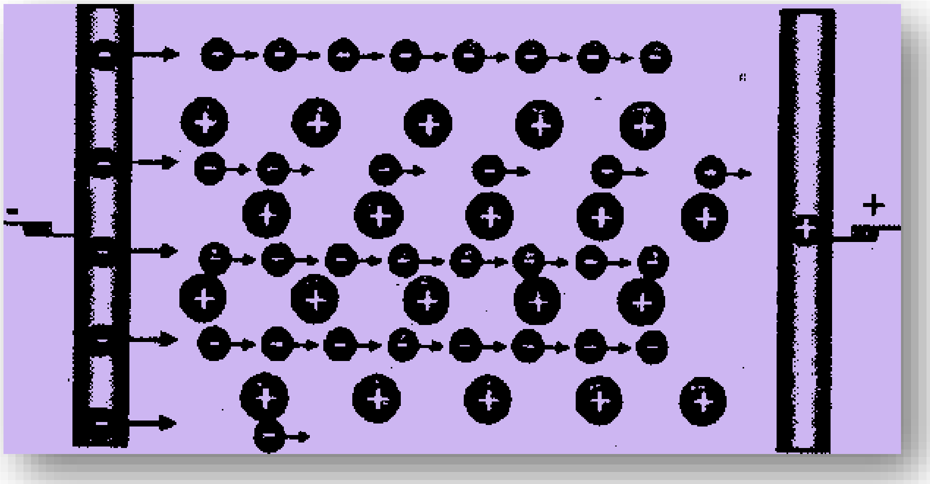
The force of attraction between Bra molecules is induced dipole due to being non-polar, The size of the Bromine molecule is large and has large polarizablity, And the force of attraction between its molecules is stronger, This is the reason why it exists as a liquid.

(iii) **Noble gases**:

The force of attraction between noble gas molecules is induced dipole due to being nonpolar, The size and polarizability of noble gases increases down the group, As a result, the force of attraction down the group becomes stronger and becomes easier to be liquefied, This is the reason why boiling point of noble gases increases down the group.

Metallic bonding in terms of a lattice of positive ions surrounded by mobile electrons Electron Gas Theory:

This theory was proposed by Drude and extended by Loren in 1923, according to this theory:

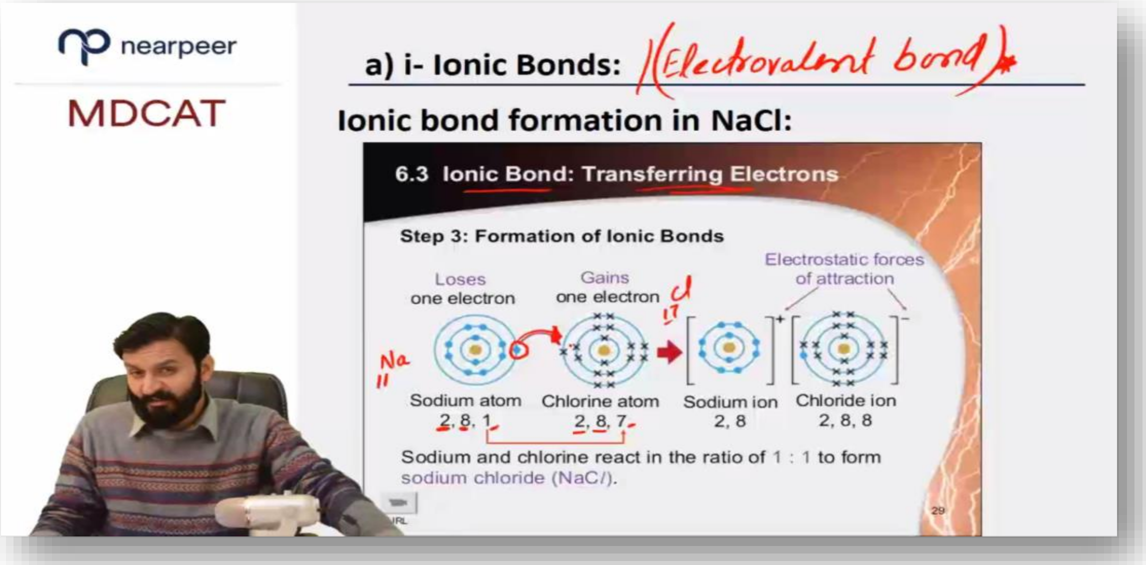


Explanation:

The cations occupy definite positions at measurable distance from each other in the crystal lattice, Valence electrons are not attached to any individual ion or pair of ions rather they belong to the crystal as a whole, these electrons are free to move about from one part of the crystal to the other.

Type of solid	Structural	Intermolecular forces	Typical properties	Examples
Metallic	cations plus delocalized electrons	metallic bonds	hardness varies from soft to very hard; melting points varied from low to very high; lustrous; ductile; malleable; very good conductors of heat and electricity	Na, Mg, Al, Fe, Zn, Cu, Ag, W
Ionic	cations and	Electrostatic attractions	hard; moderate to very high melting points; nonconductors of	MaCl, $NaNO_3$, MgO

	anions		electricity (but good electrical conductors in the molten state)	
Molecular	molecules (atoms of noble gases)	London or dipole-dipole or hydrogen bonds	soft; low melting points; nonconductors of heat and electricity; sublime easily in many cases	Noble gas elements, CH_4, CO_2, $P_4S_8I_2$, H_2O
Covalent network	Atoms	covalent bonds	very hard; very high melting points; nonconductors of electricity	C(diamond), SiC, SiO_2



a) i- Ionic Bonds: (Electrovalent bond)

Ionic bond formation in NaCl:

6.3 Ionic Bond: Transferring Electrons

Step 3: Formation of Ionic Bonds

Sodium and chlorine react in the ratio of 1 : 1 to form sodium chloride (NaCl).

PRACTICE EXERCISE

1. **Chemical property of element depends upon**

A) Atomic number C) Electron configuration

B) Mass number D) All of these

2. Which of the following element can follow extended octet rule?

A) Lithium C) Fluorine

B) Nitrogen D) Phosphorus

3. Which of the statement is incorrect?

A) Bond length of H_2 is 75.4 pm

B) Energy released in the formation of H_2 is 436.45kJ mol^{-1}

C) When bond length is less than 75.4 pm, energy of molecules decreases

D) When bond length is less than 75.4 pm, energy of molecules increases

4. Which of the following show isomorphism and polymorphism

A) Ionic compound C) Coordinate covalent compound

B) Covalent compound D) None of these

5. Which of the bond is directional and rigid?

A) Ionic bond C) Coordinate covalent bond

B) Covalent bond D) both b and c

6. Which of the molecules show bent shaped structure?

A) CCl_4 C) NH_3

B) BF_3 D) H_2O

7. Which has greater bond angle

A) $HgCl_2$ C) NH_3

B) BF_3 D) H_2O

8. Which group of element form ionic bond

A) I and II A with VI and VIIA C) II and IV A with VI and VII A

B) IIA with VA D) IIA with VA

9. Which of the following molecule belong to four electron pair system?

A) $MgCl_2$ C) BF_4^{-1}

B) $AlCl_3$ D) PCl_5

10. An ionic compound $A^+ B^-$ is most likely to be formed when

A) The ionization energy of ‘A’ is high and electron affinity of ‘B’ is low

B) The ionization energy of ‘A’ is low and electron affinity of ‘B’ is high

C) Both ionization energy of ‘A’ and electron affinity of ‘B’ is high

D) Both ionization energy of ‘A’ and electron affinity of ‘B’ is low

11. Amongst the following compounds which has greatest ionic character in it

A) HCl C) H_2

B) HF D) H_2O

12. Which of the statement is correct about the shape of NH_3 molecule

A) Square planer C) Angular

B) Pyramidal D) Tetrahedral

13. An ionic compound will dissolve in water only if

A) Hydration energy is high and lattice energy is low

B) Hydration energy is low and lattice energy is high

C) Hydration energy and lattice energy both are high

D) Hydration and lattice energy both are low

14. Which one is not the absolute term of the element:

(A) Ionization energy (C) Electron affinity

(B) Electronegativity (D) Atomic size

15. Which has the minimum bond angle:

(A) H_2O (C) H_2S

(B) NH_3 (D) NF_3

16. Which of the following molecule has zero dipole moment:

(A) ClO_2 (C) CS_2

(B) NO_2 (D) SO_2

17. Which of the following contain co-ordinate covalent bond:

(A) $BaCl_2$ **(C)** NH_4^+

(B) CsCl (D) H_2O

18. A molecule with two bond pairs and two lone pairs will have geometry:

(A) Tetrahedral **(C)** Trional plannar

(B) Bent (D) Trigonal pyramidal

19. Which of the following molecule have zero dipole moment:

(A) NH_3 (C) BF_3

(B) H_2O (D) CH_4

20. Bond energy depends upon the following factors execpt:

(A) Bond length (C) Electronegativity

(B) Sizes of the bonded atoms (D) Atomic number of atoms

21. Which of the following bonds is present in NH_4Cl?

(A) Ionic bond **(B)** Covalent bond

(C) Co-ordinate covalent bond **(D)** All the above

22. In which molecule, all atoms are coplanar?

(A) CH_4 **(B)** BF_3

(C) NH_3 **(D)** PH_3

23. For which of the following, the value of dipole moment is same as that for CCl_4?

(A) CO **(B)** $CHCl_3$

(C) NH_3 **(D)** SO_3

24. A specie that represents all the types of chemical bonds:

(A) H_3O^+ **(B)** $NaBH_4$

(C) $CuSO_4$ **(D)** $(COOH)_2.2H_2O$

25. Maximum bond angle can be reduced by replacing the 'H' in SbH_3 with:

(A) O **(B)** F

(C) Cl **(D)** N

26. How many sigma bond's are present in HCN molecule?

(A)2 **(B)** 3

(C) 4 **(D)** 5

27. 92° bond angle is present in:

(A) CH_4 **(B)** H_2O

(C) NH_3 **(D)** H_2S

28. Formation of covalent bond is:

(A) Thermodynamic approach **(B)** Quantum mechanics approach

(C) Kinetic approach **(D)** All above

29. Which of the following species has triangular pyramidal shape?

(A)H_3O^+ **(B)** CO_3^{-2}

(C) NO_3^- **(D)** BF_3

30. Bond length is minimum in:

(A) HCl **(B)** NH_3

(C) H_2O **(D)** HF

31. If ΔEN of two bonded atom is equal to 1.7 then bond is:

(A) Polar covalent (B) 100% covalent

(C) 100% ionic (D) 50% ionic and 50% covalent

32. The charge of a cation M is +2 and on anion A is -3. The compound formed has the formula:

(A) M_2A (B) MA_2

(C) M_3A_2 (D) M_2A_3

33. Lateral overlapping is expected in:

(A) σ- bond (B) π - bond

(C) Ionic bond (D) Metallic bond

34. The geometry of the molecule will be regular if central atom is surrounded by:

(A) Lone pairs only (B) Bond pairs only

(C) Both lone and bond pairs (D) All given

35. H_2S has similar geometry with:

(A) $SnCl_2$ (B) CS_2

(C) CO_2 (D) H_2O

36. Benzene –hexane pair is soluble in:

(A) H_2O (B) C_2H_5OH

(C) $CHCl_3$ (D) CCl_4

37. If bond energies of c to c bonds is in the order c ≡c > c = c > c – c their bond length are in the order.

(A) c ≡c > c = c > c – c (B) c= c > c ≡ c > c- c

(C) c– c > c = c > c ≡c (D) c= c > c - c > c ≡ c

38. Which one of the following compounds does the underlined element not have eight electrons in the outer shell?

(A) $Li_2\underline{O}$ (B) $H_2\ \underline{O_2}$

(C) $\underline{P}Cl_3$ (D) $\underline{P}Cl_5$

39. Why is the molecule of BCl_3 planar, whereas the molecule of PH_3 is pyramidal?

(A) The boron atom has no lone pair in valence shell

(B) The boron atom in BCl_3 has six electrons in its valency shell, whereas the phosphorus atom in PH_3 has eight.

(C) The repulsion between chlorine atoms is greater than that between hydrogen atoms.

(D) The covalent radius of phosphorus is greater than that of boron.

40. Which statement is incorrect?

A sigma bond is always formed before $\pi - bond$

a $\pi - bond$ is weaker than sigma bond

In $\pi - bond$ the lesser electron density lies above and below the internuclear axis

All sigma bonds have axial symmetry

ANSWER KEY

1	C	11	B	21	D	31	D
2	**D**	**12**	**B**	**22**	**B**	**32**	**C**
3	**C**	**13**	**A**	**23**	**D**	**33**	**B**
4	**A**	**14**	**C**	**24**	**B**	**34**	**B**
5	**D**	**15**	**C**	**25**	**B**	**35**	**D**
6	**D**	**16**	**C**	**26**	**A**	**36**	**D**
7	**A**	**17**	**C**	**27**	**D**	**37**	**C**
8	**A**	**18**	**B**	**28**	**A**	**38**	**D**
9	**C**	**19**	**C**	**29**	**A**	**39**	**A**
10	**B**	**20**	**D**	**30**	**D**	**40**	**D**

UHS TOPIC V A

CHEMICAL ENERGY

LEARNING OUTCOMES

In this topic, student should be able to:

a) Understand concept of energy changes during chemical reactions with examples of exothermic and endothermic reactions.

b) Explain and use the terms:

i) Enthalpy change of reaction and standard conditions, with particular reference to: formation; combustion; solution; neutralization and atomization.

ii) Bond energy (ΔH positive, i.e. bond breaking)

iii) Lattice energy (ΔH negative, i.e. gaseous ions to solid lattice)

e) Find heat of reactions/neutralization from experimental results using mathematical relationship i.e

$\Delta H = mc\,\Delta T$

d) Explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of lattice energy.

e) Apply Hess's Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to:

i) Determining enthalpy, changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy change of combustion.

ii) Born-Haber cycle of NaCl (including ionization energy and electron affinity).

THERMOCHEMISTRY

:

The study of heat changes during a chemical reaction is called thermochemistry.

ENERGY:

Ability of a body to do work is called energy.

TYPES OF ENERGIES:

(i) Kinetic energy (KE) → Energy due to motion

(ii) Potential energy (P.E) → Energy due to position, shape and orientation

(iii) Sound energy

(iv) Heat energy

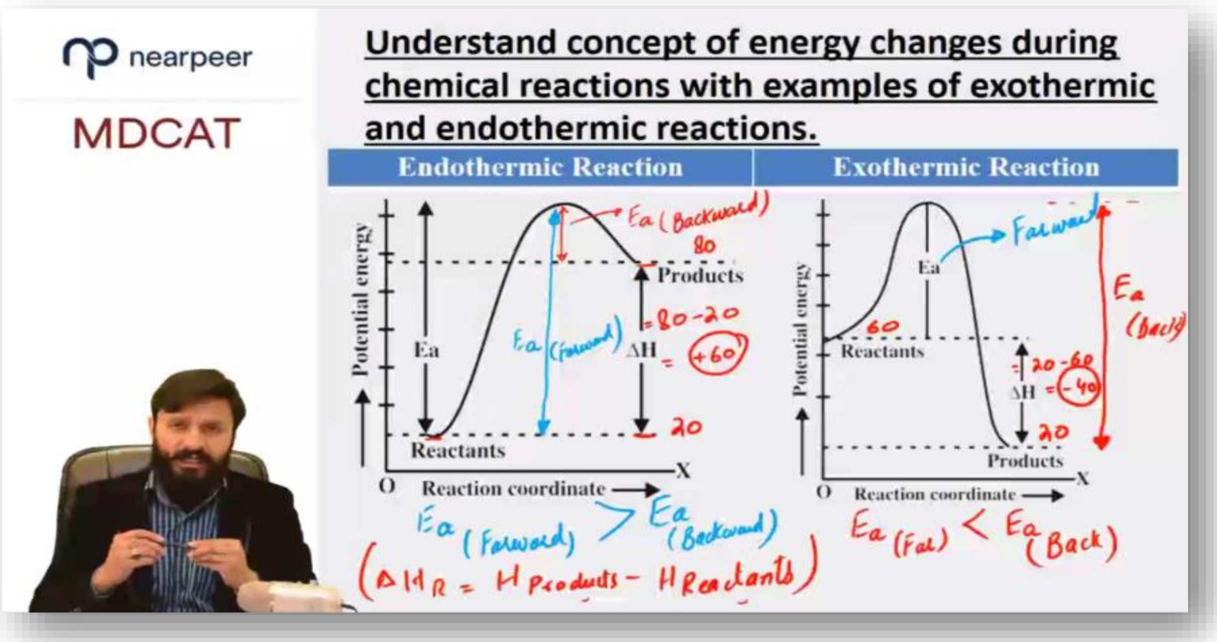
(v) Magnetic energy

(vi) Mechanical energy

(vii) Solar energy

UNITS OF ENERGY:

UNITS	RELATION
Joule (SI Unit)	$J = khm^2\ s^2$
Calorie	1 cal = 4.184 J



Understand concept of energy changes during chemical reactions with examples of exothermic and endothermic reactions.

Endothermic Reaction	Exothermic Reaction

$E_{a\,(Forward)} > E_{a\,(Backward)}$

$(\Delta H_R = H_{Products} - H_{Reactants})$

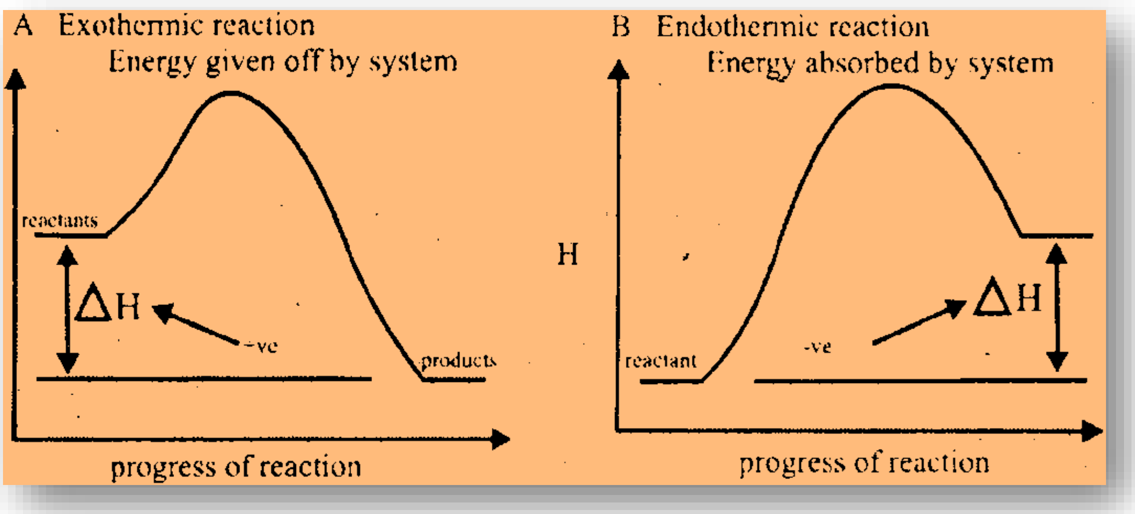
$E_{a\,(For)} < E_{a\,(Back)}$

COMPARISON OF EXOTHERMIC AND ENDOTHERMIC REACTIONS:

No.	Properties	Exothermic	Endothermic
1	Flow of heat energy	System to surrounding	Surrounding to system
2	Temperature of surrounding	Increases	Decreases
3	Temperature of the system	Decreases	increases
4	Energy of products	Low	High
5	Energy of reactants	High	Low
6	Strength of bonds in products	Strong	Weak
7	Strength of bonds in reactants	Weak	Strong
8	Enthalpy change (ΔH)	Negative	Positive
9	Examples	$C + C_2 \rightarrow CO_2$ $\Delta H = -393.7$ kmol Respiration $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ Neutralization $NaOH + HCl \rightarrow NaCl + H_2O$	$N_2 + O_2 \rightarrow 2NO$ $\Delta H = +180.51$ kj/mol Thermal decomposition $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ Dissolving $NH_4NO_{3(s)} \rightarrow NH_4NO_{3(aq)}$

POINT TO PONDER: Substance which do not support combustion like water, carbon dioxide and most other oxides, have enthalpy of combustion........

Graphical representation of exothermic and endothermic reactions:



Enthalpy	**Definition**	**Symbol**	**Positive or negative**
Enthalpy of reaction	The enthalpy change which occurs when the certain number of moles of reactants as indicated by the balanced chemical equation, react together completely to give the products under standard condition. $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)} \Delta H^\circ = -285.8 \text{ kJmol}^{-1}$	ΔH°	May be positive or negative
Enthalpy of formation	The change of enthalpy when one mole of the compound is formed from atoms of its elements. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_f^0 = -393.7 \text{ kJmol}^{-1}$	ΔH_f^0	May be Positive Or Negative

Enthalpy of atomization	The enthalpy change when one mole of gaseous atoms are formed from a molecule or an element under standard condition. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_f^0 = -393.7\ kJmol^{-1}$	ΔH_{at}^0	Always Positive
Enthalpy of neutralization	The amount of heat evolved when one mole of hydrogen ions H^+ from an acid, react with one mole of hydroxide ions (OH^-) from a base to form one mole of water. **Example:** The enthalpy of neutralization of sodium hydroxide by hydrochloric acid is $-57.4\ kJmol^{-1}$ $NaOH + HCl \rightarrow NaCl + H_2O$ $\Delta H_n = -57.4\ kJmol^{-1}$	ΔH_n^0	Always negative
Enthalpy of combustion	The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions. $C_2H_5OH_{(\ell)} + 3O_2 \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$ $\Delta H_c^0 = -1368\ kj\ mol^{-1}$	ΔH_c^0	Always negative
Enthalpy of solution	The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution result in no detectable heat change. $NH_4Cl_{(s)} + (aq) \rightleftharpoons NH_4\,Cl_{(aq)}$ $\Delta H_{sol}^0 = +16.2\ kj\ mol^{-1}$	ΔH_{sol}^0	May be negative or positive
Enthalpy of hydration	The amount of heat evolved or absorbed when one mole of gaseous ions are dissolved in water is called enthalpy of hydration. $H^+_{(g)} + H_2O_{(l)} \rightleftharpoons H_2H^+_{(aq)}$ $\Delta H_h = -1075\ kJmor^{-1}$	ΔH_h^0	may be negative or positive

Enthalpy (energy) changes:

Δ (delta means difference), H (means enthalpy), $\Delta H = E_{in} = E_{out}$ (joules)

Note:

i) ΔH_n = – 57.4 KJ / mole (maximum for strong acids and bases)

ii) ΔH_n> – 57.4 (Not possible)

iii) ΔH_n< – 57.4 (When one of the acid or base is stronger and other is weaker)

BOND ENERGY

:

The average amount of energy required to break all bonds of a particular type in one mole of the substance is called bond energy.

- Unit of bond energy is kJ/mole.

Factors Affecting Bond Energy:

The bond energy is the measure of the strength of bond. The strength of a bond depends upon the following factors.

(i) Electronegativity difference of bonded atoms

(ii) Sizes of the atoms

(iii) Bond length

Applications of bond energy:

- Relative strength of bonds
- % of ionic character in bond
- Estimation of ΔH

LATTICE ENERGY

Definition:

The amount of energy released when one mole of crystalline solid is formed from the gaseous ions is called lattice energy.

Example: $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$ $\Delta H = -787 \text{ kJ mol}^{-1}$

Lattice energy depends upon charge to size ratio of ions. For ions of same group, lattice energy depends upon size of ion.

1. Greater the size of cation (from same group) by keeping the anion same, lesser will be the charge to size ratio and lesser will be the lattice energy and vice versa.

Examples:

(i) Lattice energy of LiCl is – 833 kJ/mole

(ii) Lattice energy of NaCl is – 787 kJ/mole

2. Greater the size of anion (from same group) by keeping cation same, lesser the charge to size ratio, lesser will be the lattice energy and vice versa.

Examples:

(i) Lattice energy of NaF is – 895 kJ/mole

(ii) Lattice energy of NaCl is – 787 kJ/mole

Note: With the increasing size of either cation or anion, the packing of oppositely charged ions becomes less tight. As a result, electrostatic attraction is weak and Lattice energy is less.

Note: Heat of single step reaction can be measured by calorimeter.

Measurement of enthalpy of a reaction:

There are two basic methods to measure the enthalpy of reactions

- **Experimental methods:**

  (i) Glass Calorimeter (ΔH and ΔH_s)

(ii) Bomb Calorimeter (ΔH_c of food and fuel)

- **Theoretical methods** for calculation of enthalpy of reaction indirectly

(i) Hess's Law for constant heat summation

(ii) Born Haber's cycle

By Glass Calorimeter: (At constant pressure)

- Glass calorimeter is used to measure the enthalpy of solution and enthalpy of neutralization.

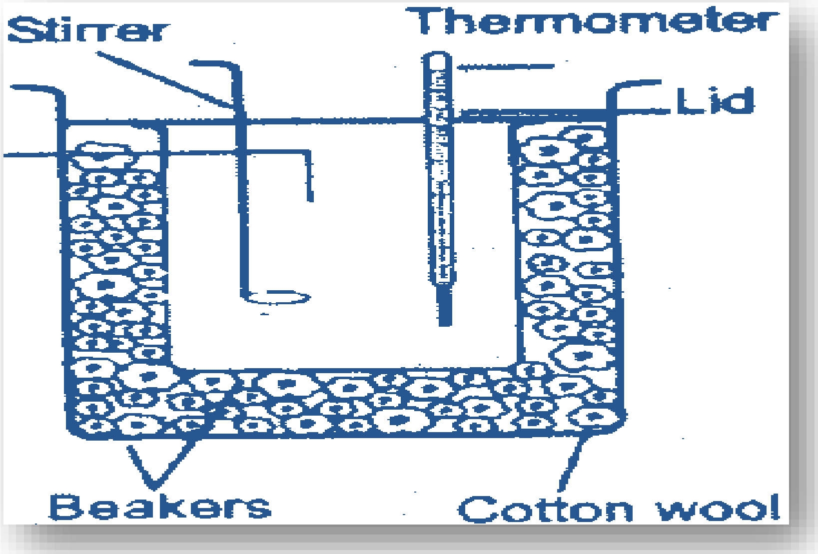
- By using following relationship, heat of reaction is calculated. $q = m \times s \times \Delta T$

Where

m = mass of reactant Units = 'g' or 'Kg'

s = specific heat of reacting mixture Units = $JK^{-1}g^{-1}$

ΔT = change in temperature Units = K



Hydrochloric Acid + sodium hydroxide

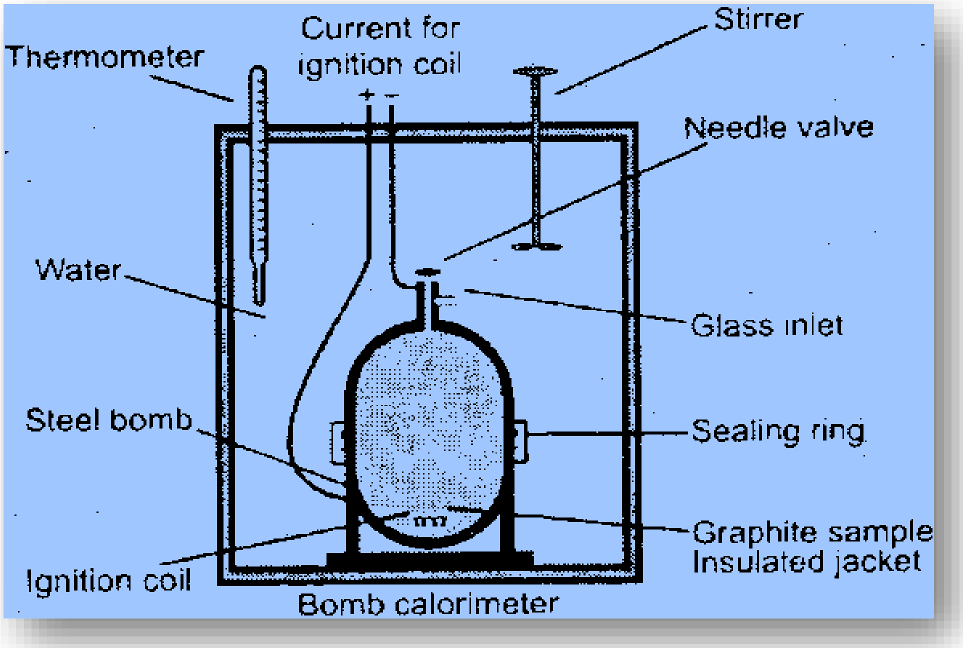
By Bomb Calorimeter: (at constant pressure)

- Bomb calorimeter is used to measure enthalpy of combustion and enthalpy of reaction
- By using following relationship, heat of reaction is calculated. $q = C \times \Delta T$

Where

C = Heat capacity Units = kJK^{-1}

ΔT = change in temperature Units = K



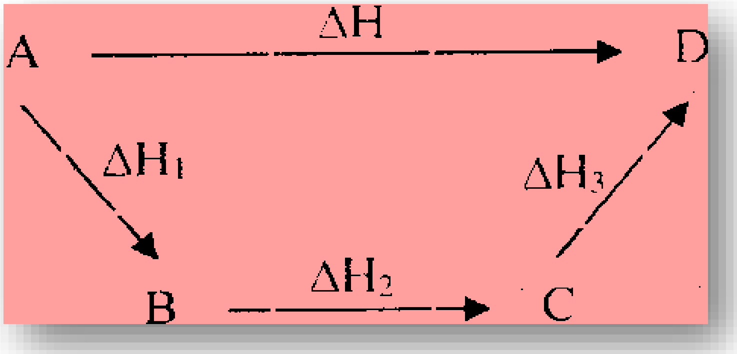
HESS's LAW OF CONSTANT HEAT SUMMATION

Energy contents of a reaction remain constant whether reaction takes place in single step or many steps.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

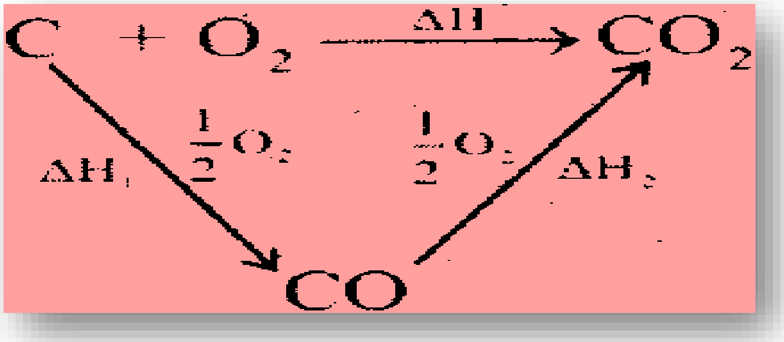
The sum of enthalpy changes in a cyclic process is zero.

$$\Sigma\ (\Delta H)\ \text{cycle} = 0$$



Example:

(i) If the enthalpy of combustion for graphite to form CO_2 and enthalpy of combustion of CO to form CO_2 are known, then by using Hess's law we can determine the enthalpy of formation of CO. Consider the following cycle:



$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ ΔH (for CO_2 from graphite) = – 393.7 KJ mol^{-1}

$CO_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$ ΔH_2 (for CO_2 from graphite) = – 283 KJ mol^{-1}

$C_{(graphite)} + \frac{1}{2}O_2 \rightarrow CO_{2(g)}$ ΔH_1 (CO) = ?

From cycle, it is clear that:

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$\Delta H_1 = \Delta H - \Delta H_2$$

$$= -393.7 - (-283)$$

$$\Delta H_1 = -110.7 \text{ kJ mol}^{-1}$$

So, the enthalpy change for the formation of $CO_{(g)}$ is –110 kJmol^{-1}.

Average bond energies:

- During a chemical reaction, the bonds in the reactants are broken. This is an endothermic process; energy is required to do this.

- After the bonds have been broken, however, the bonds in the products are formed. This is an exothermic process; energy is released when this happens.

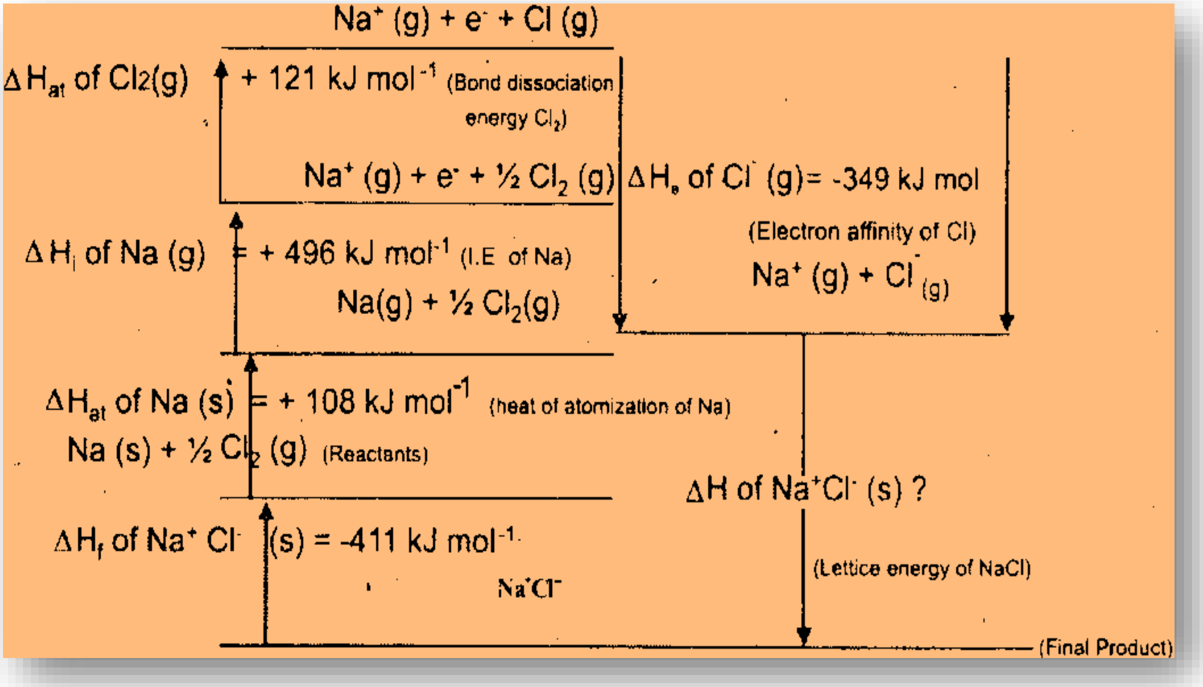
The enthalpy change for a chemical reaction can be deduced from consideration of the energy required to break bonds in the reactants and the energy released when the bonds in the products are formed. It can be calculated from the following equation:

ΔH = Energy required to break bonds in reactants – energy released to make bonds in products

This method can be used to calculate the enthalpy changes for any reaction which does not involve ionic bonds. The breaking and making of ionic bonds involve a more complicated sequence of energetic processes and thus cannot be considered in this way.

BORN HABER CYCLE

Energy change in cyclic process is always zero. It enables us to calculate the lattice energy of binary compounds (ionic); this is called Born-Haber cycle.



Lattice Energy:

- Lattice energy of an ionic crystal is the enthalpy of formation of one mole of the ionic compound from gaseous ions under STP.
- Lattice energy cannot be determined directly.
- Lattice energy can be obtained by means of Born Haber cycle.
- Lattice energy is helpful in discussing bonding and properties of ionic compounds.

Ionic Compound	Lattice energy (KJ mol^{-1})
LiCl	– 833
NaF	– 895
NaCl	– 787
KCl	– 690
NaBr	– 728

KBr	– 665
NaI	– 690

Applications:

It is applied to determine:

- Bonding in ionic compounds
- Properties of ionic compounds

❖ Lattice energy depends upon charge to size ratio of ions. Greater the charge to size ratio, greater will be the lattice energy.

PRACTICE EXERCISES

1. If an endothermic reaction takes rapidly in a container, temperature of the surrounding

A) Increases

C) Remains constant

B) Decreases

D) Difficult to predict

2. If internal energy of a system increases than which of the following change may take place?

A) State of the system may change

C) Temperature of the system may rise

B) Chemical reaction may take place

D) All of the above

3. Which of the enthalpy change is always positive

A) Heat of solution

C) Heat of combustion

B) Heat of neutralization D) Heat of atomization

4. Bomb calorimeter is used to determine

A) Heat of neutralization C) Heat of solution

B) Heat of combustion D) Heat of formation

5. Hess's law is used to calculate

A) Heat of combustion C) Heat of formation

B) Lattice energy D) All of above

6. Formula to determine lattice energy is

A) $\Delta H_{latt} = \Delta H_{form} - \Delta H_x$ C) $\Delta H_e = \Delta H_f + \Delta H_x$

B) $\Delta H_e = \Delta H_x - \Delta H_f$ D) None of above

7. Calorie is equal to

A) 0.4184J C) 4.184J

B) 41.84J D) 418.4J

8. Which is contrary to 1st law of thermodynamics

A) Energy can never be produced

B) Energy can neither be formed nor destroyed

C) In an adiabatic process, work done is independent of its path

D) continuous production of work without supply of an equivalent amount of energy

9. Which is not a spontaneous reaction

A) $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$ C) Acid base reaction

B) $H_2O_{(g)}$ □□□ $\rightleftharpoons$

D) $N_2 + O_2 \longrightarrow 2NO$

10. Born Haber cycle is application of

A) Law of mass action

C) Rate law

B) Hess’s law

D) Equilibrium law

11. In which of the following equations, enthalpy change is negative

A) $Na_{(s)} \longrightarrow Na_{(l)}$

C) $Na_{(l)} \longrightarrow Na_{(g)}$

B) $\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)}$

D) $Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)}$

12. Neutralization of strong acid with strong base is

A) Non-spontaneous reaction

C) Spontaneous and exothermic reaction

B) Spontaneous and endothermic

D) Non-spontaneous endothermic reaction

13. The value of ΔH and ΔE are approximately the same for the process in case of liquids and solids because

A) There is no change in temperature

C) Head absorbed

B) volume change is negligible

D) Heat is released

14. In the formation of 1 mole of a compound from its element, the standard enthalpy change is called

A) Internal energy change

C) Enthalpy of neutralization

B) Enthalpy of formation

D) None of these

15. The enthalpy of an element in standard states is:

(A) 1 KJ–mol^{-1}

(C) Zero

(B) 298 KJ–mol^{-1}

(D) None of these

16. First law of thermodynamics is represented as:

(A) $\Delta E = q + RT$

(C) $\Delta E = \Delta H$

(B) $\Delta E = q + W$

(D) $\Delta E = q + \Delta P$

17. The conditions for standard enthalpy change is:

(A) 1 atm and 273 K

(C) 1 atm and 298 K

(B) 1 atm and 0 K

(D) 1 atm and –273°C

18. In thermochemistry force displacement work is replaced by:

(A) Pressure volume work

(C) Pressure temperature work

(B) Temperature volume work

(D) None of these

19. The smallest unit of heat energy is:

(A) Calorie

(C) Joule

(B) Erg

(D) Kilo Joule

20. ΔH_n for the reaction NaOH + CH_3COOH is:

(A) 57 KJ

(C) Less than 57 KJ

(B) Zero

(D) More than 57 KJ

21. A chemical change occurs when:

(A) A shirt is ironed

(B) Milk sours

(C) Perfume evaporates

(D) Electricity pass through copper wire

22. Which of the following is not state function?

(A) Internal energy **(B)** Work

(C) Gibb's free energy **(D)** Enthalpy

23. If more bonds are broken than the bonds formed, the reaction will be:

(A) Exothermic **(B)** Endothermic

(C) Both **(D)** None

24. From the following data:

$C_{(graphite)} \longrightarrow C_{(g)}$ **ΔH = 716.7 kJ/mole**

$C_{(diamond)} \longrightarrow C_{(g)}$ **ΔH = 714.8 kJ/mole**

Calculate ΔH for the reaction $C_{(graphtie)} \longrightarrow C_{(diamond)}$.

(A) 714.8 kJ **(B)** –1.9 kJ

(C) Zero **(D)** 1.9 kJ

25. If heat is being given to system (reaction taking place in a solution) then q_p is related to q_v as:

(A) $q_p > q_v$ **(B)** $q_p < q_v$

(C) $q_p = q_v$ **(D)** not comparable

ΔH_n for the reaction:

26. $NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

(A) Zero **(B)**57 kJ mol^{-1}

(C) Less than 57 kJ mol^{-1} **(D)**More than 57 kJ mol^{-1}

27. The sponteinity of chemical reaction can be predicted by knowing:

(A) ΔH **(B)** ΔE

(C) ΔG **(D)** ΔP

28. At constant T and P, which is correct for the following reaction:

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$$

(A) $\Delta H = \Delta E$ **(B)** $\Delta H > \Delta E$

(C) $\Delta H < \Delta E$ **(D)** $\Delta H \simeq \Delta E$

29. When an exothermic reaction is reversed:

(A) It becomes another exothermic reaction **(B)**It attains equilibrium

(C) It becomes an endothermic process **(D)** There is no change at all

30. If $H^+ + OH^- \longrightarrow H_2O$ $\Delta H = +13.7$ **K.Cal**

Heat of neutralization for complete neutralization of one mole of H_2SO_4 by base will be:

(A) 13.7 K.Cal **(B)** 27.4 K.Cal

(C) 6.85 K.Cal **(D)** 3.425 K.Cal

31. An isolated system is the one:

(A) that can transfer matter only

(B) that can transfer energy only

(C) that can transfer matter and energy

(D) that can transfer neither matter nor energy to and from surrounding

32. A closed flask contains water in all its three states i.e., solid, liquid and vapour at 0°(C) In this situation, the average K.E. of water molecule will be:

(A) Same in all three states

(B) Greater in liquid than vapour state

(C) Maximum in solid state

(D) Maximum in vapour state

33. Which of the following changes is exothermic?

(A) $NH_4Cl_{(s)} + aq \longrightarrow NH_4Cl_{(aq)}$

(B $Br_{(g)} + e^- \longrightarrow Br^-_{(g)}$

(C) $Br_{2(g)} \longrightarrow 2Br_{(g)}$

(D) $Na_{(g)} \longrightarrow Na^+ + e^-$

34. A system absorb 30 kJ of heat and does 20 kJ of work. The net internal energy of the system:

(A) Increase by 10 kJ

(B) Decrease by 10 kJ

(C) Increase by 30 kJ

(D) Decrease by 30 kJ

35. A human being requires 2700 KCal of energy per day. If ΔH_C of glucose is –1350 KCal.mol^{-1}. How many grams of glucose a person has to consume everyday?

(A) 360 g

(B) 36.0 g

(C) 3.6 kg

(D) 360 mg

36. For which of the following equations does the enthalpy change represent the lattice energy of sodium chloride?

(A) $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$

(B) $Na^+(aq) + Cl^-(aq) \rightarrow NaCl(aq)$

(C) $Na(g) + Cl(g) \rightarrow NaCl(s)$

(D) $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

37. Which one of the following equations correctly defines the enthalpy change of formation of carbon monoxide?

(A) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ (B) $C(s) + O(g) \rightarrow CO(g)$

(C) $C(s) + CO_2(g) \rightarrow 2CO(g)$ (D) $C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

38. The value of the enthalpy change for the process represented by the equation

$\boldsymbol{Na(s) \rightarrow Na^+(g) + e^-}$ **is equal to:**

(A) the first ionization energy of sodium

(B) the enthalpy change of vaporization of sodium.

(C) The sum of the first ionization energy and the electron affinity of sodium.

(D) the sum of the enthalpy change of atomization and the first ionization energy of sodium.

39. Which one of the following processes is endothermic?

(A) Milting of ice (B) Sublimation

(C) Fusion of metal (D) All of these

40. If bond enthalpy of N-H bond is x kJ mol^{-1}, the value of enthalpy change in the process

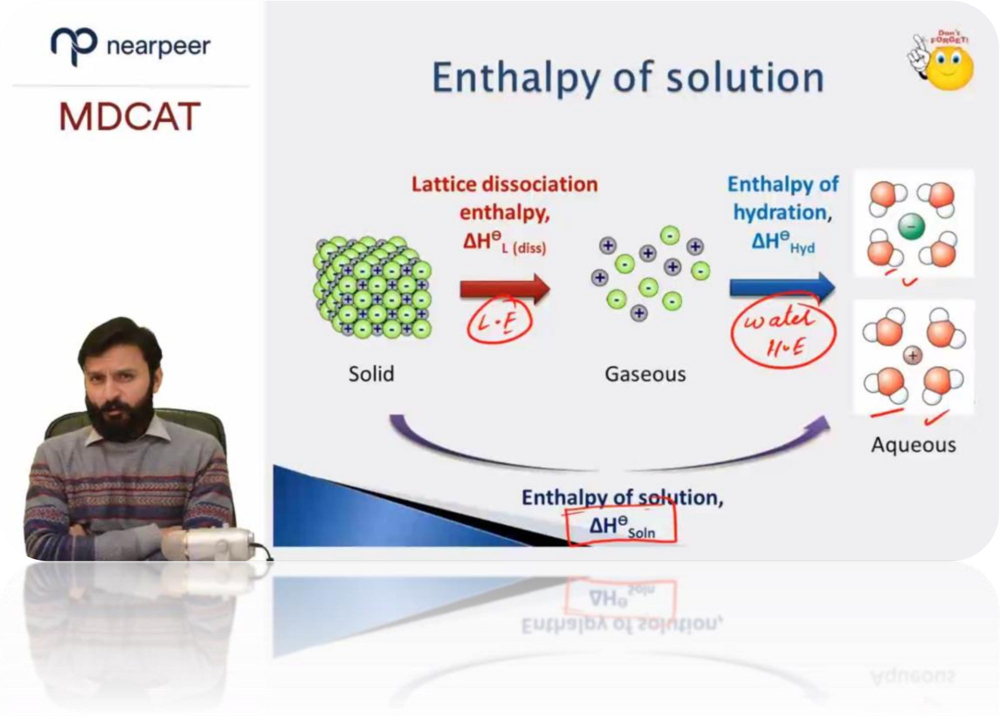
$\mathbf{NH_{3(g)} \longrightarrow N_{2(g)} + 3H_{(g)}}$ **+ ? kJ mole^{-1} is**

(A) 2x **(B)** x

(C) 3x **(D)** $\frac{x}{3}$

ANSWER KEY

1	B	11	D	21	B	31	D
2	**D**	**12**	**C**	**22**	**B**	**32**	**D**
3	**D**	**13**	**B**	**23**	**B**	**33**	**B**
4	**B**	**14**	**B**	**24**	**D**	**34**	**A**
5	**D**	**15**	**C**	**25**	**C**	**35**	**A**
6	**A**	**16**	**B**	**26**	**C**	**36**	**D**
7	**C**	**17**	**C**	**27**	**C**	**37**	**A**
8	**D**	**18**	**A**	**28**	**B**	**38**	**D**
9	**D**	**19**	**B**	**29**	**C**	**39**	**D**
10	**B**	**20**	**C**	**30**	**B**	**40**	**C**



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Enthalpy of solution

UHS TOPIC VI A

ELECTROCHEMISTRY

LEARNING OUTCOMES

In this topic, student should be able to:

a) Describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number.

b) Define the terms: Standard electrode (redox) potential and standard cell potential.

c) Describe the standard hydrogen electrode as reference electrode.

d) Describe methods used to measure the standard electrode potentials of metals - or non-metals in contact with their ions in aqueous solution

e) Calculate a standard cell potential by combining two standard electrode potentials.

f) Use standard cell potentials to:

  i) Explain/deduce the direction of electron flow in the external circuit.

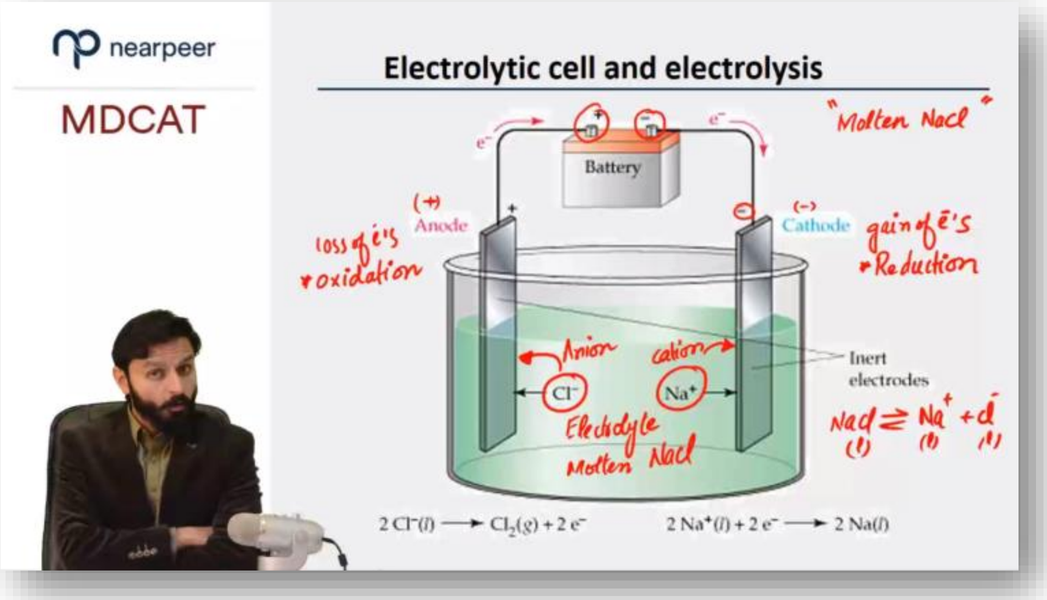
  ii) Predict the feasibility of a reaction.

g) Construct redox equations using the relevant half-equations.

h) State the possible advantages of developing the H_2/O_2 fuel cell.

i) Predict and to identify the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration e.g:

$H_2SO_{4(aq)}$ and $Na_2SO_{4(aq)}$.



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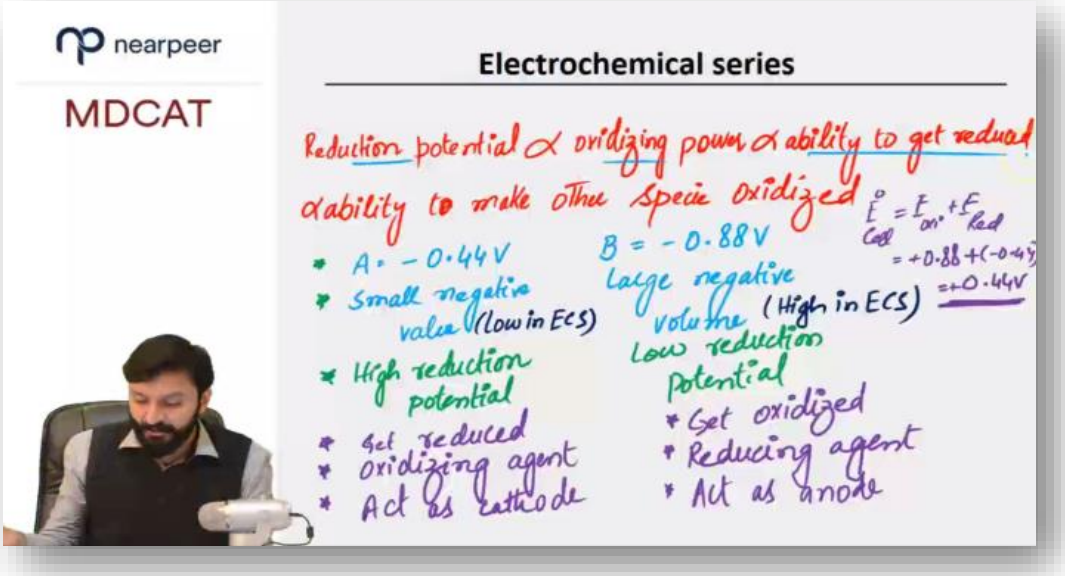
Electrolytic cell and electrolysis

"Molten NaCl"

$NaCl_{(l)} \rightleftharpoons Na^+_{(l)} + Cl^-_{(l)}$

$2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$ $2Na^+(l) + 2e^- \longrightarrow 2Na(l)$



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Electrochemical series

Reduction potential ∝ oxidizing power ∝ ability to get reduced

∝ ability to make other specie oxidized

$E^\circ_{Cell} = E_{ox} + E_{Red}$

$= +0.88 + (-0.44)$

$= +0.44V$

- A = −0.44V
- Small negative value (low in ECS)
- High reduction potential
- Get reduced
- oxidizing agent
- Act as cathode

B = −0.88V

Large negative volume (High in ECS)

Low reduction potential

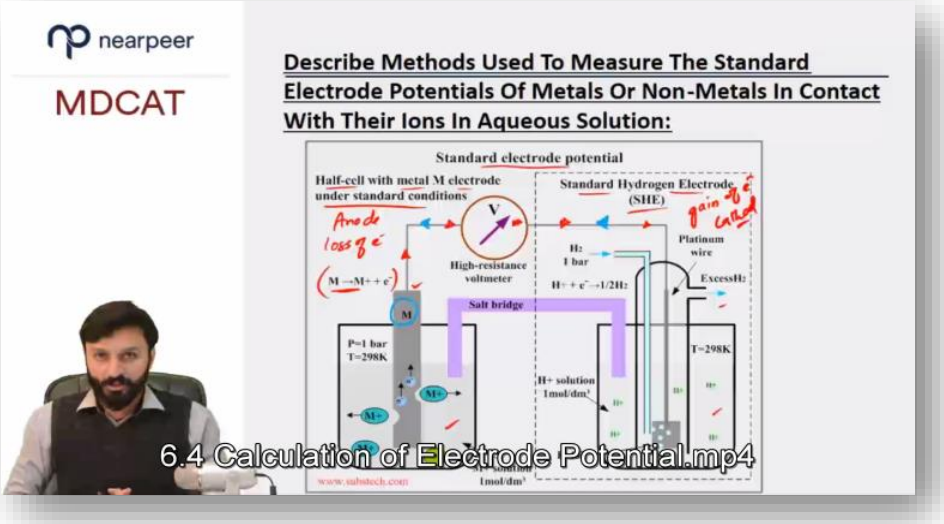
- Get oxidized
- Reducing agent
- Act as anode

ELECTROCHEMISTRY

:

It is the branch of chemistry which is concerned with the inter-conversion of chemical energy and electrical energy.

- Electrical energy is converted into chemical energy through electrolytic cells.
- Chemical energy is converted into electrical energy through galvanic or voltaic cells.



Describe Methods Used To Measure The Standard Electrode Potentials Of Metals Or Non-Metals In Contact With Their Ions In Aqueous Solution:

6.4 Calculation of Electrode Potential.mp4

POINT TO PONDER: The oxidation numbers of the elements in a compound add up to…

OXIDATION STATE OR NUMBER

It is the apparent charge on an atom of an element in a molecule or an ion. It may be positive or negative or zero.

RULES FOR ASSIGNING OXIDATION NUMBER

Element	• Molecular Form • Bulk/Chunk	H_2, S_8 0 Diamond (C) 0
Compound	• Covalent Compound → molecular / Bulk / Chunk Non-metal – non-metal • Less electronegative nonmetal = +ve • More electronegative nonmetal = – ve • Algebraic sum of oxidation numbers = 0 •Ionic Compound → Metal – None-metal Metal = + ve Non-metal = – ve Algebraic sum of oxidation numbers = 0	Molecular: HCl (+1) + (– 1) = 0 Bulk/Chunk: SiO_2 [+ 4 + 2 (– 2)] = 0 Ionic Compound NaCl (+ 1) + (– 1) = 0
Ion	Monoatomic ion → Oxidation number will be equal to the charge on the ion Poly-Atomic Ion → The algebraic sum of oxidation number is equal to charge on that ion	Mono-Atomic Ion Cl^{-1} – 1 Poly-Atomic Ion SO_4^{-2} + 6 +[– 2(4)] = – 2
Hydrogen	• Ionic Compound → Always – ve oxidation number • Covalent compound	Ionic Compound NaH (+1) + (– 1) = 0 Covalent Compound

	→ Always +ve oxidation number	H_2O [+1(2)] + (– 2) = 0
Oxygen	• With all element → – 2 oxidation number (normal oxides) → – 1 oxidation number (per oxides) → – ½ oxidation state (super oxides) • With Fluorine → + 2 oxidation state	 H_2O – 1(2) – 2 = 0 H_2O_2 + 1 – 1 = 0 KO_2 [+ 1 + 2(– ½)] = 0 OF_2 [+ 2 + 2(– 1) = 0

OXIDATION		**REDUCTION**	
→	Gain in oxygen	→	Loss in oxygen
→	Loss of hydrogen	→	Gain of hydrogen
→	Loss of electrons including anode reaction	→	Gain of electron including cathode reaction
→	Increase in oxidation	→	Decrease in oxidation state

Oxidation number of IA group	(+ 1)
Oxidation number of II-A group	(+2)
Oxidation number of III-A group	(+3)

Examples:

$K_2Cr_2O_7$ $(+1)2 + 2Cr – 2(7) = 0$

$+ 2 + 2Cr – 14 = 0$

$2Cr = + 14 – 2 = + 12$

$Cr = + 6$

$NaBrO_3$ $1 + Br + (-2)(3) = 0$

$1 + Br - 6 = 0$

$Br - 5 = 0$

$Br = +5$

Commercial preparation of sodium hydroxide:

Sodium hydroxide (caustic soda) is manufactured on a large scale by the electrolysis of aqueous solution of common salt (Brine) in a diaphragm cell.

ELECTROLYTIC CONDUCTION

:

ELECTROLYTIC CONDUCTION	ELECTRONIC CONDUCTION
• Conduction through fused or aqueous electrolyte	• Conduction through solid metal
• It is due to mobile ions	• Due to free electrons
• Conduction increases with increase in temperature due to increase in ionization	• Conduction decreases with increase in temperature due to increase in oscillations of cations

Products of Electrolysis:

(When electrodes take part in the reaction)

ELECTROLYTE	COPPER CATHODE	COPPER ANODE
$CuSO_4$ (aq)	Cu deposits	Cu(s) dissolves to form Cu^{2+} ions
Electrolyte	Ag Cathode	Ag Anode
$AgNo_3$(aq) And HNO_3 (aq)	Ag Deposits	Ag (s) dissolves to form ag^+ ions

Products of electrolysis:

(Using inert electrodes of platinum or graphite)

Electrolyte	Cathode	Anode
$PbBr_2$(molten)	Pb(s)	B_2(g)
NaCl(molten)	Na(s)	Cl_2(g)
NaCl(aq)	H_2 (g)	Cl_2(g)
$CuCl_2$(aq)	Cu(s)	Cl_2(g)
$CUSO_4$(aq)	Cu (s)	O_2 (g)
KNO_3(aq)	H_2 (g)	O_2 (g)
NaOH (aq)	H_2 (g)	O_2 (g)
H_2SO_4 (aq)	H_2 (g)	O_2 (g)
$ZnSO_4$ (aq)	H_2 (g)	O_2 (g)

Electrolysis becomes more complex when there is more than one cation and anion or water present in the electrolytic mixture. If it is so, the discharged at the cathode can be predicted from the reactivity (electrochemical series).

It's not surprising that metals like potassium and sodium which are keen to form ions don't readily reform the metal during electrolysis. So the ions of metals lower down in the electrochemical series are discharged in preference to those higher up. The simple rule is however complicated by two factors:

If a cation is present in very high concentration, it may be discharged in preference to one below it in the electrochemical series at much lower concentration. Hydrogen is discharged from the aqueous solutions of salts of metals above it in the electrochemical series. So hydrogen is produced at the cathode when aqueous sodium chloride is electrolyzed. When there is more .than one anion present in the electrolyte, experiments show that the order of increasing discharge is:

SO_4^{-2}, NO_3^{-1}, Cl^{-1}, Br^{-I}, I^{-1}, OH^{-1}

USES OF ELECTROLYSIS:

PARTICULAR	DESCRIPTION
Extraction of Na metal	Fused NaCl is used Down's cell is an example
Caustic soda from brine	Nelson cell (aqueous NaCl is used)
Mg and Ca extraction	Extraction occurs from their fused chlorides
Extraction of Al	Electrolysis of fused bauxite is conducted
Anodized Al	Prepared by making anode of Al
Purification of Cu	Anode is made up of impure copper
Electroplating	Copper, silver, nickel or chromium plating is done in electrolytic cell

POINT TO PONDER: in disproportionation part of a substance is oxidized and part is …

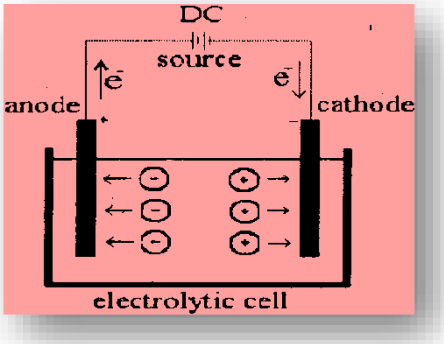
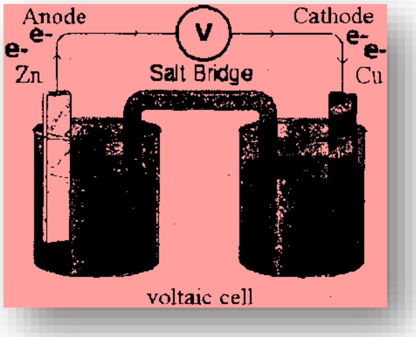
ELECTRCOCHEMICAL CELLS

The cells consisting of electrodes dipped into an electrolyte which make the inter-conversion of electrical energy and chemical energy possible are called electrochemical cells.

Types of electrochemical cells:

(i) Electrolytic cell

(ii) Voltaic or galvanic cell

ELECTROLYTIC CELL	**VOLTAIC/GALVANIC CELL**
A cell in which a redox reaction occurs at the expense of electrical energy is called electrolytic cell.	A cell in which redox reaction generates electric current through chemical reaction is called voltaic or galvanic cell.
Anode is +vely charged	Anode is – vely charged
Cathode is – vely charged	Cathode is + vely charged
Electrical energy → chemical energy	Chemical energy → electrical energy
Both reduction reaction and oxidation reaction occur in the same compartment.	Reduction reaction and oxidation reaction occur in the separate compartment.
Non-spontaneous redox reaction occurs.	Spontaneous redox reaction occurs.
Salt bridge is not used.	Salt bridge is used.
Used for the extraction of metals, purification, electroplating and anodizing.	Used for the measurement of electrode potential.
It consumes heat (endothermic)	It generates heat (exothermic)
	
Nelson's Cell and Down's Cell	Daniel's cell, Ni-Cd cell, fuel cell

VOLTAIC OR ORGANIC CELL

Two half cells are present in voltaic cell

- Left Half Cell (Oxidation Half Cell)

Zn - electrode is dipped in 1 M solution of $ZnSO_4$

- Right Half Cell (Reduction Half Cell)

Cu - electrode is dipped in 1 M solution of $CuSO_4$

- **Salt Bridge** It is aqueous solution of KCl in a gel
- Working

→ Connect both the half cells electrolytically through the salt bridge

→ Close the external circuit by connecting the Zn and Cu electrodes.

→ The electrons will flow from Zn to Cu through external circuit. The following Reactions will occur at respective electrodes.

- **At anode** $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ Oxidation
- **At cathode** $Cu^{2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ Reduction
- The voltaic cell reaction is represented by:

$$Zn^{(s)}/Zn^{2+}_{(aq)}1M \,||\, Cu^{2+}_{(aq)}1M/Cu_{(s)}$$

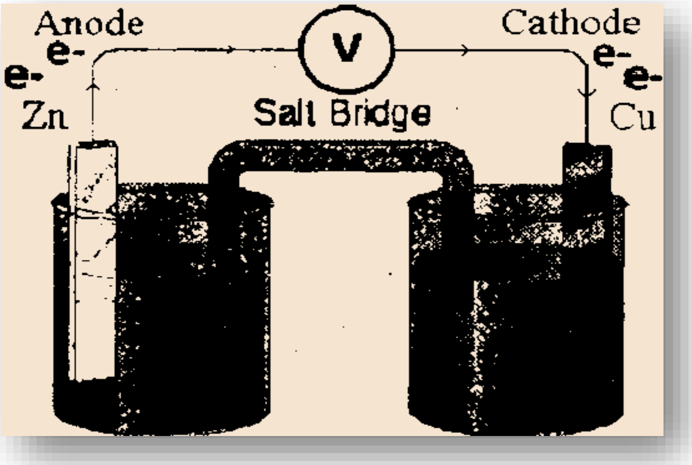
- emf of the cell

$$E^0 = 1.10\text{ V}$$

Function of salt bridge:

→ Salt bridge acts as a passage for the transfer of negative ions (SO_4^{2-}) from right half-cell to left half-cell.

→ If the exchange of SO_4^{2-} ions is stopped, then the oxidation-reduction reaction willstop due to charge accumulation in both half cells.



Zn → Zn^{+2} + ze – || Cu^{+2} + 2 e^- → Cu

Replacing the external circuit by a source of high voltage can reverse the voltaic cell reactions. Such cell is called reversible cell.

Electrode Potential:

The potential set up when an electrode is dipped in one molar solution of its own ions at 298K called standard electrode potential or standard reduction potential, denoted by E^o.

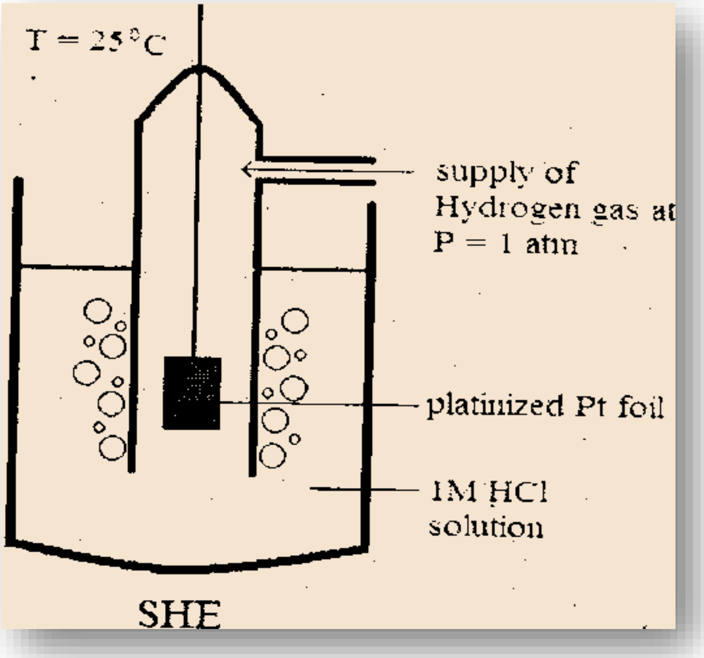
- Electrode potential, of any element, can be calculated by comparing it with standard hydrogen electrode (SHE).

Standard Hydrogen Electrode (SHE):

SHE consists of:

- Glass Tube filled with H_2 gas at 1 atm. Pt-foil, coated with finally divided platinum black is suspended in it.
- The whole system mentioned above is dipped in 1 M solution of HCl

- Electrode Potential of SHE is arbitrarily considered as zero



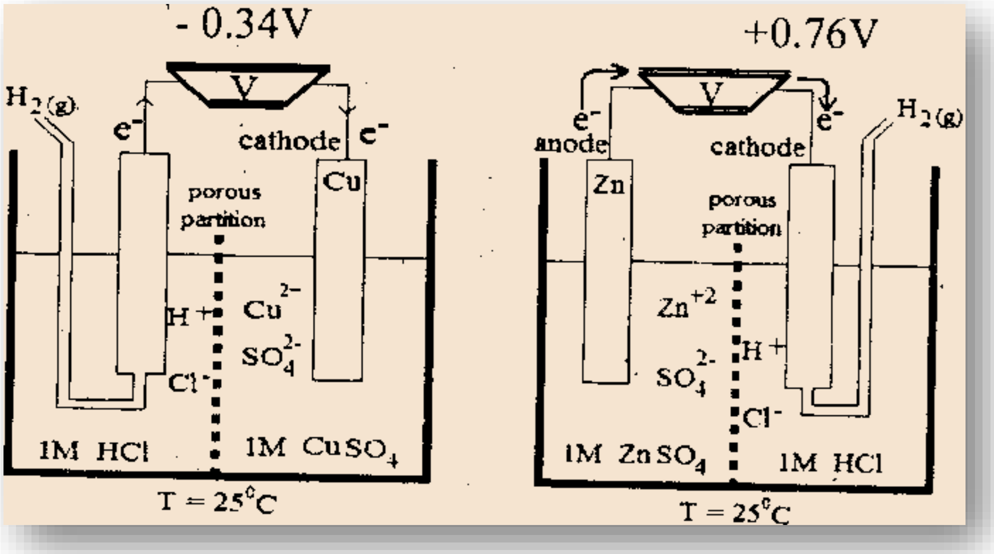
MEASUREMENT OF ELECTRODE POTENTIAL

- Concerned electrode is joined with SHE and form a voltaic cell
- Salt bridge is used to connect both cells, filled with solution of KCl
- Voltmeter is attached to measure electrode potential
- Oxidation or reduction reaction occurs at SHE depending on the nature of the concerned electrode.
- When reduction occurs on SHE then volt meter reading

will be +ve. $2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(gas)}$

- When oxidation occurs on SHE then voltmeter reading will be in – ve $H_{2(gas)} \rightarrow H^{+}_{(aq)} + 2e^{-}$

- Potential of Zn is called oxidation potential
- Potential of Cu is called reduction potential



POINT TO PONDER: An electrode potential is measured by finding the emf of a cell composed of the electrode e.g. the .... which has E = 0 or the calomel electrode

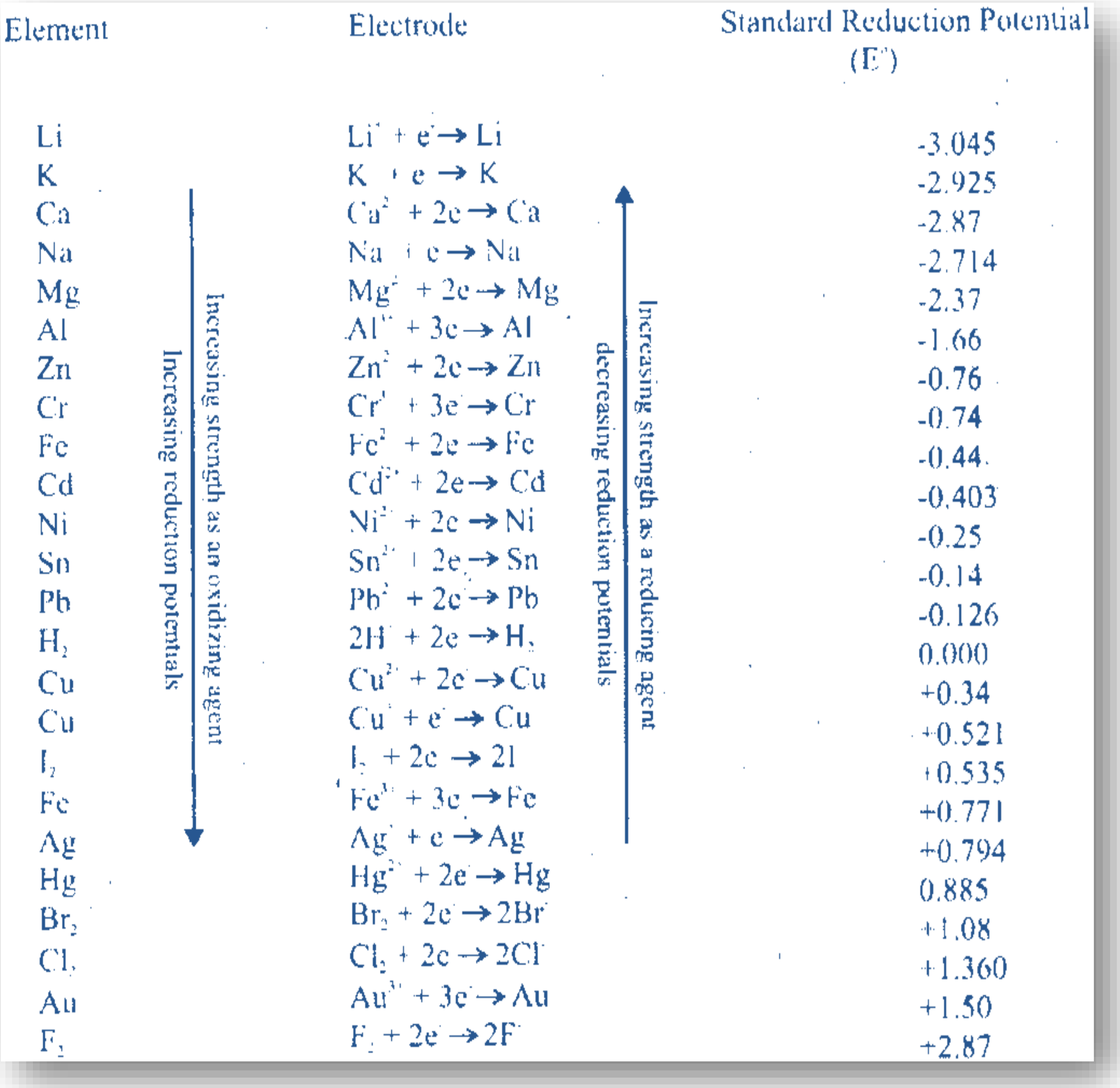
Electrode	Plate which carries electricity into the liquid
Anode	Plate at which oxidation occurs
Cathode	Plate at which reduction occurs
Conductor	A substance which conducts electricity but is not chemically changed
Insulator	A solid non-conductor
Strong electrolyte	A liquid which is fully ionized
Weak electrolyte	A liquid which is not fully ionized
Non-electrolyte	A liquid which does not undergo ionization.

Electrolysis	Decomposition of an electrolyte by passage of electricity
Anion	Negatively charged ion that travels to the anode during electrolysis
Cation	Positively charged ion that travels to the cathode during electrolysis

THE ELECTROCHEMICAL SERIES

When elements are arranged in the order of their increasing standard electrode potentials on the hydrogen scale, the resulting list is known as electrochemical series.

ELECTROCHEMICAL SERIES



Element	Electrode	Standard Reduction Potential (E°)
Li	$Li^+ + e^- \rightarrow Li$	-3.045
K	$K^+ + e^- \rightarrow K$	-2.925
Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
Na	$Na^+ + e^- \rightarrow Na$	-2.714
Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
Al	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
H_2	$2H^+ + 2e^- \rightarrow H_2$	0.000
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Cu	$Cu^+ + e^- \rightarrow Cu$	+0.521
I_2	$I_2 + 2e^- \rightarrow 2I^-$	+0.535
Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	+0.771
Ag	$Ag^+ + e^- \rightarrow Ag$	+0.794
Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	0.885
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.08
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.360
Au	$Au^{3+} + 3e^- \rightarrow Au$	+1.50
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+2.87

POINT TO PONDER: The electrochemical series lists:

- Cations in order of case of discharge at a ....
- Aninos in order of case of discharge at a ....

POINT TO PONDER: The criterion for spontaneous cell reactions is that E_{cell} is ....

Applications of Electrochemical Series:

Applications:

(i) Prediction of the feasibility of a chemical reaction:

The Electrochemical series tells us that whether are action is feasible or not. If the sum of E_o values of the two half-cell reaction is positive, the reaction is feasible and if it is negative then the reaction will not be feasible.

(ii) Calculation of the voltage or emf of the cell:

- Electrode having higher position in series will act as an anode, oxidation will take' place on it
- Electrode having lower position in series, will act as cathode, reduction will take place on it

(iii) Comparison of relative tendency of metals and non-metals to get oxidized or reduced:

- Value of the electrode potential shows, either the metal or non-metal is oxidized or reduced Greater value of standard reduction electrode potential greater will be the tendency to accept electron and undergo reduction and vice versa

(iv) Relative chemical reactivity of metals:

Greater value of the standard reduction potential of specie lesser will be its tendency to lose electron to form +ve ion hence lesser will be its reactivity.

POINT TO PONDER: A redox reaction will go almost to completion between two redox systems which differ in their ....

(v) Reaction of metals with dilute acids:

Greater the value of standard reduction potential of a metal, lesser its tendency to lose electrons to form metal ions and so weaker, its tendency to' displaced H_2 from acids. For example Au, Pt, Ag and Cu do not liberate hydrogen from acids.

(vi) Displacement of one metal by another from its solution:

Metal will displace another metal from the aqueous solution of its salt if it lies above the electrochemical series. For example Fe can displace Cu from $CuSO_4$, Zn does not displace Mg from solution of $MgSO_4$

FUEL CELL

A fuel cell is a cell which converts the chemical energy of a continuous supply of reactants into electrical energy, Fuel is supplied to one electrode and an oxidant, usually oxygen: to the other. A great deal of research is being done on fuel cells as they are a promising source of energy for the future. The American Gemini space probes and Apollo moon probes used hydrogen-oxygen fuel cells. The astronauts used the product of the reaction to supplement their drinking water.

1. Stream of hydrogen

2. Hydrogen diffuses through the porous cathode (e.g. of Ni) when it comes into contact with the electrolyte $KOH_{(aq)}$.

Absorbed H_2 is oxidized:

$$\frac{1}{2}H_2 + OH^- \rightarrow H_2O + e^-$$

3. Electron flow through an external circuit from cathode to anode.

4. Stream of oxygen

5. Oxygen diffuses through a porous anode (e.g. of nickel) absorbed oxygen is reduced to OH^- ions:

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-(eq)$$

The overall reaction is:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O\ (l)$$

PRACTICE EXERCISE (FOR UHS TOPIC)

1. **Which statement is correct for galvanic cell:**

(A) Anode = negative
(C) Cathode = negative

(B) electrons enter the cell = anode
(D) reduction occurs at anode

2. **Which is inert electrode?**

A) Zn
C) Pb

B) Pt
D) Cd

3. **During electrolysis of dilution KNO_3, which of them is collected at anode?**

A) H_2
C) K

B) O_2
D) N_2

4. **Which is electrolytic cell?**

A) Down's cell
C) Silver oxide

B) Dry alkaline cell
D) Nickle cadmium cell

5. **In which of the type of cell, electric current is consumed?**

A) Fuel cell
C) Silver oxide cell

B) Lead storage cell
D) Nelson's cell

6. **By the electrolysis of concentrated NaCl solution, which of the following is collected at cathode?**

A) Hydrogen

C) Chlorine

B) Oxygen

D) NaOH

7. By the electrolysis of dil. $CuSO_4$ solution, which is deposited at cathode?

A) H_2

C) Cu

B) O_2

D) SO_4^{2-}

8. Which of the following cell is considered as rechargeable cell / secondary cell

A) Dry alkaline cell

C) Down's cell

B) Silver oxide cell

D) Nickel cadmium cell

9. In which of the following cells, zinc is used as anode?

A) Dry alkaline

C) Galvanic cell

B) Silver oxide cell

D) All of above

10. Which is best reducing agent regarding in electrochemical series?

A) Li

C) K

B) Na

D) Ca

11. Which statement is correct about electrochemical series?

A) Smaller is the standard reduction potential, stronger is the reducing agent.

B) Greater is the standard reduction potential, greater is oxidation power.

C) Every top metal can displaces lower one while lower non-metal can displace higher one

D) All of the above

12. The electrode potentials of few elements are given:

A = -0.76V B = +0.34V C = -1.0V D = -1.5V

13. Which is the strongest reducing agent

(A) B (C) A

(B) D (D) C

14. Which of the following statements is correct

A) Mg and Ca are extracted by electrolysis of their fused chlorides.

B) Al is obtained by electrolysis of fused bauxite.

C) Electrolytic cell is used for the purification of Cu

D) All of the above

15. Which of the following is the function of salt bridge

A) To maintain flow of electric current through exterior

B) To keep separate both solutions

C) To keep electrical neutrality

D) All of the above

16. Which of the following has same oxidation state in all of its compounds:

(A) Be (C) Br

(B) Cl (D) N

17. In which of the following reactions, hydrogen behave as an oxidizing agent:

(A) $H_2 + Cl_2 \longrightarrow 2HCl$ (C) $C_2H_4 + H_2 \longrightarrow C_2H_6$

(B) $2Na + H_2 \longrightarrow 2NaH$

(D) $N_2 + 3H_2 \longrightarrow 2NH_3$

18. The change in oxidation state of nitrogen in the following reaction is:

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

(A) +5 to –2

(C) +5 to +4

(B) +5 to 0

(D) 0 to –4

19. The oxidation state of Mn in K_2MnO_4 is:

(A) +7

(C) +6

(B) +5

(D) +4

20. The oxidation number of sulphur in $Na_2S_4O_6$ is:

(A) +2

(C) +4

(B) +2.5

(D) +6

21. In which of the following compounds, oxidation number of sulphur is negative:

(A) SO_2

(C) H_2SO_4

(B) H_2S

(D) Na_2SO_4

22. Oxidation number of O in Na_2O_2:

(A) –1

(B) +1

(C) +2

(D) –2

23. $Zn_{(s)}$: Zn^{+2}_{aq} (1 M) || Cu^{+2}_{aq} (1 M) : Cu is representation of the reaction:

(A) Down's cell (B) Daniel's cell

(C) Galvanic cell (D) The reaction takes place in all the cells

24. The trend of strength as oxidizing agent down the electrochemical series is:

(A) Increasing (B) Decreasing

(C) Variable (D) Same

25. Which of the following is not redox reaction?

(A) $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(B) $2Mg + O_2 \longrightarrow 2MgO$

(C) $Mg + 2HCl \longrightarrow MgCl_2 + H_2$

(D) $MgO + 2HCl \longrightarrow MgCl_2 + H_2O$

26. A substance conducts electricity both when solid and in molten state:

(A) An alloy (B) Metal oxide

(C) A salt (D) A hydrocarbon

27. The function of SHE when connected to zinc is:

(A) Anode (B) Cathode

(C) Electrolyte (D) None of these

28. The reason for the less reactivity of Coinage metals Cu, Ag and Au is

(A) Low reduction potential (B) High reduction potential

(c) high oxidation potential (D) None of these

29. What is standard e.m.f of the cell $Mg_{(s)} \mid Mg^{+2}_{(aq)} \parallel Cu^{+2}_{(aq)} \mid Cu_{(s)}$?

$$\left(\begin{array}{lll} Mg^{+2} + 2e^- \rightleftharpoons Mg & & E = -2.38\ V \\ Cu^{+2} + 2e^- \rightleftharpoons Cu & & E = +0.34\ V \end{array}\right)$$

(A) 2.72 V

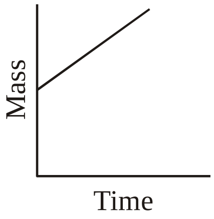
(B) 2.53 V

(C) 2.04 V

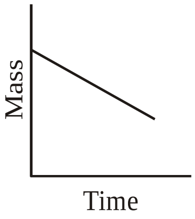
(D) 1.36 V

30. Electrolysis of aqueous $CuSO_4$ was carried out using Cu-electrodes. Which graph shows the change in mass of the cathode with time?

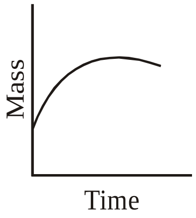
(a)



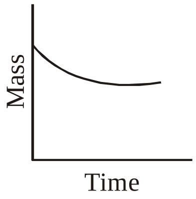
(b)



(c)



(d)



31. When 5 moles of electrons are passed through a molten aluminum salt, what is the maximum mass of aluminium deposited at cathode:

(A) 5.4 g

(B) 16.2 g

(C) 27 g

(D) 45 g

32. Metals which easily react with acid should fulfill which of the following statements?

(A) Less oxidation potential as compare to hydrogen

(B) More oxidation potential as compare to hydrogen

(C) Less reduction potential as compare to hydrogen

(D) Both (b) and (c)

33. Which of the following reactions is not feasible according to the electrochemical series?

(A) $2KCl + F_2 \longrightarrow 2KF + Cl_2$ (B) $2KF + Cl_2 \longrightarrow 2KCl + F_2$

(C) $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$ (D) $2KI + Br_2 \longrightarrow 2KBr + I_2$

34. How many electrons are required to balance the charge in the following equation:

$$2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+$$

(A) $9e^-$ on right side (B) $9e^-$ on left side

(C) $6e^-$ on the right side (D) $6e^-$ on the left side

35. Which one of the following can have positive and negative oxidation state in various compound?

(A) Fluorine (B) Sodium

(C) Iodine (D) Helium

36. Consider the following cell reaction:

$$Al, Al^{+3} \,||\, Cl_2, Cl^- \quad Al^{+3}/Al^0 = -1.67\ V \quad Cl_2/Cl^- = +1.36\ V$$

The cell voltage in this case is:

(A) 2.95 V (B) 3.0 V

(C) 3.03 V (D) 0.31 V

37. Which ion is discharged at anode, during the electrolysis of dil. aqueous NaCl?

(A) Cl^-

(B) OH^-

(C) Na^+

(D) H^+

38. The best reducing agent is:

(A) F^{-1}

(B) Cl^{-1}

(C) Br^{-1}

(D) I^{-1}

39. In hydrogen-oxygen fuel cell, the two electrodes are hollow tube made of porous compressed carbon impregnated with platinum which act as?

(A) Inhibitor

(B) Reducing agent

(C) Catalyst

(D) Oxidizing agent

40. In which of the following changes there is a transfer of five electrons

(A) $MnO_4^{2-} \rightarrow MnO_2$

(B) $MnO_4^- \rightarrow Mn^{+2}$

(C) $CrO_4^{-2} \rightarrow Cr^{+3}$

(D) $Cr_2O_7^{2-} \rightarrow 2Cr^{+3}$

41. In which one of the following reactions does hydrogen behave as an oxidizing agent?

(A) $H_2 + Cl_2 \longrightarrow 2HCl$

(B) $2Na + H_2 \longrightarrow 2NaH$

(C) $C_2H_4 + H_2 \longrightarrow C_2H_6$

(D) $N_2 + 3H_2 \longrightarrow 2NH_3$

ANSWER KEY

1	A	11	D	21	A	31	D
2	**B**	**12**	**B**	**22**	**B**	**32**	**B**
3	**B**	**13**	**D**	**23**	**A**	**33**	**C**
4	**A**	**14**	**D**	**24**	**D**	**34**	**C**
5	**D**	**15**	**A**	**25**	**B**	**35**	**C**
6	**A**	**16**	**B**	**26**	**B**	**36**	**B**
7	**C**	**17**	**C**	**27**	**B**	**37**	**D**
8	**D**	**18**	**C**	**28**	**A**	**38**	**C**
9	**D**	**19**	**B**	**29**	**C**	**39**	**B**
10	**A**	**20**	**B**	**30**	**D**	**40**	**B**

UHS TOPIC VII A

CHEMICAL EQUILIBRIUM

LEARNING OUTCOMES

In this topic, student should be able to:

a) Explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium.

b) State Le Chatelier's Principle and apply it to deduce qualitatively the effects of changes in temperature, concentration or pressure, on a system at equilibrium.

c) Deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction.

d) Deduce expressions for equilibrium constants in terms of concentrations; K_c and partial pressures K_p

e) Calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data.

f) Calculate the quantities present at equilibrium, given appropriate data.

g) Describe and explain the conditions used in the Haber process.

h) Understand and use the Bronsted-Lowry theory of acids and bases.

i) Explain qualitatively the differences in behaviour between strong and weak acids' and bases and the pH values of their aqueous .solutions in terms of the extent of dissociation.

j) Explain the terms pH; Ka; pKa; Kw and use them in calculations.

k) Calculate $[H^+(aq)]$ and pH values for strong and weak acids and strong bases.

i) Explain how buffer solutions control pH

m) Calculate the pH of buffer solutions from the given appropriate data

n) Show understanding of, and use, the concept of solubility product, Ksp.

o) Calculate Ksp from concentrations and vice versa

p) Show understanding of the common ion effect

RATE OF CHEMICAL REACTION

The change in the molar concentration of the reactants or products per unit time is called rate of chemical reaction. Its units are mol.dm $^{-1}$s $^{-1}$

CHEMICAL EQUILIBRIUM

An apparent state of rest in a reversible chemical reaction where the rate of forward chemical reaction becomes equal to the rate of reverse reaction is called chemical equilibrium.

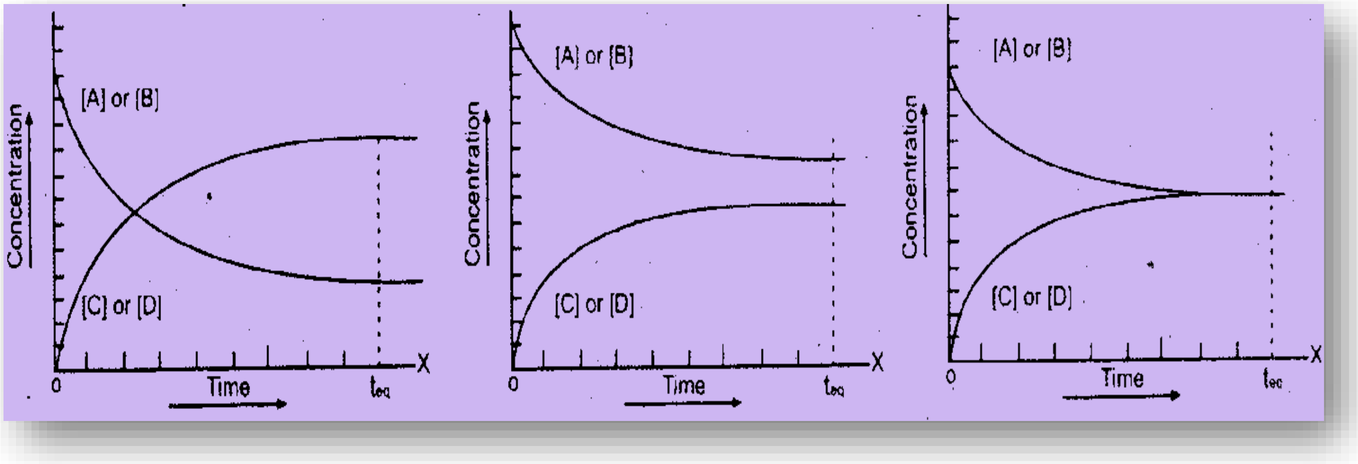
Characteristics of Chemical Equilibrium:

- It is established only in close system
- It can be established from either side
- It is a microscopic property.
- It is a dynamic state because reaction is not stationary rather moving in both directions.

Types of Equilibrium

HOMOGENEOUS EQUILIBRIUM	HETEROGENEOUS EQUILIBRIUM
A chemical equilibrium in which the reaction mixture and catalyst are in the same phase is called a homogeneous equilibrium e.g.	A chemical equilibrium in which the reaction mixture and catalyst are present in different phases is called a heterogeneous equilibrium e.g

$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO_{(g)}} 2SO_{2(g)}$	$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{Pt/V_2O_{5(g)}} 2SO_{2(g)}$



DIFFERENCE BETWEEN REVERSIBLE AND IRREVERSIBLE REACTION

REVERSIBLE REACTIONS	IRREVERSIBLE REACTIONS
Proceed in both directions i.e. forward and reverse	Proceed in one direction i.e.
Reaction does not go to completion	Reaction goes to completion
Represented by (⇌)	Represented by (→)
Dynamic equilibrium state is present	Dynamic equilibrium state is absent
Examples: $\xrightleftharpoons{Fe / 450^{o}C}$	Examples: $2Na + 2H_2O \longrightarrow 2NaOH + H_2$ $2H_2 + O_2 \longrightarrow 2NaOH + H_2$

$N_2 + 3H_2 \underset{}{\overset{Fe\ /\ 150^\circ C}{\rightleftharpoons}} 2NH_3$ $PCl_5 \overset{High\ Pressure}{\rightleftharpoons} PCl_3 + Cl_2$	

LAW OF MASS ACTION

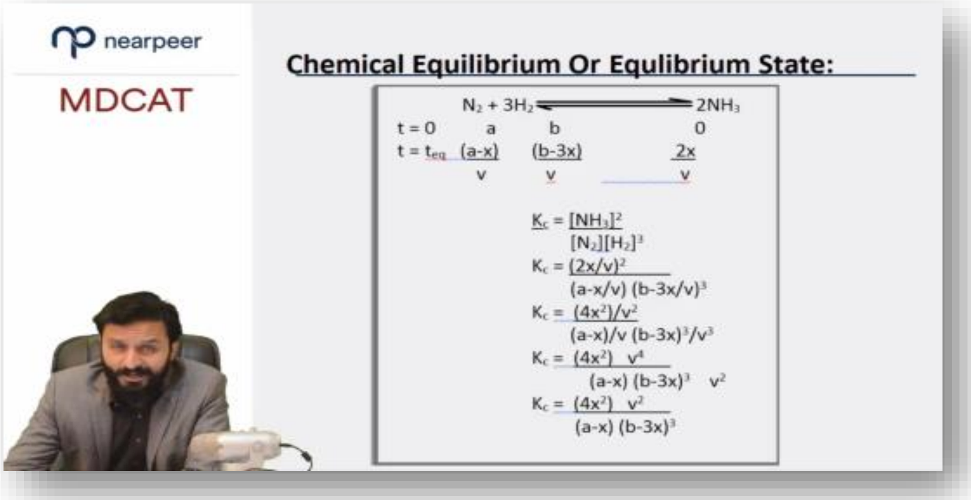
GM Guldberg and P. Waage introduced this law in 1864.

Statement:

It states that the rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants or their molar concentration.

Note:

Active mass means the concentration in mole dm^3 of the reactants which alter as a result of chemical reaction.



Chemical Equilibrium Or Equlibrium State:

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$t = 0 \quad a \quad b \quad 0$

$t = t_{eq} \quad \frac{(a-x)}{v} \quad \frac{(b-3x)}{v} \quad \frac{2x}{v}$

$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

$K_c = \frac{(2x/v)^2}{(a-x/v)\ (b-3x/v)^3}$

$K_c = \frac{(4x^2)/v^2}{(a-x)/v\ (b-3x)^3/v^3}$

$K_c = \frac{(4x^2)\ v^4}{(a-x)\ (b-3x)^3\ \ v^2}$

$K_c = \frac{(4x^2)\ v^2}{(a-x)\ (b-3x)^3}$

Explanation:

Consider a general reaction in which A and B are the reactants and C and D are the products.

$$\underset{K_r}{\overset{K_f}{\rightleftharpoons}}$$

A + B   C + D

$R_f \propto [A][B]$

$R_r = kr\ [A][B]$

$Ri \propto [C][D]$

$R_r = k_r\ [C][D]$

At equilibrium state $R_f = R_r$

$k_f\ [A]\ [B] = k_r[C]\ [D]$

On rearranging, we get $\frac{k_f}{k_r} = \frac{[C]}{[A]} \frac{[D]}{[B]}$

$\frac{k_f}{k_r} = K_c$

$$K_c = \frac{[C]}{[A]} \frac{[D]}{[B]}$$

The constant K, is called the equilibrium constant of the reaction. For a more general reaction

aA + bB   cC + dD $\underset{K_r}{\overset{K_f}{\rightleftharpoons}}$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

What is K_c:

The ratio of the product of the concentrations of the products to the product of the concentrations of the reactants is called equilibrium constant (K_c)

Characteristics of K_c:

FACTORS	EXPRESSION	
Depends upon	i)	Temperature:

	ii)	Greater the temperature, greater will be the K, value for endothermic reactions and vice versa Greater the temperature, lesser will be the K, value for exothermic reactions and vice versa
Independent of	• • • •	Initial concentration of reactants Pressure or volume Direction of reaction Catalyst
Units	• •	When number of moles of reactants = number of moles of products, then K_c has no units. When number of moles of reactants -I number of moles of products, then K_c has some units and can be calculated by using formula kc = $(\text{moles.dm}^{-3})^{\Delta n}$

Equilibrium Constant Expressions of Different Reactions:

Particular	Ester formation	Dissociation of PCl_5	Decomposition of N_2O_4	Synthesis of NH_3	Synthesis of SO_3
Reaction	$RCOOH + ROH \rightleftharpoons RCOOR + H_2O$	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	$N_2O_4 \rightleftharpoons 2NO_2$	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$2SO_2 + O_2 \rightleftharpoons 2SO_3$
Initial conc. of reaction	(a) = [RCOOH] (b) = [ROH]	(a) = $[PCl_5]$	(a) = $[N_2O_4]$	(a) = $[N_2]$ (b) = $[N_2]$	(a) = $[SO_2]$ (b) = $[O_2]$
Equilibrium conc. of reaction	(a-x) = [RCOOH] (b-x) = [ROH]	(a – x) = $[PCl_5]$	(a – x) = $[N_2O_4]$	(a – x) = $[N_2]$ (b – 3x) = $[N_2]$	(a – 2x) = $[SO_2]$ (b – x) = $[O_2]$
Rate expression	$K_c = \frac{[RCOOR][H_2O]}{[RCOOH][ROH]}$	$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5\}}$	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$	$K_c = \frac{[NH_3]^2}{[N_2][O_4]^3}$	$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]^1}$

	$K_c = \frac{x^2}{(a-x)(b-x)}$	$K_c = \frac{x^2}{V(a-x)}$	$K_c = \frac{4x^2}{V(a-x)}$	$K_c = \frac{4x^2V^2}{(a-x)(b-3x)^1}$	$K_c = \frac{4x^2V}{(a-2x)^2(b-x)}$

The Le Chatelier's Principle:

Statement:

This principle states that if a- stress is applied to a system at equilibrium. the system acts in such a way so as to nullify it, as far as possible.

Applications of Le-Chatelier's principle

Le-Chatelier's principle helps in studying effect of followings on equilibrium position and equilibrium constant.

(i) Effect of change of concentration

(ii) Effect of change of pressure or volume

(iii) Effect of change of temperature

(iv) Effect of catalyst on equilibrium.

Effect of change of concentration:

- The addition of substance among the reactants or the removal of a substance among the products at equilibrium stage disturbs the equilibrium position and reaction is shifted to forward direction.
- The addition of a substance among the products or the removal of a substance among the reactants will drive the equilibrium towards the backward direction.

Note: The reaction shifts in any direction on the addition of any substance just to keep the value of K_c constant.

Effect of change in pressure or volume:

- The change in pressure or volume is important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal.

(i) Theoretical study of effect of change of pressure or volume

The increase of pressure or decrease in volume shifts the reaction in direction of less number of moles and vice versa.

a) Examples: $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

The above increase is pressure shifts the above reaction in forward direction and vice versa.

b) Examples: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

The increase in pressure shifts the above reaction in backward direction and vice versa.

(ii) Quantitative study of effect of pressure or volume:

a) If volume term is present in the numerator of K_c expression, then increase in pressure decreases the volume and reaction will shift in forward direction to increase the value of x^2 and to keep the value of K_c constant.

$$K_c = \frac{4x^2V}{(a-2x)^2(b-x)}$$

b) If volume term is present in the denominator of Kc expression, then increase in pressure decreases the volume and reaction will shift in backward direction to decrease the value of x^2 and to keep the value of K_c constant.

$$K_c = \frac{x^2}{V(a-x)}$$

POINT TO PONDER: The equilibrium constant of an exothermic reaction ……….
With temperature and that of an endothermic reaction …… with temperature

Effect of Change in Temperature:

(i) On Endothermic reactions:

- By increasing the temperature, reaction is favoured in forward direction.
- By decreasing the temperature, reaction is favoured in backward direction.

$H_2 + I_2 \rightleftharpoons 2HI$ $\Delta H = +ve$

(ii) On Exothermic reactions:

- By decreasing the temperature, reaction is favoured in forward direction.
- By increasing the temperature, reaction is favoured in backward direction.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta H = -ve$

Effect of catalyst on Equilibrium Constant:

A catalyst does not affect the equilibrium position and equilibrium constant of the reaction. It increases the rates of both forward and backward reactions, as it reduces the time to attain the equilibrium.

Applications of Chemical Equilibrium in Industry:

Particulars	Synthesis of NH_3
Reaction	$N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta H = -92.46$ kJ (-46.23 kJ/mol)
Condition For maximum Production	• Removal of ammonia after regular intervals • Increase in pressure • Decrease in temperature
Catalyst	Pieces of iron catalyst are embedded in fused mixture of MgO, Al_2O_3 and SiO_2
Favourable Conditions	P = 200 – 00 atm T = 673 K (400° C)

Note: (For synthesis of NH_3)

- Equilibrium mixture contains 35 % NH_3 by volume
- Ammonia is separated by refrigeration of reaction mixture
- 110 million tons ammonia is produced per anum
- 80 is used in fertilizer
- 13 % Nitrogen fixation is done by Haber's process

Note: $K_p = K_c(RT)^{\Delta n}$

Δn = number of moles of products-no of moles of reactants

R = General gas constant

T = Absolute temperature When

$\Delta n = 0$ then $K_p = K_c$

Relation Between Different Equilibrium Constants:

When concentrations are expressed in mole dm^{-3}, then

$aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$K_c = \frac{C_C^c C_D^d}{C_A^a C_B^b}$$

In case of gases, we use partial pressure and K, changes to K_p

$$K_c = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

Calculate The Quantities Present at Equilibrium, Given Appropriate Data:

Consider the following reaction

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

When two moles of acetic acid and two moles of ethanol are present at equilibrium, the number of moles of ester formed ifK_c is 0.25.

$K_c = [CH_3COOH][C_2H_5OH] / [CH_3COOC_2H_5][H_2O]$

$0.25 = 2 \times 2/(x)(x)$

$0.25 = 4/[x]$

$x^2 = 4/0.25$

$x^2 = 16$

$x = 4$

Calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data:

Consider the following gaseous reaction system having partial pressure at equilibrium

$2HI \rightleftharpoons H_2 + I_2$

100 torr 50 torr 50 torr

Its Kp can be calculated as:

$K_p = P_{H_2} \, . \, P_{I_2} / (P_{HI})^2$

$= 50 \times 50 / (100)^2$

$= 2500 / 10000$

$= 0.25$

LOWRY BRONSTED ACID AND BASE CONCEPT

Lowry Bronsted Acid and Base Concept:

ACID:

Those species which donate the proton or have a tendency to donate protons are called acids. Conjugate base of a very weak acid is relatively very strong.

Base:

Those species which accept the proton or have tendency to accept the proton are called bases. Conjugate acid of a very strong base is relatively very weak.

Example:

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

(Acid) (Base) Conjugate Acid Conjugate Base

$K_a \times K_b = [H^+] [OH^-]$

$K_a \times K_b = 10^{-14}$ at 25° C

$K_a = K_w \times \frac{1}{K_b}$

$K_b \propto \frac{1}{K_b}$

$pK_a + pK_b = pK_w$ ($pK_a = 14$, at 25° C)

$pK_a + pK_b = pK_w$ ($pK_w = 14$, at 25°C)

$pK_a + pK_b = 14$ at 25°C

Ionic Product of Water (K_w):

Water undergoes self-ionization as follows and the reaction is reversible.

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$H_2O \rightleftharpoons H^+ + OH^-$

$K_c[H_2O] = [H^+][OH^-]$

$K_w = [H^+] = [OH^-] = 10^{-14}$ at 25°C

K_w is called ionic product of water or dissociation constant of water.

Kw VARIES WITH TEMPERATURE:

TEMPERATURE (°C)	**K_w**	**At(°C)**	**Change in K_w**
0	0.11×10^{-14}		
10	0.30×10^{-14}	0 – 10	Increases by 3 times
25	$I.0 \times 10^{-14}$	0 – 25	Increases by 10 times
40	3.00×10^{-14}	0 – 40	Increases by 30 times
100	7.5×10^{-14}	0 – 100	Increases by 75 times

Note:

- ■ K_w is directly related to temperature
- ■ pK_w is inversely related to temperature
- ■ K_w and pK_w are inversely related to each other

pK_w:

Negative log of K_w is called pK_w $pK_w = -\log K_w$

Note: The idea of pH and pOH was introduced by a Danish biochemist Sorenson in 1909.

- pH means potential of ……………concentration
- pOH means potential of …………concentration

pH:

The negative log of hydrogen ion concentrator $[OH^-]$ is called pH.

$pOH = -\log [OH^-]$

Note: An increase in pH of one unit is ………… to fall in the H_2O^+ concentration

pOH: The negative log of hydroxyl ion concentration $[OH^-]$ is called pOH.

$pOH = -\log[OH^-]$

Note:

- pH and hydrogen ion concentration $[H^+]$ are……………related to each other
- pOH and hydroxyl ion concentration $[OH^-]$ are …………related to each other

Conclusion:

For neutral water

$pH = -\log 10^{-7} = 7$

$pOH = -\log 10^{-7} = 7$

$pH = 7$ → solution is neutral

$pH < 7$ → solution is acidic

$pH > 7$ → solution is basic

Note: $pH + pOH = pK_w = 14$ at 25° C

Ionization Constant of Acids (Ka):

The dissociation constant of an acid is the ratio of the product of molar concentration of the ionized species to the initial molar concentration of acid.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

POINT TO PONDER: The value of K_c for an acid is a quantitative measure of the strength of the acid in all its ……….. reaction.

- Dissociation constant of an acid shows the strength of an acid.
- When $K_a = < 10^{-3}$, acid is weak
- When $K_a = 1$ to 10^{-3}, acid is moderately strong
- When $K_a > 1$, acid is strong
- Percentage of ionization = $\frac{\text{Amount of an acid ionized}}{\text{Acid initially available}} \times 100$

Dissociation Constants of Some Acids at 25° C:

ACID	K_a	RELATIVE STRENGTH
HCl	Very large	Very strong
HNO_3	Very large	Very strong
H_2SO_4	Large	Very strong
HSO_4^-	1.3×10^{-5}	Strong
HF	6.7×10^{-5}	Weak
CH_3COOH	1.85×10^{-5}	Weak
$H_2CO_3(H_2O + CO_2)$	4.4×10^{-7}	Weak
H_2O	1.0×10^{-7}	Weak
NH_4^+	1.0×10^{-7}	Weak
HCO_3	4.7×10^{-11}	Weak
H_2O	1.8×10^{-16}	Very weak

Ionization Constant of Bases (K_b):

The dissociation constant of a base is the ratio of the product of molar concentration of the ionized species to the molar concentration of unionized species.

$A^- + H_2O \rightleftharpoons BA + OH^-$

$K_b = \frac{[HA][OH^{-1}]}{[A^{-1}]}$

Strength of base is expressed by K_b.

Any substance that accepts H^+ or generates $OH^-$is a base.

Dissociation Constants of Some Bases at 25° C:

BASE	K_b	RELATIVE STRENGTH
NaOH	very high	very strong
KOH	very high	very strong
$Ca(OH)_2$	high	strong
NH_4OH	1.81×10^{-5}	weak
CH_3NH_2 (Methylamine)	4.38×10^{-4}	weak
$C_6H_5NH_2$ (Anitine)	4.7×10^{-10}	very weak

pK_a and pK_b:

The value of pK_a and pK_b can be defined and related as follow:

$pK_a = -\log K_a$ Ka is inversely related to pK_a

$pK_b = -\log K_b$ K_b os inversely related to pK_b

Conclusion:

- Greater the value of K_a, stronger will be acid and vice versa.
- Greater the value of pK_a, weaker will be the acid and vice versa.

- Greater the value of K_b, stronger will be base and vice versa.
- Greater the value of pK_b, weaker will be the base and vice versa.

Note:

(i) If the difference of pK_a values of the two acids is one, then acid with smaller pK_a is ten times stronger than the other.

$pK_a(I) - pK_a(II) =$ 1, acid II is ten times stronger than acid I

(ii) If the difference, of pK_a values of the two acids is two, then acid with smaller pK_a is hundred times stronger than the other.

$pK_a(I) - pK_a(II) =$ 2, acid II is hundred times stronger than acid I

Calculation $[H^+_{(aq)}]$ and pH values for strong and weak acids and strong bases

(i) 10^{-4} mcl.dm^{-3} of HCl

$[H^+] = 10^{-4}$ mol.dm^{-3}

$pH = -\log[H^+]$

$= -\log[10^{-4}] = 4$

(ii) 10^{-4} mol.dm^{-3} of $Ba(OH)_2$

0.0001 M $Ba(OH)_2$ solution contains 0.0002 M $OH^- = 2\times 10^{-4}$ mol/dm^3

$pOH = -\log[OH^-]$

$pOH = -\log 2\times 10^{-4}$

$pOH = 3.7$

$pH = 14 - 3.7$

$pH = 10.3$

(iii) 1.0 mol.dm^3 of H_2X, which is only 50 % dissociated:

1 .mol.dm^{-3} of H_2X 50 % Dissociated means 0.5 mol/dm$_3$ of H_2X completely dissociated.

$[H^+] = 1$ mol.dm^{-3}

$$\text{pH} = -\log[\text{H}^+] = -\log 1$$

$$\text{pH} = 0$$

BUFFER SOLUTIONS

The solutions, which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions.

How Buffer controls the pH?

Buffer action can be explained by keeping in view the concepts of common ion effect and Le-Chateliers principle.

Let us take the example of an acidic buffer consisting of CH_3COOH and CH_3COONa CH_3COOH being a weak electrolyte undergoes very little dissociation. Whereas, CH_3COONa which is a strong electrolyte, will produce CH_3COO^- ions as common ions, The dissociation of CH_3COOH is suppressed due to the common ion effect of CH_3COO^-.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$CH_3COONa_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + Nq^+_{(aq)}$$

If we go on adding CH_3COONa in CIH_3COOH solution, then common ions i.e. CH_3COO^-decreases the ionization of CH_3COOH. The solution will have less hydrogen ion concentration and high pH value. If CH_3COOH is in high concentration as compared to CH_3COONa then pH value of solution will be less.

Greater the concentration of acetic acid as compared to CH_3COONa, lesser will be the pH of the solution and vice versa. This is shown in table.

$[CH_3COOH]$ (molc dm^{-3})	**$[CH_3COO^-$ (mole dm^{-3})**	**% Dissociation**	**pH**
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44

0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

The buffer mentioned above is the large reservoir of CH_3COOH and CH_3COO^- components.

(i) Whenever an acid is added to this buffer and 'H^+' concentration increases, at this stage CH_3COO^- reacts to form un-dissociated CH_3COOH. So, pH of the buffer will remain almost same because 'H^+' ions which are added are captured by CH_3COO^- ion and pH will not vary too much.

(ii) If base is added in this' buffer, base will produce OH- ions which combine with H_3O^+ to form neutral compound i.e H_2O. So, pH will remain almost unchanged.

Note: The buffer solution consisting of NH_4Cl and NH_4OH can resist the change in pH and pOH when acid or base is added from outside.

Henderson's Equation for Acidic Buffer:

$$pH = pK_a + \log \frac{[Salt]}{[Acid\}}$$

Cases:

(i) If [salt] = [acid] then $pH = pK_a$

(ii) If [salt] > [acid] then $pH > pK_a$

(iii) If [salt] < [acid] then $pH < pK_a$

HENDERSON'S EQUATION FOR BASIC BUFFER

$$pOH = pK_b + \log \frac{[Salt]}{[Base\}}$$

Cases:

(i) If [salt] = [base] then $pOH = pK_b$

(ii) If [salt] > [base] then $pOH > pK_b$

(iii) If [salt] < [base] then $pOH < pK_b$

Solubility Product (Equilibria of slightly Soluble ionic compounds):

The product of the concentration of ions raised to an exponent equal to the co-efficient .of the balanced equation.

- If ionic product = K_{sp} solution is saturated
- If ionic product < K_{sp} solution is unsaturated
- If ionic product > K_{sp} solution is unsaturated

General Expression:

$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$

$K_{ap} = [A^{+y}]\ [B^{-x}]^y$

Examples:

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2CI^{-}_{(aq)}$ $K_{sp} = 1.6 \times 10^{-5}$

$AgCl_{(s)} \rightleftharpoons Ag^{-}_{(aq)} + 2CI^{-}_{(aq)}$ $K_{sp} = 1.8 \times 10^{-10}$

Applications:

- Determination of K_{sp} from solubility of salts
- Determination of solubility from K_{sp}
- Prediction of precipitation
- Effect of common ion effect on solubility

Note: Applicable for sparingly soluble substances $PbCb_2$, AgCl, $Ca(OH)_2$, $PbCrO_2$. it is only applicable for the sr substances whose molar concentrations are less than 0.01 M

General K_{sp} expressions for some salts:

(i) $K_{sp} = s^2$ (For AgCl)

(ii) $K_{sp} = 4s^3$ (For $PbCl_2$)

(iii) $K_{sp} = 27s^4$ (For $AlCl_2$)

Calculate K_{sp} from concentrations and vice versa

(i) The solubility of PbF^2 is 2×10^{-3} moles 1 dm^3. Its solubility product will be

$PbF_{2(s)} \rightarrow \quad Pb^{2+}_{(aq)} \quad + \quad 2F^{-}_{(aq)}$

$2 \times 10^{-3} \quad 2 \times 10^{-3} \quad 2 \times 2 \times 10^{-3}$

$K_{sp} = [Pb^{+2}][F^{-}]^{2} = [2 \times 10^{-3}][2 \times 2 \times 10^{-3}]^{2}$

$= 32 \times 10^{-3}$

(ii) The solubility product of $Ca(OH)^{2}$ is 3.6×10^{-8}. Its solubility is:

$Ca(OH)_{2(s)} \rightarrow \quad Ca^{2+}_{(aq)} \quad + \quad 2OH^{-}_{(aq)}$

$s \quad s \quad 2s$

$K_{sp} = [Ca^{+2}][F^{-}]^{2} = [S][2S]^{2}$

$3.2 \times 10^{-8} \quad =4s^{3}$

$s^{3} = 3.6 \times 10^{-8}/4$

$s = (9 \times 10^{-9})^{1/3} = 3 \times 10^{-3}$

COMMON ION EFFECT

The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as precipitates.

Common ion effect increases:

(i) Crystallization

(ii) Association of ions

Common ion effect decreases

(i) Ionization / dissociation

(ii) solubility

Examples:

The solubility of a less soluble salt $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect.

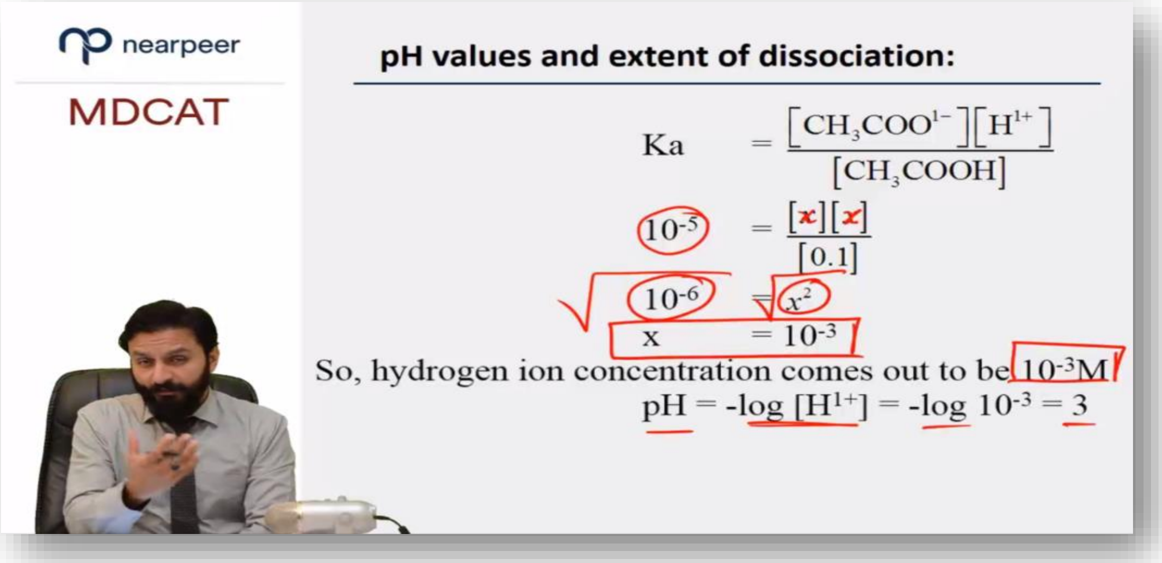
$KClo_{3(S)} \rightleftharpoons K^+_{(aq)} + ClCO^-_{(aq)}$

$KCl_{(S)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$

(ii) An addition of NH_4Cl in NH_4OH solution suppresses the concentration of $OH^{-1}_{(aq)}$ due to the presence ofa large excess of NH_4^+ from NH_4Cl.

$NH_4\,Cl_{(aq)} \rightleftharpoons NH^+_{(aq)} + Cl^-_{(aq)}$

$NH_4OH \rightleftharpoons NH^+_{(aq)} + OH^-_{(aq)}$



pH values and extent of dissociation:

$$Ka = \frac{[CH_3COO^{1-}][H^{1+}]}{[CH_3COOH]}$$

$$10^{-5} = \frac{[x][x]}{[0.1]}$$

$$\sqrt{10^{-6}} = \sqrt{x^2}$$

$$\boxed{x = 10^{-3}}$$

So, hydrogen ion concentration comes out to be $\boxed{10^{-3}M}$

$$pH = -\log[H^{1+}] = -\log 10^{-3} = 3$$

PRACTICE EXERCISE (FOR UHS TOPIC)

1. **K_c value does not depend on all the factors except**

A) Pressure

B) constant at constant temperature

C) Catalyst

D) Temperature

2. **Which of the following is correct statement about "K_c"**

A) May or may not have a units

B) Thermodynamic property

C) depend upon equilibrium concentrations

D) All of the above

3. **In which of the following reactions, K_c has moles^{-2} dm^{+6} unit**

A) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2\ NH_{3(g)}$

B) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

C) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

D) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\ SO_{3(g)}$

4. **Which of the following relationship is incorrect**

A) $Kp = Kc$ when $\Delta n = 0$

B) $Kp < Kc$ when $\Delta n < 0$

C) $Kp > Kc$ when $\Delta n > 0$

D) $Kp \neq Kc$ when $\Delta n = 0$

5. **Oxidation of SO_2 by O_2 is exothermic reaction. The yield of SO_3 will be maximum if**

A) Temperature is increased and pressure is kept constant

B) Temperature is reduced and pressure is increased

C) Both temperature and pressure are increased

D) Both temperature and pressure are decreased

6. **Which is correct statement**

A) Conjugate base of weak acid is weak

C) Greater is molar conc. Of H^+ greater is pH

B) Greater is ka value, greater is kb

D) Greater is ka value smaller is pka value

7. **Equation used to calculate pH of acidic buffer solution is pH = pka + $\log\frac{[\text{salt}]}{[\text{acid}]}$ which of the following is correct about equation**

A) pH = pka when [acid] = [salt]

C) pH < pka when [acid] > [salt]

B) pH > pka when [acid] < [salt]

D) All of the above

8. **Which is correct about common ion effect**

A) Best application of Le-Chatlier's principle

B) It is the effect of increase in concentration of product in form of common ion

C) Always in reverse direction

D) All of these

9. **Solubility product of AgCl is 2×10^{-10} mol^2dm^{-6}. Maximum Ag^+ ion in solution is**

A) $2 \times 10^{-10} moldm^{-3}$

C) $1.41 \times 10^{-5} moldm^{-3}$

B) $1 \times 10^{-10} moldm^{-3}$

D) $4 \times 10^{-10} moldm^{-3}$

10. **Given that pKa of acetic acid is 4.7, what is pH of solution of 0.1M acetic acid and 0.01 sodium acetate is**

A) 3.7

C) 5.7

B) 4.7

D) 2.7

11. The pH of 10^{-3} mol.dm^{-3} of an aqueous solution of H_2SO_4 is

A) 3.0

B) 2.7

C) 2.0

D) 1.5

12. Which statement about the following is correct

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\ SO_{3(g)} \quad \Delta H = -188.3\ kJ\ mol^{-1}$$

A) The value of K_p falls with rise of temperature

B) The value of K_p falls with increasing pressure

C) Adding V_2O_5 catalyst increase the equilibrium yield of SO_3

D) The value of K_p is equal to K_c

13. Best buffer is prepared by taking

A) Equal conc. of salt and acid

B) More conc. of salt than acid

C) More conc. of acid than salt

D) Any of these

14. Which of the followings are the applications of Ksp

A) Determination of Ksp from solubility

B) Determination of solubility from Ksp

C) saturation for a given solute in solution

D) All of these

15. In which of the following reactions, the increases in pressure moves the reaction in the forward direction

A) $H_2 + I_2 \rightleftharpoons 2HI$

B) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\ SO_3$

C) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

D) $N_2 + O_2 \rightleftharpoons 2NO$

16. Strength of an acid is directly related to the value of:

(A) pKa

(B) Ka

(C) pH

(D) Kw

17. The value of pK_w at 25°C is:

(A) 10^{14}

(B) 14

(C) 10^{-14}

(D) 7

18. Almost forward reaction is complete when:

(A) K_C is very large

(B) Moderate K_C value

(C) K_C is very small

(D) None of these

19. The pH value of 0.001 M HCl solution in water is:

(A) 3

(B) 4

(C) 2

(D) Zero

20. pOH of human blood is:

(A) 7.0

(B) 7.85

(C) 7.35

(D) 6.65

21. For what value of K_c almost forward reaction is complete?

(a) $K_c = 10^{-30}$

(c) $K_c = 1$

(b) $K_c = 10^{30}$

(d) $K_c = 0$

22. Which of the following efforts will change K_c for the reaction?

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ + Heat

(a) Adding catalyst

(b) Decreasing pressure

(c) Increasing Cl_2

(d) Increasing heat

23. Value of K_c for the given reaction is 50 at 700 K:

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

When the equilibrium concentration of both reactants is 0.5 M each, the value of K_p under same condition will be:

(a) 125

(b) 50

(c) 75

(d) 100

24. Which of the following salt solution will have pH more than (7)?

(a) NH_4Cl

(b) CH_3COONa

(c) $CuSO_4$

(d) $BaCl_2$

25. Consider the reaction:

$HCN_{(aq)} \rightleftharpoons H^{+}_{(aq)} + CN^{-}_{(aq)}$

at equilibrium, the addition of $CN^{-}_{(aq)}$ would

(a) Increase equilibrium constant

(b) Decrease $HCN_{(aq)}$ concentration

(c) Decrease H^{+} ion concentration

(d) Increase H^{+} ion concentration

26. What happens if pressure is applied to the equilibrium Ice $\rightleftharpoons$ Water?

(a) More amount of water is formed

(b) More amount of ice is formed

(c) Water changes to vapours

(d) No change

27. The value of K_c for H_2O at 25°C is:

(a) 1×10^{-14} mol dm^{-3} (b) 1.86×10^{-16} mol dm^{-3}

(c) 14 mol dm^{-3} (d) 1.0×10^{-7} mol dm^{-3}

28. Which of the following is wrong statement?

(a) Strong acid has weak conjugate base (b) Weak acid has weak conjugate base

(c) K_a is inversely proportional to K_b (d) K_a is inversely proportional to pK_a

29. If molar conc. of HCl solution is 0.001 M then pOH of solution is:

(a) 3 (b) 4

(c) 11 (d) 10

30. Dissociation of H_2S in water is suppressed by the addition of HCl because:

(a) H_2S weaker acid than HCl (b) H_2S is stronger acid than HCl

(c) HCl reacts chemically with H_2S (d) Size of H_2S smaller than HCl

31. What will be the direction of reversible reaction when one of the product of the reaction is removed?

(a) Forward direction (b) Backward direction

(c) The reaction is stopped (d) At equilibrium

32. The precipitation occurs if the ionic conc. is:

(a) Less than K_{sp} **(b)** More than K_{sp}

(c) Equal to K_{sp} **(d)** is present in any amount

33. The pH of a solution is 5. To this solution sufficient acid was added and is pH decreases to 2. The increase in hydrogen ions concentration is:

(a) 100 times **(b)** 1000 times

(c) 3 time **(d)** 10 time

34. The molar solubility of $Ca(OH)_2$ in water in term of its K_{sp} can be written as:

(a) $S = (K_{sp})^{1/2}$ **(b)** $S = (K_{sp})^{1/3}$

(c) $S = (K_{sp}/4)^{1/3}$ **(d)** $S = (K_{sp/6})^{1/3}$

35. Which one of the following solutions have zero pH?

(a) 0.5 M HCl **(b)** 0.5 M H_2SO_4

(c) 0.1 M HNO_3 **(d)** 0.5 M CH_3COOH

36. To prepare a buffer with pH close to 9.0, you could use a mixture of:

(a) NH_4OH and NH_4Cl **(b)** CH_3COOH and CH_3COONa

(c) HNO_2 and $NaNO_2$ **(d)** $NaHCO_3 + H_2CO_3$

37. The pK_b value for aqueous ammonia at 25°C is 4.8. What is the correct pK_a value for the ammonium ions at this temperature?

(a) –4.8 **(b)** 2.2

(c) 4.8 **(d)** 9.2

38. 1 mole of N_2O_4 was decomposed according to the given equation in 1 dm^3 contain

$N_2O_4 \rightleftharpoons 2NO_2$

At equilibrium “x” mole of N_2O_4 have dissociated. What is the value of K_c?

(a) $\frac{2x}{(1-x)}$ **(b)** $\frac{4x}{(1-x)}$

(c) $\frac{2x}{(1-x)^2}$ **(d)** $\frac{4x^2}{(1-x)\ V}$

39. For a reaction A + B $\rightleftharpoons$ C + D when we start with 2 moles of each A and B, K_c = 25. What will be the value of K_c? If we start with 1 mole of each A and B.

(a) 25 **(b)** 5

(c) 12.5 **(d)** 50

40. A salt "X" is dissolved in water of PH = 7 the resulting solution becomes alkaline in nature. The salt "X" is made of:

(a) Strong acid and strong base **(b)** Strong acid and weak base

(c) Weak acid and strong base **(d)** Weak acid and weak base

ANSWER KEY

1	**D**	**11**	**B**	**21**	**B**	**31**	**A**
2	**D**	**12**	**A**	**22**	**D**	**32**	**B**
3	**A**	**13**	**A**	**23**	**B**	**33**	**B**
4	**D**	**14**	**D**	**24**	**B**	**34**	**C**
5	**B**	**15**	**B**	**25**	**C**	**35**	**B**
6	**D**	**16**	**B**	**26**	**A**	**36**	**A**
7	**D**	**17**	**B**	**27**	**A**	**37**	**D**
8	**D**	**18**	**A**	**28**	**B**	**38**	**D**
9	**C**	**19**	**A**	**29**	**C**	**39**	**A**
10	**C**	**20**	**C**	**30**	**B**	**40**	**C**

UHS TOPIC VIII A

REACTION KINETIC

LEARNING OUTCOMES

`In this topic, student should be able to:

a) Explain and use the terms: rate of reaction; activation energy; catalysis; rate equation; order of reaction; rate constant; half-life of a reaction; rate determining step.

b) Explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction.

c) Explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy.

d) Describe enzymes as biological catalysts which may have specific activity.

e) Construct and use rate equations of the form:

Rate = $k[A]^m[B]^n$ with special emphasis on:

i) Zero order reaction

ii) 1st order reaction

iii) 2nd order reaction

f) Show understanding that the half-life of a first-order reaction is independent of initial concentration and use the half-life to calculate order of reaction.

g) Calculate the rate constant from the given data

h) Name a suitable method for studying the rate of a reaction, from given information

REACTION KINETICS

The studies concerned with rates of chemical reactions and factors that affect the rates of chemical reactions and the mechanism of reactions constitute the subject matter of reaction kinetics.

CHEMICAL REACTIONS

The breaking of pre-existing bonds and the formation of new bond is called chemical change or chemical reaction. On the basis of rate of reaction, chemical reactions can be broadly classified into three types.

(1) Very fast reaction ($AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$)

(2) Very slow reaction ($2Fe + 3H_2O + O_2 \rightarrow Fe_2O_3.3H_2O$)

(3) Moderately slow reactions ($C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O$)

RATE OF REACTION

The change in concentration of a reactant or a product divided by the time taken for the change is called rate of reaction.

$$\text{Rate of Reaction} = \frac{\text{Change in concentration of the substance}}{\text{Time taken for the change}}$$

$$\text{Rate of reaction} = dx/dt$$

The rate of a general reaction:

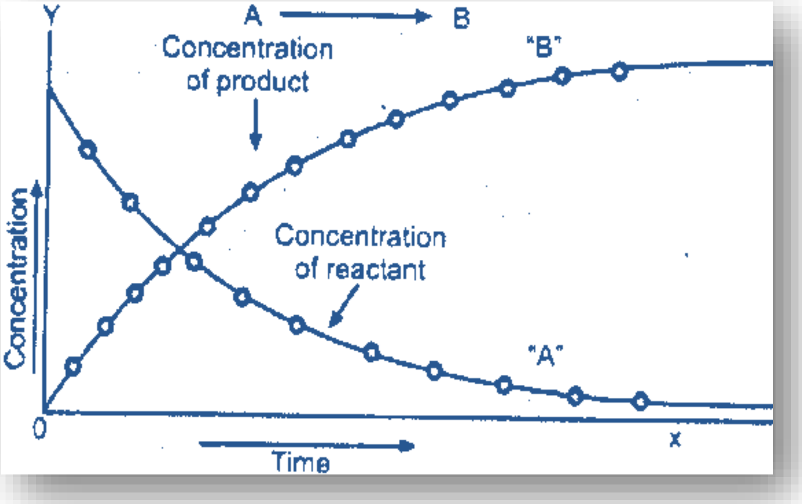
$A \rightarrow B$ can be expressed as:

$$\text{Rate of reaction} = \frac{-\mathrm{d}[A]}{dt} = \frac{+\mathrm{d}[B]}{dt}$$

Units of rate of reaction:

The units for rate of reaction are moles $dm^{-3}s^{-1}$

Note: For a gas phase reaction units of pressure are used in place of molar concentration.



TYPES OF REACTION RATE

The rate of reaction between two specific time intervals is called average rate.

Instantaneous Rate:

The rate at anyone instant during a specific interval of time is called instantaneous rate.

Comparison of Instantaneous and Average Rate:

- The average rate and instantaneous rate are equal for only one instant in any time interval.

- At the beginning of reaction, the instantaneous rate is higher than the average rate.

- At the end of reaction, the instantaneous rate is less than the average rate.

- The average rate will be equal to instantaneous rate, when the time interval approaches zero.

ENERGY OF ACTIVATION

The minimum amount of energy, in addition to the average kinetic energy, which the particles must have for effective collisions, is called activation energy.

Important Points:

- Reactants go into transition state before going into product called activated complex.
- Energy of activated complex is higher than reactants and products.
- Amount of energy to form transition state is called energy of activation.
- Effective collision produces products.
- In effective collision, molecules have certain amount of energy and collide in certain orientation.
- When the energy of products is lesser than reactants, the reaction is exothermic.
- When the energy of products is higher than reactants, the reaction is endothermic.
- Energy of activation of forward reaction is less than backward reaction for an exothermic reaction.
- Energy of activation for backward reaction is less than forward reaction for an endothermic reaction.

Arrhenius Equation:

According to Arrhenius Equation $k = Ae^{-Ea/RT}$

In this equation k = specific rate constant

A = Arrhenius constant

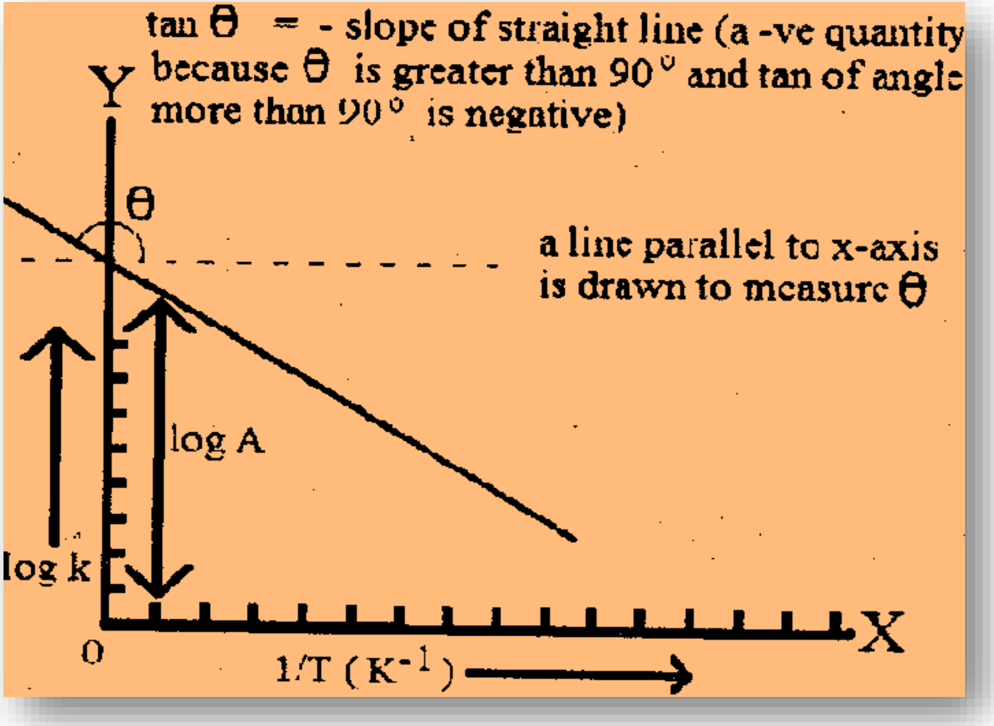
It tells us about collision frequency.

Points To Be Remembered:

→ This equation explains the effect of temperature on the rate constant of reaction.

→ k is exponentially related to activation energy and temperature.

→ When a graph 'is plotted between $\frac{1}{T}$ on x-axis and log k at y-axis, a straight line isobtained with a negative slope. Actually, $\frac{E_a}{RT}$ has negative sign so the straight linehas two ends in second and fourth quadrants.



tan θ = - slope of straight line (a -ve quantity because θ is greater than 90° and tan of angl more than 90° is negative)

a line parallel to x-axis is drawn to measure θ

→ Slope = $\frac{E_a}{2.303\ R}$ unit of slope is Kelvin

→ This equation helps us to determine activation energy of the reaction.

→ $E_a = -\text{Slope} \times 2.303\ R$

→ Unit of activation energy is Joule mole^{-1}, greater is value of activation energy smaller is k value hence smaller will be the rate.

CATALYSIS

The process, which takes place in the presence of a catalyst, is called catalysis.

Types of Catalysis:

(i) Homogeneous Catalysis:

In this type of catalysis, the catalyst and the reactants are in the same phase and the reacting system is homogenous throughout.

Examples:

$$2SO^{2(g)} + O_{2(g)} \xrightleftharpoons{NO_{(g)}} SO_{3(g)}$$

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \xrightleftharpoons{H^+} CH_3COOC_2H_{5(aq)} + H_2O(\ell)$$

(ii) Heterogeneous Catalysis:

When the phase of catalyst differs from phase of reactant, catalysis is called heterogeneous catalysis.

Example:

$$4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt_{(s)}} 4NO_{(g)} + 6H_2O_{(g)}$$

RATE LAWS FOR ELEMENTARY REACTIONS		
ELEMENTARY REACTION	**MOLECURITY**	**RATE LAW**
A → Product	Uni-molecular	Rate = $k[A]$
A + A → Product	Bi-molecular	Rate = $k[A]^2$
A + B → Product	Bi-molecular	Rate = $k[A]\,[B]$

A + A + B → Product	Ter-molecular	Rate = $k[A]^2 [B]$
A + A + C → Product	Ter-molecular	Rate = $k[A] [B] [C]$

Order of Reaction:

The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction.

OR

The number of reacting molecules, whose concentration alter as a result of the chemical change, is called order of reaction.

$$aA + bB \rightarrow P$$

$\frac{dx}{dt} = k[A]^a[B]^b$ Order of reaction = a + b

- Under the given conditions, k remains constant, but it changes with temperature.

Note: There is only one factor i.e. temperature which affects the specific rate constant.

DIFFERENCE BETWEEN RATE OF REACTION AND RATE CONSTANT OF REACTION

RATE OF REACTION	RATE CONSTANT OF REACTION
• The change in concentration of a reactant or a product divided by the time taken for the change is called rate of reaction.	• It is the proportionality constant, which is represented by k, in rate equation.
• Its unit is mol $dm^{-3}s^{-1}$	• Its units depend on the order of reaction

•	It depends upon concentrations of reactants	•	It is independent of the concentration of reactant or products
•	It varies with the passage of time under given conditions	•	It always remains constant under the given conditions
•	Example: aA + bB → cC + dD Rate of reaction = $k[A]^a[B]^b$	•	Example: aA + bB → Product $k = \frac{Rate}{[A]^a[B]^b}$

Half-Life Period:

The time required to convert 50% of the reactants into products is called half-life period.

Example:

(i) Half-life period of N_2O_4 at 45° C is 24 minutes.

(ii) Half-life period of $^{235}_{92}U$ is 7.1 × l0^{8} or 710 million years

Important Points:

- Half-life period of second order reaction is inversely proportional to the initial concentration of the reactants
- Half-life period of third order reaction is inversely proportional to the square of initial concentration of reactants

In general for the reaction of nth order: $[I_{1/2}]_n \alpha \frac{1}{a^{n-1}}$

Rate Determining Step:

When the reaction completes in more than one step, then the slowest step will give the overall rate of reaction, thus slowest step of such a reaction is called rate determining step side the following reaction:

$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$

The rate equation of this reaction is found to be:

Rate = $k[NO_2]^2$

This equation shows that rate of reaction is independent of the concentration of CO. In other words, the equation gives us information that.

(j) Reaction takes place in more than one step i.e the mechanism of this reaction is different than as shown in balanced chemical equation.

(ii) Two molecules of NO_2 are involved in the rate determining step. The proposed mechanism for this reaction is as follows.

$$NO_{2(g)} + NO_{2(g)} \xrightarrow{\text{slow}} NO_{3(g)} + NO_{(g)}$$

$$NO_{3(g)} + CO_{(g)} \xrightarrow{\text{fast}} NO_{2(g)} + CO_{2(g)}$$

The first step is the slowest step and the rate determining step. So, order of reaction is two with respect to NO_2 but it is independent of CO concentration. NO_3 which does not appear in balanced chemical equation is reaction intermediate.

Reaction Intermediate:

A species which has temporary existence and it is unstable relative to the reactants and products and does not appear in the balanced chemical equation is called reaction intermediate.

This is a specie with normal bonds and may be stable enough to be isolated under special conditions.

Example:

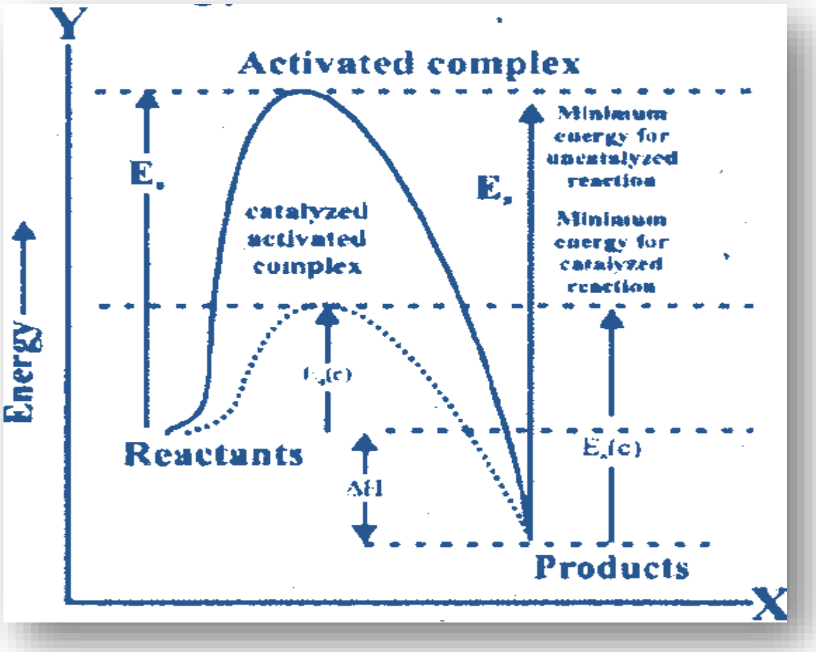
In above reaction, NO_3 is reaction intermediate.

In the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy

A substance which alters the rate of chemical reaction but remains chemically unchanged at the end of the reaction is called a catalyst. The process which takes place in the presence of a catalyst is called catalysis. Basically, a catalyst provides a new reaction path with a low activation energy barrier as shown in the following figure. A greater number of molecules are now able to get over new low energy barrier and reaction rate increases.

POINT TO PONDER: Many transition metals act as heterogenous ………….

In autocatalysis the product of the reaction is a ………… for the reaction.



Examples:

(i) The reaction between 112 and 02 to form water is very slow at ordinary temperature, but proceeds more rapidly in the presence of platinum which acts as catalyst.

$2H_2 + O_2$ $2H_2O$ $\xrightarrow{Pt}$

(ii) Decomposition of KC_1O_3 is more rapid in the presence of a small amount of MnO_2 which acts as a catalyst.

$2KClO_3$ $2KCl + 3O_2$ $\xrightarrow[\Delta]{MnO_2}$

POINT TO PONDER: The reason for the specification is that the substrate fits the active sits of the enzyme as a key fits a lock the active sits binds the ……. and …….. its reaction.

Enzyme Catalysis:

Enzymes are biochemical proteins, which increase the rate of biochemical reactions:

- The substance on which an enzyme can attack is called substrate.
- The point through which an enzyme attacks on substrate called active site.
- Each enzyme has its own active site.
- Enzymes are highly specific for substrate.
- Enzyme and substrate form enzyme substrate complex, which then breaks into product and enzyme.
- The name of enzyme usually ends on "ase".

Examples:

Urease, Zymase, Dehydrogenase, Hydrolase, Maltase

Characteristics of Enzyme Catalysis:

- The catalytic activity of enzymes is greatly enhanced by the presence of a co- enzyme or activator
- Enzyme catalysis is highly specific e.g. urease catalysis the hydrolysis of urea only and it cannot hydrolyse any other amide even methyl urea.
- Enzyme catalytic reactions have the maximum rates at an optimum temperature.
- The pH of the system also controls the rates of the enzyme catalyzed reaction and the rate passes through a maximum at a particular pH known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.

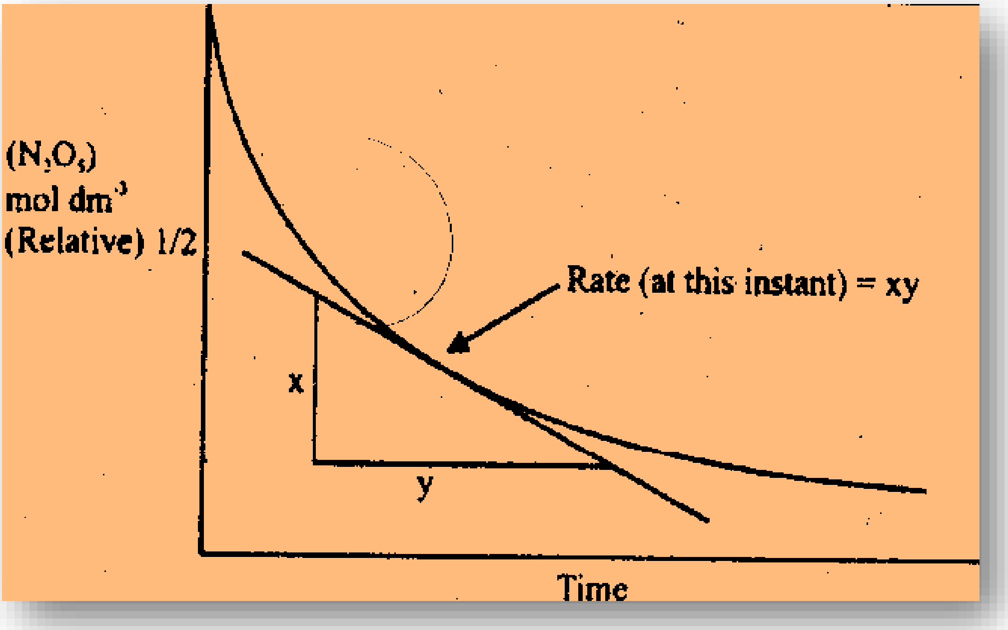
Use rate equations súch as, Rate = k $[A]^m$ $[B]^n$:

Consider the reaction involving the decomposition of dinitrogen pentoxide dissolved in tetra chiorome thane at 30° C) (Temperature must be kept constant since rate of reaction is also affected by temperature.)

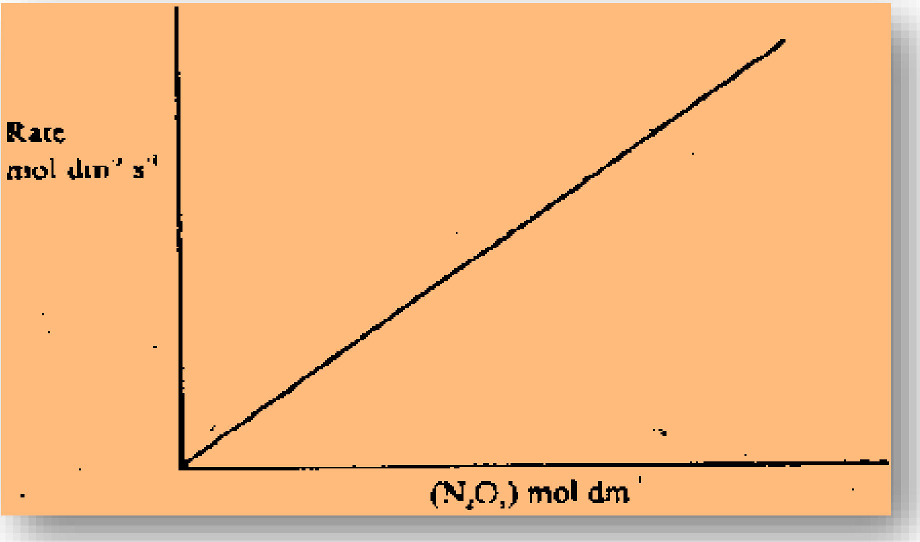
$N_2O_{5(sol)} \rightarrow 2NO_{2(sol)} + \frac{1}{2}O_{2(g)}$

As this reaction proceeds from start to finish, its rate will diminish as the N_2O_5 is used up and its concentration decreases. This changing rate could be observed by monitoring the concentration of $N_2O_{5(sol)}$ (written as $[N_2O_{5(sol)}]$) during the reaction. For example, the increase in pressure of 02 is related to the decrease in concentration of N_2O_5. For each ½ mole of O_2 formed, 1 mole of N_2O_5 is consumed.

The concentration against time graph for the reaction is shown below:



During the reaction, the rate at any instant of time can be determined by measuring the gradient of the tangent to the curve at that time. This also corresponds to the rate at an instant of concentration. For the above reaction, if the rate is measured at a range of instants of concentration during the experiment, a Rate against Concentration graph can be plotted the resulting graph is given below:



This graph shows that the rate of reaction is directly proportional to the concentration of $[N_2O_{5(sol)}]$:

Rate α $[N_2O_{5(sol)}]$ or Rate = constant x $[N_2O_{5(sol)}]$

Rate = k $[N_2O_{5(sol)}]$

- This expression is called a rate determining equation, where k is called the rate constant. The concentration of $N_2O_{5(sol)}$ is raised to the power 1. We say that the reaction is first order with respect to the $[N_2O_{5(sol)}]$. That is:

- When the concentration of $N_2O_{5(sol)}$ is doubled, the rate doubles.

- The rate constant, k, can be calculated from the rate equation: k Rate/ $[N_2O_{5(sol)}]$

This shows that the value of k is equal to the gradient of the graph. In this case the units of k are s^{-1}. The units of k are dependent on the particular rate expression. However, for the decomposition of $[N_2O_{5(sol)}]$ a plot of rate against concentration is not needed to show that the reaction rate is first order with respect to $\{N_2O_{5(sol)}]$.

- The concentration against time' curve shows repeating constant half-lives for a reaction that is first-order with respect to a reactant.

- Half-life is the time required for one-half of a given quantity of a reactant to react. h is commonly used as a measure of the rate of first-order reactions: the shorter the half-life, the faster the reaction. It indicates the kinetic stability of a reactant: the longer the half-life, the greater the stability. Read more about half-life. Read more about chemical stability.

- The rate equation has to be experimentally determined Consider the reaction between hydrogen peroxide and iodide ions in acidic solution.

$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \rightarrow 2H_2O_{(l)} + I_{2(aq)}$

The rate equation for this reaction can be written as:

Rate = $k[H_2O_{2(q)a}]\ [I^-_{(aq)}]^b[H^+_{(aq)}]^c$

The orders of reaction, a, b and c, have to be determined by experiment. This is why the rate equation is said to be experimentally determined.

A catalyst may appear in the experimentally determined the equation......

But it is not usual to include it in the balanced chemical equation for the reaction. For example, the acid-catalyzed hydrolysis of the ester methyl methanoate yields...

$HCOOCH_3 + H_2O + H^+ \rightarrow HCOOH + CH_3OH + H^+$

Rate = k $[HCOOCH_3]$ $[H^+]$

Here we are going to determine the order of reaction with respect to $[H_2O_2$ For this to be done, only the $[H_2O_{2(aq)}]$ can be allowed to change, so the concentrations of the other reactants have to be kept constant. Having them ¡resent in large excess so their concentrations change so little during the reaction that they remain effectively constant achieves this. Under these circumstances the rate equation becomes:

Rate = k – 1 $[H_2O_{2(aq)}]^a$

Where k' is a modified rate constant which includes the constant concentrations of the other reactants. An instrumental method called spectrometry could be used to monitor the increasing concentration of $1_{2(aq)}$ during the experiment. This is related to the intensity of light reaching the photocell in the spectrometer. Knowing the starting concentration of $H_2O_{2\,(aq)}$, its diminishing concentration can be determined at time intervals. Finding the order of reaction with respect to $[H_2O_{2(aq)}]$ follows the method already described. It is first order with respect to $[H_2O_{2(aq)}]$ that is a = 1 in the equation above.

So, the experiments referred to above have been used to find the order of reaction with respect to a reactant. The experimental method used is a progressive curve method.

DETERMINATION OF RATE OF REACTION

- Determination of rate of reaction involves the measurement of concentration of reactants.
- Graph is plotted between concentration of reactant and time and we get a curve.
- Select any two points in a curve.
- Make a right angle triangle of these points.
- Getting the tan θ of right angle triangle, we shall get

Rate of reaction = $\frac{\text{Change in concentration of reactant}}{\text{Change in time}}$

Half-life of a first-order reaction is independent of initial concentration:

The half-life period for the decomposition of N_2O_5 at 45° C is 24 minutes. It means that if we decompose 1 mol/dm^3 of N_2O_5 at 45°C then:

- After 24 minutes, half amount will he decomposed and 0.5 mol/dm^3 will he left behind.
- After 48 minutes, further half amount will be decomposed and 0.25 mol/dm^3 will be left behind.
- After 72 minutes, 0.125 mol/dm^3 of N_2O_5 will be decomposed and 0.125 mol/dm^3 will be left behind.

Note: This example shows that half-life of first order reaction always remains same with different initial concentration.

Half-life to calculate order of reaction:

It is mentioned earlier, half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction.

Therefore, $(t_{½}) \propto \frac{1}{a^{n-1}}$

Let us perform a reaction twice by taking two different initial concentrations 'a_1' and a_2 their half-life periods are found to be t_1 and t_2 respectively

$t_1 \propto \frac{1}{a_1^{n-1}}$ and $t_2 \propto \frac{1}{a_2^{n-1}}$

Dividing the two relations:

$$\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}}$$

$$\frac{t_1}{t_2} = \left[\frac{a_2}{a_1}\right]^{n-1}$$

Taking log on both sides:

$$\log \frac{t_1}{t_2} = (n - 1) \log \left[\frac{a_2}{a_1}\right]$$

On rearranging the above equation:

$$(n - 1) = \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

So, if we know the two' initial concentrations and two half-life values we can calculate the order of reaction (n)

Methods for the determination of rate of a chemical reaction:

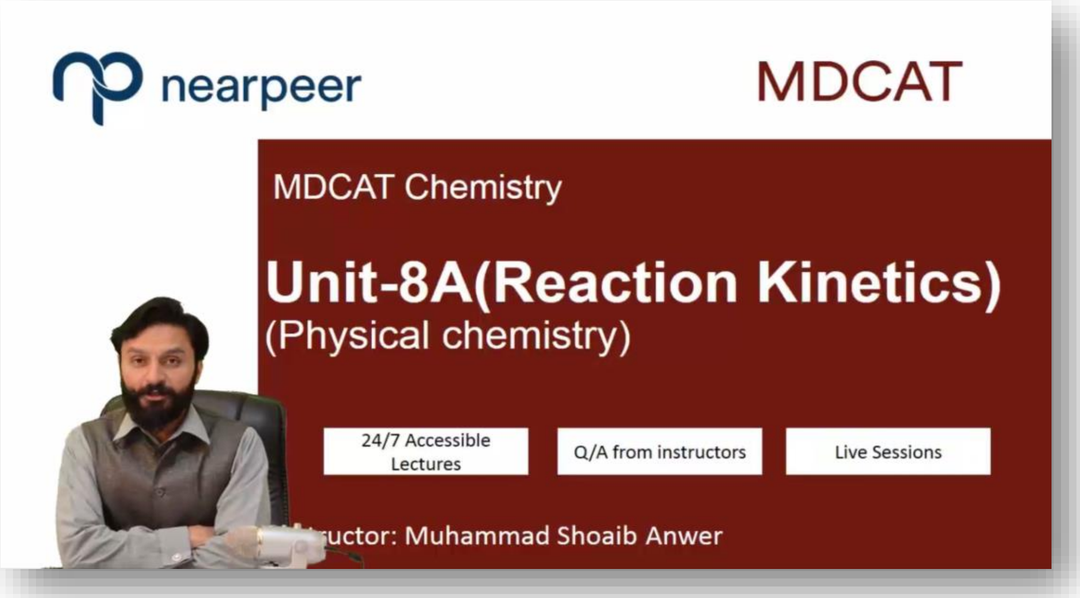
Physical Methods:

TECHNIQUES	DETAILS
Spectrometry	❖ Spectrophotometer is used. ❖ Reactants and products absorbs UV, IR radiations ❖ Amount of radiation absorbed give rate of reaction
Electrical Conductivity Method	❖ Conduc to meter is used ❖ Conductivity depends on the concentration of ions in the solution ❖ Conductivity of ions of reactants give rate of reaction
Dilatometric Method	❖ It is applied to the reaction in which volume of solution is changed ❖ Volume change of a reaction is proportional to extent of reaction
Optical Rotation Method	❖ Polarimeter is used ❖ Reacting molecules rotates angle of rotation of plane polarized light ❖ Value of angle of rotation gives information about rate of reaction

Refractometric Method	❖ Refractometer is used ❖ It is applied to the reaction in which change in refractive indices occurs ❖ Transformation of glucose into alcohol can be analyzed regarding rate of reaction through this method

Chemical Method

- Titration



nearpeer MDCAT

MDCAT Chemistry

Unit-8A(Reaction Kinetics)
(Physical chemistry)

uctor: Muhammad Shoaib Anwer

PRACTICE EXERCISE (FOR UHS TOPIC)

1. **Reaction kinetics deals with**

A) mechanism of reaction C) factors affecting rate of reaction

B) Rate of reaction D) All of these

2. **Which of the following factors affect rate of reaction?**

A) concentration C) surface area

B) catalyst D) all of the above

3. **Unit of rate of reaction**

A) $moldm^{-3}\ sec^{-1}$ C) $mol^{-}\ dm^{+3}\ sec^{-1}$

B) sec^{-1} D) $mol^{-}dm^{-3}\ sec^{+1}$

4. **In which of the following techniques, rate of reaction is directly related with number of ions**

A) spectrometry C) conductometric method

B) dilatometric method D) refractrometrc method

5. **Which of the following affect specific rate constant**

A) concentration C) temperature

B) catalyst (D) Surface area

6. **Consider the following reaction**

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

The molecularity and order of reaction for this reaction is

A) 1, 1 C) 2, 0

B) 1, 2 D) 2, 1

7. **Which statement is correct about order of reaction?**

A) order of reaction can be 0,1,2, or 3

B) Order of reaction can be related with rate law

C) Order of reaction tells us about mechanism of reaction

D) all of above

8. **Consider the following reactions**

$\rightleftharpoons$

I. $2N_2O_5$ 2] $\rightleftharpoons$ $+O_2$ **II.** $NO+O_3$ NO_2+O_2

$\rightleftharpoons$

III. $6CO_2+6H_2O$ $C_6H_{12}O_6+6O_2$

Which of these is zero order reaction

A) I C) III

B) II D) all of these

9. **Which statement is correct**

A) activation energy of exothermic reaction is smaller one

B) activation energy of endothermic reaction is greater one

C) activation energy for exothermic reaction for forward and reverse direction is different

D) all of above

10. **Which of the equation is used to determine activation energy**

A) Henderson equation C) Arrhenius equation

B) Van der Waal equation D) general gas equation

11. Which is not a characteristic of catalyst?

A) it accelerate the reaction but does not involve in the product

B) it can't affect equilibrium constant

C) it is specific in its action

D) Δ H of catalyzed and uncatoalyzed reaction is not same

12. The unit of rate constant 'K' for a first order reaction:

(A) sec^{-1} (C) $mol.dm^{-3}. sec$

(B) $mol.dm^{-3}. sec^{-1}$ (D) $mol^{-1}.dm^{3}. sec$

13. If the rate of decay of radio-active isotope decreases from 200 cpm to 25 cpm after 24 hours. What is its half life:

(A) 3 hours (C) 4 hours

(B) 6 hours (D) 8 hours

14. In a multistep reaction, the slowest step is:

(A) Mechanism step (C) Rate determing step

(B) Enthalpy determing step (D) None of above

15. The rate of reaction between two specific time intervals is called:

(A) Rate of reaction (C) Average rate

(B) Instantaneous rate (D) None of these

16. Rate = $K[A]^2[B]$ for the reaction $2A + B \longrightarrow$ Product and 'A' is present is large excess, then order or reaction is:

(A) 1 (C) 2

(B) 3 (D) 4

17. The unit of the rate constant is the same as the of the rate of reaction is:

(A) 1st order reaction (C) 2nd order reaction

(B) Zero order reaction (D) 3rd order reaction

18. The rate equation for a reaction is Rate = K[A], what are the units of K:

(A) s^{-1} (C) $mol.dm^{-3}$

(B) $mol.dm^{-3}.s^{-1}$ (D) $mol^{-1}.\ dm^{3}.s^{-1}$

19. The half life of zero order reaction is:

(A) Proportional to initial concentration of reactants

(B) Independent of initial concentration of reactants

(C) Inversely proportional to initial concentration of reactants

(D) None of these

20. The unit of rate constant "K" is $mol^{-1}.dm^{3}.sec^{-1}$ for a chemical reaction the order of reaction is:

(A) 0 (C) 1

(B) 2 (D) 3

21. The rate of reaction:

(A) Increases as the reaction proceeds

B) Decreases as the reaction proceeds

(C) Remains the same as the reaction proceeds

(D) May decrease or increase as the reaction proceeds

22. For the reaction, $2NO + Br_2 \longrightarrow 2NOBr$, the proposed mechanism is:

$NO + Br_2 \xrightleftharpoons{\text{Slow}} NOBr_2$

$NOBr_2 + NO \xrightleftharpoons{\text{Fast}} 2NOBr$

23. The rate law for this reaction is:

(A) Rate = $K[NOBr_2][NO]$

(B) Rate = $K[NO][Br_2]$

(C) Rate = $K[NO]^2 [Br_2]$

(D) Rate = $K[NO][Br_2]^2$

24. The half-life period for the reaction $2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$ is 24 minutes at 45°C. What will be the amount of N_2O_5 left behind after 96 minutes? When 10 g is starting amount.

(A) 2 g

(B) 5 g

(C) 12.5 g

(D) 0.625 g

25. Collision theory explain:

(A) Rate of reaction

(B) Order of reaction

(C) Moleculerity of reaction

(D) All of these

26. $2A + B \longrightarrow$ Product

Rate = $k[A]^2[B]$

If B is present in large excess, the order of reaction is:

(A) Zero

(B) 1

(C) 2

(D) 3

27. Which of the following is zero order reaction?

(A) $N_2O \xrightarrow{hv} N_2 + \frac{1}{2} O_2$

(B) $2HI \xrightarrow{Au} H_2 + I_2$

(C) $H_2 + Cl \xrightarrow{hv} HCl$

(D) All of these

28. The order of reaction can be measured by:

(A) Dilatometric method

(B) Electrical conductivity method

(C) Half life method

(D) Absorption of radiation

29. $X + Y \longrightarrow Z$

[X]	[Y]	Rate
1.0	1.0	0.25
2.0	1.0	0.50
1.0	2.0	0.25
1.0	3.0	0.25

Which of the following is the rate equation?

(A) Rate = $K[X][Y]$

(B) Rate = $K[X][Y]^0$

(C) Rate = $K[X]^0[Y]^1$

(D) Rate = $K[X][Y]^2$

30. The slope of the Arrhenius equation can be represented as:

(A) $\frac{Ea}{2.303\ RT}$

(B) $-\frac{Ea}{2.303\ RT}$

(C) $-\frac{Ea}{2.303\ R}$

(D) $-\frac{Ea}{RT}$

31. The rate expression of a reaction is "Rate = K [A]^2 [B]. What becomes to rate of reaction if 'A' and 'B' concentration are doubled? Rate of reaction is:

(A) Doubled

(B) Increased four times

(C) Increased six times

(D) Increased eight times

32. Which of the following statement is true?

(A) In the beginning instantaneous rate is smaller than average rate

B) In the beginning average rate is smaller than instantaneous rate

(C) At the end instantaneous rate is greater than the average rate

(D) All

33. If for a reaction, half-life period is independent of the concentration of the reactants, then the reaction is:

(A) 3rd order

(B) 2nd order

(C) Zero order

(D) None

34. The % age of reactant left behind after four half time of chemical reactions one hour:

(A) 3.125%

(B) 12.5%

(C) 6.25%

(D) 25%

35. The half life period for 3rd order reaction is:

(A) $[t_{1/2}] \propto 1/a^0$

(B) $[t_{1/2}] \propto 1/a^1$

(C) $[t_{1/2}] \propto 1/a^2$

(D) $[t_{1/2}] \propto 1/a^3$

36. Which one of the following is heterogeneous catalysis?

(A) $HCOOH \xrightarrow{H_2SO_4} H_2O + CO$

(B) $H_2C = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$

(C) $CH_3COOC_2H_5 + H_2O \xrightleftharpoons{H^+} CH_3COOH + C_2H_5OH$

(D) $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$

37. With increase of 10°C temperature the rate of reaction doubles. This increase in rate of reaction is due to:

(A) Decreases in activation energy of reaction

B) Decrease in the number of collisions between reactant molecules

(C) Increase in activation energy of reactants

(D) Increase in number of effective collisions

38. If the rate of decay of a radioactive isotopes decreases from 200 cpm to 25 cpm after 24 hours, what is its half life?

(A) 3 hours (B) 4 hours

(C) 6 hours (D) 8 hours

39. If the temperature of the reaction is increased from 0°C to 50°C how many times rate will increase?

(A) 5 times (B) 2 times

(C) 10 times (D) 32 times

40. Decomposition of Ozone take place according to the following equation to the following equation:

$2O_{3(g)} \longrightarrow 3O_{2(g)}$ **Rate equation for the reaction is Rate K =** $[O_3]^2\ [O_2]^{-1}$

What is the order of the reaction?

(A) 3 (B) zero

(C) 2 (D) 1

41. Energy required to form transition state is called:

(A) ⍰H (B) Ea

(C) ⍰E (D) All

ANSWER KEY

1	**D**	**11**	**D**	**21**	**A**	**31**	**B**
2	**D**	**12**	**A**	**22**	**B**	**32**	**D**
3	**A**	**13**	**D**	**23**	**D**	**33**	**C**
4	**C**	**14**	**C**	**24**	**D**	**34**	**C**
5	**C**	**15**	**C**	**25**	**C**	**35**	**B**
6	**D**	**16**	**A**	**26**	**D**	**36**	**D**
7	**D**	**17**	**B**	**27**	**C**	**37**	**D**
8	**C**	**18**	**A**	**28**	**B**	**38**	**D**
9	**D**	**19**	**A**	**29**	**C**	**39**	**D**
10	**C**	**20**	**B**	**30**	**D**	**40**	**B**

SOLUTION TO PROBLEMS

UNIT 1

Fundamental Concepts

2)

No. of Neutron = $A - \lambda$

$$^{32}_{16}S = 32 - 16 = 16$$

$$^{31}_{15}P = 31 - 15 = 16$$

Note: Suck specie3s having same no. of neutrons are called isotones.

3)

$$\frac{1.4}{28} \times 22.414dm^3 = 1.1207dm^3$$

4)

$$2Al + 3O \rightarrow Al_2O_3$$

Al : Al_2O_3 O : Al_2O_3

moles moles moles moles

$$\begin{tikzcd} 2 \arrow[drr, leftrightarrow] & : & 1 \arrow[dll, leftrightarrow] \\ 0.36 & : & x \end{tikzcd} \qquad \begin{tikzcd} 3 \arrow[drr, leftrightarrow] & : & 1 \arrow[dll, leftrightarrow] \\ 0.36 & : & x \end{tikzcd}$$

$x = \frac{0.36}{2}$ $x = \frac{0.36}{3}$

$x = 0.18$ $x = 0.12$

As, oxygen is producing less moles of Alumina so, it is limiting reactant and Aluminium is non limiting reactant

6)

0.55 mg of electron = 1 mole

1g = 1000 mg

$$Mass\ in\ mg : Moles$$

$$0.55 : 1$$

$(0.55 \times 1000)g : x$

$$x = \frac{0.55 \times 1000}{0.55} = 1000 moles$$

7)

$$Moles\ of\ NO_2 : Mass\ of\ O_2$$

$$\begin{tikzcd} 1 \arrow[drr, leftrightarrow] & : & 32g \arrow[dll, leftrightarrow] \\ x & : & 16g \end{tikzcd}$$

$$x = \frac{16}{32} = 0.50 mole$$

8)

$$\frac{2}{20} \times 22.414 dm^3 = 2.2414 dm^3$$

10)

Formula of Glucose $C_6H_{12}O_6$

$$= \frac{180}{180} \times 6.02 \times 10^{23} \times 12$$

$$= 7.2 \times 10^{24} H - atoms$$

13)

$$\frac{16}{16} = 1\ Mole \times NA = 6.02 \times 10^{23} Molecules$$

14)

$$Mass\ of\ Na_2CO_3 : Mass\ of\ Na$$

$$106g : 46g$$

$$53g : x$$

$$x = \frac{46 \times 53}{106} = 23g$$

15)

$$2Mg + O_2 \rightarrow 2MgO$$

$$Moles\ of\ Mg : Moles\ of\ MgO$$

$$2 : 2$$

$$20 : x$$

$$x = 20\ moles$$

$$Moles\ of\ O : Moles\ of\ MgO$$

$$1 : 2$$

$$20 : x$$

$$x = 40 moles$$

Mg is limiting reactant

MgO mass = $n \times Mr$

MgO mass = $20 \times 40 = 800g$

17)

$$CaCO_3 = 40 + 12 + 48 = 100$$

$$\% \; of \; O = \frac{48}{100} \times 100 = 48\%$$

23)

$$Moles \; of \; SO_2 \; : \; Mass \; of \; S$$

1 : 3

$$0.5 \quad : \quad x$$

$$x = 0.5 \times 3 = 1.5 mol$$

$$Moles \; of \; H_2S \; : \; Moles \; of \; S$$

2 : 3

As SO_2 is producing less moles of product so it is limiting reactant.

24)

E.F mass = C_3H_3O = (12x3)+(1x3)+(16)

= 55

M.F mass = 110

$$n = \frac{M.F \; mass}{E.F \; mass} = \frac{110}{55} = 2$$

$$M.F = n \times E.F$$

$$M.F = 2 \times C_3H_3O = C_6H_6O_2$$

27)

$$1e^- \; charge = 1.602 \times 10^{-19} \, C$$

$$6.02 \times 10^{23} e's \; charge = 1.602 \times 10^{-19} \, Cx \; 6.02 \times 10^{23} = 96500C = 1 \; Faraday$$

28)

$$C \quad : \quad H$$

$$\frac{80}{12} : \frac{20}{1} \,(Mole\ ratio)$$

$$6.66 \quad : \quad 20$$

$$\frac{6.66}{6.66} \quad : \quad \frac{20}{6.66}\,(Atomic\ ratio)$$

$$1 \quad : \quad 3.00$$

So, E.F = CH_3

29)

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

$$Moles\ of\ CH_4 \ : \ Moles\ of\ CO_2$$

$$1 \ : \ 1$$

$$5ml \ : \ 5ml$$

$$Moles\ of\ C_2H_6 \ : \ Moles\ of\ CO_2$$

$$1 \ : \ 2$$

$$10 \ : \ x$$

$$x = 20ml$$

Total vol of CO_2 = 20 + 5 = 25ml

30)

$$H_2moles \ : \ CH_4\ moles$$

$$\frac{1}{2} = 0.5 \ : \ \frac{16}{16} = 1$$

So

$$2:1$$

(Ration between moles is ration between volumes)

35)

$$H_2O_l \xrightarrow{Electrolysis} H_{2_g} + \frac{1}{2}O_{2_g}$$

$$Mole\ of\ H_2O : Moles\ of\ O_2$$

1 : 0.5

$$\frac{90}{18} = 5 : \quad x$$

$$x = 5 \times 0.5 = 2.5\,mole$$

36)

$$Moles\ of\ CH_4 : \ Mass\ of\ C$$

$$1 : 12g$$

$$x : 3g$$

$$x = \frac{3}{12} = \frac{1}{4} = 0.25 mole$$

41)

$$M = \frac{10}{40} \times \frac{1}{1} = \frac{1}{4} = 0.25$$

44)

$$0.3 = \frac{x}{60} \times \frac{1}{0.1}$$

$$x = 0.3 \times 60 \times 0.1 = 1.8g$$

45)

$$'n'of\ C_2H_5OH = \frac{92}{46} = 2$$

$$'n'of\ CH_3OH = \frac{96}{32} = 3$$

$$'n'OF\ H_2O = \frac{90}{18} = 5$$

$$'X'of\ C_2H_5OH = \frac{2}{2+3+5} = \frac{2}{10} = 0.2$$

$$'X'of\ CH_3OH = \frac{3}{10} = 0.3$$

$$'X'OF\ H_2O = \frac{5}{10} = 0.5$$

47)

$$10\% = \frac{180g}{x} \times 100$$

$$x = \frac{180}{10} \times 100 = 1800ml$$

$$x = \frac{1800}{1000} = 1.8dm^3$$

50)

$$Moles\ of\ sucrose = 1$$

$$Moles\ of\ H_2O = \frac{1000g}{18} = 55.5$$

$$'x'of\ sucrose = \frac{1}{1+55.5} = \frac{1}{56.5}$$

UNIT 2

States of Matter

33)

$$PV = nRT$$

$$n = \frac{m}{M} = \frac{2.8}{28} = 0.1 mole\ of\ CO$$

$$V = \frac{nRT}{P} = \frac{0.1 \times 0.0821 \times 300}{0.0821}$$

$$V = 30dm^3$$

35)

$$P_1V_1 = P_2V_2 \quad , \quad V_2 = \frac{P_1V_1}{P_2}$$

$$V_2 = \frac{1 \times 0.25}{10} = 0.025dm^3$$

$$No.of\ baloon : Volume\ of\ each\ baloon$$

$$1 \ : \ 0.025$$

x : 5(Total volume of gas)

$$x = \frac{5}{0.025} = 200$$

36)

Ratio between moles is ratio between volumes

$$O_2 \ : \ H_2 : \ CH_4$$

$$n = \frac{m}{M} = \frac{32}{32} : \frac{32}{2} : \frac{32}{16}$$

$$1 \ : \ 16 \ : \ 2$$

37)

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1 \times T_2}{T_1 \times P_2} = \frac{2 \times 5 \times 273}{546 \times 1}$$

$$V_2 = 5dm^3$$

UNIT 3

Atomic Structure

31)

$$Proton\ :\ \alpha - particle$$

$$\frac{e}{m}\frac{+1}{1.008}\ :\ \frac{+2}{4}$$

$$1\ :0.5$$

So

$$2\ :\ 1$$

32)

Formula:

$$No. of\ orbitals\ in\ a\ shell = n^2$$

So,

$$(3)^2 = 9$$

33)

$$n\ =\ 4 \quad l\ = n - 1$$

$$l = 4 - 1 = 3$$

So,

$l = 0,1,2,3$ Total four values

34)

$$Cr_{24} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$$

$$l = 1\ \ P - subshell = 6 + 6 = 12e$$

$l = 2 \quad d - subshell = 5\text{e}$

35)

$$n + l = 3 + 2 = 5$$

UNIT 5

Chemical Energetics

24)

i) $C \rightarrow C \qquad \Delta H = +716.7KJmol^{-1}$

(graphite) (g)

ii) $C \rightarrow C \qquad \Delta H = 714.81CJmol^{-1}$

(Diamond) (g)

$$C \rightarrow C \qquad \Delta H = ?$$

(graphite) (Diamond)

Inverting equation ii and then adding both equations

$$C \rightarrow C \qquad \Delta H = +716.7KJmol^{-1}$$

(graphite) (g)

$$C \rightarrow C \qquad \Delta H = -714.8KJmol^{-1}$$

(g) (Diamond)

$$C \rightarrow C \qquad \Delta H = +1.9KJmol^{-1}$$

(graphite) (Diamond)

30)

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{-2}$$

It is dibasic acid so,

$$2H^{+} + 2OH^{-} \rightleftharpoons 2H_2O \ \Delta H = +13.7 \times 2$$

$$\Delta H = 27.4cal$$

34)

$$\Delta E = q + w$$

$$\Delta E = 30 - 20 = 10$$

As work is done by the system so negative

$$\Delta E = q - w$$

35)

$$Mass\ of\ Glucose \ : \ \Delta H_{comb}\ of\ Glucose$$

$$180g \ : \ -1350\ kcal$$

$$x \ : \ -2700kcal$$

$x \times -1350 = 180 \times -2700$

$$x = \frac{180 \times -2700}{-1350}$$

$$x = 360g$$

3)

$$\begin{array}{ccccc} H & - & N & - & H \\ & & | & & \\ & & H & & \end{array}$$

No. of N – H bonds = 3

So, total energy 3 x x = 3x

UNIT 6

Electrochemistry

21)

$$Na_2O_2$$

$$(+1)2 + 2x = 0$$

$$+2 + 2x = 0$$

$$+2x = -2$$

$$x = -\frac{2}{2} = -1$$

28)

$$E_{cell} = E_{oxi} + E_{Red}$$

Mg will oxidized due to low R.P

Cu will reduced due to high R.P

$$Mg \rightleftharpoons Mg^{+2} + 2e^{-} E_{oxi} = +2.38V$$

$$Cu^{+2} + 2e^{-} \rightleftharpoons Cu_{(s)} \quad E_{Red} = +0.34V$$

$$E_{cell} = 2.38 + 0.34 = 2.72V$$

29)

Mass of cathode will increase due to deposition of Cu^{+2} ions after reduction

30)

$$Al^{+3} + 3e^{-} \rightarrow Al^{o}$$

$$27g \qquad\qquad 27g$$

$$Mass\ of\ Al\ :\ Moles\ of\ e^{-}$$

$$27\ :\ 3$$

$$x\ :\ 5$$

$$x = \frac{5 \times 27}{3} = 45g$$

33)

$$2Cr^{+3} + 7H_2O \rightarrow Cr_2O_7^{-2} + 14H^+$$

$$+6 \qquad\qquad\qquad +12$$

Charge on right side is greater by a numerical value of +6. So $6e^-$ on right side will make charge balance.

35)

$$Al \rightarrow Al^{+3} + 3e^- E_{oxi} = 1.67V$$

$$\frac{1}{2}Cl_2 + e^- \rightarrow Cl^{-1} \quad E_{Red} = +1.36V$$

So

$$E_{cell} = E_{oxi} + E_{Red}$$

$$E_{cell} = 1.67 + 1.36 = 3.03V$$

39)

$$MnO_4^- \rightarrow Mn^{+2}$$

$$Mn^{+7} \rightarrow Mn^{+2}$$

According to oxi-state, there is transfer of $5e^-$

40)

Hydrogen charges its oxi-state from 0 to -1. So, it act as oxi-agent and itself get reduced.

UNIT 7

Chemical Equilibrium

9)

$$AgCl \rightleftharpoons Ag^{+} + Cl^{-}$$

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

$$K_{sp} = S.S$$

$$K_{sp} = S^{2}$$

$$\sqrt{2 \times 10^{-10}} = \sqrt{S^{2}}$$

$$1.41 \times 10^{-5} = S$$

10)

$$pH = 4.74 + \log\frac{(0.01)}{(0.1)}$$

$$pH = 4.74 + log10^{-1}$$

$$pH = 4.74 - 1 = 3.74$$

11)

$$H_2SO_4 \rightleftharpoons 2H^{+} + SO_4^{-2}$$

$$1M \qquad 2MH^{+} + ions$$

$$10^{-3}M \qquad 2 \times 10^{-3}M \;\; H^{+}ions$$

$$[H^{+}] = 2 \times 10^{-3}$$

$$-\log[H^{+}] = -log2 \times 10^{-3}$$

$$pH = 2.7$$

12)

Because in exothermic reaction

$$\left(K_c \propto \frac{1}{Temp}\right)$$

19)

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$1M \qquad 1M\ H^+\ ions$$

$$10^{-3}M \quad 10^{-3}M \quad H^+\ ions$$

$$[H^+] = 10^{-3}$$

$$-\log[H^+] = -log10^{-3}$$

$$pH = 3$$

23)

$$K_p = K_c(RT)^{\Delta n}$$

$$\Delta n = 2 - 2 = 0$$

$$K_p = 50(8.3143 \times 700)^o$$

$$x^o = 1$$

$$K_p = 50 \times 1 = 50$$

29)

$$[H^+] = 10^{-3}$$

$$-\log[H^+] = -log10^{-3}$$

$$pH = 3$$

$$pH = pOH = 14$$

$$3 + pOH = 14$$

$$pOH = 14 - 3 = 11$$

33)

$$pH = 5 \ \ Means \ \ [H^+] = 10^{-5}$$

$$pH = 2 \ \ Means \ \ [H^+] = 10^{-2}$$

$$10^{-5} \rightarrow 10^{-2}$$

$$\downarrow$$

$$1000 \ times \ change$$

34)

$$Ca(OH)_2 \rightleftharpoons Ca^{+2} + 2OH^-$$

S 2S

$$K_{sp} = [Ca^{+2}][OH^-]^2$$

$$K_{sp} = (S)(2S)^2$$

$$K_{sp} = 4S^3$$

$$S^3 = \frac{K_{sp}}{4}$$

$$\sqrt[3]{S^3} = \sqrt[3]{\frac{K_{sp}}{4}}$$

$$S = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$$

35)

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{-2}$$

$$1M \qquad 2M$$

$$0.5 \qquad 1M$$

$$[H^+] = 1$$

$$-\log[H^+] = log1$$

$$pH = 0$$

37)

pka + pkb = 14

pka + 4.8 = 14

pka = 14 – 4.8 = 9.2

pka = 9.2

38)

$$N_2O_4 \rightleftharpoons 2NO_2$$

$$t = 0 \quad 1 \qquad 0$$

$$t = t_{eq} \frac{(1-x)}{V} \quad \frac{2x}{V}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{(2x/v)^2}{(1-x/v)}$$

$$K_c = \frac{4x^2/v^2}{(1-x/v)}$$

$$K_c = \frac{4x^2}{(1-x)v}$$

39)

Because K_c value is temp dependent.

UNIT 8

Reaction Kinetics

23)

Formula

$$Total\ time = t_{1/2} \times No.of\ t_{1/2}$$

$$96min = 24min \times No.of\ t_{1/2}$$

$$No.of\ t_{\frac{1}{2}} = \frac{96}{24} = 4$$

$$10g \xrightarrow[\substack{1st \\ t_{1/2}}]{} 5g \xrightarrow[\substack{2nd \\ t_{1/2}}]{} 2.5g \xrightarrow[\substack{3rd \\ t_{1/2}}]{} 1.25g \xrightarrow[\substack{4th \\ t_{1/2}}]{} 0.625g$$

28)

$$Rate \propto [x]$$

But independent of $[y]$

33)

$$100g \xrightarrow[\substack{1st \\ t_{1/2}}]{} 50g \xrightarrow[\substack{2nd \\ t_{1/2}}]{} 25g \xrightarrow[\substack{3rd \\ t_{1/2}}]{} 12.5g \xrightarrow[\substack{4th \\ t_{1/2}}]{} 6.25g$$

37)

$200cpm$ $\downarrow 1st\ t_{1/2}$ $100cpm$ $\downarrow 2nd\ t_{1/2}$ $50cpm$ $\downarrow 3rd\ t_{1/2}$ $25cpm$	$t_{1/2} = \frac{Total\ time}{No.of\ t_{1/2}}$ $t_{1/2} = \frac{24}{3}$

	$t_{1/2}=8\ hrs$

38)

For every $10°C$ rise in temperature approximately double. So, by changing temperature $0°C$ to $50°C$ change in reaction rate is

$$0°C \rightarrow 10°C \rightarrow 20°C \rightarrow 30°C \rightarrow 40°C \rightarrow 50°C$$

$$2 \times 2 \times 2 \times 2 \times 2 = 32\ timeS$$

UHS TOPIC 1 – B

PERIODS

LEARNING OUTCOMES

In this topic, student should be able to:

Discuss the variation in the physical properties of elements belonging to period 2 and 3 and to describe and explain the periodicity in the following physical properties of elements.

a) Atomic radius

b) Ionic radius

e) Melting .point

d) Boiling point

e) Electrical conductivity

f) Ionization energy

MODERN PERIODIC TABLE

Modern Periodic Law (Moseley):

The physical and chemical properties of elements are the periodic function of their atomic numbers.

MODERN PERIODIC TABLE	
Periodic Table	Elements arranged in order of increasing proton number
Group Number	Number of electrons in outermost shell (valence electrons)
Period Number	Number of shells of electrons
Valence Electron	Electron in outermost shell
Metals	Elements with 1-3 valence electrons except boron
Non-metals	Elements with 4-7 valence electrons
Inert gases	Elements with full outermost-shell

PERIODS:

- The horizontal rows of elements in the periodic table are called periods
- All elements in a period have same number of shells
- There are seven periods ii the periodic table that are known by Arab numerals 1 to 7

No.	Peculiarity	Sub-groups Present	No. of element	s-block element	p-block element	d-block element	f-block element
1	Shortest	A	2	2	0	0	0
2	Short	A	8	2	6	0	0
3	Short	A	8	2	6	0	0
4	Long	A and B	18	2	6	10	0
5	Long	A and B	18	2	6	10	0
6	Longest	A and B	32	2	6	10	14
7	Incomplete	A and B	26	2	-	10	14

FEATURES OF THE PERIODS

(i) There are seven periods numbered by Arabic numerals from 1 to 7

(ii) **The period 1** contains only two elements (Hydrogen and helium) and is called shortest period

(iii) **The period 2 and 3** contain eight elements each and are called short periods. All the elements in these periods are representative and belong to A subgroups. In these periods, every eighth element resembles in. properties with the first one.

Example:

(i) Lithium and Beryllium in the second period resemble in most of their properties with Sodium, and Magnesium in the third period respectively.

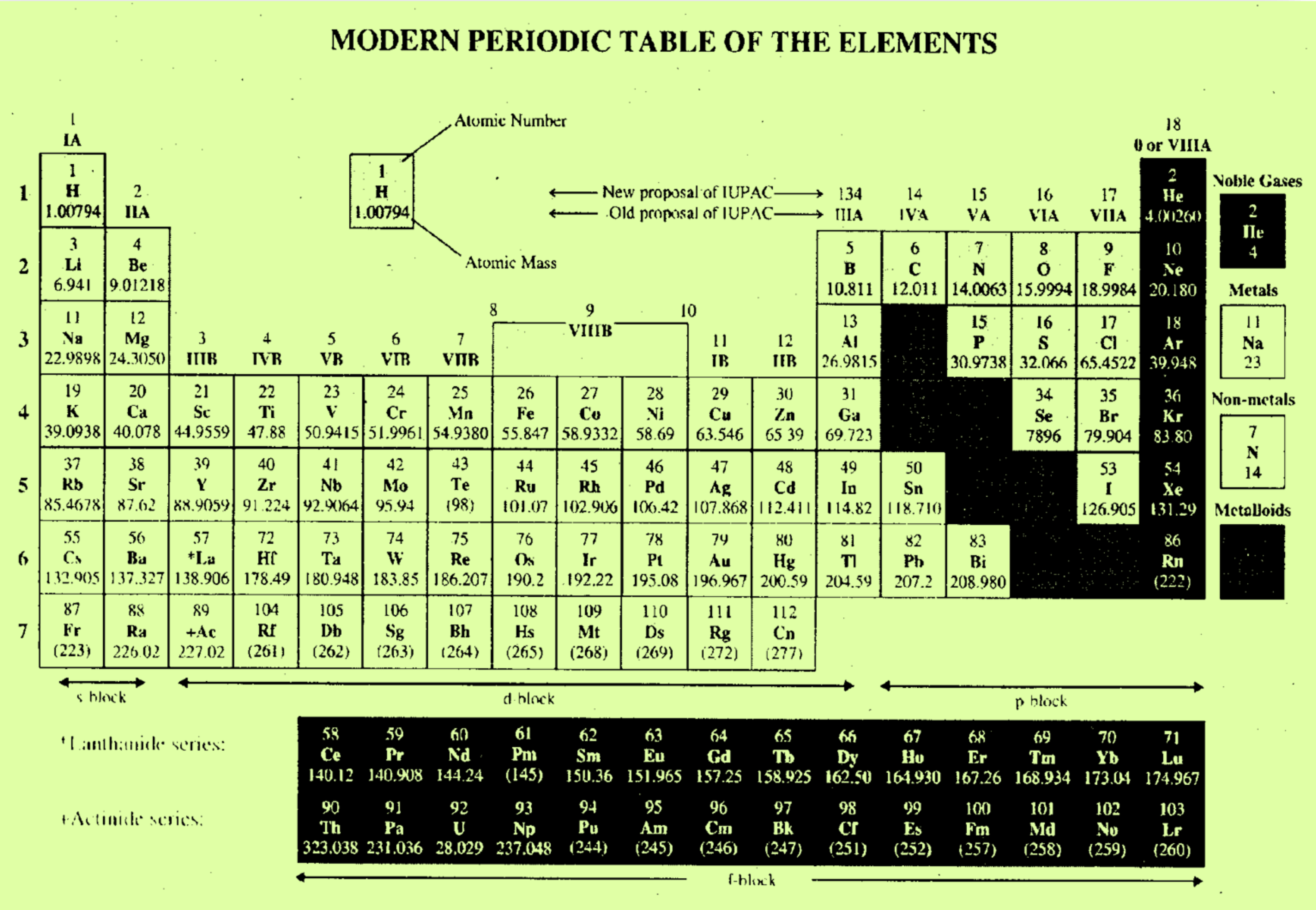
(ii) Boron in the second period and Aluminum in the third period have same oxidation state of +3

(iii) Fluorine in the second period has close resemblance with Chlorine in the third period

PERIODIC TRENDS IN PHYSICAL PROPERTIES

Property	Definition	Trend in a group (down the group)	Responsible factors	Trend along a period (from left to right)
Atomic radius	Half of the distance between the centers of two adjacent atoms of any element.	Increases	Nuclear charge and no. of shells	Decreases
Ionic radius	Distance between center of ion and the outer boundary of its electron cloud.	(for similar charged ions) increases	Nuclear charge and no. of shells	Decrease for iso-electronic +ve and – ve ions

Ionization energy	Minimum quantity of energy which is required to remove an electron from the outer most shell of its isolated, gaseous atom in its ground state	Decreases	Nuclear charge atomic size and shielding effect	Generally Increases
Electron affinity	Energy released or absorbed, when an electron is added to a gaseous atom to form a negative ion	Generally Decreases	Size of atom, nuclear charge and vacancies in valence shell	Increases
Metallic character	Tendency to lose electron and form cations and basic oxides	Increases	Atomic size and nuclear charge	Decreases
Melting and boiling Points	Specific temperature at which an element changes to liquid or gaseous state	for IA and IIA decreases for VIIA increases	No. of valence electrons	I-A to IV-A increases V to VIII decreases
Oxidation state	Charge, which an element could carry in a compound	Usually same	Electrons lost or gamed	I to IV same as group number V, VI, VII is equal to vacancy or group number
Electrical conductance	Ability to conduct electricity	(increases for IA and IIA) no regular trend for transition metals	Free electrons in outer shell	Increase from IA to IIIA and then decreases except B group
Hydration energy	Heat absorbed or evolved, when one mole of gaseous ion dissolves in water to give and infinity dilute solution	Decreases	Charge to size ratio	Increase



MODERN PERIODIC TABLE OF THE ELEMENTS

1
H
1.00794
Atomic Number
Atomic Mass

← New proposal of IUPAC →
← Old proposal of IUPAC →

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	134 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 0 or VIIIA
1	1 H 1.00794																	2 He 4.00260
2	3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0063	8 O 15.9994	9 F 18.9984	10 Ne 20.180
3	11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815		15 P 30.9738	16 S 32.066	17 Cl 65.4522	18 Ar 39.948
4	19 K 39.0938	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65 39	31 Ga 69.723			34 Se 7896	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Te (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710			53 I 126.905	54 Xe 131.29
6	55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.59	82 Pb 207.2	83 Bi 208.980			86 Rn (222)
7	87 Fr (223)	88 Ra 226.02	89 +Ac 227.02	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (268)	110 Ds (269)	111 Rg (272)	112 Cn (277)						

s block

d block

p block

*Lanthanide series:	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
+Actinide series:	90 Th 323.038	91 Pa 231.036	92 U 28.029	93 Np 237.048	94 Pu (244)	95 Am (245)	96 Cm (246)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

f-block

Noble Gases	2 He 4
Metals	11 Na 23
Non-metals	7 N 14
Metalloids	■

PRACTICE EXERCISE (FOR UHS TOPIC)

1. **Newland classified the number of elements in the increasing order of their atomic mass is**

(A) 62

(B) 64

(C) 66

(D) 68

2. **Mendeleev's periodic table has number of groups and number of periods**

(A) 6, 7

(B) 8, 7

(C) 8, 12

(D) 7, 8

3. **Uniqueness of Mendeleev's periodic table is that**

(A) Atomic mass of element

(B) Classified elements into 12 periods

(C) Placed Na, K with Ca and Mg

(D) He left empty spaces for undiscovered elements

4. **Which is the drawback of Mendeleev's periodic table?**

(A) He placed alkali metal with alkaline earth metal

(B) He could not specify the position of isotopes

(C) He could not explain the structure of atom

(D) Both a and b

5. **For which of the element, separate group was not mentioned in the Mendeleef's periodic table?**

(A) IV A

(B) VIII A

(C) VI A

(D) II A

6. Which of the scientist experimentally proved that element should be arranged in the periodic table on the basis of atomic numbers and not on the basis of atomic mass

(A) Mendeleeve

(B) Newland

(C) Dobereiner

(D) Mosley

7. *f*-block elements are also called

(A) Outer transition element

(B) Inner transition elements

(C) Alkaline earth elements

(D) Coinage metal

8. Elements in the periodic table are classified into four blocks. This classification is based upon

(A) Valence orbital

(B) sub-shell

(C) Shell

(D) All of the above

9. Which of the elements has comparatively greater reduction in size

(A) Lanthanide series

(B) Actinide series

(C) Chalcogen

(D) Halogen

10. Which statement is incorrect

(A) Size of the positive ion is smaller than its parent atom

(B) Size of the negative ion is greater than its parent atom

(C) In positive ion, number of proton exceed the number of electrons

(D) In negative ion, number of proton exceed the number of electrons

11. Which of the species is not isoelectromic others

(A) F^{-1} (C) O^{-2}

(B) N^{-3} (D) C^{-3}

12. Which has highest value of ionization energy

(A) He (C) O

(B) N (D) F

13. Which element has greater 1st ionization energy?

(A) Lithium (C) Beryllium

(B) Sodium (D) Boron

14. Which element is the most electro positive in periodic table?

(A) Barium (C) Potassium

(B) Calcium (D) Cesium

15. Which of the following elements has greatest value of first ionization energy

(A) N (C) C

(B) O (D) B

16. Which halogen has greatest value of electron affinity

(A) F (C) Br

(B) C1 (D) I

17. Ionization energy is the index to the metallic character. The elements which have

(A) Low energy – metal (C) High ionization energy – non metal

(B) Intermediate - metalloid (D) All of the above

18. Which is correct statement?

(A) 1st electron affinity value is always negative

(B) Term electro negativity is associated with molecule

(C) Electron affinity is associated with atom

(D) All of the above

19. The melting point and boiling point is highest for

(A) N_2 (C) C

(B) Be (D) Na

20. Which of the element is the best conductor of electricity?

(A) Zn (C) Cu

(B) Fe (D) Ca

21. Which of the following set of ions represents the collection of isoelectrnic species?

(A) Na^+, Mg^{2+}, Al^{3+}, Cl^- (B) Na^+, Ca^{2+}, Sc^{3+}, F^-

(C) Sc^{3+}, K^+, Cl^-, Mg^{2+} (D) K^+, Ca^{2+}, Sc^{3+}, Cl^-

22. The 1st I.E energies of Na, Mg, Al and S are in the order:

(A) Na > Mg > Al > Si (B) Na < Mg > Al < Si

(C) Na > Mg > Al < Si (D) Na < Mg < Al < Si

23. Which of the following have similar properties?

(A) 13, 31 (B) 11, 20

(C) 12, 10 (D) 21, 33

24. The highest ionization energy is shown by:

(A) Alkaline earth metal (B) Halogens

(C) Noble gases (D) Transition elements

25. On descending a group, electropositive character of elements:

(A) Increases (B) Decreases

(C) Remain same (D) None

26. In a period, the alkali metals have:

(A) Highest ionization energy (B) Largest atomic radii

(C) Highest density (D) Highest electronegativity

27. Which of the following has the largest ionic radius?

(A) Be^{2+} (B) Mg^{2+}

(C) Ca^{2+} (D) Sr^{2+}

28. Which of the following has first two electron affinities zero?

(A) Na (B) N

(C) C (D) None

29. Which one of the following properties is common to Li, Na and K?

(A) All the elements form hydride (B) High 2nd I.P

(C) High ionic radius (D) High electronegativity

30. Which of the following is correct order for the decreasing 1st I.E energy?

(A) C > B > Be > Li
(B) C > Be > B > Li
(C) B > C > Be > Li
(D) Be > Li > B > C

31. Which of the period consists of all types of elements?

(A) 2nd and 3rd
(B) 4th and 5th
(C) 6th and 7th
(D) All period

32. Which of the following element possess greatest value of electronegativity when combined with hydrogen?

(A) Be
(B) Na
(C) C
(D) Cl

33. The decrease in atomic sizes is not much prominent across rows containing elements of:

(A) s-block
(B) p-block
(C) d-block
(D) f-block

34. Which of the following will form largest ion with noble gas electronic configuration?

(A) Al
(B) K
(C) P
(D) S

35. 7th period of the periodic table contains normal elements:

(A) 2
(B) 3
(C) 4
(D) 8

36. Which of the following properties increases up to the middle of the period and then decreases?

(A) Ionization energy
(B) Melting and boiling point
(C) Atomic radii
(D) Atomic volume

37. Keeping in view the size of atoms, which order is the correct one:

(A) Mg > Sr

(B) Ba > Mg

(C) Lu > Ce

(D) Cl > I

38. The melting point is highest for:

(A) Ca

(B) S

(C) Be

(D) Ba

39. The formula of ions of some elements are shown below N^{-3}, O^{-2}, F^{-1}, Li^{+1}, Mg^{+2}. Which statement about these ions is correct? They all have same.

(A) Number of electrons in their outer shells

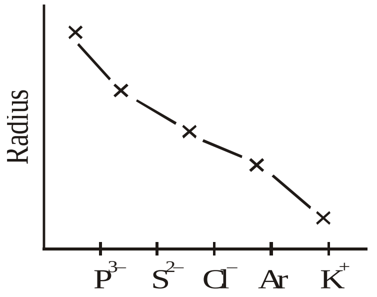
(B) Electronic structure as noble gases

(C) Number of neutrons in their nuclei

(D) Number of protons and electrons

40. Which one of the graph is correct?

(a)



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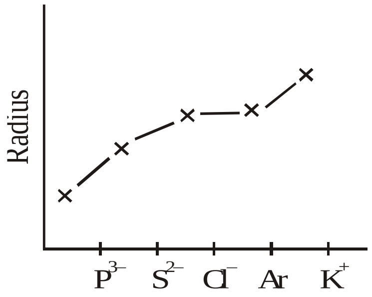
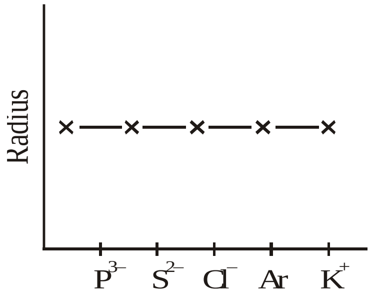
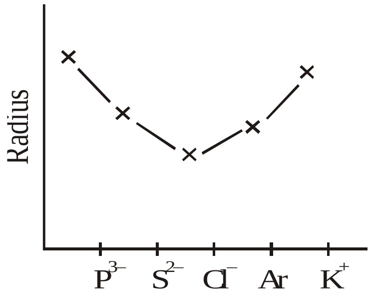


(c)



(d)



ANSWWER KEY

1	**A**	**11**	**D**	**21**	**D**	**31**	**C**
2	**C**	**12**	**A**	**22**	**D**	**32**	**D**
3	**D**	**13**	**C**	**23**	**A**	**33**	**A**
4	**D**	**14**	**D**	**24**	**C**	**34**	**C**
5	**B**	**15**	**A**	**25**	**A**	**35**	**A**
6	**D**	**16**	**B**	**26**	**B**	**36**	**B**
7	**B**	**17**	**A**	**27**	**D**	**37**	**B**
8	**A**	**18**	**D**	**28**	**D**	**38**	**C**
9	**A**	**19**	**D**	**29**	**B**	**39**	**B**
10	**C**	**20**	**C**	**30**	**B**	**40**	**A**

UHS TOPIC 2 – B

GROUPS

LEARNING OUTCOMES

In this topic, student should be able to:

Describe and explain the variation in the properties of group II and VII elements from top to bottom with special emphasis on:

a) Reactions of group-II elements with oxygen and water.

b) Properties of halogens and uses of chlorine in water purification and as bleaching agent.

c) Reaction of chlorine with sodium hydroxide (disproportionation reactions of chlorine).

d) Uses of Nobel gases (group VIII).

GROUPS

- The vertical columns of elements in the periodic table are called groups. Each group represents number of valence electrons.
- All the elements in a group have similar properties and similar electronic configuration of valence shell
- There are eight groups that are shown by Roman numerals Ito VIII.
- Each group has two sub-groups A and B. A’ contains normal or typical elements while B contains transition elements.

ALKALI METALS

- Alkali metals have only one electron in the s' orbital of their valence shell (ns^1).
- All alkali metals lose one electron of the valence shell to form mono-positive ion (M), because their ionization energy values are very low, e.g. $M_1 \rightarrow M_1^+ + Ie^-$
- They form ionic compounds and show +1 oxidation state.

The electronic configuration and some physical constants of alkali metals are given in the table below

PROPERTIES	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Electronic configurations	$1s^2 2s_1$	$[Ne]3s^1$	$[Kr]4s^1$	$[Kr]5s^1$	$[Xe]6s^1$
Ionization energy (kJ/mol)	520	496	419	403	376
Electron affinity (kJ/mol)	– 60	– 53	– 48	– 47	– 46
Electro negativity	1.0	0.9	0.8	0.8	0.7
Atomic radius	123	158	203	216	235
Ionic radius of 1+ ion (pm)	60	95	133	148	169
Melting points (°C)	187.0	97.5	63.6	39.0	28.5
Boiling points (°C)	1325	889	774	688	690
Density gm/cm^3 at (20° C)	0.53	0.97	0.86	1.53	1.9
Heat of hydration (kJ/mol)	505	475	384	345	310

ALKALINE EARTH METALS

- Alkaline earth metals have two electrons in the s' orbital of their valence shell (ns^{-2})

- All alkaline earth metals lose their two electrons to form di-positive ions (M^{+2}) because their ionization energies are low, e.g. $M \rightarrow M^{2} + 2e^{-}$

- They form ionic compounds and show +2 oxidation states.

The electronic configuration and some physical constants of alkaline earth metals are given in the table.

PROPERTIES	Be	Mg	Ca	Sr	Ba
Atomic number	4	12	20	38	56
Electronic configurations	$1s^{2}2s_{1}$	$[Ne]3s^{1}$	$[Ar]4s^{1}$	$[Kr]5s^{1}$	$[Xe]6s^{1}$
Ionization energy (kJ/mol)	899	738	590	549	503
Electron affinity (kJ/mol)	540	230	156	168	52
Electro negativity	1.5	1.2	1.0	1.0	0.9
Atomic radius	89	136	147	191	198
Ionic radius of 2+ ion (pm)	31	65	99	113	135
Melting points (°C)	1289	649	839	769	725
Boiling points (°C)	2970	1107	1484	1384	1640
Density gm/cm^{3} at (20° C)	1.85	1.74	1.55	2.6	3.5
Heat of hydration (kJ/mol)	1337	1897	1619	1455	1250

HALOGENS

Group VII-A of the periodic table consists of five elements i.e.

(1) Fluorine (F)

(2) Chlorine (Cl)

(3) Bromine (Br)

(4) Iodine (I)

(5) Astatine (At)

They are called halogens. The term “halogen” is derived from two Greek words:

“hals” means salt and Gennan means lo form or generate’ Hence, they are literally the salt formers.

PROPERTIES	Fluorine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Electronic configurations	[He]$2s^2$ $2p^5$	[Ne] $3s^2$ $3p^5$	[Ar] $3d^{10}$, $4s^2$, $4p^5$	[Kr] $4d^{10}$, $5s^2$, $5p^5$
Physical appearance	Pale yellow gas	Greenish yellow gas	Red brown Liquid	Shiny grayish black solid
Ionization energy (kJ mole^{-1})	1681	1251	1140	1008
Electron affinity (kJ mole^{-1})	– 322	– 349	– 325	– 295
Electro negativity	4.00	3.00	2.8	2.5
Ionic radius of (pm)	136	181	196	216
Covalent radius (pm)	72	99	114	133
Melting point (°C)	– 220	– 101	– 7.2	114
Boiling points (°C)	– 188	– 34.6	58.8	184.4
Density (g/cm^3)	0.00181	0.00321	3.12	4.93
Oxidation states	– 1	– 1 + 1, +3, +5, +7	– 1, +1, +3, +5, +7	– 1, +1, +3, +5, +7
Bond energy (KJ mole^{-1}) (X – X)	154.80	242.67	192.46	150.6

ALKALINE EARTH METAL OXIDES

:

(i) **Solubility:** The solubility of alkaline earth metal oxides increases down the group due to decreasing lattice energy of oxides and charge density of cations, e.g. BeO, MgO are insoluble but CaO, BaO and SrO are soluble.

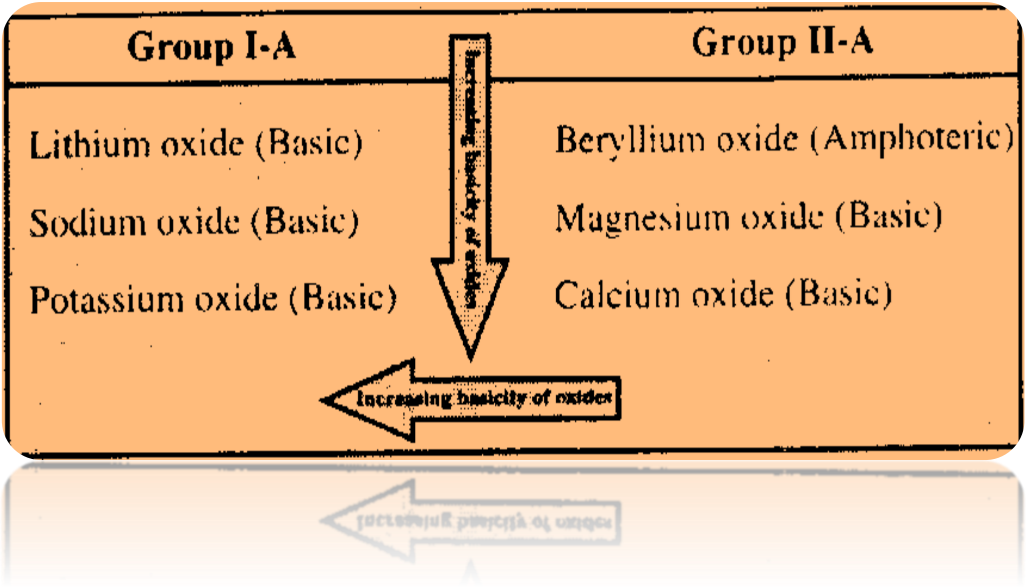
(ii) **Basic character**:

- The oxides of lower members of II-A are soluble and react with water to form corresponding Hydroxides.
- The Basic character of alkaline earth metal oxides increases down the group due to increasing dissociation and decreasing lattice energy of oxides.
- The tendency of II-A group oxides to form alkaline solution is relatively less than that of alkali metals due to high lattice energy of oxides.
- BcO oxides are the only oxide in II-A group that is amphoteric in nature.

$BcO + H_2SO_4 \rightarrow BeSO_4 + H_2O$

$BcO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$

b



Group I-A	Group II-A
Lithium oxide (Basic)	Beryllium oxide (Amphoteric)
Sodium oxide (Basic)	Magnesium oxide (Basic)
Potassium oxide (Basic)	Calcium oxide (Basic)

Increasing basicity of oxides

Increasing basicity of oxides

ALKALINE EARTH METAL HYDROXIDES:

a) Solubility:

- The solubility of alkaline earth metal hydroxides increases down the group due to decreasing lattice energy of hydroxides and decreasing charge to size ratio of cations.

- $Be(OH)_2$ is quite, insoluble, Mg(OH)2 is sparingly soluble and $Ca(OH)_2$ is more soluble.

b) Basic character:

- The basic character of alkaline earth metal hydroxides increases down the group due to increasing dissociation and decreasing lattice energy of hydroxides.

- Ca(OH) is more basic than Mg(OH)2 due to being more soluble.

- The basic character of alkaline earth metal hydroxides is less than that of alkali metal hydroxides due to greater lattice energy.

c) Thermal stability:

- Alkaline earth metal hydroxides are thermally unstable and decompose on heating to their oxides. E.g. $Mg(OH)_2$ and $Ca(OH)_2$ decompose on heating as follows.

$Mg(OH)_2 \rightarrow MgO + H_2O$

$Ca(OH)_2 \rightarrow CaO + H_2O$

Lime water:

- A saturated solution of $Ca(OH)_2$ is called lime water.

- It is used for the test of Carbon dioxide.

Milk of lime:

- A suspension of $Ca(OH)_2$ in water is called milk of lime.

- It is used for white wash.

Milk of Magnesia:

- A suspension of $Mg(OH)_2$ in water is called milk of magnesia.
- It is used to treat the acidity of stomach.

Note: When carbon dioxide is passed through lime water it turns milky due to formation of:

$CaCO_3 + CO_2 \rightarrow CaCO_3 + H_2O$

When excess of carbon dioxide is passed through lime water it turns due to formation of $Ca(HCO_3)_2$ which is soluble. $CaCO_3 + CO_2 + H_2O \rightarrow Ca(CHO_3)_2$

Properties of Halogens:

(1) First four members are common elements of the halogen family but Astatine is a rare halogen. It was first prepared artificially in 1940. All its known isotopes are radioactive and the longest lived isotope ${}^{210}_{85}\mathrm{At}$, has a half-life of 8.3 hours.

(2) First four members are stable and they resemble each other in physical and chemical properties, some of which have been given here.

(i) Physical State:

First two member fluorine and chlorine are gases, bromine is a liquid and iodine is a solid.

(ii) Colour:

All the halogens are coloured and there is a gradual darkening of colour from Fluorine to Iodine.

(a) Fluorine is a pale yellow gas.

(b) Chlorine is a greenish yellow gas

(c) Bromine is a red-brown liquid

(d) Iodine is a shiny grayish black solid

(iii) Odour:

They have irritating odour and they attack the skin. Bromine in particular causes burns which heal slowly.

(iv) Ionization energy:

They have high ionization energies. Anyhow, ionization energies decrease down the group. So, the tendency to form the positive ion goes on increasing down the group.

(v) Electron affinity:

They have large and negative electron affinity values. So they gain electrons readily to form uni negative ions.

(vi) Electrode potential:

They have large, positive standard electrode potentials. As a result, they have strong tendency to accept electron and hence act as good oxidizing agents. However their oxidizing ability decreases down the group.

(vii) Electronic configuration:

The electronic configuration of outer most shell of halogen is ns^2, np^5.

(viii) Atomic size:

Atomic radii, ionic radii and covalent radii increase down the group in the halogens. This is due to increasing number of shells and increasing shielding effect.

(ix) Melting and Boiling Points:

Their melting and boiling points gradually increase from top to bottom in the group. Down the group, Van Der Waal's forces increase due to increase in the polarizability which in turn is due to increase in the size of atom.

(x) Diatomic nature:

They exist in the form of diatomic molecules i.e. F_2, Cl_2, Br_2, I_2.

(xi) Oxidation state:

All halogens show '– 1' oxidation state. Except fluorine, rest of the halogens i.e. Cl, Br, I may also how +1, +3, +5, and +7 oxidation states as well.

(xii) Electro negativity:

Halogens have large values of electro-negativities. However, electro-negativities decrease down the group. Fluorine is the most electronegative element in the periodic table.

USES OF CHLORINE

Chlorine is used:

(i) For preparing bleaching powder

(ii) For preparing a number of antiseptics, weed killers and herbicides.

(iii) For preparing hydrochloric acid, a cheapest industrial acid

(iv) For preparing polyvinyl chloride (PVC) plastics.

(v) For preparing chloroform ($CHCl_3$) and carbon tetrachioride (CCl_4) which are used as solvents.

(vi) As a disinfectant in swimming pools and water treatment plants.

(vii) For preparing explosives.

(viii) For preparing poisonous gases like mustard gas and phosgene.

WATER ISINFECTION BY CHLORINE

Introduction:

Chlorine is frequently used to disinfect water. It is effective in killing pathogens which may cause serious water-burn diseases like

(a) typhoid and

(b) cholera

Disinfection by chlorine is also inexpensive.

Chlorinating Agent for Disinfection:

The most commonly used disinfectant is hypochlorous acid. HClO. It is not a stable molecule, hence it cannot be stored.

Generation of Hypochlorous Acid:

(i) It can be generated by dissolving molecular chlorine gas in water,

$Cl_2+H_2O \rightarrow HC1+HC1O$

(ii) It may also be generated by dissolving sodium and calcium hypochlorites in water.

$NaClO + H_2O \rightarrow NaOH + HClO$

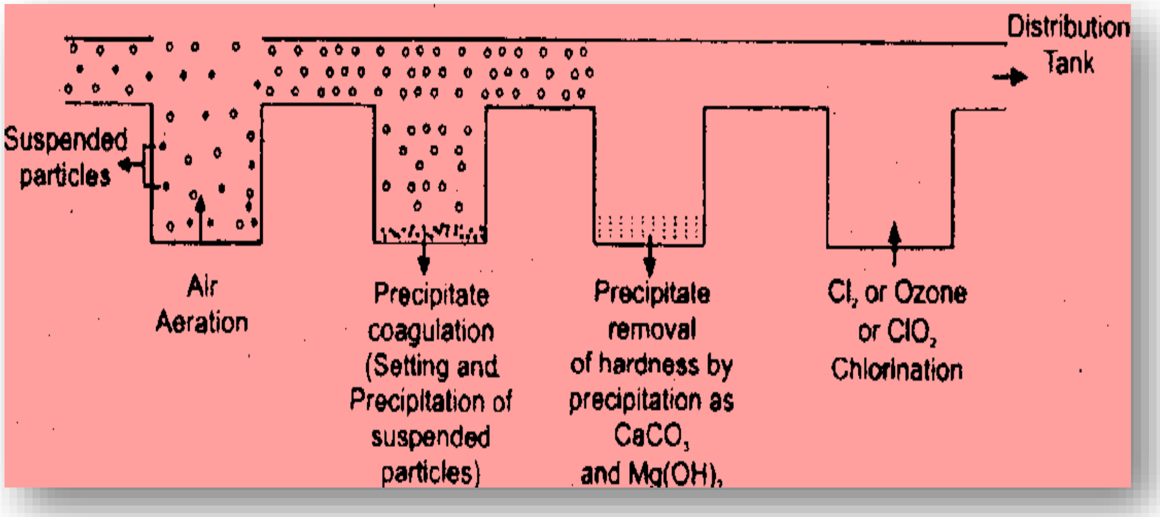
$Ca(ClO)_2 + 2H_2O \rightarrow C(OH)_2 + 2HC1O$

How HClO kills the microorganisms?

HClO a neutral covalent compound kills microorganisms readily by passing through their cell membranes. Generating HClO from sodium or Calcium hypochlorite avoids the:

(a) transportation (b) use of chlorine cylinders

Diagrammatic representation of purification of water:



Following diagram helps to understand how water undergoes the various stages of purification.

Harmful Effects of Chlorination:

Following are the some harmful effects of chlorination.

(a) Formation of chloramines:

HClO reacts with dissolved ammonia to form chloramines NH_2Cl, $NHCl_2$ and NCl_3.

$NH_3 + 3HClO \rightarrow NCl_3 + 3H_2O$

NCl_3 is a powerful eye irritant. The alkaline pH can prevent the formation of chloramines.

(b) Formation of chlorinated phenols:

If phenol is present in water, then chlorination of water produces chlorinated phenols.

Chlorinated phenols:

(i) Have offensive odour and taste

(ii) Are toxic as well

(c) Formation of chloroform:

Chloroform is formed when HClO reacts with organic matter (humic acid) dissolved in water.

Demerits of chloroform:

(i) It is a suspected liver carcinogen

(ii) It has negative reproduction and development effects in human beings

(iii) If chlorinated water is used for drinking, there may be risk of bladder and rectal cancer.

Alternative to chlorination:

In order to avoid the formation of toxic compounds with chlorine, some alternative substance can be used e.g.

(i) Ozone O_3

(ii) Chlorine dioxide, ClO_2

Bleaching Powder $CaOCl_2$ OR Ca(OCl)C:

Physical properties:

(i) It is a yellowish white powder

(ii) It has a strong smell of chlorine

Chemical properties:

(i) Oxidizing agent:

- It is a good oxidizing agent. This property is due to generation of hypochlorite ion ClO^{-1} when bleaching powder is dissolved in water.

$$CaOCl_2\ H_2O \xrightleftharpoons{H_2O} Ca_2 + C1 + ClO$$

This hypochlorite ion decomposes to release Oxygen and is responsible for oxidation of other substances.

(2) Reaction with Acid:

(i) When bleaching powder reacts with dilute acid in small quantity, hypochlorous acid is formed

$2CaOCl_2 + H_2SO_{4(Dd)} \rightarrow CaSO_4 + CaCl_2 + 2HClO$

(ii) When bleaching powder reacts with excess of acid (weak or strong) chlorine gas is evolved.

$CaOCl_2 + H_2SO_{4(Excess)} \rightarrow CaSO_4 + H_2O + Cl_2$

Available Chlorine:

The amount of chlorine which is set free during the reaction of bleaching powder with acid is called available chlorine.

Explanation:

The activity of bleaching powder is measured in terms of available chlorine. The average percentage of available chlorine in bleaching .powder is 35-40 percent. The bleaching action of bleaching powder is due to its oxidizing property.

3) Reaction with Halogen acids:

It oxidizes halogen acids to corresponding halogens:

$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$
$CaOCl_2 + 2HBr \rightarrow CaCl + H_2O + Br_2$
$CaOCl_2 + 2HI \rightarrow CaCl + H_2O + I_2$

4: Reaction with Ammonia:

It oxidizes ammonia to nitrogen.

$3CaOCl_2 + 2NH_3 \rightarrow 3CaCl_2 + H_2O + N_2$

5: Reaction with Hydrogen peroxide:

It oxidizes hydrogen peroxide to oxygen:

$CaOCl_2 + H_2O \rightarrow CaCl + H_2O + O_2$

6: Reaction with carbon dioxide:

It reacts with carbon dioxide and chlorine evolved:

$CaOCl_2 + CO_2 \rightarrow CaCO + Cl_2$

Uses of Bleaching powder:

Bleaching powder is used:

(i) For the laboratory preparation of Cl_2 and O_2

(ii) For the manufacture of chloroform $CHCl_3$

(iii) As a disinfectant and in the sterilization of water

(iv) For making un-shrinkable wool

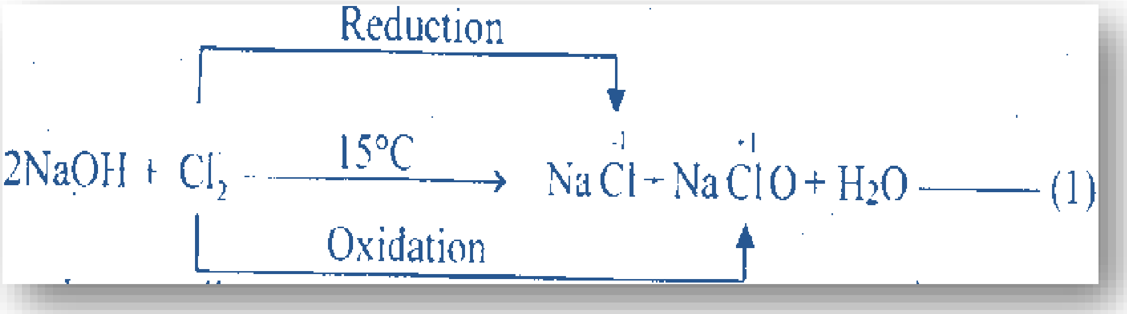
(v) For bleaching cotton, linen and paper pulp. Anyhow, delicate fabrics like wool, silk etc. cannot be bleached with it as these could be damaged by chlorine.

Reaction of chlorine with cold and hot NaOH:

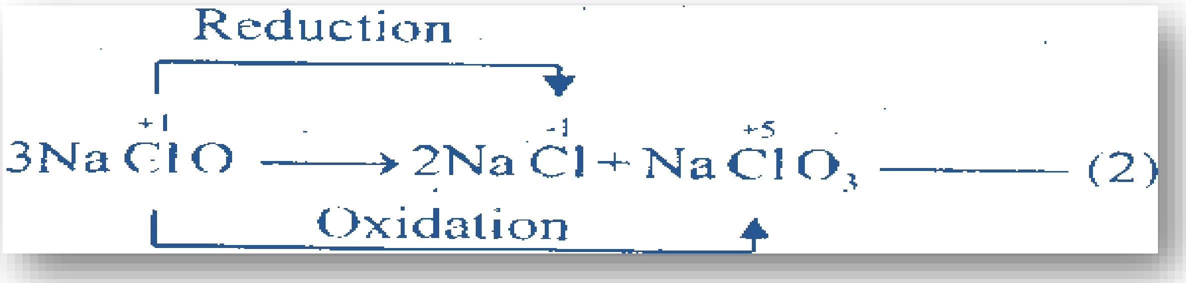
Disproportionation Reaction:

"A reaction in which an atom, ion or molecule is oxidized and reduced simultaneously is called disproportionation reaction". It is a self-oxidation-reduction reaction.

Chlorine reacts with NaOH at 15° C to give NaCl and NaClO. The chlorine Cl_2^0 is in zerooxidation state. It is reduced to + 1 in NaClO and is oxidized to + 1 in Na ClO.



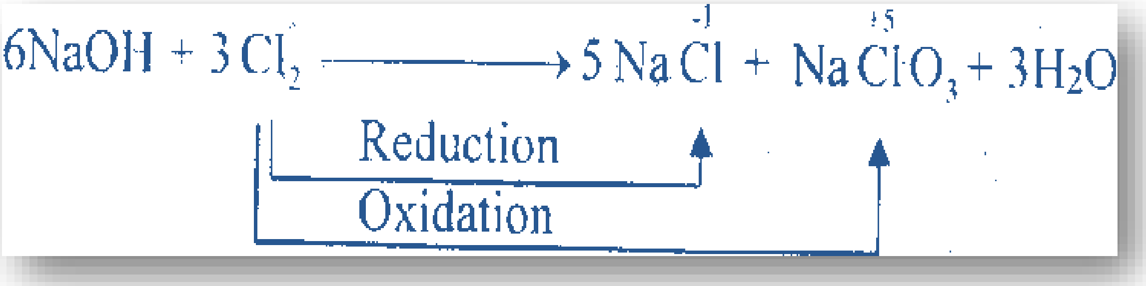
So, Cl_2^0 has undergone disproportionation reaction. When the above reaction is heated upto 70° C then NaClO is converted to NaCl and $NaClO_3$.



Now, NaClO has undergone disproportionation reaction. Multiplying eq (1) by 3 and then adding in eq (2), we get.

6NaOH + 3Cl2 → + 3NaClO + $3H_2O$

$3NaClO \rightarrow 2NaCl + NaClO_3$



$$6NaOH + 3Cl_2 \longrightarrow 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$$

APPLICATION OF NOBLE GASSES

Helium:

Helium is used:

(i) In weather balloons

(ii) For producing inert atmosphere in welding

(iii) In traffic signal lights

(iv) As a mixture of 80% helium and 20% oxygen by the sea divers for breathing

(v) As a cooling medium for nuclear reactors

Neon:

Neon is used:

(i) In making neon advertising signs

(ii) In high voltage indicators

(iii) In TV tubes

(iv) Neon and helium arc is used in making glass lasers

POINT TO PONDER: A radioactive tracer can be used to demonstrate the dynamic nature of the ………

Argon:

Argon is used:

(i) In electric light bulbs

(ii) In fluorescent tubes

(iii) In radio tubes

(iv) In Geiger counters to detect radioactivity

(v) For arc welding and cutting

Krypton:

Krypton is used:

(i) In filling fluorescent tubes

(ii) In flash lamps for high speed photography

Xenon:

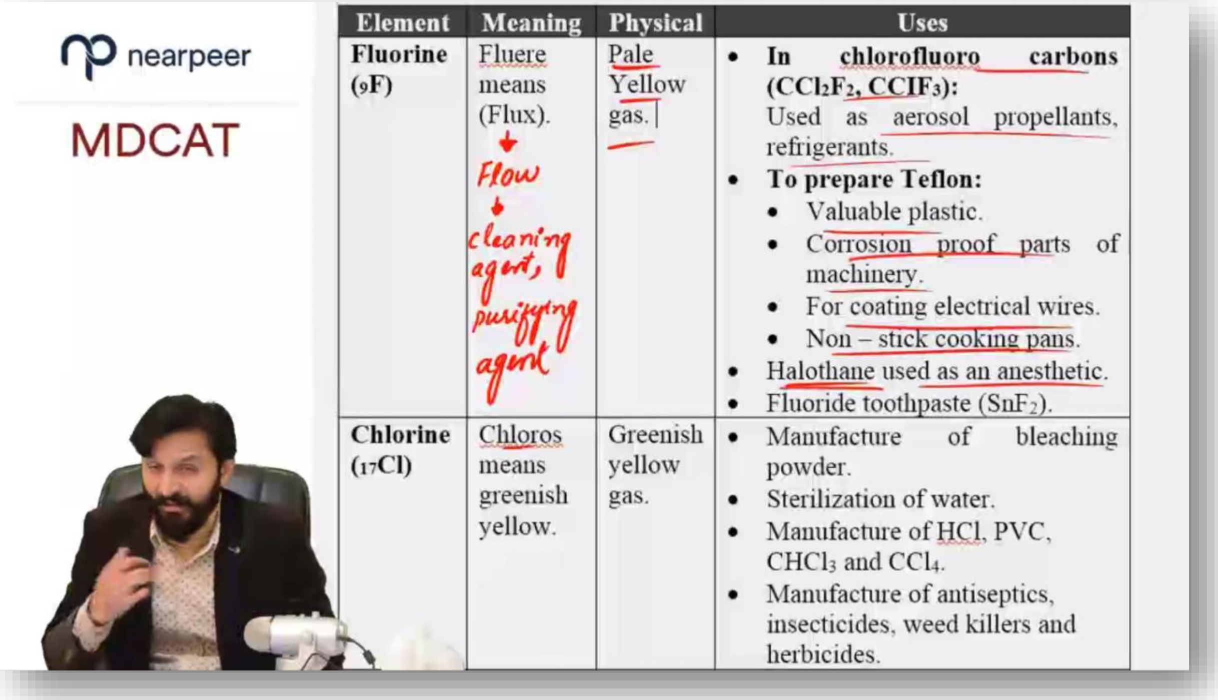
It is used in bacterial lamps.

Radon:

Radon is used:

(i) In radiotherapy of cancer

(ii) For earthquake prediction



Element	Meaning	Physical	Uses

Fluorine ($_9F$)	Fluere means (Flux).
	↓
	Flow
	↓
	cleaning agent, purifying agent
		Pale Yellow gas.	• **In chlorofluoro carbons (CCl_2F_2, $CClF_3$):** Used as aerosol propellants, refrigerants.
			• **To prepare Teflon:**
			  • Valuable plastic.
			  • Corrosion proof parts of machinery.
			  • For coating electrical wires.
			  • Non – stick cooking pans.
			• Halothane used as an anesthetic.
			• Fluoride toothpaste (SnF_2).

Chlorine ($_{17}Cl$)	Chloros means greenish yellow.	Greenish yellow gas.	• Manufacture of bleaching powder. • Sterilization of water. • Manufacture of HCl, PVC, $CHCl_3$ and CCl_4. • Manufacture of antiseptics, insecticides, weed killers and herbicides.

Video lectures of Unit 2(b) along with practice questions at www.nearpeer.org

PRACTICE EXERCISE (FOR UHS TOPIC)

1. Which of the following elements only forms normal oxide?

(A) LiO_2	(C) K_2O
(B) Na_2O	(D) Rb_2O

2. **Which of the following elements is the most reactive**

(A) Li (C) K

(B) Na (D) Rb

3. **Which of the following salts is not soluble in water?**

(A) LiF (C) $CaCl_2$

(B) KBr (D) $BaSO_4$

4. **Which of the following salt can't be decomposed on heating**

(A) Li_2CO_3 (C) $CaCO_3$

(B) Na_2CO_3 (D) $MgCO_3$

5. **Which of the following elements can only react with NaOH**

(A) Be (C) Ca

(B) Mg (D) Ba

6. **Which of the salts of IIA group is soluble in water?**

(A) $BeCO_3$ (C) CaC_2O_4

(B) $CaCO_3$ (D) $MgCO_3$

7. **Which of the bicarbonate decompose on heating?**

(A) $LiHCO_3$ (C) Ca(HCO)

(B) $NaHCO_3$ (D) all of the above

8. **Which of the following oxides is insoluble in H_2O?**

(A) BeO

(B) MgO

(C) CaO

(D) both a and b

9. Which of the following hydroxides is more soluble in water?

(A) $Be(OH)_2$

(B) $Mg(OH)_2$

(C) $Ba(OH)_2$

(D) $Ca(OH)_2$

10. Which of the following hydroxide do not decompose on heating?

(A) $Mg(OH)_2$

(B) $Ca(OH)_2$

(C) LiOH

(D) NaOH

11. Which of the following nitrate gives a nitrite on heating?

(A) $NaNO_3$

(B) $Mg(NO_3)_2$

(C) $Ca(NO_3)_2$

(D) $LiNO_3$

12. Highest bond energy exists for?

(A) F_2

(B) Br_2

(C) Cl_2

(D) I_2

13. The chemical name of bleaching powder is?

(A) Calcium chloride hypochlorite

(B) calcium chlorate

(C) calcium hypochlorite

(D) calcium perchlorate

14. Chlorine bleaches only in

(A) absence of acid

(B) absence of moisture

(C) presence of alkali

(D) presence of moisture

15. The anhydride of carbonic acid is

(A) C_2O_3 (C) CO_2

(B) CO (D) Na_2CO_3

16. The element which forms neutral as well as acidic oxide

(A) Si (C) C

(B) Ge (D) Pb

17. Which one of the following is not an alkali metals:

(A) Fr (C) Cs

(B) Rb (D) Ra

18. Which ion will have the maximum value of heat of hydration:

(A) Na^+ (C) Cs^+

(B) Ba^{+2} (D) Mg^{+2}

19. One of the following alkali metals is the most reactive which is that:

(A) Cs (C) K

(B) Na (D) Li

20. Which of the following statement/statements about Barium are true?

(A) Its compounds tend to be covalent rather than ionic

(B) It has oxidation number of +2 in most of its compounds.

(C) Its red in color.

(D) All of these

21. Which one is more basic in nature?

(A) $Ba(OH)_2$ **(B)** $Be(OH)_2$

(C) $Mg(OH)_2$ **(D)** $Ca(OH)_2$

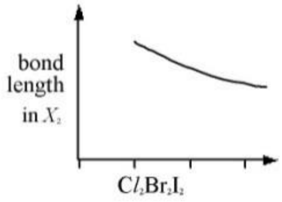
22. Which one of the following alkaline earth metal form peroxide when heated with oxygen at 600°C?

(A) Magnesium **(B)** Calcium

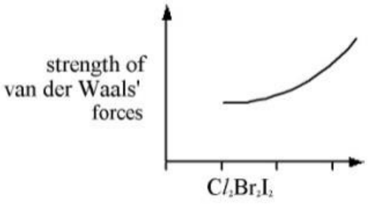
(C) Strontium **(D)** Barium

23. Which graph correctly describes a trend found in the halogen group?

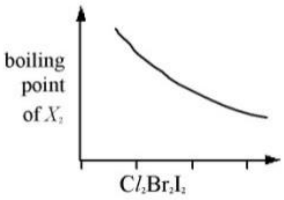
A



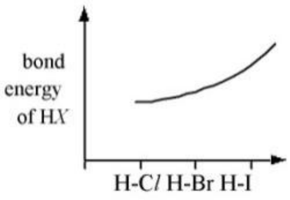
B



C



D



(A) A (B) B

(C) C (D) D

24. The element of group II-A that is quite resistant towards complete oxidation?

(A) Beryllium (B) Magnesium

(C) Calcium (D) Radium

25. Alkali and alkaline earth metals are:

(A) Oxidizing agent **(B)** Reducing agent

(C) Acidic **(D)** Amphoteric

26. Which one of the following elements burns in air to form an oxide which, when shaken with water, gives a solution with a pH greater than 7?

(A) Carbon **(B)** Magnesium

(C) Sulphur **(D)** Hydrogen

27. An element that has a high ionization energy and tends to be chemically inactive would most likely to be:

(A) An alkali metal **(B)** Transition elements

(C) A noble gas **(D)** A halogen

Which of the following pairs of compounds of alkaline earth metals have opposite solubility trend?

(A) Carbonates and sulphates **(B)** Oxides and hydroxide

(C) Nitrates and sulphates **(D)** Sulphates and hydroxides

28. **Compounds of alkaline earth metals are less soluble in water than the corresponding alkali metals because of their:**

(A) Increased covalent character **(B)** High ionization energies

(C) High lattice energy **(D)** None

29. When magnesium is burnt in air, magnesium oxide alongwith small amount of:

(A) Magnesium hydride **(B)** Magnesium nitride

(C) Magnesium nitrate **(D)** Magnesium sulphate

30. Milk of magnesia is:

(A) KOH **(B)** NaOH

(C) $Mg(OH)_2$ **(D)** $Ca(OH)_2$

31. The most soluble in water among the following is:

(A) BeO **(B)** MgO

(C) BaO **(D)** CaO

32. The correct order of radii of Ca, Ca^{1+}, Ca^{2+} is:

(A) $Ca > Ca^{2+} > Ca^{1+}$ **(B)** $Ca > Ca^{1+} > Ca^{2+}$

(C) $Ca^{2+} > ca^{1+} > Ca$ **(D)** $Ca^{2+} > Ca > Ca^{1+}$

33. The correct order of solubility of hydroxides of alkaline earth metals in water is:

(A) Be > Ca > Mg > Ba > Sr **(B)** Mg > Be > Ba > Ca > Sr

(C) Ba > Sr > Ca > Mg > Be **(D)** Mg > Ca > Ba > Be > Sr

34. A mixture of oxides of two elements of third period is dissolved in water. The solution is neutral. What is the mixture?

(A) Al_2O_3 + MgO **(B)** Na_2O + MgO

(C) Na_2O + P_4O_{10} **(D)** SO_3 + MgO

35. All pathogenic micro-organisms are killed by:

(A) CO **(B)** Cl_2

(C) H_2S **(D)** HCl

36. Cl_2 reacts with cold and dilute NaOH to form:

(A) Hypochlorite **(B)** Chlorite

(C) Chlorate **(D)** Per chlorate

37. Bleaching powder is an example of:

(A) Normal salt **(B)** Double salt

(C) Mixed salt **(D)** Complex

38. Fluorine is in group VIIA of periodic table. Its chemistry will most closely resembles that of:

(A) Argon **(B)** Boron

(C) Iodine **(D)** Sulphur

39. Which of the following has highest boiling point?

(A) He **(B)** Ne

(C) Ar **(D)** Kr

40. In the halogens, which is rarely found:

(A) Fluorine **(B)** Chlorine

(C) Iodine **(D)** Astatine

41. Vander Waal's forces are stronger in:

(A) F_2 **(B)** Cl_2

(C) Br_2 **(D)** I_2

42. The halogen which reacts with Xe:

(A) F_2 **(B)** Cl_2

(C) Br_2 **(D)** I_2

43. Consider the reaction:

$$3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

(A) Oxidation reaction **(B)** It is double displacement reaction

(C) Disproportionation reaction **(D)** Reduction reaction

44. Oxidation state of Ca in Ca(OCl)Cl (bleaching powder):

(A) +3 **(B)** +4

(C) +2 **(D)** +1

45. Which of the following is used in radiotherapy?

(A) Rn **(B)** Xe

(C) Kr **(D)** Ar

46. Neon is extensively used in:

(A) Cold storage units **(B)** Organic compounds

(C) Medicines **(D)** Coloured electric discharge lamps

47. With cold caustic soda, what are possible changes of oxidation state of Cl_2:

(A) 0 to +1, +3 **(B)** 0 to –1, +5

(C) 0 to +1, –1 **(D)** 0 to –1, +3

48. Fluorescent tubes:

(A) Rn **(B)** He

(C) Ne **(D)** None

49. Which of the following is used in arc welding?

(A) Ar

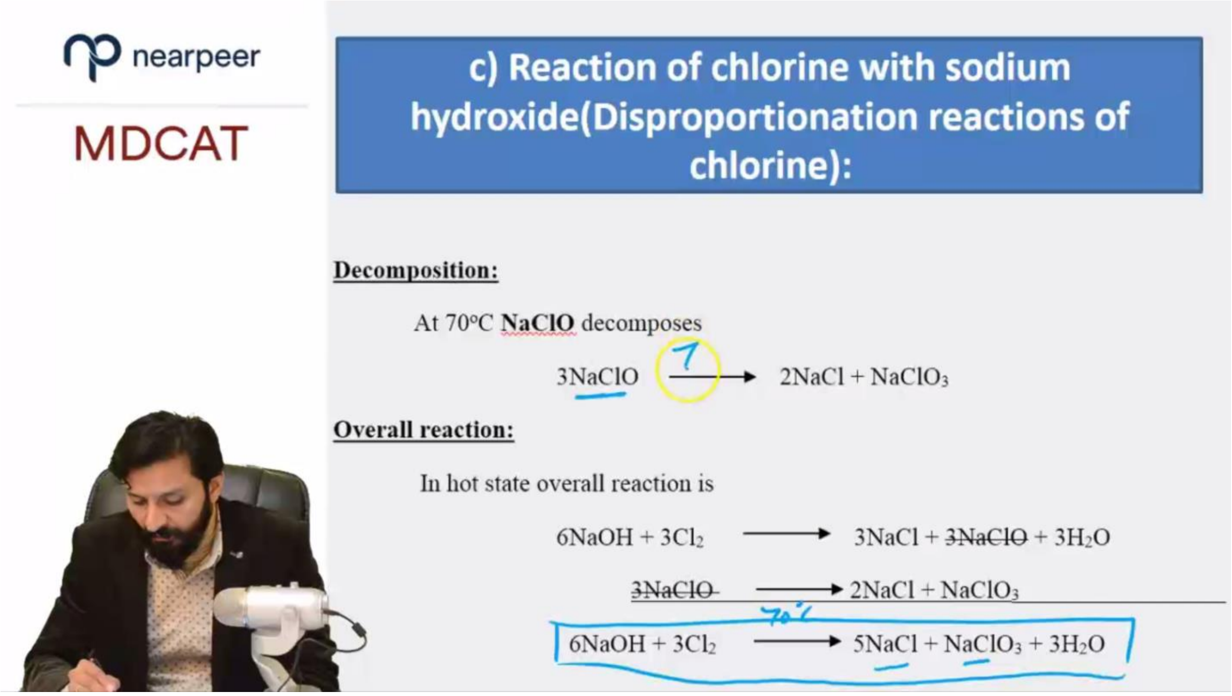
(B) Ne

(C) He

(D) Rn

ANSWER KEY

1	A	11	D	21	A	31	C	41	D
2	**D**	**12**	**C**	**22**	**D**	**32**	**C**	**42**	**D**
3	**D**	**13**	**A**	**23**	**B**	**33**	**B**	**43**	**A**
4	**D**	**14**	**D**	**24**	**A**	**34**	**C**	**44**	**C**
5	**B**	**15**	**C**	**25**	**B**	**35**	**D**	**45**	**C**
6	**A**	**16**	**C**	**26**	**B**	**36**	**B**	**46**	
7	**A**	**17**	**B**	**27**	**C**	**37**	**A**	**47**	**D**
8	**D**	**18**	**A**	**28**	**D**	**38**	**C**	**48**	**C**
9	**D**	**19**	**D**	**29**	**C**	**39**	**C**	**49**	**C**
10	**C**	**20**	**D**	**30**	**B**	**40**	**D**	**50**	**A**



c) Reaction of chlorine with sodium hydroxide(Disproportionation reactions of chlorine):

Decomposition:

At 70°C **NaClO** decomposes

$$3NaClO \xrightarrow{7} 2NaCl + NaClO_3$$

Overall reaction:

In hot state overall reaction is

$$6NaOH + 3Cl_2 \longrightarrow 3NaCl + \cancel{3NaClO} + 3H_2O$$

$$\cancel{3NaClO} \longrightarrow 2NaCl + NaClO_3$$

$$\boxed{6NaOH + 3Cl_2 \xrightarrow[]{70^\circ C} 5NaCl + NaClO_3 + 3H_2O}$$

Visit: www.nearpeer.org for recorded video lectures

UHS TOPIC III B

TRANSITION ELEMENTS

LEARNING OUTCOMES

In this topic, student should be able to:

Discuss the chemistry of transition elements of 3-d series with special emphasis on:

a) Electronic configuration

b) Variable oxidation states

c) Use as a catalyst

d) Formation of complexes

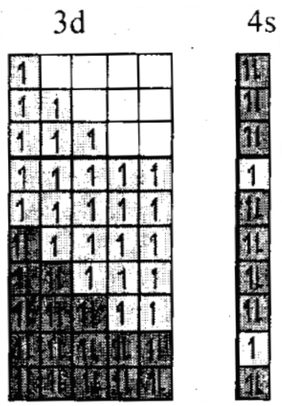
f) Colour of transition metal complexes

INTRODUCTION

Transition elements may be defined as those elements which have partially filled 'd' o 'f' sub shells in atomic state or in any of their commonly occurring oxidation states.

PROPERTIES

Transition elements usually show variable oxidation states, coloured compounds and form complex compounds.

3D - SERIES ELEMENTS		
ELEMENTS	**ELECTRONIC CONFIGURATION**	
Sc (21)	[Ar] $3d^1 4s^2$	
Ti (22)	[Ar] $3d^2 4s^2$	
V (23)	[Ar] $3d^3 4s^2$	
Cr (24)	[Ar] $3d^5 4s^1$	
Mn (25)	[Ar] $3d^5 4s^2$	
Fe (26)	[Ar] $3d^6 4s^2$	
Co (27)	[Ar] $3d^7 4s^2$	
Ni (28)	[Ar] $3d^8 4s^2$	
Cu (29)	[Ar] $3d^{10} 4s^1$	
Zn (30)	[Ar] $3d^{10} 4s^2$	

TYPICAL AND NON TYPICAL TRANSITION ELEMENTS

- Elements of group II-B(Zn, Cd and Hg), III-B(Sc, Y and La) are non-typical transition elements. Coinage metals (Cu, Ag and Au) are considered as transition elements as their d-orbitals are in process of completion in their ionic states.

→ Cu^{+2} ------------ $3d^9$

→ Ag^{+2} ------------ $4d^9$

→ Au^{+3} ------------ $5d^8$

- d-block elements are called outer transition elements while f-block elements are called inner transition elements.

GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS	
Characteristics	Description
Oxidation State	❖ Elements shows variable oxidation state +2, +3, ………. +7
	❖ It is due to the involvement of unpaired d-electrons in bonding in addition to outer s electrons.
	❖ Sc upto Mn oxidation states increases and after that it decreases
Colour	❖ When d-orbitals are involved in the bonding they split up into two energy levels. One set has a higher energy than the other.
	❖ d-d transition occur when light energy is absorbed by electrons of lower atomic orbital
	❖ Each ions absorb a particular set of wavelength and transmits the remaining set of wavelength giving colour
	❖ Energy difference between two sets of d-orbitals varies from ion to ion

POINT TO PONDER: Many important reactions are catalyzed by ………

Transition metals ion are often coloured because electrons move between non degenerate ……….

COMPLEX COMPOUNDS

:

The compound containing the complex molecules or complexions and capable of independent existence are called coordination compounds complexes.

A complex compound may contain:

(i) A simple cation and a complex anion

(ii) A complex cation and a simple anion

Component of Complex Compound:

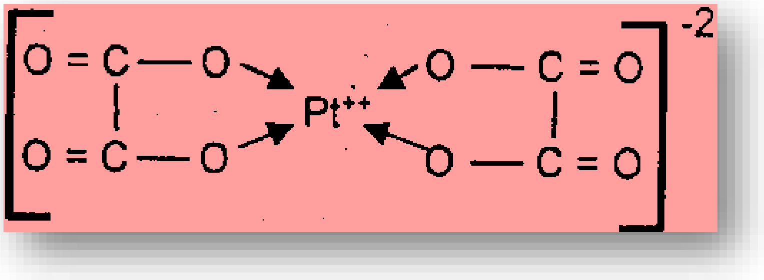
Component	Description
Central Metal Atom or Ion	Metal atom or metal ion surrounded by number of ligands in the complex compound
Ligand	Ion, atom or neutral molecule that donates electron pairs to central metal atom/ion
	Ligand with two donor atoms is called bi-dentate
Co-ordination Number	Thenumberoflonepairofelectronsprovidedbyligandstocentralatomorion
Co-ordination Sphere	The central metal atom or ion along with ligands is called co-ordination sphere
Charge on co-ordination sphere	Algebraic sum of charges present on central metal ion and the total charge on the ligands

CHELATES

:

A complex compound, in which one or more than one ring is formed due to donation of electrons by poly dentate ligand e.g. $[Pt(C_2O_4)_2]^{2-}$

$[Pt(C_2O_4)_2]^{-2}$ Dioxalato-platinate (II) ion



Nomenclature:

The IUPAC rules for naming the complex compounds are as follows:

(i) Cations are named before anions

(ii) In naming the coordination sphere, ligands are named in alphabetical order regardless of the nature and number of each followed by the name of central metal ion

(iii) The prefixes di, tri, tetra, penta, hexa, etc, are used to specify *thy* number of coordinated same ligand

(iv) The names of anionic ligands end in suffix "O" e.g. hydroxo, OH^-carbonato CO_3^{-2}

(v) The names of neutral ligands are usually unchanged, e.g. for NH_3 ammine and for H_2O, aqua etc.

(vi) The suffix 'ate' comes at the end of the name of metal if the co-ordination sphere is negative otherwise it remains unchanged

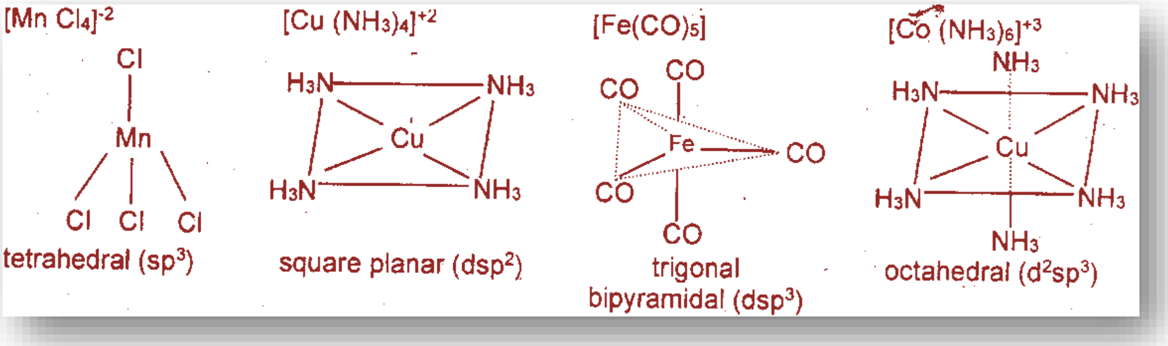
(vii) The oxidation number of the metal ion is represented by a Roman numeral in parenthesis following the name of the metal

Examples:

$K_4[Fe(CN)_6]$ Potassium hexacayno ferrate(II)

$[PtCl(NO_2)(NH_3)_4]SO_4$ Tetraammine chloronitro-platinum (IV) sulphate

Geometry of Complex Compound:



Use as a Catalyst:

The following reactions are the bare minimum examples of transition metals acting as catalysts that everyone studying chemistry and general science should know. Catalysts are written over the reaction arrow, sometimes with (cat) after the formula, to distinguish them from reactants and products.

The Haber's Process:

This is one of the best known reactions involving a transition metal catalyst. It is the formation of ammonia from nitrogen and hydrogen using iron as the catalyst. This is a heterogeneous system.

Contact Process:

This reaction is part of the production of sulphuric acid the reaction between sulphur dioxide and oxygen to form sulphur trioxide is catalyzed by vanadium (V) oxide, V_2O_5. This is a heterogeneous system.

Hydrogenation (Reduction):

Raney nickel, which is very finely divided nickel powder, is a catalyst for the addition of hydrogen across $C = C$ and $C \equiv C$ bonds. Finely divided platinum, and finely dividedpalladium also catalysis this sort of reaction but are a hit expensive this is a heterogeneous system.

The margarine industry uses the above type of reaction to convert unsaturated vegetable oils into higher metal point saturated fats i.e. margarine.

Decomposition:

Manganese dioxide catalysis the decomposition of hydrogen peroxide, lots of other things catalyze this reaction too, but MnO_2 is one of the best. This is a heterogeneous system.

PRACTICE EXERCISE

1. **Which is non-typical transition elements:**

(A) Cr (B) Mn

(C) Zn (D) Fe

2. **In which compound, the oxidation state of Mn is highest:**

(A) K_2MnO_4 (B) $KMnO_4$

(C) MnO (D) MnO_2

3. **The trace metal present in insulin is:**

(A) Mn (B) Co

(C) Fe (D) Zn

4. **The hybridization of Ni in $[Ni(CN)_4]^{-2}$ ion is:**

(A) sp^3 (B) dsp^3

(C) d^2sp^3 (D) dsp^2

5. **Which of the following cation has maximum unpaired electrons:**

(A) Ni^{+2} (B) Co^{+2}

(C) Mn^{+2} (D) Fe^{2+}

6. **Which is the configuration of Cr:**

(A) $3d^4\ 4s^2$ (B) $3d^5\ 4s^1$

(C) $3d^6\ 4s^1$ (D) $2d^1\ 4s^2$

7. The black image on an exposed and developed photographic film is composed of:

(A) Ag (B) Ag_2O

(C) AgBr (D) $Ag[(SrO_3)_2]^-$

8. The binding energy of transition elements depend upon:

(A) No. of electron pair (B) No. of unpaired electrons

(C) No. of neutron (D) No. of proton

9. No. of electron pairs accepted by the central atom in a transition metal complex is called:

(A) Co-ordination sphere (B) Co-ordination complex

(C) Co-ordination number (D) Chelate

10. Group VIB of transition elements contains:

(A) Zn, Cd, Hg (B) Fe, Ru, Os

(C) Cr, Mo, W (D) Mn, Te, Re

11. Which of the following is a typical transition metal:

(A) Sc (B) Y

(C) Hg (D) Co

12. Co-ordination number of Pt in $[PtCl(NO_2)(NH_3)_4]^{2-}$ is:

(A) 2 (B) 4

(C) 1 (D) 6

13. f-block element are called:

(A) Typical transition elements (B) Non-typical transition elements

(C) Outer-transition elements (D) Inner transition elements

14. The colour of transition metal complexes is due to:

(A) d-d transition of electrons (B) Paramagnetic nature

(C) Ionization (D) Loss of s-electron

15. Which of the following do not have variable valency?

(A) Cobalt (B) Iron

(C) Manganese (D) Zinc

16. Which of the following exist as liquid at room temperature?

(A) Aluminium (B) Mercury

(C) Copper (D) Iron

17. Type of hybridization in PCl_5 is:

(A) sp^3 (B) sp^2

(C) dsp^2 (D) dsp^3

18. Which of the following is bidentate ligand?

(A) Ammine (B) Carboxyl

(C) Oxalato (D) Acetato

19. Which of the following is not neutral ligand?

(A) NH_3 (B) H_2O

(C) CO (D) CN^-

20. The diamagnetic cation among the following is:

(A) Sc^{+3} (B) Fe^{+3}

(C) Co^{+2} (D) Ni^{+}

21. Which element has three unpaired electrons?

(A) Al (B) Sc

(C) Cr (D) Ni

22. The geometry of which complex is square planar:

(A) $[MnCl_4]^{2-}$ (B) $[Cu(NH_3)_4]^{2+}$

(C) PCl_5 (D) $[Co(NH_3)_6]^{3+}$

23. Which one of the following sets has coinage metals in it?

(A) Cu, Hg, Au (B) Cu, Ag, Au

(C) Ag, Au, Hg (D) Cu, Fe, Au

24. Geometry of complex compound depends upon:

(A) No of ligands (B) No of chelates

(C) Hybridization of central metal (D) All the above

25. When a compound of transition element is dissolved in a solution, it produces:

(A) Simple ion (B) Complex ions

(C) Double salt (D) Strong anions

26. In the silver ammine complex $[Ag(NH_3)_2]^{+}$, the co-ordination number of Ag is:

(A) Zero (B) One

(C) Two (D) Three

27. Co-ordination number of Fe in $K_4[Fe(CN)_6]$ is:

(A) 2
(B) 4
(C) 6
(D) Zero

28. The following is not a monodentate ligand:

(A) Ammonia
(B) Oxalate
(C) Carbonyl
(D) Cyanide

29. For $sp^3 d^2$ hybridization, the expected shape is:

(A) Tetrahedral
(B) Square planar
(C) Trigonal bipyramidal
(D) Octahedral

30. The central atom along with ligand is called:

(A) Complex ion
(B) Ligand
(C) Co-ordination sphere
(D) Complex compound

31. An ion with maximum paramagnetic character:

(A) Ni^{+2}
(B) Fe^{+2}
(C) Fe^{+3}
(D) Mn^{+3}

32. For transition elements in ionic state, paramagnetic character and covalent radii along the period:

(A) Increases
(B) Decreases
(C) Remains same
(D) Variable trend

33. Which of the following d-block elements can show highest oxidation number in its compounds?

(A) Cr

(B) Cu

(C) Mn

(D) Ni

34. What is the configuration of Cr?

(A) $3d^4\ 4s^2$

(B) $3d^5\ 4s^1$

(C) $3d^6\ 4s^1$

(D) $2d^1\ 4s^2$

35. Coordination number of Pt in $[PtCl(NO_2)(NH_3)_4]^2$ is:

(A) 2

(B) 4

(C) 1

(D) 6

36. The least paramagnetism is shown by:

(A) V^{3+}

(B) Cu^{2+}

(C) Cr^{3+}

(D) Mn^{2+}

37. The general configuration of transition element:

(A) $(n-1)\ d^{1-5}$

(B) $(n-1)\ d^{1-10}\ ns^1$

(C) $(n-1)\ d^{1-10}\ ns^{1-2}$

(D) $(n-1)\ d^{1-10}\ ns^{0-2}$

38. Which is not true in case of transition metal?

(A) Variable oxidation state

(B) Complex formation

(C) Partially filled d-orbitals

(D) All ions are colourless

39. Which would be coloured cation?

(A) Sc^{2+}

(B) Ni^{2+}

(C) Cr^{3+} (D) All of these

40. Which of the following is a chelate?

(A) $[Pt(Py)_4]Cl_2$ (B) $Na_3[Fe(CN)_6]$

(C) $Na[Co(C_2O_4)_2(NH_3)_2]$ (D) $[Ni(CO)_4]$

41. Octahedral:

(A) Triammine trinitroobalt (III)

(B) Potassium hexacyano ferrate (II)

(C) Tetrammine chloronitro platinum (IV) sulphate

(D) All of these

42. Which of the following is more stable then others?

(A) d^5 (B) d^{10}

(C) d^4 (D) d^1

43. How many coordinate covalent bonds are there in tetra ammine copper (II) sulphate?

(A) 2 (B) 4

(C) 8 (D) 10

44. dsp^2 hybridization is present in complexes:

(A) Tetrahedral (B) Octahedral

(C) Square planar (D) Tetragonal

45. The oxidation number of Fe in $[Fe(H_2O_3)(CN)_3]$ is:

(A) +1 (B) +2

(C) +3 (D) +4

46. Which of the following has the strongest shielding effect?

(A) Half-filled d-subshell (B) Completely filled d-subshell

(C) Outermost d-subshell (D) Inner f-subshell

47. Which of the following is a polydentate ligand?

(A) H_2O (B) NH_3

(C) Ethylenediamine (D) Pyridine

48. Which of the following is correct?

(A) $[Fe(NH_3)_4Cl_3]$ (B) $Fe[Fe(CN)_6]$

(C) $[Co(SO_4)_2(NH_3)_4]$ (D) $[Cu(NH_3)_2(OH)_2]$

49. Which of the following is paramagnetic atom?

(A) $_{26}Fe$ (B) $_{24}Cr$

(C) $_{29}Cu$ (D) All of these

50. If a complex absorb red light then the color of complex most likely to be

(A) Red (B) Green

(C) Yellow (D) Orange

ANSWER KEY

1	C	11	D	21	D	31	C	41	D
2	**B**	**12**	**D**	**22**	**B**	**32**	**D**	**42**	**B**
3	**C**	**13**	**D**	**23**	**B**	**33**	**C**	**43**	**B**
4	**A**	**14**	**A**	**24**	**D**	**34**	**B**	**44**	**C**
5	**C**	**15**	**D**	**25**	**B**	**35**	**D**	**45**	**C**
6	**A**	**16**	**B**	**26**	**C**	**36**	**B**	**46**	**B**
7	**A**	**17**	**D**	**27**	**C**	**37**	**C**	**47**	**C**
8	**B**	**18**	**C**	**28**	**B**	**38**	**D**	**48**	**D**
9	**C**	**19**	**D**	**29**	**D**	**39**	**D**	**49**	**D**
10	**C**	**20**	**A**	**30**	**C**	**40**	**C**	**50**	**B**

UHS TOPIC IV B

ELEMENTS OF BIOLOGICAL IMPORTANCE

LEARNING OUTCOMES

In this topic, student should be able to:

a) Describe the inertness of Nitrogen

b) Manufacture of ammonia by Haber's process

c) Discuss the uses nitrogenous fertilizers

e) Describe the presence of sulphur dioxide in the atmosphere which causes acid rain

c) Describe only manufacturing of Sulphuric acid by contact method

INERTNESS OF NITROGEN

Molecular nitrogen is inert under ordinary conditions existing as diatomic molecules, N_2. The presence of a very strong triple covalent bond in the N_2 molecule renders it un-reactive under normal circumstances. Nevertheless, nitrogen gas does react with the alkali metal lithium to form compound lithium nitride (Li_3N), even under ordinary conditions. Under high pressures and temperatures and with the right catalysts, nitrogen becomes more reactive; the Haber's process uses such conditions to produce ammonia from atmospheric nitrogen.

Inert atmospheres consisting of gases such as argon, nitrogen, or helium are commonly used in chemical reaction chambers and in storage containers for air-sensitive or water-sensitive substances, to prevent unwanted side-reactions of these substances with air and water. The extremely strong bond in elemental nitrogen dominates nitrogen chemistry, causing difficulty for both organisms and industry in breaking the bond to convert the N_2 into useful compounds, but at the same time causing release of large amounts of often useful energy when the compounds bum, explode, or decay back into nitrogen gas.

Synthesis of Ammonia by Haber's Process:

Formation of ammonia gas from nitrogen and hydrogen gas is reversible process. We apply the concept of equilibrium constant to maximize the yield of ammonia by keeping in view the chemical reaction for the formation of ammonia.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92.46\ kJ/mol$$

(i) By continual removal of ammonia, reaction will move in forward direction.

(ii) Increase in pressure decreases the volume that causes the reaction to proceed in forward direction and yield of ammonia increases.

(iii) Decrease in temperature favours exothermic reactions. As forward reaction is exothermic, the decrease in temperature favours the reaction in forward direction. So, high pressure, low temperature and continual removal of ammonia increase the yield of ammonia.

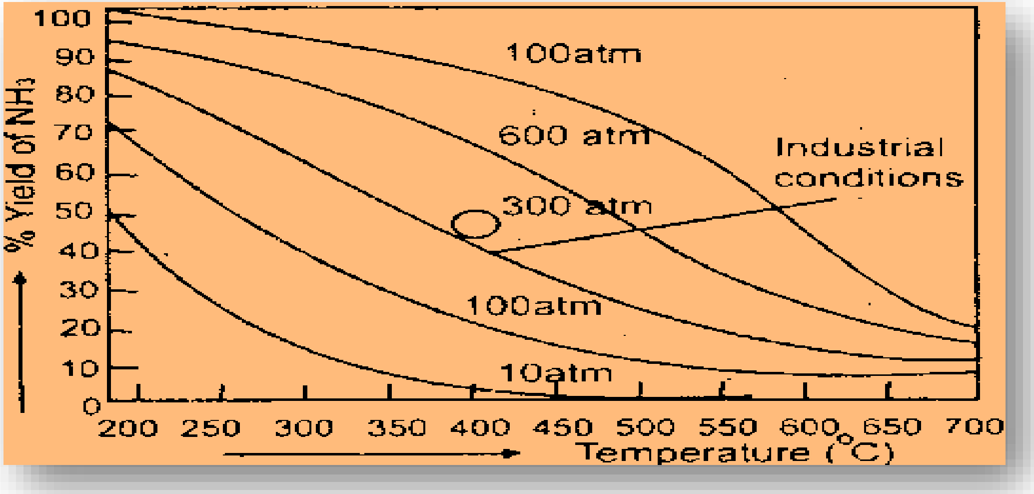
Rate of Formation and Yield:

The yield of ammonia is favoured at low temperature, but at low temperature rate of reaction is very slow and process becomes uneconomical. Temperature is raised to a moderate value and catalyst is added to increases the rate of reaction. Without a catalyst, faster rate is only achieved .at higher temperature where yield of ammonia decreases.

Optimum Conditions for the Reasonable Yield of Ammonia:

(i) Temperature around 673 K (400° C) Pressure about 200-300 atm. Pieces of iron crystals embedded in fused mixture of MgO, Al_2O_3 and SiO_2. These conditions will optimize the yield of ammonia. Table below shows the effect of rise in temperature on K_c value. At 200 C^o k, value is very high but rate is too slow to make the process economical, figure shows percentage yield of NH_3 versus temperature at five different, operating pressures. At very high pressure and low temperature, the yield of ammonia is high but rate of formation is slow. So industrial conditions are denoted by circle are between 200-300 atm pressure and 400° C.

T(K)	K_c
200	7.17×10^{15}
300	2.69×10^{8}
400	3.94×10^{1}
500	1.72×10^{2}
600	4.53×10^{0}
700	2.96×10^{-1}
800	3.69×10^{-2}



ELEMENTS OF BILOGICAL IMPORTANCE

Removal of Ammonia:

The equilibrium mixture has 35 % by volume of M 90 NH_3. The mixture is cooled by refrigeration coils until ammonia condenses (RP = –33.4° C) and is removed. The boiling points of $N_{2(g)}$ and $H_{2(g)}$ are very low and they remain in gas phase and are recycled by pumps back into reaction chamber.

Note: H_2SO_4 is a king of chemicals. A country's industrial progress is measured by the amount of H_2SO_4 manufactured each year.

Application of Haber's Process and Uses of Ammonia:

- Nearly 13 % of all nitrogen fixation on earth is accomplished through Haber's process.
- This process produces 110 million tons of ammonia annually
- About 80 % of NH_3 is used for the production of fertilizers.
- Ammonia is also used in the manufacture of explosives.

It is also used for the production of nylon and other polymers

Nitrogenous Fertilizers:

These fertilizers provide nitrogen to plants

Importance

These fertilizers are required because nitrogen is required by plants

- During early stage of plant grow.

→ Development of stems

→ Development of leaves

- Nitrogen is the main constituent of proteins
- It imparts green colour to the leaves
- It enhances the yield and quality of the plant

Examples:

(i) Ammonia

(ii) Urea

(iii) Ammonium Nitrate

(iv) Ammonium Sulphate

(v) Calcium nitrate

(vi) Calcium cyanamide

(vii) Calcium ammonium nitrate

(viii) Ammonium phosphate

(ix) Ammonium chloride

A) Ammonia (NH_3):

- It is used only in liquid state
- It is used in anhydrous form
- It is directly applied to the soil by injecting about 6 inches under the surface of soil to avoid it form seeping out.

%of Nitrogen:

It contains about 82 % nitrogen

C) Urea:

- It is high quality nitrogenous fertilizer
- It is most widely used nitrogen fertilizer in Pakistan
- It is most concentrated solid nitrogen fertilizer

% of Nitrogen:

It contains 46 % nitrogen

Manufacturing:

The following steps are involved in the manufacture of urea

(i) Preparation of Hydrogen gas:

- Water gas method

$CH_4 + H_2O \rightarrow H_2 + CO$

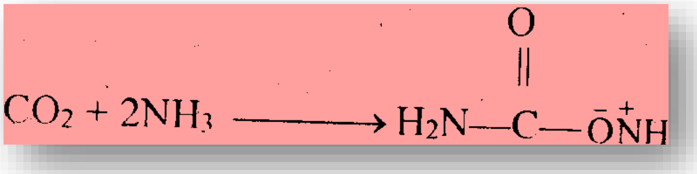
(ii) Preparation of Ammonia:

- Haber's Process

$$N_2 + 3H_2 \xrightarrow[200\ \text{atm}.450^{o}\ C]{Fe+MgO+AI_2O+SiO} 2NH_3$$

(iii) Preparation of Ammonium Carbonate:

Gaseous CO_2 is mixed with ammonia in the volume ratio of 1 : 2 in a reactor to produce ammonium carbonate.



$$CO_2 + 2NH_3 \longrightarrow H_2N - \overset{\overset{O}{\|}}{C} - \bar{O}\overset{+}{N}H$$

(iv) Preparation of Urea / Dehydration of Ammonium Carbonate:

Dehydration of ammonium carbonate gives urea

O O

| | | |

$NH_3 – C – C\ NH_4 \rightarrow H_3N – C – NH_4 + H_2O$

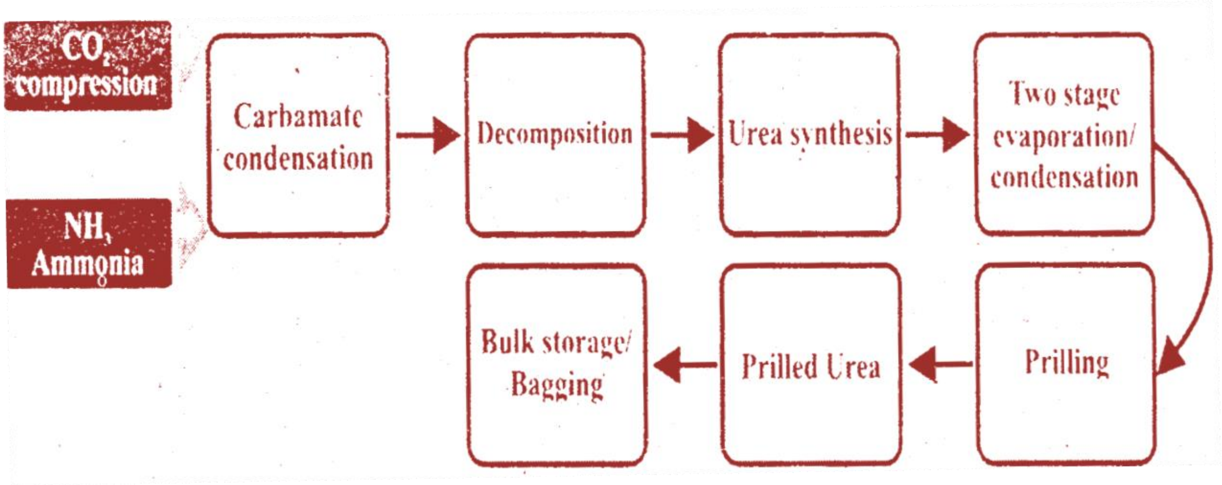
(v) Concentration of Urea Solution:

The urea solution is concentrated in an evaporation section where water is evaporated by heating with steam under vacuum in two evaporation stages.

This results in the formation of 99.7 % molten urea.

(vi) Prilling:

The molten urea is sprayed at the prilling tower by means of prilling bucket where it is cooled by the air rising upward; molten droplets solidify into the form of prills. Urea prills thus produced arc either sent to the bagging section or to the bulk storage.



FLOW SHEET DIAGRAM FOR MANUFACTURE OF UREA

b) Ammonium nitrate (NH_4NO_3):

- It is hygroscopic in nature
- It is not useful for paddy rice

REASON: Microbial bacteria in the flooded fields decompose NH_4NO_3 to nitrogen gas.

- It is also used in combination with lime stone.

% of Nitrogen:

It contains 33 - 33.5 % nitrogen

Manufacturing:

It is manufactured by the neutralization between ammonia and nitric acid.

$NH_{3(g)} + HNO_{3(g)} \rightarrow NH_4NO_{3(s)}$

After this reaction the following steps are followed

(i) **Evaporation**:

Evaporation results in the formation of solid ammonium nitrate.

(ii) Fusion of solid ammonium nitrate

(iii) Prilling

The molten ammonium nitrate is then sprayed down from a tall tower. The falling droplets are dried by upward current of air. Ammonium nitrate solidifies as tiny hard pellets. This is called prilling.

ACID RAIN (ACID DEPOSITION):

Acid rain which now-a-days is termed as acid deposition was first discovered by Angus Smith in Great Britain in the mid-17th century. However, this phenomenon gained importance as a serious environmental problem in 1950's.

pH of acid rain:

The pH of unpolluted rain water should be 5.6. The rain water having pH less than 5 is considered truly acidic.

Sources of acid rain:

The oxides of carbon; nitrogen and sulphur are responsible for acid rain.

(i) Due to the presence of CO_2 in the atmosphere the natural rain itself forms carbonic acid.

$CO_2 + H_2O \rightarrow H_2CO_3$

(ii) NO_2 in the atmosphere combines with water to form nitric acid.

$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$

(iii) SO_2 and SO_3 react with water to give sulphuric acid

$SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$

$SO_3 + H_2O \rightarrow H_2SO_4$

These acids get mixed with rain. The acid deposition includes both wet (rain. snow. fog) and dry acidic deposition.

(iv) In some countries due to release of hydrogen chloride gas (HCl) by volcanic eruption there is temporary acid rain.

Adverse Effects of acid rain:

(i) Acidification of the soil and rocks can leach metals like Al, Hg, Pb and Ca. These metals are discharged into water bodies. These heavy metals are accumulated in the fish and are health hazards for humans and birds as they eat these fish.

(ii) The high concentration of aluminum is harmful for fish as it clogs the gills thus causing suffocation.

(iii) Acidification of the soil can also leach nutrients. It will damage leaves, plants and growth of forest.

(iv) The acid rain also damages building materials such as:

  (a) Steel

  (b) Paint

  (c) Plastic

  (d) Cement

  (e) Masonry work

  (f) Sculptural work

(g) Material especially of marble and lime stone

POINT TO PONDER: Sulphur dioxide is the anhydride of sulphurous acid. Which is a …

MANUFACTURE OF SULPHURIC ACID

On large scale it can be manufactured by following two processes:

  (i) Contact process

  (ii) Lead Chamber Process

Contact Process:

It has four major parts.

(i) Sulphur burners
(ii) Purifying Unit
(iii) Contact Tower
(iv) Absorption Unit

Principle:

SO_2 obtained by burning sulphur or iron pyrites is oxidized to SO_3 in the presence of V_2O_5 which acts as a catalyst. SO_3 formed is absorbed in concentrated H_2SO_4 to form oleum. "Oleum" ($H_2S_2O_7$) formed can be converted into sulphuric acid of any strength by mixing adequate quantities of water.

Conditions to get maximum yield of SO_3:

(i)	Temperature	400 – 500° C
(ii)	Pressure	2 atm
(iii)	Concentration	continuous supply of oxygen
(iv)	Catalyst	V_2O_5

Sulphur Burners:

Sulphur or iron pyrites are burnt in excess of air to produce SO_2.

$S(s) + O_{2(g)} \rightarrow SO_{2(g)}$

$4FeS_{2(s)} + HO_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$

Purifying Unit:

SO_2 is purified from impurities like dust and arsenic oxide, to avoid poisoning of the catalyst. Purifying unit consists of the following parts.

(i) Dust remover:

Steam is injected to remove dust particles from the gases

(ii) Cooling Pipes:

The gases are passed through lead pipes to cool them to 100° C

(iii) Scrubbers:

The cooled gases are washed by a spray of water, SO_2 is not soluble' in water at high temperature

(iv) Drying Tower:

The moisture of gases is removed by concentrated H_2SO_4 trickling down through the coke filled in this tower.

(v) Arsenic Purifier:

Arsenic oxide is then removed by passing the gases through a chamber provided with shelves packed with freshly prepared ferric hydroxide.

(vi) Test Box:

In this box a beam of light is introduced which indicates the presence or absence of solid particles. If solid particles are present, then gases are sent back for further purification.

c) Contact Tower:

Preheated gases at 400 – 500° C are passed through vertical iron columns packed with the catalyst V_2O_5. Here SO_2 is oxidized to SO_3.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons[V_2O_5]{400\text{-}500^\circ C} 2SO_{3(g)}$$

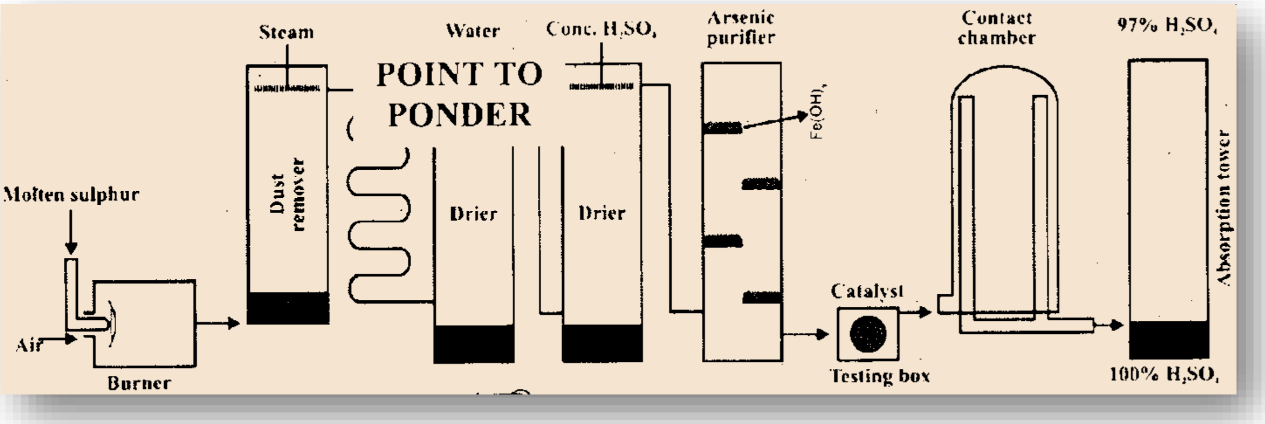
The reaction is highly exothermic so no heating is required once the reaction is started.

d) Absorption Unit:

The SO_3 obtained from the contact tower is dissolved in 98 H_2SO_4 to form pyrosulphuric acid (oleum), $H_2S_2O_7$. It can be diluted with water to get any required concentration of sulphuric acid.

$H_2SO_{4(aq)} + SO_{2(g)} \rightarrow H_2S_2O_{7(l)}$

$H_2S_2O_{7(l)} + H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)}$



POINT TO PONDER: Gases are dried by bubbling them through concentrated sulhuric acid for basic gases …………… drying agent must be used.

PRACTICE EXERCISE

1. **Which is a reducing agent?**

(A) HNO_3 (C) H_3PO_4

(B) H_2SO_4 (D) HCl

2. **Which of the substance acts both as oxidizing and reducing agent?**

(A) HNO_3 (C) H_2SO_3

(B) H_2SO_4 (D) HNO_2

3. **The percentage of nitrogen in urea is**

(A) 36% (C)) 46%

(B) 56% (D) 66%

4. For $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(A) $K_C = Kp$ (C) $Kp = K_C(RT)^1$

(B) $Kp = K_C(RT)^{-2}$ (D) $Kp = K_C(RT)^{-1}$

5. SO_3 is not absorbed in water directly to form H_2SO_4 because

(A) The reaction does not go to completion (C) The reaction is quite slow

(B) The reaction is exothermic (D) SO_3 is insoluble in water

6. Acid Rain first of all observed by

(A) Robert Hook (C) Mosely

(B) Augus Smith (D) Watson

7. The pH of unpolluted rain water should be

(A) 5.6 (C) 5

(B) greater than 5.6 (D) less than 5.6

8. Which catalyst is used in contact process?

(A) Fe_2O_3 (C) V_2O_5

(B) SO_3 (D) Ag_2O

9. Which statement is incorrect about O_2

(A) It is divalent

(B) It shows allotropic form

(C) Combine with non metals to from covalent compound

(D) It is only found in free state

10. H_2SO_4 does not act as

(A) Dehydrating agent

(B) Oxidizing agent

(C) Acid producing acid

(D) Reducing agent

11. H_2SO_4 by contact process is prepared by

(A) Homogenous catalysis

(B) Both a and b

(C) Hetergenous catalysis

(D) None of these

12. H_2SO_4 is used in

(A) Refining of petroleum

(B) Electrical battery

(C) Producing acids

(D) All of these

13. Which catalyst is used in contact process?

(A) Fe_2O_3

(B) V_2O_5

(C) SO_3

(D) Ag_2O

14. Most electro negative element in group VA is

(A) N

(B) P

(C) AS

(D) Sb

15. Which of the following compound acts as oxidizing agent only

(A) HNO_2

(B) H_2O_2

(C) HNO_3

(D) H_2SO_3

16. Laughing gas is chemically

(A) N_2O (C) NO_2

(B) NO (D) N_2O_4

17. Which of the following metal liberates hydrogen from dilute nitric acid?

(A) Sn (C) Cu

(B) Zn (D) Mn

18. Which one of the following compounds is not known:

(A) $SbCl_3$ (C) NCl_3

(B) NI_3 (D) NCl_5

19. How much nitrogen fixation on earth is being done by Haber process

(A) 10% (C) 13%

(B) 16% (D) 25%

20. Yellow colour of Nitric Acid is due to the presence of:

(A) NO_2 (C) NO

(B) N_2O (D) N_2O_4

21. SO_3 is not absorbed in water directly to H_2SO_4 because:

(a) The reaction does not go to completion (b) The reaction is quite slow

(c) The reaction is exothermic (d) SO_3 is insoluble in water

22. Arsenic impurities in contact process are removed:

(a) by prolong heating the gases (b) by treatment with $Fe(OH)_3$

(c) in scrubbing tower (d) in absorption tower

23. Which one of the following gases cannot be dried over conc. H_2SO_4?

(a) SO_2

(b) N_2

(c) H_2

(d) NH_3

24. In purifying unit of contact process, As_2O_3 reacts with freshly prepared ferric hydroxide to produce:

(a) H_2S

(b) H_2SO_4

(c) $FeAsO_3$

(d) All

25. As_2O_3 is removed in the purifying unit of contact process for the manufacture of H_2SO_4:

(a) to act as a catalyst

(b) to act as an autocatalyst

(c) to avoid poisoning of a catalyst

(d) to act as scrubber

26. Which one is not a quality of a fertilizer?

(a) Fairly soluble

(b) Stable in soil

(c) Deliquescent

(d) Non-toxic for plants

27. The role of nitrogen in plant development is as:

(a) Resistant against diseases

(b) To develop healthy root system

(c) To help in photosynthesis

(d) To stimulate seed and fruit formation

28. The fertilizer among following which provide maximum % of N to plants:

(a) Ammonia

(b) Urea

(c) Ammonium nitrate

(d) Diammonium phosphate

29. Select the fertilizer which contain 16% nitrogen:

(a) Urea
(b) Ammonium nitrate
(c) DAP
(d) Potassium nitrate

30. Which element is essential component of most of the fertilizers?

(a) C
(b) N
(c) P
(d) K

31. Which fertilizer is used in gaseous form?

(a) Urea
(b) NH_4NO_3
(c) Ammonia
(d) None

32. Ammonium nitrate fertilizer is not used for which crop?

(a) Cotton
(b) Wheat
(c) Sugarcane
(d) Paddy rice

33. Which nitrogen fertilizer will make soil acidic?

(a) KNO_3
(b) $NaNO_3$
(c) $Ca(NO_3)_2$
(d) NH_4NO_3

34. $N_2H_6CO_2$ can be the composition of:

(a) Diammonium hydrogen phosphate
(b) Urea
(c) Ammonium carbonate
(d) Ammonium carbamate

35. Which of the following is main component of temporary acid rain?

(a) Sulphuric acid
(b) Nitric acid

(c) Carbonic acid
(d) Hydrochloric acid

36. The acid which is not a component of acid rain:

(a) Sulphuric acid
(b) Nitric acid
(c) Carbonic acid
(d) Acetic acid

37. Major cause of SO_2 on global scale is:

(a) Volcanoes
(b) Combustion of coal
(c) Fossil fuels in power plants
(d) Chemical industries

38. SO_2 and SO_3 through various reactions in the atmosphere form:

(a) Sulphur
(b) CFCs
(c) Ozone
(d) Sulphate aerosols

39. Nitrogen is less reactive due to

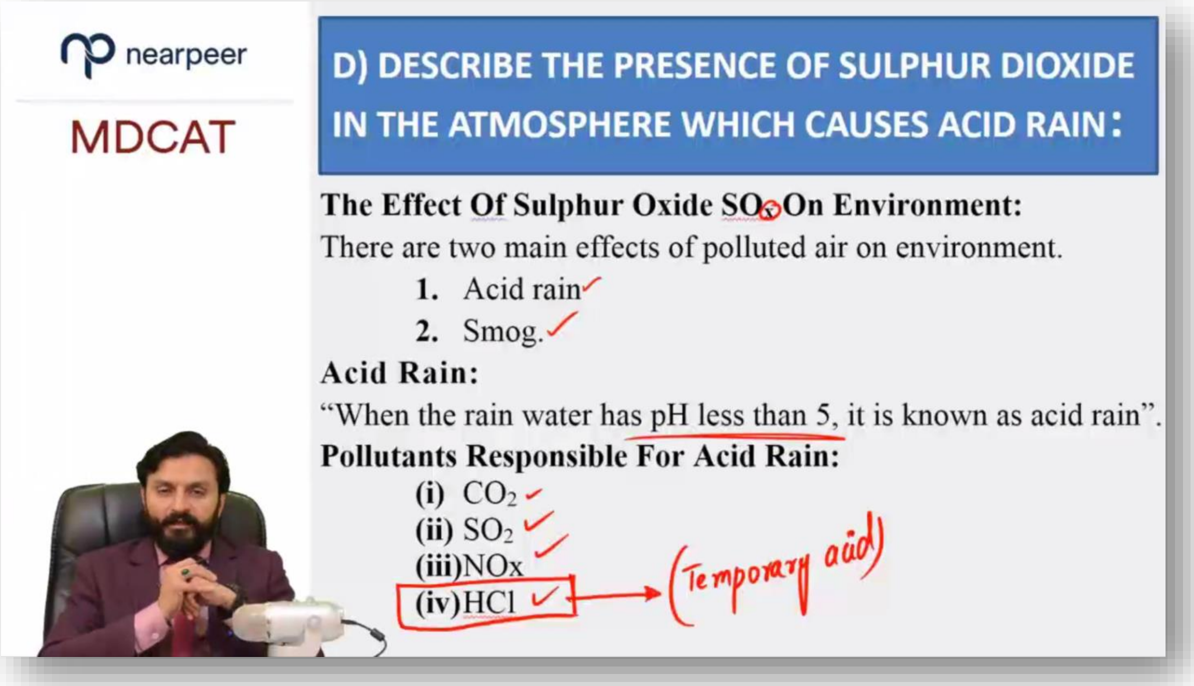
a. High electro-negativity
b. Stable electronic configuration
c. High dissociation energy
d. Small atomic radius.

40. Which condition is not applied in the manufacture of NH_3 by Haber's process?

a. pressure between 200-300
b. temperature 400-500 C^0
c. Ni/Pt catalyst
d. N_2, H_2 in 1:3 ratios

ANSWER KEY

1	D	11	B	21	C	31	C
2	D	12	D	22	B	32	D
3	C	13	B	23	D	33	D
4	B	14	A	24	C	34	D
5	B	15	C	25	C	35	D
6	B	16	A	26	B	36	D
7	A	17	D	27	C	37	A
8	C	18	D	28	A	38	D
9	D	19	C	29	C	39	C
10	D	20	A	30	B	40	C



D) DESCRIBE THE PRESENCE OF SULPHUR DIOXIDE IN THE ATMOSPHERE WHICH CAUSES ACID RAIN:

The Effect Of Sulphur Oxide SO_x On Environment:

There are two main effects of polluted air on environment.

1. Acid rain ✓
2. Smog. ✓

Acid Rain:

"When the rain water has pH less than 5, it is known as acid rain".

Pollutants Responsible For Acid Rain:

(i) CO_2 ✓
(ii) SO_2 ✓
(iii) NOx ✓
(iv) HCl ✓ → (Temporary acid)

UHS TOPIC 1 – C

FUNDAMENTAL PRINCIPLES

LEARNING OUTCOMES

In this topic, student should be able to:

a) Classify the organic compounds.

b) Explain the types of bond cleavage, homolytic and heterolytic

c) Suggest how cracking can be used to obtain more useful alkanes and alkenes of lower masses

d) Discuss the types of reagents; nucleophile, electrophile and free radicals

e) Explain isomerism; structural and cis-trans

f) Discuss the functional group and nomenclature of organic compounds with reference to IUPAC names of Alkanes, Alkenes, Alcohols, Haloalkanes and Carboxylic acids

INTRODUCTION

On the basis of origin, chemical compounds were classified as:

(i) Organic compounds (compounds obtained from living things)

(ii) Inorganic compounds (compounds obtained from mineral sources)

ORGANIC CHEMISTRY:

The branch of chemistry that deals with the study of compounds of carbon and hydrogen(hydrocarbons) and their derivatives is called organic chemistry.

VITAL FORCE THEORY:

Introduction:

This theory was proposed by Berzelius.

Definition:

Organic compounds could be manufactured only by and within living things and these compounds could never be synthesized from inorganic materials as these compounds required vital force for their synthesis.

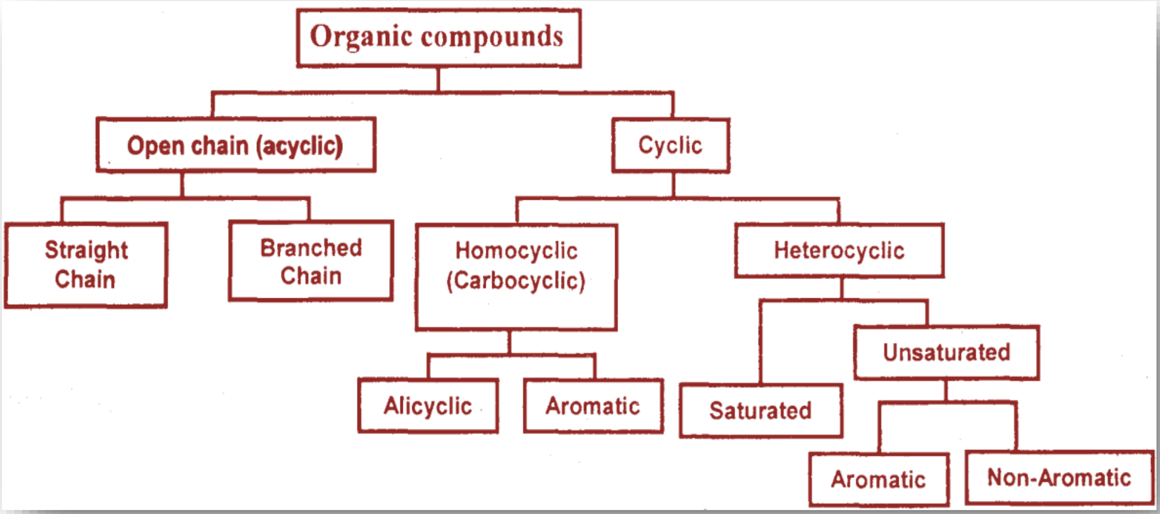
POINT TO PONDER: Fuels are obtained from crude oil by?

FEATURES OF ORGANIC COMPOUNDS:

- Peculiar nature of carbon
- Catenation
- Moderate electropositivity
- Tetravalency
- Covalent nature (non-ionic character)
- Similarity in behaviour (homologous series)
- Complexity in structure
- Isomerism
- Solubility only in non-polar solvents
- Low melting and boiling points
- Volatility and highly flammable characters

- Non-conductance of electricity
- Slow rates of organic reactions with low yield
- Polymerization

CLASSIFICATION OF ORGANIC COMPOUNDS:



POINT TO PONDER: Why butane has a larger surface area than 2-methyl propane although they have the same molecular formula (C_4H_{10})?

Photochemical hemolysis of Cl_2 is?

TYPES OF BOND FISSION

When organic compounds react, their bonds can split in either of two ways, by homolytic or heterolytic fission.

Homolytic Fission:

When the bond breaks, each of the bonded atoms takesone of the pair of electrons. Free radicals are formed. These are atoms or groups of atoms .With unpaired electrons.

$HC_3CH_2CH_3 \xrightarrow{Heat} CH_3CH_2\bullet + \dot{C}H_3$

Propane Ethyl radical Methyl radical

$Cl_2 \xrightarrow{Straight} 2\dot{C}l$

Chlorine molecule Chlorine atoms or free radicals

Energy must be supplied, either as heat or light, to break the bond. The free radicals formed possess this energy, and are very reactive. The steps in a free radical reaction are initiation, propagation and termination.

Heterolytic Fission:

When the bond breaks, one of the bonded atoms takes both of the bonding electrons to form an anion. The rest of the molecule becomes a caution. An ion with a positively charged carbon atom is called a carbocation. An ion with negativity charged carbon atom is called a carbanion:

$(CH_3)_3\,C - Cl \rightarrow (CH_3)_3\,C^+ + Cl^-$

2-Chloro-2-methylpropane → A carbocation + Chloride ion

$CH_3COCH_2\,CO_2C_2H_5 + OH^- \rightarrow CH_3COC^-\,HCO_2C_2H_5 + H_2O$

Ethyl-3-oxobutanoate A carbanion + Water

Cracking of Petroleum (Pyrolysis):

(Cracking increases the percentage of gasoline)

(1) **Definition**:

Break down of higher hydrocarbons (alkanes) into lower hydrocarbons (alkenes and alkanes) by heating in the absence of air is called cracking.

Example:

$$C_{16}H_{34} \xrightarrow{Heat} C_7H_{16} + 3CH_2 = CH_2 + CH_3 - CH{=}CH_2$$

(2) Importance Of Cracking Of Petroleum:

The fractional distillation of petroleum only gives us 20 % gasoline. This is very small fraction of the total gasoline used by the world. The higher demand of the present civilization can be fulfilled by cracking of higher alkanes. These higher alkanes are mostly consisted of kerosene oil. In fact, approximately 50 % of Gasoline is now prepared by this method.

(3) Types Of Cracking:

(i) Thermal Cracking:

A type of cracking in which higher hydrocarbons are heated at high temperature (700°C) to break them down into lower alkenes and alkanes.

Example:

$$2CH_3 - CH_2 - CH_3 \xrightarrow{Heat} CH_3 - CH{=}\,CH_2 + CH_2{=}\,CH_2 + CH_4 + H_2$$

It is particularly useful for the production of unsaturated hydrocarbon such as and propene.

(ii) Catalytic Cracking:

Breaking down of higher hydrocarbons into lower hydrocarbons in the presence of catalyst (Al_2O_3+SiO_2) at lower temperature (500° C) is called catalytic cracking. In the process of cracking, bigger alkane molecules are heated to in the absence of air and in the presence of a mixture of silica (SiO_2) and alumina (Al_2O_3) as a catalyst. Hexadecane breaks up further to give even smaller molecules.

Example: $C_{16}H_{34} \xrightarrow[500°C]{Al_2O_3+SiO_2} C_8H_{18}+C_8H_{16}$

Hexadecane n-Octane Octene

It produces gasoline of high octane number which is a better quality gasoline.

(iii) Steam Cracking

Break down of higher hydrocarbons in vapour phases mixed with steam into lower hydrocarbons by heating for short duration to about 900° C and then cooled rapidly is called steam cracking.

It is useful for obtaining lower unsaturated hydrocarbons.

(4) Applications of Cracking:

(i) Used to produce gasoline
(ii) Increases production of petrol
(iii) Used to produce, propene, butane and benzene
(iv) Used to form drugs, fertilizer, plastic, synthetic fibers and detergents
(v) About 50 of petrol is synthesized

Used to produce certain solvents, phenol, ethanol and acetone

POLAR REACTIONS

Polar reactions occur with the bonding electron pair remaining intact. Polar reactions

(i) Usually occur in solution [can occur on polar surfaces]

(ii) Are often catalyzed by acids and bases

(iii) Often proceed at a rate strongly influenced by the polarity of the solvent

(iv) Are not affected by light, oxygen, or peroxides

(v) Are rarely chain reactions

Examples:

(a) Typical acid/base reactions of inorganic chemistry
(b) Solvolysis (the solution process)
(c) Most organic reactions that occur in solution

FREE RADICAL REACTIONS

A free radical reaction is any chemical reaction involving free radicals. This reaction type is abundant in organic reactions. When radical reactions are part of organic synthesis the radicals are often generated from radical initiators such as peroxides or azobis compounds. Many radical reactions are chain reactions with a chain initiation step, a chain propagation step and a chain termination step. Reaction inhibitors slow down a radical reaction. Radical reactions, occur frequently in the gas phase, are often initiated by light are rarely acid or base catalyzed and are not dependent on polarity of the reaction medium. Reactions are also similar whether in the gas phase or solution phase.

REACTIONS OF ORGANIC COMPOUNDS

Types of Reactions:

The reactions of organic compounds fall into four classes. These are listed below.

Substitution:

An atom or group of atoms replaces another, e.g. in hydrolysis:

C_2H_5Cl + OH^- → C_2H_5OH+ Cl^-

Chloroethane + Hydroxide ion → Ethanol+ Chloride ion

Addition:

Two molecules react to form one:

$Br_2 + CH_2 = CH2 \rightarrow BrCH_2CH_2Br$

Bromine + Ethene → 1,2-Dibromoethane

Elimination:

One molecule reacts to form more than one:

$C_2H_5OH \rightarrow C_2H_4 + H_2O$

Ethanol → Ethene + Water

Rearrangement:

One molecule reacts to give different molecule

CH_3– CH – CH= CH ⇌ CH_3– CH= CH – CH_2– Cl

|

Cl

3 = Chlorobut – 1 – ene ⇌ 1 – Chlorobut2 – ene

Types of Reagent:

In a covalent bond between A and B, if A is more electronegative than B, the distribution of bonding electrons can be represented as:

$$A^{\delta+} - B^{\delta+}$$

The bond is described as **polar.** The reagents which attack organic compounds seek out either the slightly positive ($\delta +$) end of the bond or the slightly negative ($\delta -$) end of the bond. There are two main classes of reagent.

Nucleophilic Reagents:

Negative ions, e.g., OH –, CN – and compounds in which an atom has an unshared pair of electrons, e.g., NH_3, are nucleophilic (nucleus – seeking). They attack the electron – deficient end of a polar bond, the $\delta +$ end.

Examples are the hydrolysis of a primary halogenoalkane.

$$\mathrm{R}^{\delta+} - \mathrm{X}^{\delta+} + \mathrm{OH}^- \rightarrow \mathrm{ROH} + \mathrm{X}^-$$

And the substitution of a cyanide group for a halogen atom:

$$\mathrm{R}^{\delta+} - \mathrm{X}^{\delta+} + \mathrm{CN}^- \rightarrow \mathrm{RCN} + \mathrm{X}^-$$

Electrophilic reagents:

A reagent which attacks a region where the electron density is high is called an:

Electrophile.

Examples of electrophilic reagents are the nitryl cation, NO_2^+ and sulphur (VI) oxide, SO_3.The nitryl cation is involved in the nitration of benzene. Sulphur (VI) oxide is involved in introducing a sulphonic acid group - SO_3H into benzene ring.

A reaction may involve.

- Substitution by a nucleophile – calledan S_N reaction
- Substitution by an electrophile – calledan S_E reaction
- Addition by an electrophile – calledan A_E reaction
- Addition by a nucleophile – calledan A_N reaction

Reaction Mechanism:

The stoichiometric equation for an organic reaction does not tell you how the reaction takes place. There may be a series of reactions in between the mixing of the reactants takes place is called the reaction mechanism.

ISOMERISM (Iso = same ; Merose = units)

Two or more compounds· having same molecular formula but different structures are called isomers and the phenomenon is known as isomerism.

- In saturated hydrocarbons methane, ethane and propane (amongst alkanes) have one structural form only i.e. no isomerism
- Isomerism is possible for compounds having at least four carbon atoms
- Number of isomers increases with increase in number of carbon atoms in saturated hydrocarbon

No. of carbons	No. of Isomers
4	2
5	3
6	5
7	9
8	18
9	35
10	75

TYPES OF ISOMERISM:

A. Structural Isomerism

Type	Reason of isomerism	Functional groups	Example
Chain or skeletal Isomerism	Difference in nature Of carbon chains	same	n-pentane, iso-pentane and neo-pentane
Position isomerism	Difference in position of same functional group on the carbon chain	same	1-butene and 2-butene
Functional group Isomerism	Same molecular formula, but different	different	Propanal and propanone

	functional groups		
Metamerism	Unequal distribution of carbon atoms (R) on either side of functional group	same	diethyl ether and methyl n- propyl ether

B) Cis-Trans Isomerism or Geometric Isomerism:

Two compounds that possess the same structural formula but differ with respect to the positions of the identical groups in space are cis-trans isomers.

Reason:

Two carbon atoms with double bond cannot rotate freely, however relative position of the attachments get fixed.

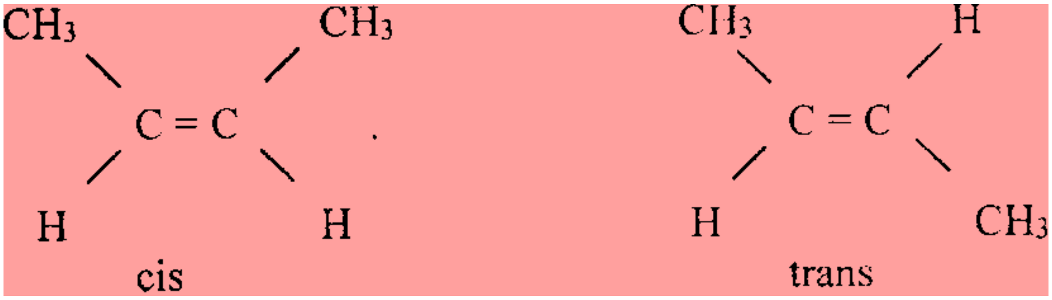
Condition:

Two groups attached to same carbon atom must be different

In cis form, similar groups lie on same side of double bond while in trans form similar groups lie on opposite sides of double bond.

Example:

2-butene

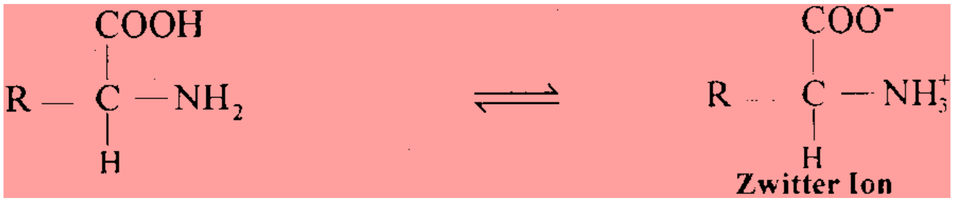


cis

trans

(III). Tautomerism:

This type of isomerism arises due to shifting of proton from one atom to other in the same molecule.



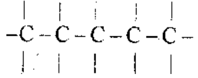
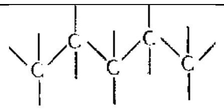
C. Tautomerism

Difference Between Homologues and Isomers:

	HOMOLOGOUS	ISOMER
General Formula	Applicable	No
Functional Group	Same	Mayor may not be same
Periodic Difference of CH_2	Present	Absent
Structural Formula	Similar	Different
Molecular Formula	Different	Same
Molecular Weight	Different	Same

FORMULAE OF ORGANIC COMPOUNDS

The molecular formula of organic compound may be expressed as e.g. pentane.

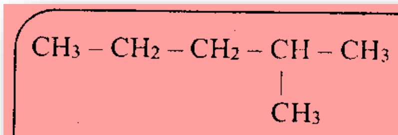
Condensed Structural Formula	Displayed Formula	Skeletal Formula
(a) Simple molecular formula: C_5H_{12}		
(b) Simple structural formula: $CH_3(CH_2)_3CH_3$		

Nomenclature of Alkanes, Alkenes, Alcohols and Acids:

System of Naming Alkanes and Alkenes:

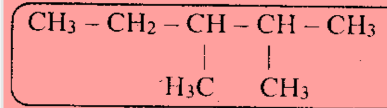
The names of these isomers are given in accordance with the international union of pure and applied chemistry (IUPAC) system of nomenclature. The procedure followed is:

- Name the longest un-branched carbon chain
- Name the substituent groups
- Give the positions of the substituent groups



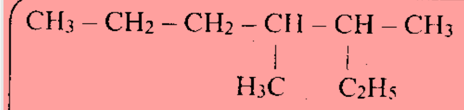
$CH_3-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

2- Methylpentane.
One could count from the other end and call it 4 – methylpentane, but the IUPAC system is to count from the end which will give the lower locant (number) for the position of a substituent group.



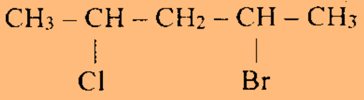
$CH_3-CH_2-\underset{H_3C}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

2,3 – Dimethylpentane



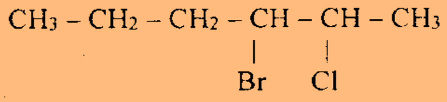
$CH_3-CH_2-CH_2-\underset{H_3C}{\underset{|}{CH}}-\underset{C_2H_5}{\underset{|}{CH}}-CH_3$

3,4 – Dimethylheptane
In spite of the way it is written, you should be able to see that the longest unbranched chain has seven carbon atoms.



$CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Br}{\underset{|}{CH}}-CH_3$

2–Bromo 4 – chloropentane
The substituent groups are named in alphabetical order.



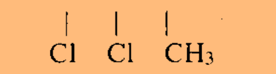
$CH_3-CH_2-CH_2-\underset{Br}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-CH_3$

3 – Bromo – 2 – chlorohexane.
The substituents are named in alphabetical order, not in the numerical order of the locants.

To construct formula of a compound from its name, e.g. 2,3–dichloro–4– methylhexane, first write the carbon atoms of the hexane part of the molecule:

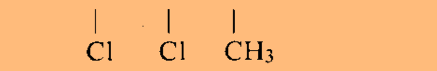
$C-C-C-C-C-C$

Then put in Cl atoms on carbons 2 and 3, and a CH_3 group on carbon 4:



$C-\underset{Cl}{\underset{|}{C}}-\underset{Cl}{\underset{|}{C}}-\underset{CH_3}{\underset{|}{C}}-C-C$

Full in the hydrogen atoms to give each carbon atom a valency of four:



$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

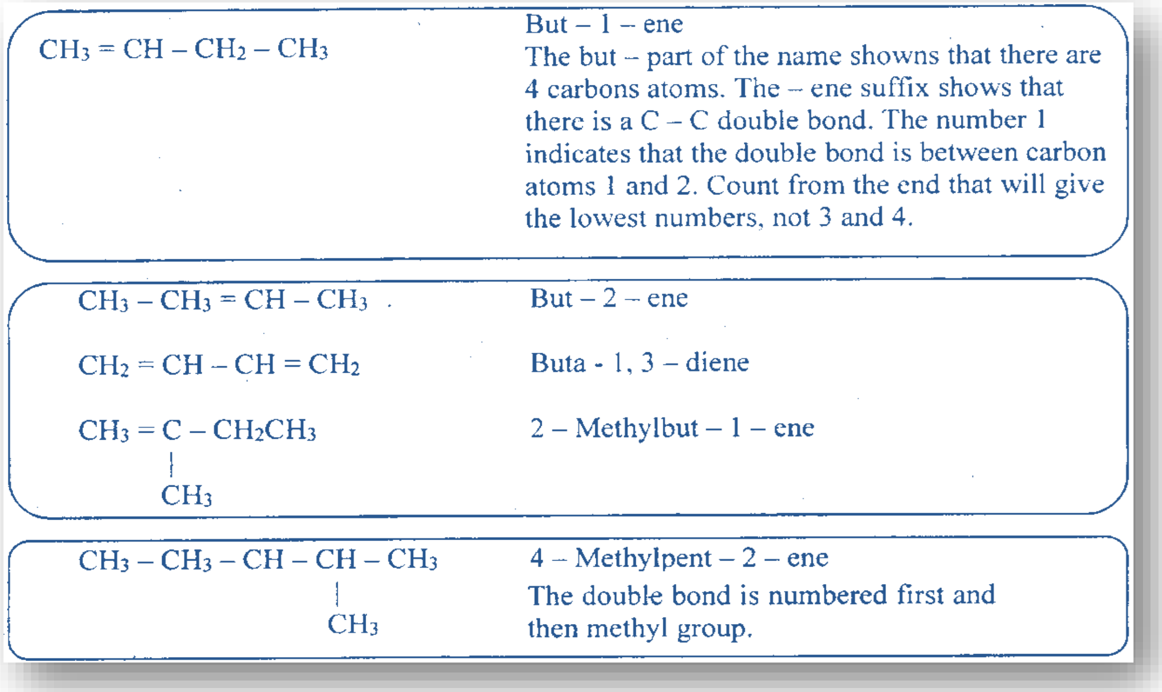
UNSATURATED HYDROCARBONS

The alkanes are not the only hydrocarbons. There are also alkenes and alkynes. Alkanes are said to be saturated hydrocarbons as they contain only single bonds between carbon atoms. Alkenes and alkynes are unsaturated hydrocarbons: they contain multiple bonds between carbon atoms. The simplest alkene is ethene $H_2C = CH_2$. Formerly called ethylene, it is the first members of the homologous series of alkenes, which have general formula C_nH_{2n}. Alkynes, contain one or more carbon-carbon triple bonds. Ethyne $HC = CH$ is the first member of the homologous series of alkynes, which have the general formula C_nH_{2n-2}.

No. of C atoms	**Alkane**		**Alkene**		**Alkyl group**	
	Formula	**Name**	**Formula**	**Name**	**Formula**	**Name**
1	CH_4	Methane			CH_3	Methyl
2	C_2H_6	Ethane	C_2H_4	Ethane	C_2H_5	Ethyl
3	C_3H_8	Propane	C_3H_6	Propane	C_3H_2	Propyl
4	C_4H_{10}	Butane	C_4H_8	Butane	C_4H_9	Butyl
5	C_5H_{12}	Pentane	C_5H_{10}	Pentane	C_5H_{11}	Pentyl
N	C_nH_{2n+2}	Alkane	C_nH_{2n}	Alkane	C_nH_{2n+1}	Alkyl

The names of the other members of the series are given in table. All these hydrocarboi are classified as aliphatic hydrocarbons. Aliphatic means 'fatty' in Greek, the connectic being that fats contain largealkyl groups, e.g. $C_{15}H_{31}$ –.

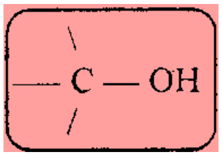
In naming alkenes and alkynes, the positions of the multiple bonds must be stated:



$CH_3 = CH - CH_2 - CH_3$	But – 1 – ene The but – part of the name showns that there are 4 carbons atoms. The – ene suffix shows that there is a C – C double bond. The number 1 indicates that the double bond is between carbon atoms 1 and 2. Count from the end that will give the lowest numbers, not 3 and 4.
$CH_3 - CH_3 = CH - CH_3$	But – 2 – ene
$CH_2 = CH - CH = CH_2$	Buta - 1, 3 – diene
$CH_3 = \underset{\substack{\mid \\ CH_3}}{C} - CH_2CH_3$	2 – Methylbut – 1 – ene
$CH_3 - CH_3 - CH - \underset{\substack{\mid \\ CH_3}}{CH} - CH_3$	4 – Methylpent – 2 – ene The double bond is numbered first and then methyl group.

ALCOHOLS:

Aliphatic alcohols are a homologous series. They all possess the same B functional group, a hydroxyl group attached to a saturated carbon atom. They all have the formula ROH, where R is an alkyl group C_nH_{2n+1} –.

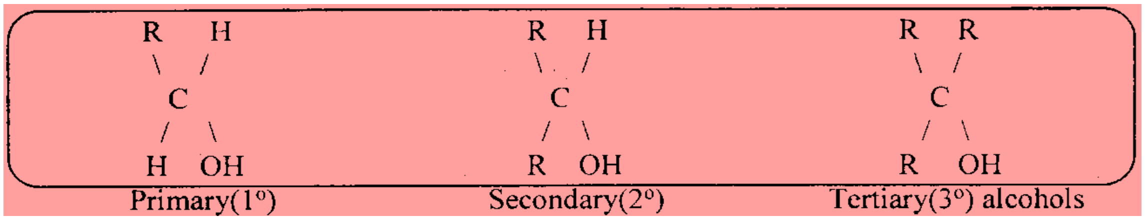


NOMENCLATURE:

They can be regarded as alkanes in which one H atom is replaced by a -OH group and are often called the alkanols. The names are arrived at by adapting the name of the parent alkane by changing the terminal ane to aneto anol. The first members of the series are:

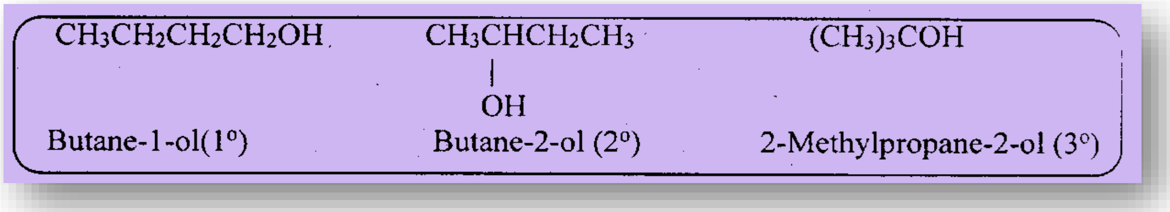
Formula	IUPAC Name	Formula	IUPAC Name
CH_3OH	Methanol	C_4H_9OH	Butanol
C_2H_5OH	Ethanol	$C_5H_{11}OH$	Pentanol
C_3H_7OH	Propanol	$C_6H_{13}OH$	Hexanol

Monohydric Alcohols: Primary (1°), Secondary (2°) and Tertiary (3°) alcohols:



Primary(1°) Secondary(2°) Tertiary(3°) alcohols

The three isomeric butanols, of formula C4H9OH, are:



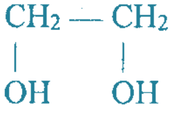
$CH_3CH_2CH_2CH_2OH$ Butane-1-ol(1°)

$CH_3\underset{\displaystyle OH}{\underset{|}{C}H}CH_2CH_3$ Butane-2-ol (2°)

$(CH_3)_3COH$ 2-Methylpropane-2-ol (3°)

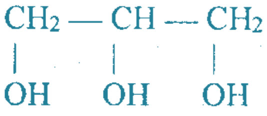
POLYHYDRIC ALCOHOLS

Polyhydric alcohols contain more than one -OH group. Diols contain two, and triols contain three hydroxyl groups.



$\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$

Ethane-1,2-diol



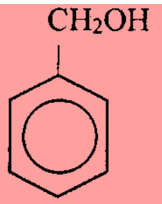
$\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$

Propane-1,2,3-triol (glycerol)

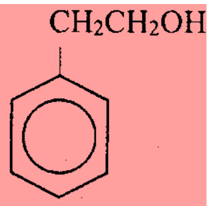
ARYL ALCOHOLS

:

Aromatic alcohols or aryl alcohols contain a benzene ring



Phenylmethanol



2-Phenylethanol

CARBOXYLIC ACIDS

Organic compounds containing – COOH as a functional group are called carboxylic acids (carb from carbonyl and oxyl from hydroxyl).Their general formula is R-COOH.

Nomenclature

No.	Formula	IUPAC Name	Common Name
1	HCOOH	Methanoic acid	Formic acid
2	CH_3COOH	Ethanoic acid	Acetic acid
3	CH_3CH_2COOH	Propanoic acid	Propionic acid
4	$CH_3(CH_2)_2COOH$	Butanoic acid	Butyric acid
5	$CH_3(CH_2)_2COOH$	Pentanoic acid	Valeric acid
6	$CH_3(CH_2)_2COOH$	Hexanoic acid	Caproic acid
	DICARBOXYLIC ACID		
7	HOOCCOOH	Ethanedioic acid	Oxalic acid

8	$HOOC(CH_2)COOH$	Propanedioic acid	Malonic acid
9	$HOOC(CH_2)_2COOH$	Butanedioic acid	Succinic acid
10	$HOOC(CH_2)_3COOH$	Pentanedioic acid	Glutaric acid
11	$HOOC(CH_2)_4COOH$	Hexanedioic acid	Adipic acid
	AROMATIC ACID		
12	C_6H_5COOH	Benzoic acid	Benzenecarboxylic acid
13	$C_6H_4(COOH)_2$	Phthalic acid	Benzenedicarboxylic acid

PRACTICE EXERCISE (FOR UHS TOPIC)

1. **The mains reason for a large number of compounds is unique property of**

(A) Isomerism (C) Homologous series

(B) Catenation (D) Complexity of organic compound

2. **Which is not organic in nature**

(A) Na_2CO_3 (C) CH_3COOH

(B) Formic acid (D) $CO(NH_2)_2$

3. **Friederick Wohler rejected vital force theory by artificially synthesizing urea as a result of heating of**

(A) Ammonium nitrate (C) Ammonium sulphate

(B) Ammonium chloride (D) Ammonium cyanate

4. **Which type of coal has maximum percent of carbon?**

(A) Peat

(B) Lignite

(C) Bituminous

(D) Anthracite

5. **Which is truce for organic compound**

(A) Petroleum is combination of two Greek words petra and oleum

(C) It has non renewable energy

(B) It is formed by decomposition of living organism

(D) All of above

6. **Which property is only shown by organic compound?**

(A) Isomosphism

(B) Polymorphism

(C) Isomerism

(D) Fast rate of reaction

7. **Nucleophilicity order is correctly represented by:**

(A) $CH_3^- < NH_2^- < OH^- < F^-$

(B) $CH_3^- \simeq NH_2^- > OH^- \simeq F^-$

(C) $CH_3^- > NH_2^- > OH^- > F^-$

(D) $NH_2^- < F^- < OH^- < CH_3$

8. **Which technique is used to separate various fractions from petroleum?**

(A) Dry distillation

(B) Fractional distillation

(C) Vaccum distillation

(D) Destructive distillation

9. **Which term is used to convert higher alkane into lower alkane / alkene**

(A) Pyrolysis

(B) Catalysis

(C) Hydrolysis

(D) Electrolysis

10. Which type of cracking is used to produce gasoline of higher octane number?

(A) Thermal cracking (C) Steam cracking

(B) Catalytic cracking (D) All of these

11. Main application of cracking is

(A) To increase production of gasoline petrol (C) To produce petrochemicals

(B) To produce low boiling hydrocarbons (D) All of these

12. Which process is used to improve quality of petrol

(A) Cracking (C) Anealing

(B) Reforming (D) Pickling

13. Which method is used for improving octane number of gasoline?

(A) Isomerisation (C) aromatization

(B) reforming (D) Both (A) and (B)

14. The homocyclic compound which contain a ring of three or more carbon atoms and resembling aliphatic compound are called

(A) Alicyclic (C) Acyclic

(B) Hetrocyclic (D) Aromatic

15. Which heterocyclic compound has six membered ring?

(A) Pyridine (C) Pyrole

(B) Furan (D) Thiophene

16. Which is amino functional group

(A) –CN (C) C = NH

(B) $-NH_2$ (D) $-C = NH_2$

17. Which is mercapto functional group?

(A) –SH(C) –COOH

(B) –OH (D) –CHO

18. The reaction $C_8H_{18} \xrightarrow{\Delta} C_3H_6$ **+ Fragments is:**

(A) Catalytic oxidation (C) Isomerisation

(B) Synthesis (D) Cracking

19. The octane number is 100% in petroleum:

(A) Neo-octane (C) n-Hexane

(B) Neo-pentane (D) Iso-octane

20. Carbon atom of HCHO (methanol, formaldehyde) is:

(A) sp hybridized (C) sp^2 hybridized

(B) Sp^3 hybridized (D) Not hybridized

21. Which of the following is not heterocyclic compound?

(A) Furan (B) Pyridine

(C) Thiophene (D) Aniline

22. The compound which is not isomeric with diethyl ether:

(A) n-propyl-methyl ether (B) 1-butanol

(C) 2-butanone (D) 2-methyl-2-propanol

23. Heteroatom in Furan:

(A) N (B) O

(C) N (D) S

24. Glucose and fructose are:

(A) Cis-trans isomers (B) Metamers

(C) Chain isomers (D) Functional group isomers

25. Ethers can be presented by:

(A) –OH (B) R–COOH

(C) R–CO–R (D) R–O–R

26. These are geometrical isomers:

(A) Maleic acid and maleic anhydride (B) Maleic acid and fumaric acid

(C) Ethylene dichloride and 1, 2-dichloroethene (D) None of these

27. All the following compounds have benzene ring in their fused form except:

(A) Phenanthrene (B) Diphenylmethane

(C) Naphthalene (D) Anthracene

28. Cir-trans isomers can be differentiated by:

(A) Melting point (B) Boiling point

(C) Dipole moment (D) All of these

29. As the number of carbon atoms in the homologous series of alkanes increase numerical value the following property decrease:

(A) Number of isomers (B) Density

(C) Enthalpy of vaporization
(D) Vapour pressure

30. Tautomerism can also to called:

(A) Chain isomerism
(B) Metamerism
(C) Prototropism
(D) Geometrical isomerism

31. Benzene is:

(A) Alicyclic
(B) Aliphatic
(C) Aromatic
(D) Heterocyclic

32. Cracking gives gasoline:

(A) 10%
(B) 20%
(C) 30%
(D) More than 50%

33. C_4H_4O i.e.,  **is:**

(A) Pyridine
(B) Furan
(C) Thiophene
(D) Pyrrol

34. Urea has the functional group:

(A) Amine
(B) Carboxylic acid
(C) Ether
(D) Acid amide

35. Hexane has number of chain isomers:

(A) 4
(B) 5
(C) 6
(D) 7

36. Fumaric acid and maleic acid are:

(A) Metamers (B) Chain isomers

(C) Functional group isomers (D) Cis-trans isomers

37. Alkanone is another name of:

(A) Carboxylic acids (B) Alcohols

(C) Aldehydes (D) Ketones

38. Pyrrol is:

(A) Homocyclic compound (B) Heterocyclic compound

(C) Acyclic compound (D) Carbocyclic compound

39. The general formula $(RCO)_2O$ represents:

(A) An ester (B) An ether

(C) An acid anhydride (D) An aldehyde

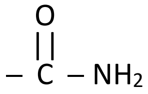
40. Which of the following has zero dipole moment?

(A) 2-methyl-1-propene (B) 1-butene

(C) Trans-2-butene (D) Cis-2-butene

41. Which of the following is amino group?

(A) $-NH_2$ (B) $C = NH$

(C) $-C \equiv N$ (D) 
$-\overset{O}{\overset{||}{C}}-NH_2$

42. The reaction $C_8H_{18} \xrightarrow{D} C_3H_6$ + Fragments is:

(A) Catalytic oxidation (B) Isomerization

(C) Synthesis (D) Thermal Cracking

43. How many ester are these with the molecular $C_4H_8O_2$?

(A) 2 (B) 3

(C) 4 (D) 6

44. Heterolysis of carbon – chlorine bond produces:

(A) two free radicals (B) two cabonium ions

(C) two carbanions (D) one cation and one anio

45. In CH_3 CH_2 OH, the bond that undergoes heterolytic cleavage most readily is:

(A) C – C (B) C – O

(C) C – H (D) O – H

46. Carbonium ion is formed in:

(A) Homolytic fission (B) Heterolytic fission

(C) in both of the above (D) in none of the above

47. The central C – atom of free radical possesses:

(A) 6 electrons (B) 8 electrons

(C) 7 electrons (D) none of the above

48. Which of the following free radicals is most stable?

(A) Primary (B) methyl

(C) secondary (D) tertiary

49. Which of the following ions is most stable?

A) $CH_3\,\mathit{C}H2$ (B) $(CH_3)_2CH$

(C) $(CH_3)_3C$ (D) $C_6H_5CH_2$

50. Which of the following has the highest nucleophilicity?

(A) F^- (B) OH^-

(C) CH_3^- (D) NH_2^-

ANSWER KEY

1	**B**	**11**	**D**	**21**	**D**	**31**	**C**	**41**	**A**
2	**A**	**12**	**B**	**22**	**C**	**32**	**B**	**42**	**D**
3	**D**	**13**	**D**	**23**	**B**	**33**	**B**	**43**	**C**
4	**D**	**14**	**A**	**24**	**D**	**34**	**D**	**44**	**D**
5	**D**	**15**	**A**	**25**	**D**	**35**	**B**	**45**	**D**
6	**C**	**16**	**B**	**26**	**B**	**36**	**D**	**46**	**B**
7	**C**	**17**	**A**	**27**	**B**	**37**	**D**	**47**	**C**
8	**B**	**18**	**D**	**28**	**D**	**38**	**B**	**48**	**A**
9	**A**	**19**	**D**	**29**	**D**	**39**	**C**	**49**	**C**
10	**B**	**20**	**C**	**30**	**C**	**40**	**C**	**50**	**C**

UHS TOPIC 2 – C

HYDRO CARBONS

LEARNING OUTCOMES

In this topic, student should be able to:

Describe the chemistry of Alkanes with emphasis on:

a) Combustion

b) The mechanism of free radical substitution reaction of methane with particular reference to the initiation, propagation and termination

Discuss the chemistry of Alkenes with emphasis on:

i) Preparation of alkenes by elimination reactions:

→ Dehydration of alcohols

→ Dehydrohalogenation of Alkyl halide

ii) Reaction of Alkenes such as

→ Cataytic hydrogenation

→ Halogenation (Br_2 addition to be used as a test of an alkene)

→ Hydration of alkenes

→ Reaction with HBr with special reference to Markownikoff's rule

→ Oxidation of alkenes using cold alkaline or acidic $KMnO_4$ (Bayer's reagent) and using hot concentrated acidic or alkaline $KMnO_4$ for cleavage of double bond in 2-butene

→ Polymerization of ethane

Discuss chemistry of Benzene with examples

a) Structure of benzene showing the delocalized 7r -orbital which causes stability of benzene

b) Electrophilic substitution reactions of benzene including mechanism of:

- i) Nitration
- ii) Halogenation (chlorination and bromination)
- iii) Friedel Craft's reaction (Alkylation and acylation)

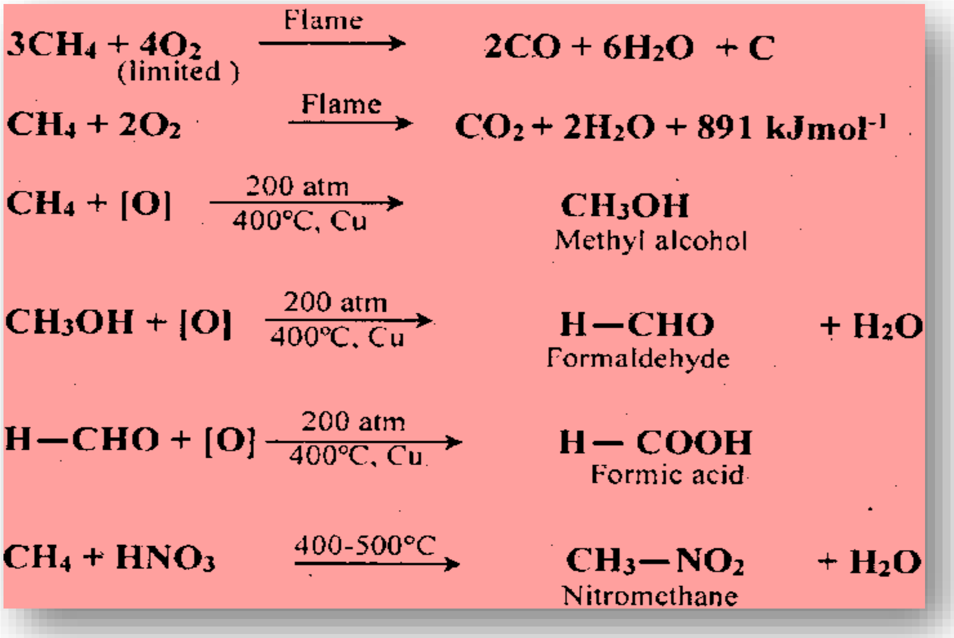
c) Hydrogenation of benzene ring to form cyclohexane ring

d) Side chain oxidation of methyl benzene (toluene) and ethyl benzene

e) Directive influence of substituent’s on the benzene ring by 2,4 directing and 3,5 directing groups

(orientation in Electrophilic Substitution reactions of Benzene)

CHEMISTRY OF METHANE:



$$3CH_4 + \underset{\text{(limited)}}{4O_2} \xrightarrow{\text{Flame}} 2CO + 6H_2O + C$$

$$CH_4 + 2O_2 \xrightarrow{\text{Flame}} CO_2 + 2H_2O + 891\ kJmol^{-1}$$

$$CH_4 + [O] \xrightarrow[\text{400°C, Cu}]{\text{200 atm}} \underset{\text{Methyl alcohol}}{CH_3OH}$$

$$CH_3OH + [O] \xrightarrow[\text{400°C, Cu}]{\text{200 atm}} \underset{\text{Formaldehyde}}{H{-}CHO} + H_2O$$

$$H{-}CHO + [O] \xrightarrow[\text{400°C, Cu}]{\text{200 atm}} \underset{\text{Formic acid}}{H{-}COOH}$$

$$CH_4 + HNO_3 \xrightarrow{\text{400-500°C}} \underset{\text{Nitromethane}}{CH_3{-}NO_2} + H_2O$$

FREE RADICAL SUBSTITUTION REACTION:

$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl \quad + HCl$

Methyl chloride

$CH_3Cl + Cl_2 \xrightarrow{hv} CH_2Cl_2 \quad + HCl$

Methylene chloride

$CH_4Cl_2 + Cl_2 \xrightarrow{hv} CH_3Cl \quad + HCl$

Chloroform

$CHCl_3 + Cl_2 \xrightarrow{hv} CCl_4 \quad + HCl$

Carbon tetrachloride

Mechanism:

HALOGENATION:

Halogenation is the replacement of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine or iodine). Unlike the complex transformations of combustion, the halogenation of an alkane appears to be a simple substitution reaction in which a C-H bond is broken and a new C-X bond is formed.

If a stoppered test-tube containing hexane and a drop of liquid bromine are left to stand at room temperature in the dark, nothing happens. The colour of the bromine is still as intense after three or four days. If the solution is exposed to sunlight, the colour fades in a few minutes and the acidic, fuming gas hydrogen bromide can be detected. The reaction that has occurred is:

$C_6H_{14}\,(l) + Br_2\,(l) \rightarrow C_6H_{13}Br(l) + HBr(g)$

When ethane reacts with chlorine in sunlight one or more chlorine atoms may replace hydrogen atoms depending on the amounts of halogen and alkane present. The formation of chloroethane:

$CH_3CH_3\ (g) + Cl_2\ (g) \rightarrow CH_3CH_2Cl(g) + HCl(g)$

May be followed by the formation of dichloroethane, $(CH_2)_2Cl_2$, trichloroethane CH_3CCl_3, Tetrachloroethane $ClCH_2CCl_3$, Pentachloroethane Cl_2CHCCl_3, and Hexachloroethane, C_2Cl_6.

$CH_3CH_2Cl(g) + Cl_2(g) \rightarrow CH_3CHCl_2(g) + HCl(g)$

$CH_3CHCl_2(g) + Cl_2(g) \rightarrow CH_3CCl_3(g) + HCl(g)$

$CH_3CHCl_3(g) + Cl_2(g) \rightarrow CH_2ClCCl_3(g) + HCl(g)$

$CH_2ClCCl_3\ (g) + Cl_2\ (g) \rightarrow CHCl_2CCl_3\ (g) + HCl(g)$

$CHCl_2CCl_3(g) + Cl_2(g) \rightarrow C_2Cl_6(g) + HCl(g)$

Chloroalkanes are useful solvents, and the mixture of products formed in the chlorination of an alkane may find use as a solvent, without the need for isolation of individual compounds.

The mechanism of the chlorination of Ethane:

Step 1:

Homolysis of the Cl– Cl bond. The necessary energy comes from the light absorbed or the heat supplied. It is easier to split the Cl – Clbond than the C – H bond. (Bond energy terms are Cl-Cl, 242.

KJmol^{-1}, C-H, 435 KJ mol^{-1}.

$$Cl_2 \xrightarrow[\text{or heat}]{\text{light}} 2Cl^{\bullet}$$

Step 2:

The chlorine atoms formed are very reactive. Since they are surrounded by ethane molecules:

$Cl\bullet + CH_3 - CH_3 \rightarrow HCl + CH_2 - CH_3$

The second possibility is more likely because the formation of an H – CI bond is more exothermic than the formation of a C – CI bond. (Bond energy terms are H – CI, 431 kjmol^{-1}, C – CI, 350 KJ mol^{-1})

Step3:

The methyl radicals formed collide with methane molecules and chlorine molecules. The reaction:

$\bullet CH_2\text{-}CH_3 + CH_3 - CH_3 \rightarrow CH_3 - CH_3 + \bullet CH_2 - CH_3$

Results in no net change.

The reaction $\bullet CH_2 - CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + \bullet Cl$

leads to a chain reaction.

Step 4:

Thousands of molecules of chloroethane are formed for every photon of light absorbed. The high yield is due to the chain reaction – steps 2 and 3. The reason why they yield is not higher is that radicals can combine with each other and bring the chain to an end. The reactions:

$2Cl\bullet \rightarrow Cl_2$

$2CH_3 - \bullet CH_2 \rightarrow C_4H_{10}$

$Cl\bullet + \bullet CH_2 - CH_3 \rightarrow CH_3CH_2Cl$

Bring the chain reaction to an end. Some ethane can be detected in the product.

Formation of CH_3CHCl_2:

Step 3 can give rise to the chain:

$CH_3CH_2Cl + Cl \rightarrow HCl + \bullet CH_2 - CH_2Cl$

$\bullet CH_2\text{-}CH_2Cl + Cl_2 \rightarrow (CH_2)_2Cl_2 + Cl\bullet$

$(CH_2)_2Cl_2$ can undergo further chlorination to CH_3CCl_3, CH_2ClCCl_3, $CHCl_2CCl_3$ and C_2Cl_6.

Points to Remember:

The following facts must be accommodated by any reasonable mechanism for the halogenation reaction.

(i) The reactivity of the halogens decreases in the following order: $F_2 > Cl_2 > Br_2 > I_2$

(ii) We shall confine our attention to chlorine and bromine since fluorine is so explosively reactive it is difficult to control and iodine is generally unreactive.

(iii) Chlorination and bromination are normally exothermic.

(iv) Energy input in the form of heat or light is necessary to initiate these halogenations.

(v) If light is used to initiate halogenation thousands of molecules react for each photon of light absorbed

(vi) Halogenation reactions may be conducted in either the gaseous or liquid phase.

(vii) In gas phase chlorination the presence of oxygen (a radical trap) inhibits the reaction.

In liquid phase halogenation radical initiators such as peroxides facilitate the reaction.

General Reaction:

$$CH_4 + Cl_2 \xrightarrow{Sunlight} CH_3 - Cl + HCl$$

Mechanism:

(i) Initiation Step:

$$Cl \bullet\!\!-\!\!\bullet Cl \xrightarrow{\text{sunlight}} Cl^{\bullet} + Cl^{\bullet}$$

Chlorine Molecule

Chlorine free Radicals

(ii) Propagation Step:

$$\text{(a)} \quad CH_3 \bullet \boxed{\bullet H + Cl^{\bullet}} \longrightarrow \underset{\text{Methyl free radical}}{\overset{\bullet}{C}H_3} + HCl$$

$$\text{(b)} \quad \boxed{\overset{\bullet}{C}H_3 + Cl\bullet}\bullet Cl \longrightarrow \underset{\text{Methyl Chloride}}{CH_3 - Cl} + \underset{\text{Chlorine free radical}}{Cl^{\bullet}}$$

(iii) Termination Step:

•$CH3 + Cl\bullet \rightarrow CH_3 - Cl$

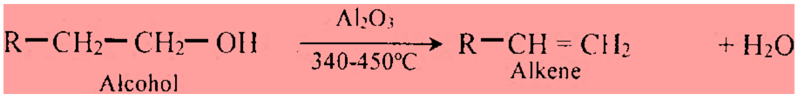
Methyl chloride

Preparation of Alkenes:

REACTION	**REMARKS**
Dehydrohalogenation	Removal of hydrogen and halogen from two adjacent carbon atoms is called dehydrohalogenation.
Dehydration of Alcohol	• Removal of water molecule is called dehydration •Tendency of dehydration is as given below Tertiary > Secondary > Primary alcohol alcohol alcohol
Dehalogenation of vic-dihalide	Removal of halogen is called dehalogenation

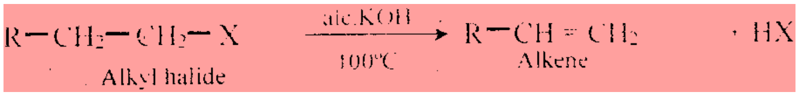
General Methods of Preparation:

- Dehydration of Alcohols:



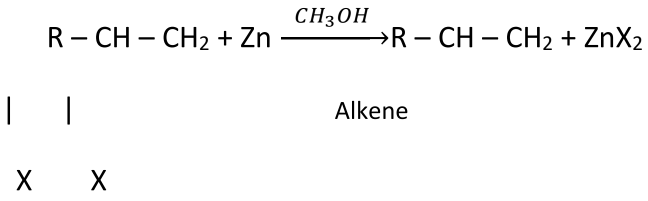
$$\underset{\text{Alcohol}}{R-CH_2-CH_2-OH} \xrightarrow[340\text{-}450^\circ C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

- Dehydrohalogenation of Alkyl Halide:



$$\underset{\text{Alkyl halide}}{R-CH_2-CH_2-X} \xrightarrow[100^\circ C]{alc.KOH} \underset{\text{Alkene}}{R-CH=CH_2} + HX$$

- Dehalogenation of Vic-Dihalides:



$$\underset{X}{\underset{|}{R - CH}} - \underset{X}{\underset{|}{CH_2}} + Zn \xrightarrow{CH_3OH} \underset{\text{Alkene}}{R - CH - CH_2} + ZnX_2$$

REACTIONS OF ALKENES (ETHENE):	
REACTION	REMARKS (ADDITION REACTION)
Hydrogenation	• Raney Nickel is used as catalyst
	• Raney Ni is produced after the reaction of Ni-Al alloy with caustic soda
	• Reaction is exothermic
Addition of HX	• Alkenes react with dry gaseous hydrogen halides
	• Order of reactivity of halogen acid is HI > HBr > HCl
	• Reaction mechanism involve carbocation formation
	• Markownikov's rule implements on asymmetric alkenes
Sulphonation	• Addition of sulphonic acid group is called sulphonaton
Halohenation	• Reaction take place in inert solvent
	• It does not react with alkene
	• Reaction mechanism involve carbonium ion formation
Addition of hypohalous acid	• Halohydrins are produced in this reaction
	• The compound in which X and OH groups are on vicinal C atoms called halo-hydrins
OXIDATION REACTION	
Addition of Oxygen	• Epoxide is reduced
	• Epoxides are used in glycol formation

Ozonolysis	•	Addition of ozone is called ozonolysis
	•	Ozonide due to instability, changes into aldehydes or ketones or both depending upon alkyl group
Combustion	•	Burning of alkene is called combustion
	•	Exothermic reaction
	•	Reaction occur in kitchen (stores) and in petrol engine
Hydroxylation	•	1 % alkaline $KMnO_4$ is also called Baeyer's reagent (Cold)
	•	$KMnO_4$ colour is discharged during reaction
Oxidative Cleavage	•	Baeyer's reagent (Hot concentrated) is used
	•	Alkenes form carboxylic acids

POLYMERIZATION

:

In this process small organic molecules (monomers) combine together to form larger molecules known as polymers, Ethene at 400° C and 100 atm pressure, polymerize to polythene or polyethylene. 400° C 100 atm pressure

$$nCH_2 = CH_2 \xrightarrow{400^{o}C\ 100\ atm\ pressure} -[CH_2 - CH_2 -]_{n\,-}$$

Polyrhtylene

Traces of O_2 (0.1 %)

A good quality polythene is obtained, when ethane is polymerized in the presence of aluminum triethyl Al $(C_2H_5)_3$ and titanium tetrachloride catalysts ($TiCl_4$).

POINT TO PONDER: A test for a multiple bond is the decolourisation of a bromine solution without?

CHEMICAL REACTIONS OF ETHENE:

$$CH_2 = CH_2 + 3O_2 \xrightarrow{Flame} 2CO_2 + 2H_2O + heat$$

$$CH_2 = CH_2 + H_2 \xrightarrow[100^\circ C, 3atm]{Raney\ Ni} \underset{Ethane}{CH_3 - CH_3}$$

$$CH_2 = CH_2 + Br_2 \rightarrow BrCH_2 - CH_2Br$$

Vicinal dihalide

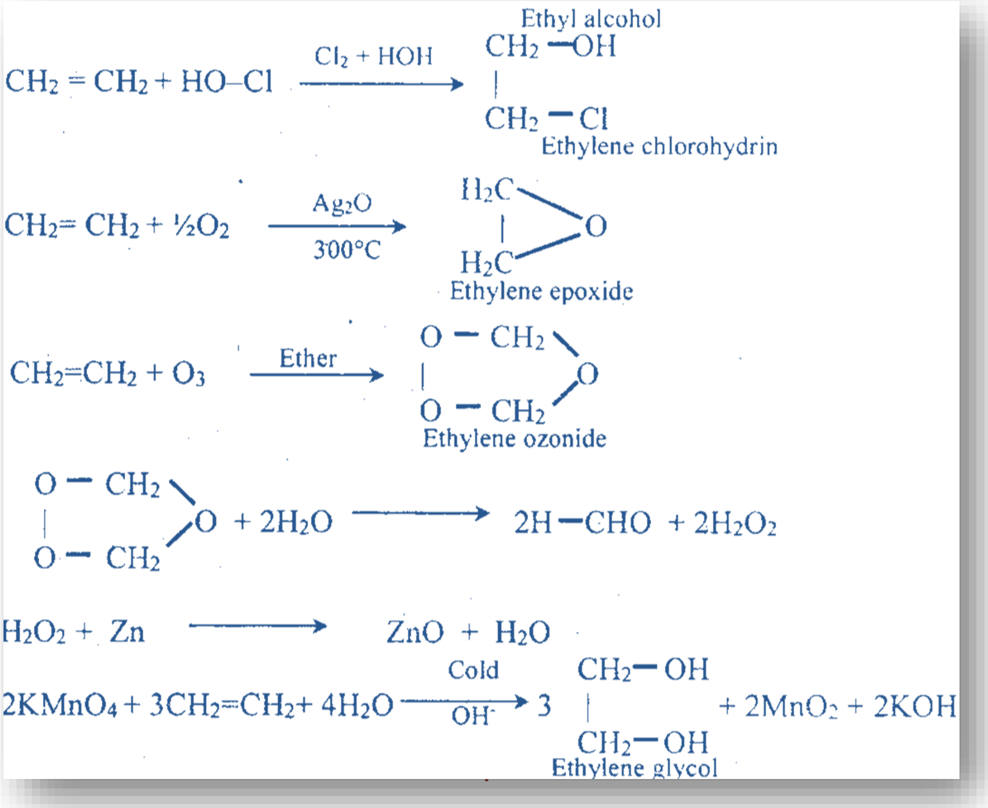
$$CH_2 = CH_2 + HBr \rightarrow CH_3 - CH_2 - Br$$

Ethyl bromide

$$CH_2 = CH_2 + H_2SO_4 \xrightarrow{(conc.)} CH_3 - CH_2 - OSO_3H$$

(Cold) Ethyl hydrogen sulphate

$$CH_3 - CH_2 - OSO_3H + H_2O \xrightarrow{100^o\ C} CH_3 - CH_2 - OH + H_2SO_4$$



$CH_2 – CH_2 – Cl$

/

$2CH_2 = CH_2 + S_2Cl_2 \rightarrow S$ + S

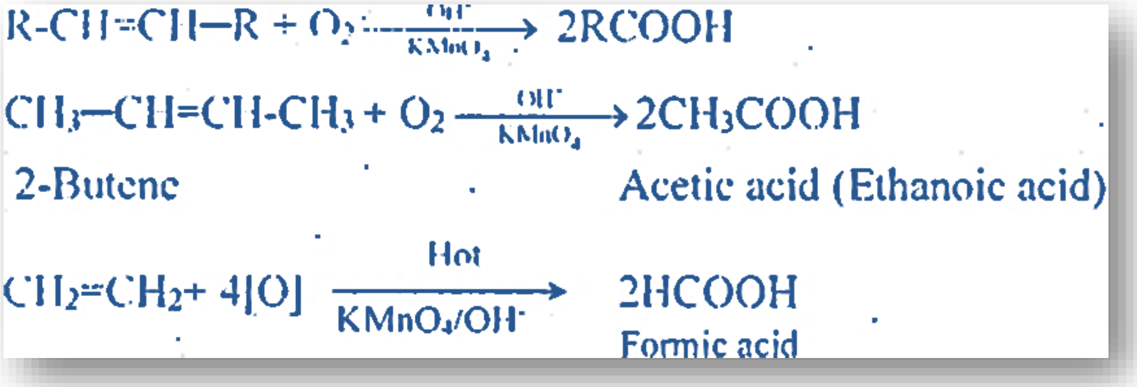
\

$CH_2 – CH_2 – Cl$

β, β-dichloroethyl sulphide (Mustard gas)

Commercial method / By the Oxidative Cleavage of Alkenes:

When alkenes arc heated with alkaline $KMnO_4$ solution, they undergo a cleavage at carbon to carbon double bond. This results in carboxylic-acids:



$$R-CH=CH-R + O_2 \xrightarrow[KMnO_4]{OH^-} 2RCOOH$$

$$CH_3-CH=CH-CH_3 + O_2 \xrightarrow[KMnO_4]{OH^-} 2CH_3COOH$$

2-Butene Acetic acid (Ethanoic acid)

$$CH_2=CH_2 + 4[O] \xrightarrow[KMnO_4/OH^-]{Hot} 2HCOOH$$

Formic acid

PHYSICAL PROPERTIES OF ALKANES AND ALKENES

Alkanes	Alkenes
• Alkanes containing → $C_1 – C_4$ are colourless and odourless gases → $C_5 – C_{17}$ are colourless and odourless liquid → C_{18} onwards are colourless and odourless waxy solids	• First three members' i.e ethene, propene and butene are gases at room temperature while C_5 to C_{15} are liquids and the higher members are solid.

•	Being non-polar they are insoluble in water but soluble in non-polar solvents	•	They are insoluble in water but soluble in alcohol
•	Their physical constants (Boiling point Melting Point. density etc) increase with the increase in number of carbon atoms	•	They have characteristic smell and burn with luminous flame
•	Solubility decreases with increase in molecular mass.	•	Unlike alkanes, they show weakly polar properties because of sp^2 hybridization
•	The boiling points of alkanes having branched chain structures are lower than their isomeric normal chain alkanes		
USES			
			Polyethylene
•	Illuminating gas cylinder	•	Anesthesia
•	$CHCl_3$, CCl_4 CH_3OH, HCOH, HCN	•	Mustard gas
•	Carbon black, printing ink, auto mobile tyres	•	Glycols (antifreeze) Artificial ripening of fruit

CHEMISTRY OF BENZENE

Structure of Benzene:

Straight Chain Structure:

- Possible chain structures are:

a) $HC{=}C - CH_2 - CH_2{-}C{=}CH$

1.5-hexadiyne

b) $CCH_2=C-CH=C-CH=CH_2$

1 ,5-hexadiene-3-yne

- Benzene does not decolorize $KMnO_4$, while alkene and alkyne decolorize $KMnO_4$.

- Benzene gives addition reaction with hydrogen and halogens

- Benzene gives substitution reaction with cone HNO_3 conc. H_2SO_4 which shows its saturation

- Benzene gives only one mono substitute product which is against its straight chain structure that may form three

- The molecular formula of benzene is C_6H_6 which does not correspond to open chain hydrocarbon like alkane (C_6H_{14}), alkene (C_6H_{12}) and alkyne (C_6H_{10}).

KEKULE STRUCTURE

- He proposed planner hexagonal structure of benzene containing three double bonds alternate to single bond

- Kekule structure gives only one mono-substituted benzene.

- It gives three di-substituted benzene isomeric products i.e. ortho, meta, para

- As benzene adds three molecules of hydrogen and chlorine, it favours presence of three double bonds alternate to the single bond

Objection to the Kekule's formula:

- Kekulcs structure favours the un-saturation of benzene while benzene acts as saturated hydrocarbon in most of the reactions. Benzene is stable compound.

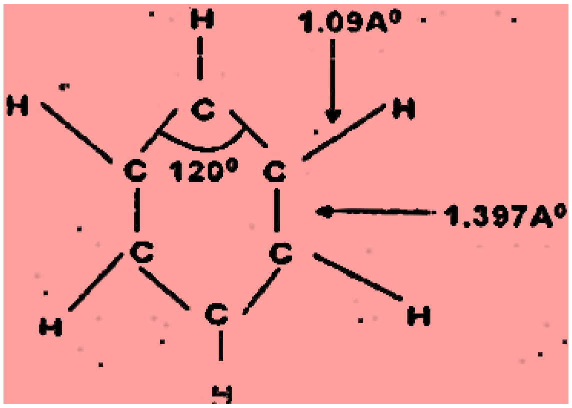
X-ray studies of benzene structure:

- Benzene is hexagonal structural compound

- C – C-H and C – C – C bond angle is 120^o

- Bond length of C-C bond is 1.397 A^o

- Bond length of C-H bond is 1.09 A°



Modern Concept about Structure of Benzene:

- Each carbon atom in benzene is sp^2 hybridized, which forms σ bonds with one of hydrogen atom and two with adjacent carbon atoms.
- All of bonds formed by $sp^2 – sp^2$ and $sp^2 – s$ orbitals are co-planner.
- All bond angles are 120° so the structure of benzene is regular co-planner hexagonal.
- Un-hybridized $2p_z$ atomic orbital of C atoms overlaps above and below the framework and forms diffused or delocalized continuous sheath of π electron cloud.

	Cyclohexene	**1, 3-dohexadiene**	**l, 3, 5-Cyelohexatriene**
Expected hydrogenation energy	$– 119.5$ kJ mol^{-1}	$– 239$ kJ mol^{-1}	$– 358.5$ kJ mol^{-1}
Actual hydrogenation energy	$– 119.5$ kJ mol^{-1}	$– 231.5$ kJ mol^{-1}	$– 208$ kJ mol^{-1}
Resonance energy	0.0	7.5 kJ mol^{-1}	150.5 kJ mol^{-1}

Delocalized Electron: When shared electrons are attracted by more than two nuclei such electrons are called delocalized electrons

The Stability of Benzene:

The stability of benzene is due to the extensive delocalization of electron cloud The delocalized electrons increase the stability of benzene.

- Heat of hydrogenation of cyclohexene and 1,3-cyclohexadicne is – 119.5 kJ mol and

– 231.5 kJ/mole respectively.

- Duetothephenomenon of resonance and resonance energy, the heat of hydrogenation of benzene is lesser (– 208 kJ mol) than that of 1,3,5-cyclohexatriene.

POINT TO PONDER: Is the standard enthalpy of benzene equal to the sum of the standard bond enthalpies.

THE RESONANCE METHOD

Resonance:

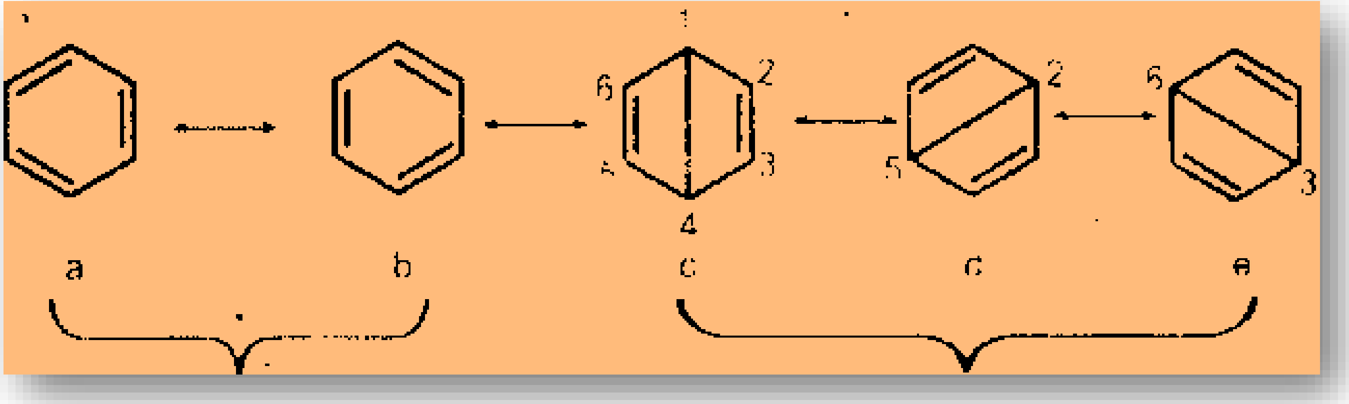
The possibility of different pairing schemes of valence electrons of atoms is called resonance and the different structure this arranged are called resonance structure.

- Different Lewis structures are called resonance contributing structures or canonical forms.
- The resonance structures are represented by (↔) double headed arrow.
- Dewar is the scientist who gave the concepts of para bonds in structure of benzene, but his structure contributes very little in prediction of actual structure of benzene
- Kekule s structure of benzene (alternate double bonds in planner hexagonal ring) contributed more in prediction of actual structure of benzene.
- Bond lengths in hydrocarbon are as under:

Nature of bond	Bond length
C – C	1.54 A^o
C = C	1.34 A^o
C ≡ C	1.20 A^o
C – C in benzene	1.397 A^o

Bond length in C-C in benzene (1.397 A^o) shows that it is in between single and double bond

- Due to fact of bond length it was proposed that actual structure of benzene will be hybrid if Kekul's and Dewar's structure.



Kakule's structures Dewar structures

Electrophile for nitration: NO_2

Sulphonation: SO_3

Alkylation: R^-

O

||

Aevlation: R – C

REACTIONS OF BENZENE:

Electrophiles:

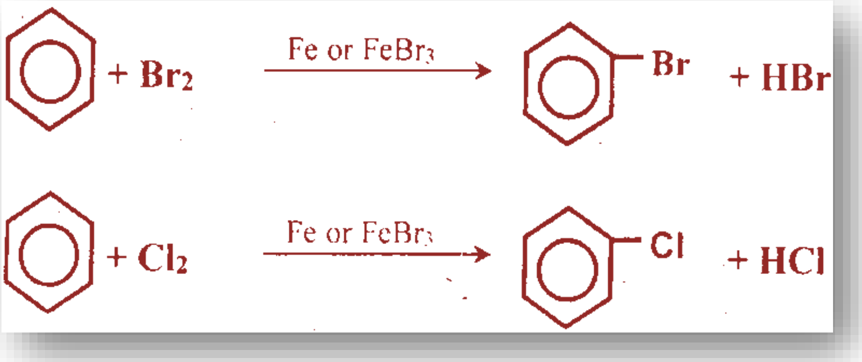
The species which are electron deficient called electrophiles

- Presence of delocalized electrons in benzene increases the stability of benzene, so very strong electrophile is required I'm attacking purpose

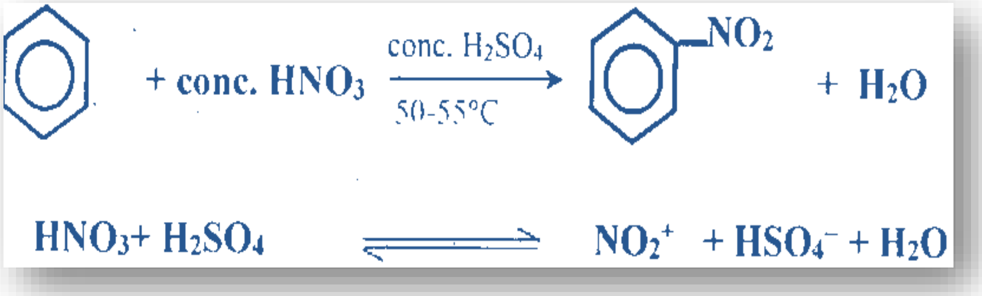
ELECTROPHILIC SUBSTITUTION REACTIONS

Electrophilic substitution reaction involves carhonium ion formation.

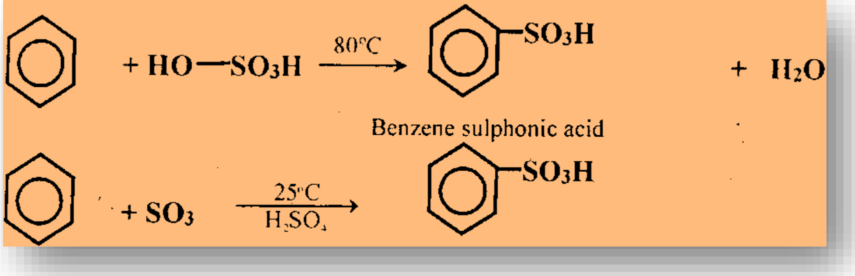
- Introduction of halogen in a molecule is called halogenation,
- Mono substituted benzene is produced during the halogenation in which FeX, or Fe act as catalyst.



- Introduction of – NO_2 in a molecule is called nitration.



- Introduction of – HSO_3^+ group in a molecule is called sulphonation.

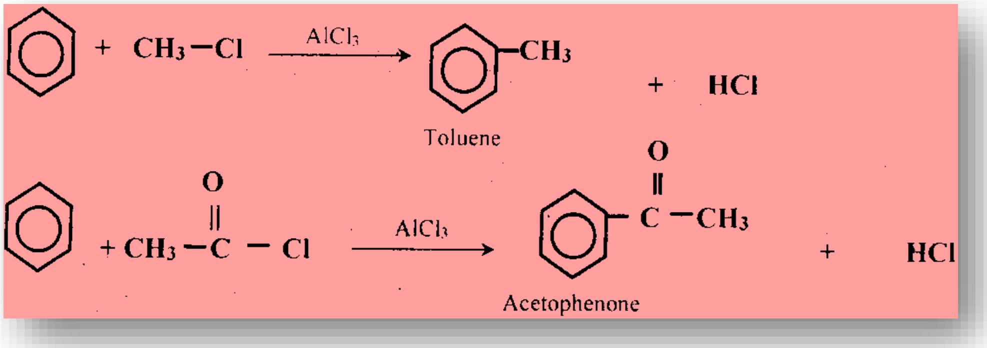


Benzene Sulphuric Acid

Friedel Craft Alkylation and Acylation:

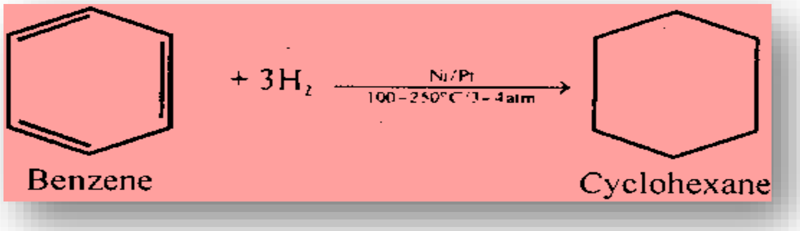
The reaction in which alkyl group or acyl group replaces the hydrogen of benzene is called Friedel Craft alkylation and acylation respectively.

- $AlCl_3$ is used as catalyst in Friedel craft alkylation or acylation:



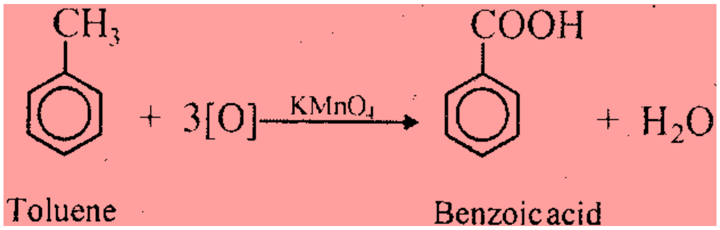
Hydrogenation of Benzene:

Addition of hydrogen is called hydrogenation. When benzene is passed over Pt or Pd at 250°C, it undergoes hydrogenation to produce cyclohexane.

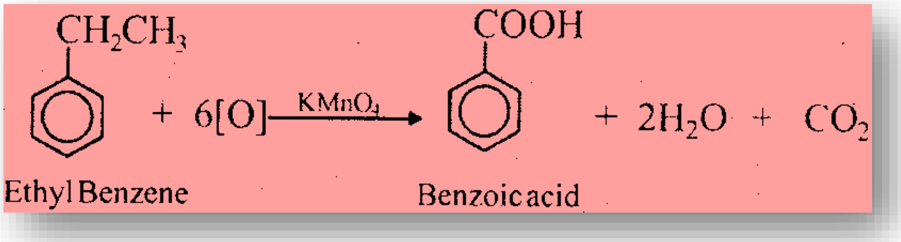


Side Chain oxidation:

Alkyl benzenes are readily oxidized by acidified $KMnO_4$ or $KCnO_7$. In these reactions the alkyl groups are oxidized keeping the benzene ring intact.

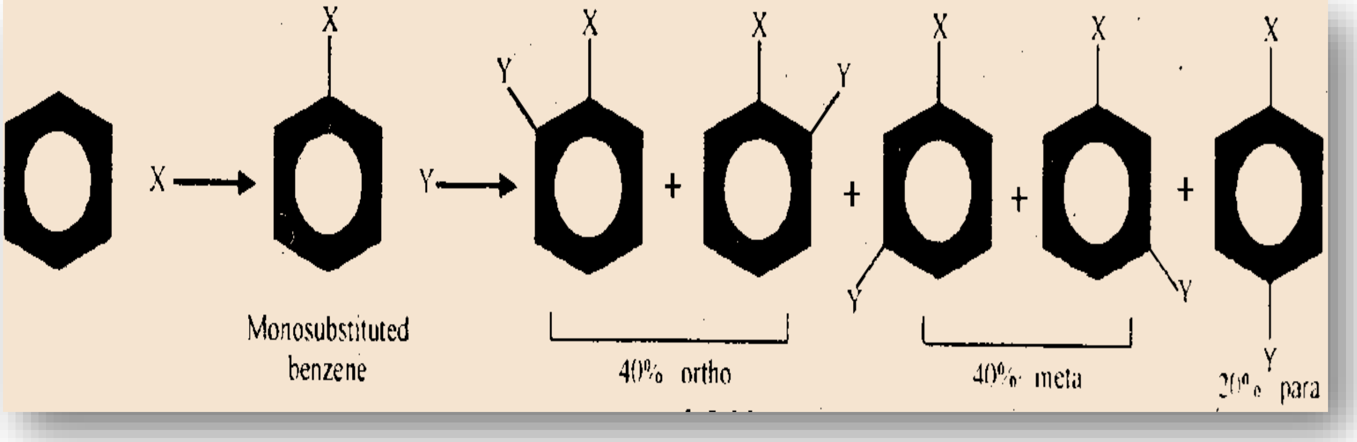


Whatever the length of an alkyl group may be it gives only one carboxyl group. Moreover, the colour of $KMnO_4$ is discharged. Therefore this reaction is used as a test for alkyl benzenes.

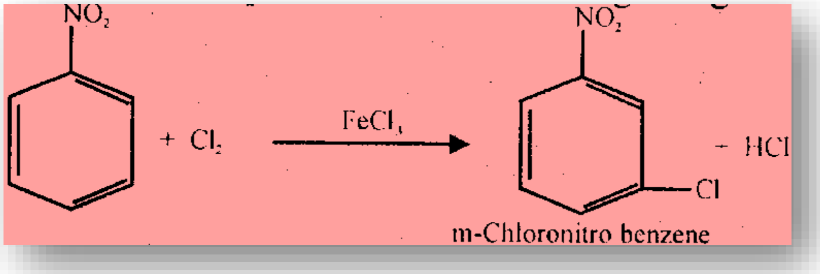


Orientation in Benzene (Electrophilic Substitution Reactions):

When an electrophilic substitution reaction takes place on benzene ring we get only one mono-substituted benzene because all the six positions in the ring are equivalent. However, the introduction of a second group into the ring may give three isomeric di-substituted products ortho, meta and para.

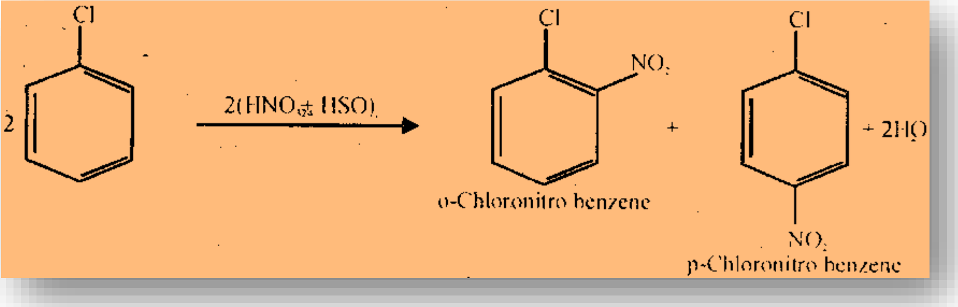


On chance basis 40 % ortho, 40 % meta and 20 % para di-substituted products are expected. But the actual di-substitution of benzene does-not follow this principle of chance. e.g m-nitrochlorobenzene is the main product of the following halogenation reaction.



m-Chloronitro benzene:

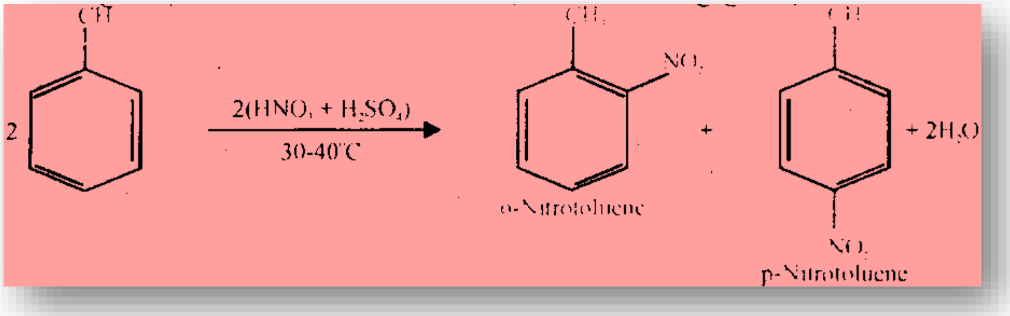
On the other hand, a mixture of o-nitro-chlorobenzene and p-nitrochlorobenzene is obtained from the nitration of chlorobenzene.



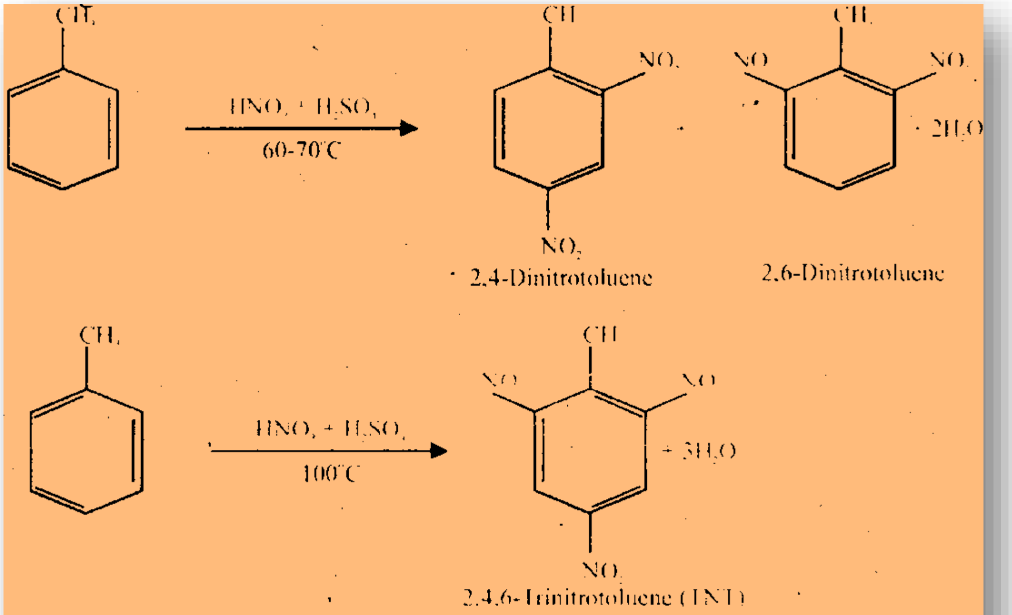
It means that the group present in the mono-substituted benzene ring has the directive effect and thus determines the position or orientation for the new incoming groups. There are two types groups, I-ortho and para-directing group's 2-meta-directing groups.

Ortho-and para directing groups:

These groups release electrons to the benzene ring thereby facilitating the availability of electrons to the electrophiles at ortho and para positions. This results in the increased chemical reactivity of benzene ring towards electrophiles. The benzene ring can offer more than one positions (ortho and para) to the new incoming groups. These groups are called ortho and para directing groups.



The electron releasing effect of methyl group is significant and it makes the ring a good nucleophile. Due to this increased reactivity more nitro groups can be substituted on benzene ring.

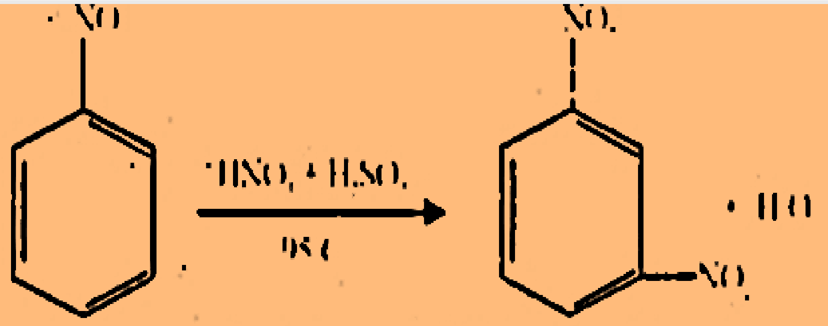


$-N(CH_3)_2$, $-NH_2$, $-OH$, $-OCH_3$, $-Cl$, $-Br$, $-I$

Meta-Directing Groups:

(deactivators of benzene ring)

These groups withdraw electron of the benzene ring towards themselves. There by reducing the availability of electrons to the electrophiles at ortho and para positions. This results in the decreased chemical activity of benzene. Moreover, due to the electron withdrawing effect of such sub-stituents the ortho and para positions are rendered more electron deficient than the meta-position. Thus the incoming electrophile will prefer to attack on meta position rather than ortho and para positions. These groups arc called meta directing groups e.g.



Other examples:— NR_3, — C ≡ N, — COOH, — CHO, — RCO

PRACTICE EXERCISE (FOR UHS TOPIC)

1. **In hot alkaline $KMnO_4$ 2-butene gives**

(A) glycol	(C) Acetic acid
(B) Glycerol	(D) Alcohol

2. The reaction of alcoholic KOH on ethyl chloride gives

(A) Ethane (C) Ethene

(B) Methane (D) Acetylene

3. The temperature during the polymerization of ethene is maintain at

(A) 200°C (C) 300°C

(B) 400°C (D) 100°C

4. Acetylene and ethylene reacts with alkaline $KMnO_4$ to give:

(A) Oxalic acid and a formic acid (C) ethyl alcohol and ethylene glycol

(B) Acetic acid and ethylene glycol (D) oxalic acid and ethylene glycol

5. Propyne and propene can be distinguished by:

(A) Conc. H_2SO_4 (C) Dil. $KMnO_4$

(B) Br_2 in CCl_4 (D) $AgNO_3$ in ammonia solution

6. Methane reacts with oxygen at 100 atm. and 300°C in presence of Cu to give

(A) Acetaldehyde (C) Acetic acid

(B) Methyl alcohol (D) Ethyl alcohol

7. Methyl free radical involve:

(A) Sp hybridisation (C) Sp^3 hybridisation

(B) Sp^2 hybridisation (D) sp^3d hybridisation

8. Which gives the most stable alkene:

(A) Ethyl alcohol (C) Sec. butyl alcohol

(B) n-butyl alcohol (D) ter. Butyl alcohol

9. The hybridization of tertiary carbon atom in isobutane is:

(A) sp (C) sp^3

(B) sp^2 (D) dsp^3

10. The chemical reactivity of ethylene is due to:

(A) Short carbon to carbon bond distance (C) Trigonal planar structure

(B) High couble bond energy (D) Presence of π electrons

11. The bond present in ethylene are:

(A) 3 sigma and 3 π bond (C) 1 π and 3 sigma bond

(B) 1 sigma and 1 π bond (D) 1 π and 5 sigma bond

12. Molecule in which the distance between the adjacent carbon atoms is largest is:

(A) Ethan (C) Ethyne

(B) Ethene (D) Benzene

13. Baeyer's reagent is:

(A) Alkaline permanganate solution (C) Neutral permanganate solution

(B) Acidified permanganate solution (D) Aqueous bromine solution

14. Preparation of vegetable ghee involves:

(A) Halogenation (C) Hydrogenation

(B) Hydroxylation (D) Dehydrogenation

15. Which type of reactions are given by alkanes:

(A) Polymerization	(C) Elimination
(B) Addition	(D) Substitution

16. The most reactive hydrocarbon is:

(A) Ethene	(C) Acetylene
(B) Heptane	(D) Ethane

17. Unsaturated nature of alkene can be detected by:

(A) Decolorization of red Br_2 water in CCl_4

(B) Decolorization of pink colour of $KMnO_4$ solution

(C) Ozonolysis

(D) All of these

18. The addition of unsymmetrical reagent to an unsymmetrical alkene is in accordance with the rule:

(A) Hund's rule	(C) Markownikov's rule
(B) Pauli's exclusion principle	(D) Aufbau principal

19. The carbon-carbon and C-H bond lengths in benzene molecule are respectively

(A) 1.54 A^o, 1.08 A^o	(C) 1.397 A^o, 1.09 A^o
(B) 1.33 A^o, 1.08 A^o	(D) 1.20 A^o, 1.08 A^o

20. The electrophile in aromatic sulphonation is:

(A) H_2SO_4	(C) HSO_4

(B) SO_3^+ (D) SO_3

21. Ethene is produced from ethyl chloride by the process:

(A) Hydration (B) Dehydration

(C) Dehalogenation (D) Dehydrohalogenation

22. Which forms alkene on dehalogenation?

(A) Vicinal dihalide (B) Geminal dihalide

(C) Tetrahalide (D) All the above

23. Which of the following does not change when ethene is polymerized to polyethylene?

(A) M-P (B) Density

(C) Molar mass (D) % composition

24. Raney Nickel is prepared by reacting an alloy with caustic soda:

(A) Ni – Cu (B) Ni – Fe

(C) Ni – Al (D) Ni – Mg

25. Ethyl chloride when boiled with alcoholic KOH gives:

(A) Ethyne (B) Ethylene

(C) Ethane (D) Benzene

26. The conversion of Ethanol to ethene is:

(A) Hydration (B) Hydrogenation

(C) Dehydration (D) Oxidation

27. Which of the following is not observed in the combustion of pure methane in a plenty of air?

(A) Water is produced (B) CO_2 is produced

(C) The flame is smoky (D) Energy is released

28. When toluene is oxidized in the presence of $KMnO_4$, the product is:

(A) benzopheone (B) Benzyl acetate

(C) Picric acid (D) Benzoic acid

29. Which alcohol will undergo dehydration easily to give alkene in the presence of acidic dichromate?

(A) Primary alcohol (B) Secondary alcohol

(C) Tertiary alcohol (D) All above

30. **An alkene is treated with cold alkaline $KMnO_4$ in experiment –1 and with hot alkaline $KMnO_4$ in experiment-2 separately. What will be pair of products in the two experiment?**

(A) Glycol and glycerol (B) Glycerol and aldehyde

(C) Glycol and carboxylic acid (D) Glycol and ketone

31. During halogenation, if an excess of methane reacts with chlorine in sunlight to form chloromethane, what will be the major product?

(A) Monochloro methane (B) Dichloromethane

(C) Trichloromethane (D) Tetrachloro methane

32. An addition of water to ethene and ethyne produces a pair of compounds:

(A) Both produces alcohol (B) An alcohol and ketone

(C) Ketone and aldehyde (D) An alcohol and aldehye

33. VinyL chloride on dehydrohalogenation gives:

(A) Ethyne (B) Ethene

(C) Ethane (D) Methane

34. Which of the following is not alicyclic aromatic?

(A) Cyclopropane (B) Cyclobutane

(C) Toluene (D) Cyclopentane

35. 1-chlorobutane on react with alcoholic KOH gives in excess:

(A) 1-butene (B) 2-butene

(C) 1-butanol (D) 2-butyne

36. Enthalpy of combustion of methane in kJ mol^{-1} is:

(A) –891 (B) –358.5

(C) –208 (D) –240

37. A hydrocarbon which is liquid at room temperature decolourizes aqueous solution of bromine. The formula of the compound is:

(A) C_2H_2 (B) C_2H_4

(C) C_7H_{16} (D) $C_{10}H_{20}$

38. Cloalkanes and monoalkenes have general formula:

(A) C_nH_{2n+2} (B) C_nH_{2n}

(C) C_nH_{2n-2} (D) C_nH_n

39. 2-methyl 1, 3 butadiene is called:

(A) Styrene
(B) Isoperene
(C) Cumene
(D) Vinyl acetylene

40. Aromatic hydrocarbons containing two or more benzene rings in their molecules can be divided into main classes:

(A) Two
(B) Three
(C) Four
(D) Five

41. Benzene reacts with HNO_3 in the presence of H_2SO_4 to form nitrobenzene. What is the role of H_2SO_4?

(A) Solvent
(B) Removing H_2O produced
(C) Protonating HNO_3
(D) Forming unstable complex with benzene

42. Benzene is made up of:

(A) 12 bonds ($3\pi + 9\sigma$)
(B) 12 bonds ($6\pi + 6\sigma$)
(C) 15 bonds ($3\pi + 12\sigma$)
(D) 16 bonds ($4\pi + 12\sigma$)

43. Which of the following is not meta directing group?

(A) –CN
(B) –OH
(C) –COOH
(D) –CHO

44. Which compound will readily undergo sulphonation?

(A) Benzene
(B) Nitrobenzene
(C) Toluene
(D) Chlorobenzene

45. Which compound will form benzoic acid on oxidation with strong oxidizing agent:

(A) Toluene

(B) Ethyl-benzene

(C) n-Propyl benzene

(D) All

46. Hydrolysis of benzene sulphonic acid with super heated steam or by boiling with dil. HCl gas:

(A) Toluene

(B) Benzene

(C) Xylene

(D) Chlorobenzene

47. The active specie involved in the nitration of benzene is:

(A) NO^+

(B) NO_2^+

(C) NO_3^+

(D) NO_2

48. Which of the following is most stabilized by resonance?

(A) Cyclohexadiene

(B) Benzene

(C) Naphthalene

(D) Anthracene

49. The oxidation of which compound yields benzoic acid:

(A) Isopropyl benzene

(B) n-propyl benzene

(C) Isobutyl benzene

(D) All

50. Which of the following is not ortho-para directing group?

(A) $-NH_2$

(B) $-OCH_3$

(C) $-CHO$

(D) $-OH$

51. Which of the following is meta directing group?

(A) CN (B) COOH

(C) COR (D) All

52. Which one of the following is used as a catalyst in Friedel-Craft reaction?

(A) HNO_3 (B) $BeCl_2$

(C) $CuCl_2$ (D) $AlCl_3$

53. Toluene can be converted into benzoic acid on reacting with:

(A) dil. NaOH (B) dil. HNO_3

(C) Conc. HNO_3 (D) Acidified $KMnO_4$

54. Benzene does not undergo reaction:

(A) Addition (B) Substitution

(C) Polymeriation (D) Aromatization

55. Arrange the following ortho-para directing groups in increasing order to increase the reactivity of benzene ring.

(i) –OH (ii) –R (iii) –Cl

(A) OH > Cl > R (B) R > OH > Cl

(C) Cl < R < OH (D) OH = Cl = R

56. 1,2 Dichloroethane treated with Acoholic 'Zn' Product will be.

(A) Ethene (B) Ethyne

(C) Ethyl alcohol (D) Ethyl Chloride

57. Which is a test to distinguish b/w ethene & ethane.

(A) $KMnO_4/OH^-$
(B) Br_2/CCl_4
(C) Cl_2/CCl_4
(D) All of these

58. Which group is otrho and para directing as well as ring de-activator?

(A) -OH
(B) -OR
(C) -Cl
(D) Not Possible

59. Which one is more reactive specie?

(A) Phenol
(B) Nitrobenzene
(C) Toulene
(D) Chlorobenzene

60. The order of reactivity of halogens with alkanes is?

(A) $I_2 < F_2 < Cl_2 < Br_2$
(B) $F_2 < I_2 < Cl_2 < Br_2$
(C) $I_2 > F_2 > Cl_2 > Br_2$
(D) $F_2 < Cl_2 < Br_2 < I_2$

ANSWER KEY

1	**C**	**11**	**D**	**21**	**D**	**31**	**A**	**41**	**C**	**51**	**D**
2	**C**	**12**	**A**	**22**	**A**	**32**	**D**	**42**	**C**	**52**	**D**
3	**B**	**13**	**A**	**23**	**D**	**33**	**A**	**43**	**B**	**53**	**D**
4	**D**	**14**	**C**	**24**	**C**	**34**	**C**	**44**	**C**	**54**	**D**
5	**D**	**15**	**D**	**25**	**B**	**35**	**A**	**45**	**D**	**55**	**C**
6	**B**	**16**	**A**	**26**	**C**	**36**	**A**	**46**	**B**	**56**	**B**
7	**C**	**17**	**D**	**27**	**C**	**37**	**D**	**47**	**B**	**57**	**D**
8	**D**	**18**	**C**	**28**	**D**	**38**	**B**	**48**	**D**	**58**	**C**
9	**C**	**19**	**C**	**29**	**C**	**39**	**B**	**49**	**D**	**59**	**A**
10	**D**	**20**	**D**	**30**	**C**	**40**	**A**	**50**	**C**	**60**	**D**

UHS TOPIC 3 – C

ALKYL HALIDES

LEARNING OUTCOMES

In this topic, student should be able to:

a) Discuss importance of halogeno alkanes in everyday life with special use of CFCs, halothanes, $CC1_4$ – $CHCl_4$ and Teflon.

b) Reaction of alkyl halides such as:

i) SN-reactions, (Reactions of Alkyl halides with aqueous KOH, Alcoholic / aqueous KCN and Alcoholic / aqueous NH_3)

ii) Describe SN_1 and SN_2 mechanisms for tertiary butyl chloride and methyl bromide respectively using aqueous KOH

iii) Elimination reaction with alcoholic KOH to give alkenes

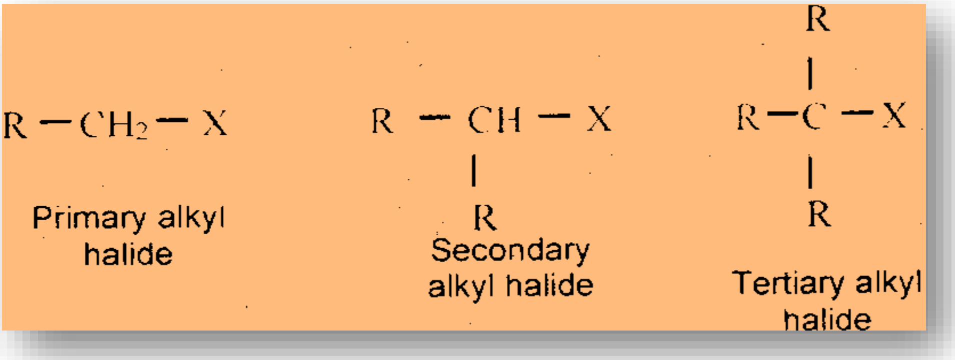
POINT TO PONDER: Monohalogeno alkanes are known as …………

INTRODUCTION:

Those organic compounds which are derived from the hydrocarbons by the replacement of one hydrogen atom by the halogen atoms are called alkyl halides.

- The general formula of alkyl halides is C_nH_{2n+1} X or R-X in which 'X' stands for a halogen atom.

- An alkyl halide may be a primary secondary or tertiary.



Haloalkanes may be mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present.

Importance of halogenoalkanes in Everyday Life:

CFCs are non-flammable and not very toxic. They therefore had a large number of uses. They were used as refrigerants, propellants for aerosols, for generating foamed plastics like expanded polystyrene or polyurethane foam, and as solvents for dry cleaning and for general degreasing purposes.

Unfortunately CFCs are largely responsible for destroying the ozone layer. In the high atmosphere the carbon-chlorine bonds, break to give chlorine free radicals. It is these radicals which destroy ozone. CFCs are now being replaced by less environmentally harmful compounds.

CFCs can also cause global warming. One molecule of CFC-11, for example has a global warming potential about 5000 times greater than a. molecule of carbon dioxide.

On the other hand, there is far more carbon dioxide in the atmosphere than CFCs. so global warming is not the major problem associated with them.

Halothanes:

It is the only inhalational anesthetic agent containing a bromine atom; there are' several other halogenated anesthetic agents which lack the bromine atom and do contain the fluorine and chlorine atoms present in halothane. It is colourless and pleasant-smelling, but unstable in light.

CCl4:

Carbon tetrachloride, also known by many other names (notably, **carbon tetrachloride** in the cleaning industry, and as a Halon or Freon in HVAC is the organic compound with the formula $CCl_{4,}$ It was formerly widely used in tire extinguishers, as a precursor to refrigerants, and as a cleaning agent. It is a colourless liquid with a "sweet" smell that can be detected at low levels.

POINT TO PONDER: The stability of the C – CI bond makes organic compounds of chlorine non-bio gradable and therefore ………..

Halogenoalkanes are also used as?

$CHCl_3$:

Formerly, chloromethane was a widely used as refrigerant, but due to its toxicity this use has been discontinued. Chloromethane was also once used for producing lead-based additives for gasoline, but leaded gasoline has been phased out in most of the industrialized world (an important exception being the former Soviet Union).

The most important use of chloromethane today is as a chemical intermediate in the production of silicone polymers. Smaller quantities are used as a solvent in the manufacture of butyl rubber andinpetroleum refining.

Chloromethane is also employed as a methylating and biodegradable and therefore chlorinating agent inorganic chemistry. It is also used in a variety of other fields: as an extractant for greases, oils and resins, as a propellant and blowing agent in polystyrene foam production, as a local anesthetic, as an intermediate in drug manufacturing, as a fluid for thermometric and thermostatic equipment and as a herbicide.

Teflon:

PTFE is used as a non-stick coating for pans and other cookware. It is non-reactive, partly because of the strength of carbon-fluorine bonds, and so it is often used in containers and pipe work for reactive and corrosive chemicals. Where used as a lubricant. PTFE reduces friction, wear, and energy consumption of machinery.

POINT TO PONDER: The stability of the hydrogen halides decreases in the order in which the standard bond enthalpy …………

Reactivity of Alkyl Halides:

The reactivity of alkyl halides depends upon the following factors:

(i) C – XBond energy

(ii) C – XBond polarity

- Greater the bond energy of R-X, greater will be the stability and lesser the reactivity.
- Greater EN difference (bond polarity) of R – X greater will be the stability and lesser the reactivity.

Conclusion:

Experiments have shown that the strength of carbonhalogen bond is the main factor which decides the reactivity of alkyl halides.

R – I> R – Br> R – Cl> R – F

Important:

If an electrophile is the attacking reagent then R-F will be the most reactive.

Reactions of Alkyl Halides:

Alkyl halides show two types of reactions generally.

i) Those reactions in which the halogen is replaced by some other atom or a group (nucleophilic substitution, or S_N reactions)

ii) Those reactions that involve the removal of HX from the halide (elimination or E reactions)

Nucleophilic Substitution (S_N) Reactions:

Electrophiles (Electron Loving):

The electron-deficient molecules or ions, which have a tendency to accept a pair of electrons from other species to make a new covalent bond, are called "electrophiles":

The electrophiles may be:

- A positive ion e.g. H^+, H_3O^+, NO_2^+, CH_3^+
- A neutral molecule e.g, SO_3, $AlCl_3$, BF_3^+
- A carbon atom bearing partial positive charge in a partially ionic covalent molecule

e.g. $R-\overset{\delta+}{C}H=\overset{\delta-}{O}$

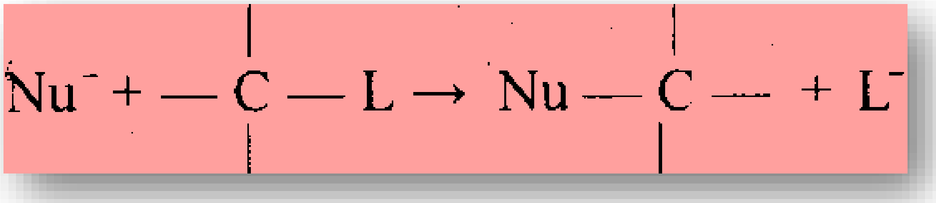
Nuceophiles (nucleus loving):

The electron rich molecules or ions, which have a tendency to donate a pair of electrons to other species to make a new covalent bond, are called "nucleophiles". The nucleophiles may be:

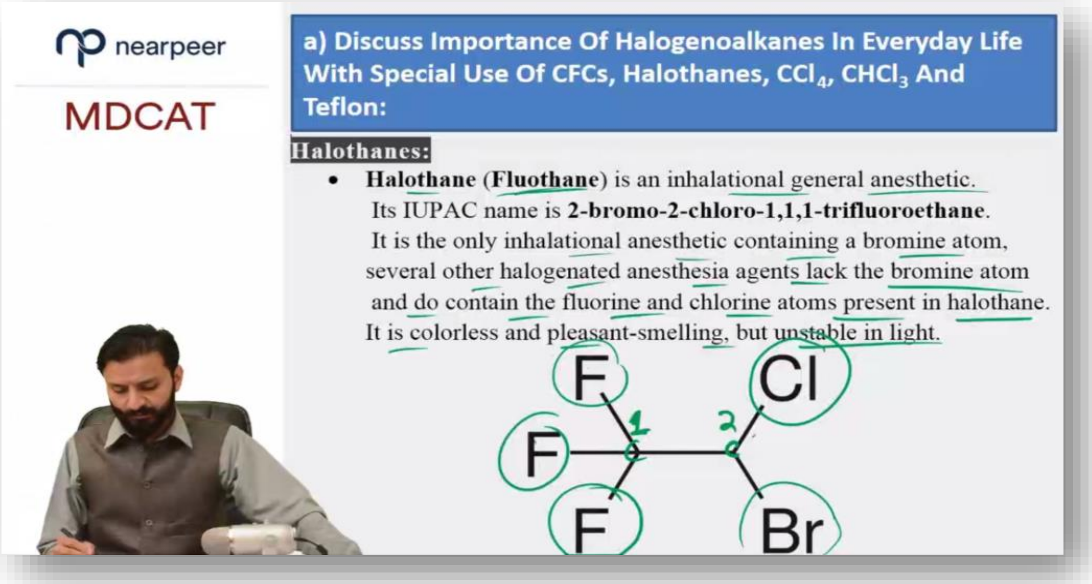
- A negative ion e.g. OH^-, CH_3COO^-, Br^-, CN^-, NO_3^{-1}.
- A molecule having lone pairs e.g. NH_3, H_2O, $R-NH_2$
- A molecule having pi-electrons e.g. C_2H_2, C_2H_4
- A carbon bearing partial negative charge in organometallic compounds e.g. Grignard's reagent.

Leaving Group:

The group that departs with an unshared pair of electrons, For S_N reactions the incoming nucleophile must be stronger than the leaving one:



$$Nu^- + -\overset{|}{\underset{|}{C}}-L \rightarrow Nu-\overset{|}{\underset{|}{C}}- + L^-$$



a) Discuss Importance Of Halogenoalkanes In Everyday Life With Special Use Of CFCs, Halothanes, CCl_4, $CHCl_3$ And Teflon:

Halothanes:

- **Halothane** (**Fluothane**) is an inhalational general anesthetic. Its IUPAC name is **2-bromo-2-chloro-1,1,1-trifluoroethane**. It is the only inhalational anesthetic containing a bromine atom, several other halogenated anesthesia agents lack the bromine atom and do contain the fluorine and chlorine atoms present in halothane. It is colorless and pleasant-smelling, but unstable in light.

Mechanism:

There are two ways by which SN reactions can occur:

(i) Nucleophilic substitution uni-molecular (S_N1)

(ii) Nucleophilic substitution bimolecular (S_N2)

	S_N1 REACTION	**S_N2 REACTION**
1	Molecularity of S_N1 reaction is one	Molecularity of S_N2 reaction is two
2	The reaction is: $R – X \rightarrow R+ + X^-$ (slow) $R^+ + Nu^- \rightarrow R – Nu$ (fast)	The reaction is: $R – X + Nu^- \rightarrow R – Nu + X^-$ (slow)
3	Rate α $[R – X]$ Rate = $k [R – X]$	Rate α $[R – X] [Nu^-]$ Rate = $k [R – X] [Nu^-]$

4	Coming nucleophile may attack from any side	Coming nucleophile may attack from any backside
5	Tertiary alkyl halides generally give S_N1 reactions.	Primary alkyl halides generally give S_N2 reactions.
6	The product is a racemic mixture i.e. 50 % inversion and 50 % retention of configuration	The product is with 100 % inversion of configuration
7	Order of reaction is one	Order of reaction is two
8	It is a two steps mechanism	It is a single step mechanism
9	It is favoured in polar solvents	It is favoured in non-polar solvents

Note:

Secondary alkyl halide can give both reactions depending upon the structure of alkyl group or nature of the solvent.

Mechanism of Nucleophilic Substitution Reactions:

Alkyl halides may undergo nucleophilic substitution reactions in two different ways:

i) Nucleophilic substitution bimolecular (S_N2) (occurs in single step)

ii) Nucleophilic substitution uni-molecular (SN 1) (occurs in two steps)

Explanation:

The nucleophilic substitution reactions on alkyl halides involve two main processes:

i) Breakage of C – L/ C – X bond

ii) Formation of C – Nu bond

The mechanism of the nucleophilic substitution reactions depends upon the timing ofthese two processes.

- If the two processes occur simultaneously, the mechanism is called S_N2.
- If bond breaks first followed by the formation of a new bond, the mechanism is called S_N1.

1-Nucleophilic substitution bimolecular (S_N2):

A mechanism in which arrival and departure of nucleophiles takes place simultaneously is S_N2 mechanism.

1) **Introduction**:

- This is a single step mechanism
- Primary alkyl halides give this reaction
- As soon as the nucleophile starts' attacking the electrophilic carbon of the substrate, the bond with which the leaving group is attached, starts breaking. In other words, the extent of bond formation is equal to the extent of bond breakage. This is called transition state.

2) Direction of attack of Nucleophile:

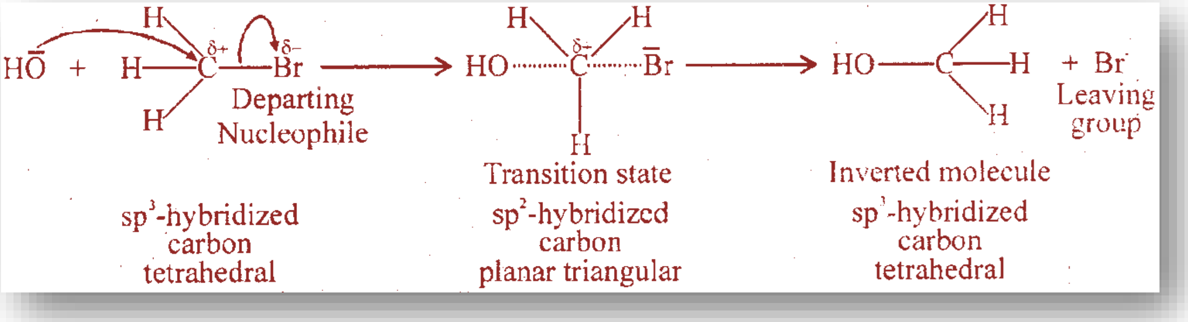
The important feature of this mechanism is the direction of the attack of the attacking nucleophile. It attacks from the side which is opposite to the leaving group. This backside attack is possible due to least crowding around electrophilic carbon.

3) Variation in hybridization:

In order to give enough room to the nucleophile to attack, the substrate carbon atom changes its state of hybridization from tetrahedral $sp^3$to planar sp^2.

Note: The attack of the nucleophile, change in the state of hybridization and the departure of leaving group, everything occurs at the same time.

4) Mechanism of reaction:



5) Inversion of configuration of molecule:

During the S_N2 reaction, the configuration of the molecule of the product as compared to alkyl halide molecule gets inverted. This inversion is 100 %. This is due to the fact that 100 % backside attack is possible.

6) Molecularity of reaction:

The molecualrity of S_N2 reactions is 2 because there are two species (primary alkyl halide and nucleophile) are taking part in the rate determining step. That is why it is called bimolecular reaction.

7) Rate of reaction:

Kinetic studies of the reactions involving S_N2 mechanism have shown that the rates of such reactions depend upon the concentration of alkyl halide as well as that of attacking nucleophile. Mathematically, the rate can be expressed as:

Rate = k $[\text{alky 1 halide}]^1[\text{Nucleophile}]^1$

8) Order of reaction:

The some of the exponents of the concentration terms in the rate expression is unity, so the order of typical S_N2 reaction will be 1 + 1 = 2

Note: Among the alkyl halides, the primary alkyl halides always follow S_N2 mechanism whenever they are attacked by nucleophiles.

II-Nucleophilic substitution uni-molecular (S_N1):

1) **Introduction**:

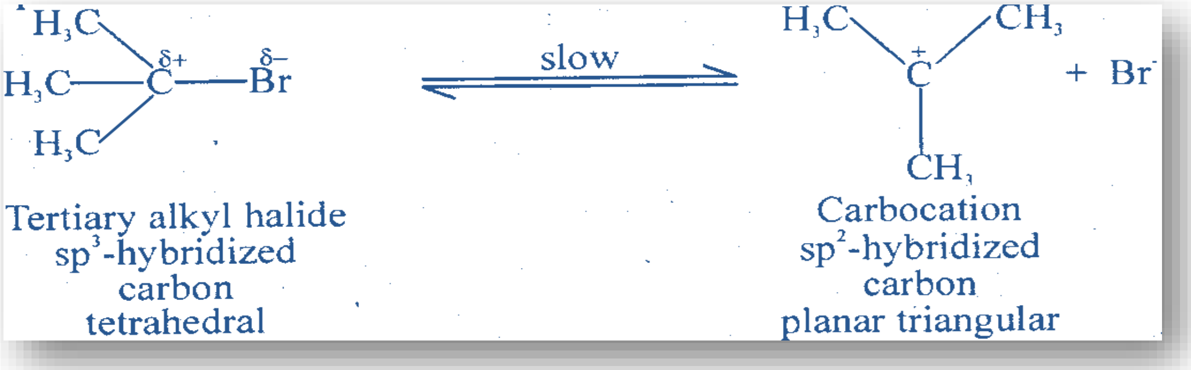
It is two step mechanism. These steps are following:

i) Ionization of R – X/ alkyl halide (tertiary alkyl halide)

ii) Attack of nucleophile

Step 1:

- This step involves the ionization of tertiary alkyl halide in the presence of polar solvent.
- This step is reversible in the presence of aqueous acetone or aqueous ethyl alcohol.
- This step results in the formation of carbocation as an intermediate.



- This step involves the breakage of covalent bond, so it is a slow step. This step is rate determining step.

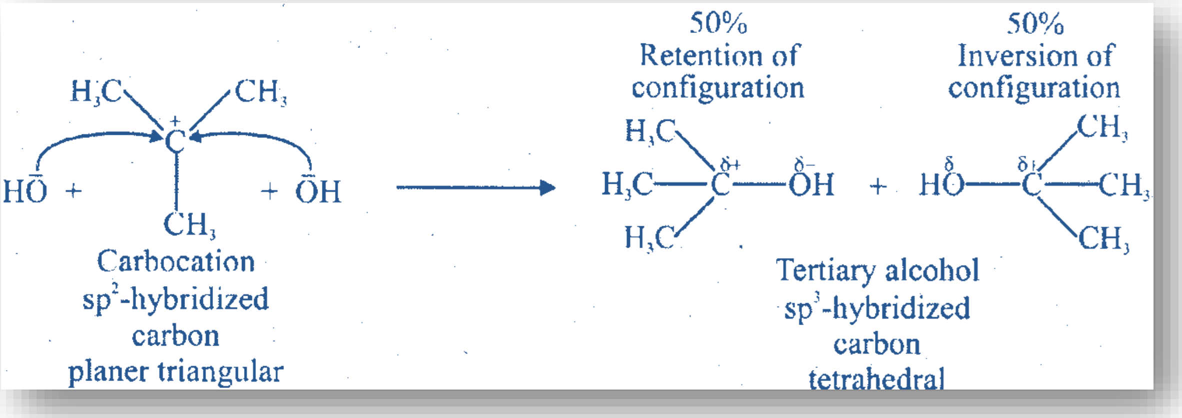
- During this step, there is variation in hybridization form tetrahedral sp^3 to planar triangular sp^2.

Step 2:

- This step involves the attack of nucleophile on carbocation:

i) The nucleophile attacks when the leaving group had already gone. So, the question of the direction of the attack does not arise.

ii) The intermediate carbocation is planar specie allowing the nucleophile to attack on it from both the directions with equal ease. Therefore, there is 50 % inversion of configuration and 50 % retention of configuration.



- This step involves the combination of ions (nucleophile and carbocation) which is energetically favourable, that is why it is a fast step.
- This step results in the formation of product.
- During this step hybridization varies from planar triangular $sp^2$to tetrahedral sp^3.

2. **Molecularity of the reaction:**

The rate determining step involves only one molecule (alkyl halide) that's why it's molecularity is one. So it is called uni-molecular reaction.

3. Rate of reaction:

Kinetic studies of the reactions involving S_N1 mechanism have shown that the rates of such reactions depend upon the concentration of alkyl halide only. Mathematically, the rate can be expressed as:

Rate = k[alkyl halide]^1

4. **Order of reaction:**

The some of the exponents of the concentration terms in the rate expression is unity, so the order of typical S_N1 reaction will be one.

Note: Among the alkyl halides, the tertiary alkyl halides always follow S_N1 mechanism whenever they are subjected to substitution.

Examples of S_N reactions are given below. These reactions show the usefulness of alkyl halides as synthetic reagents.

β-Elimination or E-Reaction:

The reactions where the attack takes place on electrophilic hydrogen attached to B-carbon of alkyl halide, resulting in formation of alkene are known as β-reactions.

- E and S_N reactions can take place simultaneously and often competition occurs.
- E can take place in two ways:

	E1 REACTION	E2 REACTION
1	Two steps mechanism	One step mechanism
2	Molecularity is one	Molecularity is two

3	Rate α [R – X] Rate = k [R – X]	Rate α [R – X] [base] Rate = k [R – X] [base]
4	Tertiary alkyl halides generally give E1 reactions.	Tertiary alkyl halides generally give E2 reactions.
5	Order of reaction is one	Order of reaction is two
6	The reaction is: $R - X \xrightarrow{slow} \text{carbocation} + X^-$ $\text{Carbcation + base} \xrightarrow{fast} \text{alkane} + H^2O$	The reaction is: $R - X + OH^- \xrightarrow{slow} \text{Alkene + Hwo} + X^-$ $\text{Carbcation + base} \xrightarrow{fast} \text{alkane} + H^2O$

Examples of S_N Reactions:

$$C_2H_5 - Br + OH^- \rightarrow Br^- + C_2H_5 - OH$$

$$2C_2H_5 - Br + 2Na \xrightarrow{ether} C_2H_5 + C_2H_5 + 2NaBr$$

n-butane

$$C_2H_5 - Br + 2[H] \xrightarrow{Zn\ /\ dil.\ HCI} C_2H_6 + HBr$$

n-butane

$$C_2H_5 - Br + CN^- \rightarrow C_2H_5 - CN + Br$$

Ethyle nitrile

$$4CH_3 - Cl + Na_4\,Pb \rightarrow (CH_3)_4\,Pb + 4NaCl$$

Sodium lead alloy Tetra methl lead

$$4C_2H_5 - Cl + Na_4\,Pb \rightarrow (C_2H_5)_4\,Pb + 4NaCl$$

Sodium lead alloy Tetra ethyl lead

$$C_2H_5Br + I^- \rightarrow C_2H_5\,I + Br^-$$

Ethyl iodide

$C_2H_5Br + NO_2^- \rightarrow C_2H_5NO_2 + Br^-$

Ethylr iodide

$C_2H_5Br + NO_2^- \rightarrow C_2H_3NO_2^- + Br^-$

Nitroethane

$C_2H_5Br + CH_3O^- \rightarrow C_2H_5 - O - CH_3 + Br^-$

Ethyl methyl ether

$C_2H_5 - Br + SH^- \rightarrow C_2H_5 - SH + Br^-$

Ethyl thioalcohol

$C_2H_5 - Br + CH3COONa \rightarrow CH_3COOC_2H_5 + NaBr$

Ethyl acetate

S_N Reaction with Aqueous NH_3:

$C_2H_5 - Br + NH_3 \rightarrow C_2H_5 - NH_2 + HBr$

Ethyl amine

$C_2H_5 - Br + C_2H_5 - NH_2 \rightarrow (C_2H_5)_2\ NH + HBr$

Diethyl amine

$(C_2H_5)_2\ NH + C_2H_5Br \rightarrow (C_2H_5)_3N + HBr$

Triethyk aminr

$(C_2H_5)_3N + C_2H_5Br \rightarrow (C_2H_5)_4N^+ + HBr$

Quaternary ethyl ammonium bromide

S_N Reaction with alcoholic KOH:

$C_2H_5 - Br + KOH \xrightarrow{Alcoholic} CH_2 = CH_2 + H_2O + KBr$

S_N Reaction with Alcoholic KOH:

$C_2H_5 - Br + KCN \xrightarrow{Alcoholic} C_2H_5CN + KBr$

EXCLUSIVE PRACTICE EXERCISE (UHS TOPIC ONLY)

1. In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how may carbon atoms

A) Two

B) Three

C) One

D) Four

2. Which one of the following is not a nucleophile:

A) H_2O

B) H_2S

C) BF_3

D) NH_3

3. Akkyl halides are considered to be very reactive compounds toward nucleophiles, because:

A) They have an electrophilic carbon

B) They have an electrophilic carbon and a bad leaving group

C) They have an electrophilic carbon and a good leaving group

D) They have an nucleophlic carbon and a good leaving group

4. The reactivity order of alkyl halides for a particular alkyl group is:

A) Fluride > Chloride > Bromide > Iodide

B) Chloride > Bromide > Fluride > Iodide

C) Iodide > Bromide > Chloride > Fluoride

D) Bromide > Iodide > Chloride > Fluoride

5. Alkyl iodide is reactive due to:

A) Primary nature of alkyl halides

B) The low dissociation energy of C-I bond

C) The presence of I atom

D) secondary nature of alkyl halides

6. S_N1 mechanism of reaction depends on all the factors except

A) Nature of solvent

B) Structure of alkyl halides

C) Nature of leaving group

D) Strength of attacking nucleophile

7. Which of the following C-X bond has least value of bond energy

A) C-F

B) C-Br

C) C-Cl

D) C-I

8. Which of the following is poor leaving group:

A) Cl^-

B) Br^-

C) HSO_4^-

D) OH^-

9. Which of the following is the best method to prepared alcohol from alkyl halilde?

A) Reaction with HX in the presence $ZnCl_2$

B) Reaction with $SOCl_2$ in the presence of pyridine solvent

C) Reaction with PCl_3

D) Reaction with PCl_5

10. Consider the following reaction $CH_3\text{-}CH_2{}^-Br + OH^- \longrightarrow C_2H_5OH + Br^-$. The mechanism of above reaction is

A) Elimination reaction

B) Electrophilic substitution reaction

C) Nucleophilic substitution reaction

D) Acid base reaction

11. The compound having no dipole moment is:

A) CH_3Cl

B) CH_2Cl_2

C) CCl_4

D) $CHCl_3$

12. When the reaction between methyl iodide and sodium ethoxide occurs, we get

A) Methyl acetate

B) Ethyl acetate

C) methyl ethyl ketone

D) Methyl ethyl ether

13. Which of the following types of alkyl halides follows only S_N2 mechanism reaction

A) Primary alkyl halide

C) Secondary alkyl halide

B) tertiary alkyl halide

D) All of the above

14. Which of the following type of mechanism of reaction has 50% inversion and 50% retention of configuration

A) S_N1

C) E1

B) S_N2

D) E2

15. In which of the following mechanism of reactions of alkyl halide first step is common

A) S_N2 and E1

C) S_N2 and E2

B) S_N1 and E1

D) None of the above

16. **Carbocation is a/an:**

(A) Electrophile

(C) Nucleophile

(B) Free radical

(D) Group of atoms

17. **1-bromobutane on reaction with alocoholic potassium hydroxide gives:**

(A) 1-butanol

(C) 1-butene

(B) 2-butene

(D) 1-butyne

18. **In the transition state of SN_2 mechanism reaction of alkyl halides, which of the following orbital hybridization is involved:**

(A) sp^3

(C) sp^2

(B) sp

(D) dsp^2

19. In β-elimination reaction, nucleophile attacks on:

(A) α-hydrogen

(C) β-hydrogen

(B) Hydrogen

(D) α-carbon

20. **Which one the following will be present at the position of letter B**

$C_2H_5Br \xrightarrow[\text{Alcohol}]{\text{KOH}} A \xrightarrow{H_2/Pt} B$:

(A) Ethyl alcohol

(C) Acetaldehyde

(B) Ethene

(D) Ethane

21. Carbonium ion is:

(A) Electrophile

(B) Nucleophile

(C) Free radical

(D) Group of atoms

22. Which of the following is not good leaving group?

(A) HSO_4^-

(B) Cl^-

(C) OH^-

(D) Br^-

23. For which mechanism the first step involved is the same:

(A) E_1 and E_2

(B) E_2 and SN_2

(C) SN_1 and E_2

(D) E_1 and SN_1

24. Which of the following factors does not affect the S_N1 rate is:

(A) Nucleophilicity of the attacking nucleophile

(B) Stability of the carbonium ion

(C) Solvent system

(D) The nature of leaving group

25. When achiral alkyl halide is subjected to S_N1 reaction, inversion of configuration takes places:

(A) 40%

(B) 50%

(C) 60%

(D) 80%

26. An amine is produced in the following reaction:

$$C_2H_5I + 2NH_3 \longrightarrow C_2H_5NH_2 + NH_4I$$

What is the mechanism?

(A) Electrophilic addition

(B) Electrophilic substitution

(C) Nucleophilic addition

(D) Nucleophilic substitution

27. Select a nucleophile from the following:

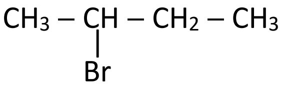
(A) Nitronium ion
(B) Carbonium ion

(C) Carbanion
(D) Ammonium ion

28. The major reactions occur in alkyl halides are:

(A) Electrophilic addition reaction
(B) Nucleophilic substitution reaction

(C) Free radical substitution reaction
(D) Free radical addition reaction


$CH_3 - \underset{Br}{\underset{|}{CH}} - CH_2 - CH_3$

29. If ⍰-elimination takes place in above reactant which statement is true about products.

(A) 1-butene is major product
(B) 2-butene is minor product

(C) 50% 1-butene 50% 2-butene
(D) 2-butene is major product

30. Nucleophilic substitution reaction in the presence of polar solvent for secondary alkhyhalide will favour mechanism:

(A) 100% SN1
(B) 100% SN2

(C) 50% SN1 & 50% SN2
(D) More % age of SN1 than SN2

31. The order of reactivity of the following alkyl halides for SN2 reaction is

(A) RF > RCl > RBr > RI
(B) RF > RBr >RCl> RI

(C) RCl > RBr > RF > RI
(D) RI> RBr >RCl >RF

32. The elimination of hydrogen halide molecule from two adjacent Carbon atom of an alkyl halide is called

(A) Dehalogenation
(B) Dehydrohalogenation

(C) Dehydration
(D) Dehydrogenation

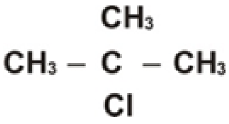
33. The order of the ease of formation of cabonium ion of alkyl halide is

(A) Prim. > Sec. > Tert
(B) Tert. > Sec. > Prim.
(C) Sec. > Prim. > Tert
(D) Tert > Pri. > Sec.

34. During elimination reactions the KOH used is

(A) Neutral
(B) Acidic
(C) Basic
(D) Alcoholic

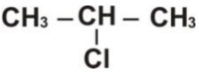
35. The compound is



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_3$$

(A) a primary alkyl halide
(B) a secondary alkyl halide
(C) a tertiary alkyl halide
(D) not an alkyl halide

36. The IUPAC name for the compound is



$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

(A) isopropyl chloride
(B) 2 chloro 1,3 dimethyl methane
(C) 2- chloro propane
(D) monochloro propane

37. Which one of the following is more reactive

(A) Methyl bromide
(B) Ethyl bromide
(C) Propyl bromide
(D) All have same reactivity

38. The charge on intermediate product of SN1 reaction is

(A) Neutral
(B) Positive
(C) Negative
(D) Both b and c

39. When alkyl halide reacts with excess of ammonia the final product will be

(A) Primary ammine
(B) Secondary ammine
(C) Tertiary ammine
(D) Quaternary alkyl ammonium ion

40. When ammonia reacts with excess of alkyl halide the final product will be

(A) Primary ammine (B) Secondary ammine

(C) Tertiary ammine (D) Quaternary alkyl ammonium ion

ANSWER KEY

1	**C**	**11**	**C**	**21**	**A**	**31**	**D**
2	**C**	**12**	**D**	**22**	**A**	**32**	**B**
3	**C**	**13**	**A**	**23**	**D**	**33**	**B**
4	**B**	**14**	**A**	**24**	**A**	**34**	**D**
5	**B**	**15**	**B**	**25**	**B**	**35**	**C**
6	**D**	**16**	**A**	**26**	**D**	**36**	**C**
7	**D**	**17**	**C**	**27**	**C**	**37**	**A**
8	**C**	**18**	**C**	**28**	**B**	**38**	**B**
9	**B**	**19**	**C**	**29**	**D**	**39**	**D**
10	**C**	**20**	**D**	**30**	**D**	**40**	**A**

UHS TOPIC 4 – C

ALCOHOLS AND PHENOLS

LEARNING OUTCOMES

In this topic, student should be able to:

Discus Alcohols with reference to:

a) Classification of alcohols into primary, secondary and tertiary

b) Preparation of ethanol by hydration of ethene using cone. H_2SO_4 or conc. H_3PO_4.

c) Reaction of alcohol with:

   i) $K_2Cr_2O_7 + H_2SO_4$ (oxidation)

   ii) PCl_5

iii) Na-metal

   iv) Alkaline aqueous Iodine (Iodoform Test)

   v) Carboxylic acid (Esterification)

d) Dehydration of alcohol to give alkene

Phenols

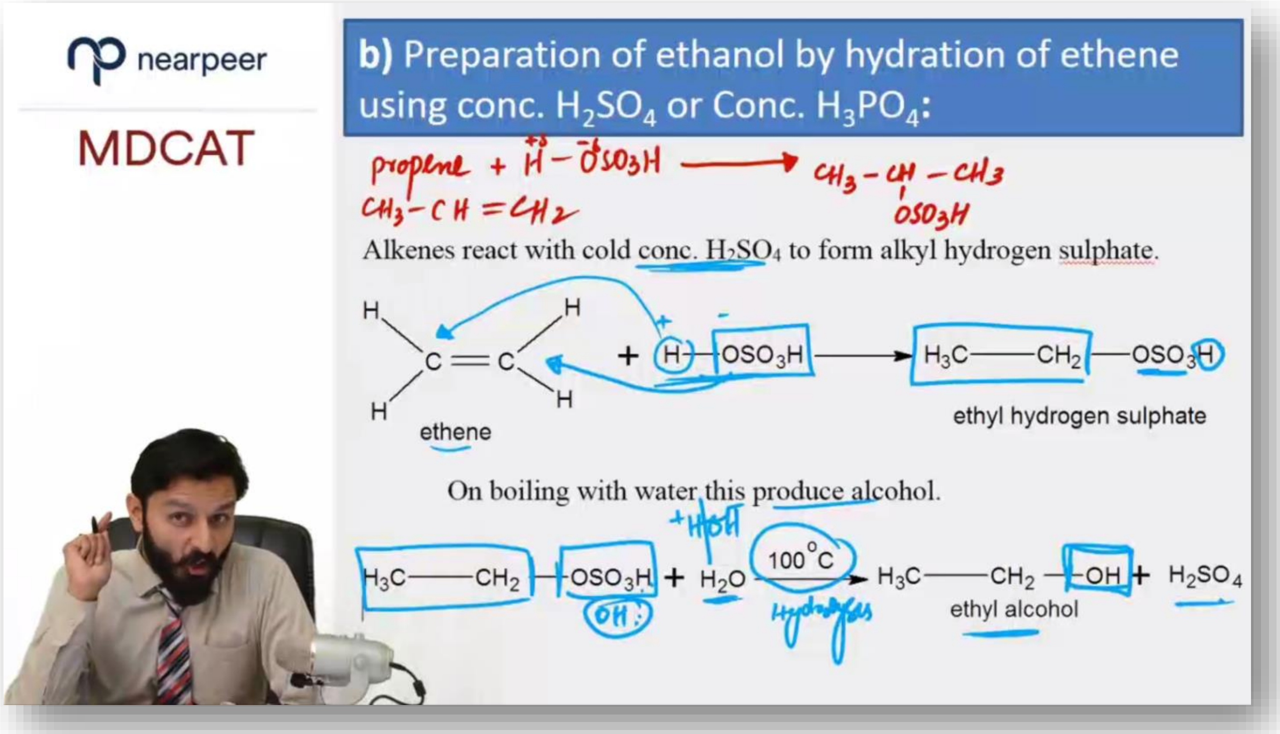
a) Discuss reactions of phenol with:

   i) Bromine

   ii) HNO_3

   iii) NaOH

b) Explain the relative acidity of water, ethanol and phenol



nearpeer MDCAT

b) Preparation of ethanol by hydration of ethene using conc. H_2SO_4 or Conc. H_3PO_4:

propene + $\overset{+}{H}-\overset{-}{O}SO_3H \longrightarrow CH_3-\underset{OSO_3H}{CH}-CH_3$

$CH_3-CH=CH_2$

Alkenes react with cold conc. H_2SO_4 to form alkyl hydrogen sulphate.

$H_2C=CH_2 + H-OSO_3H \longrightarrow H_3C-CH_2-OSO_3H$

ethene

ethyl hydrogen sulphate

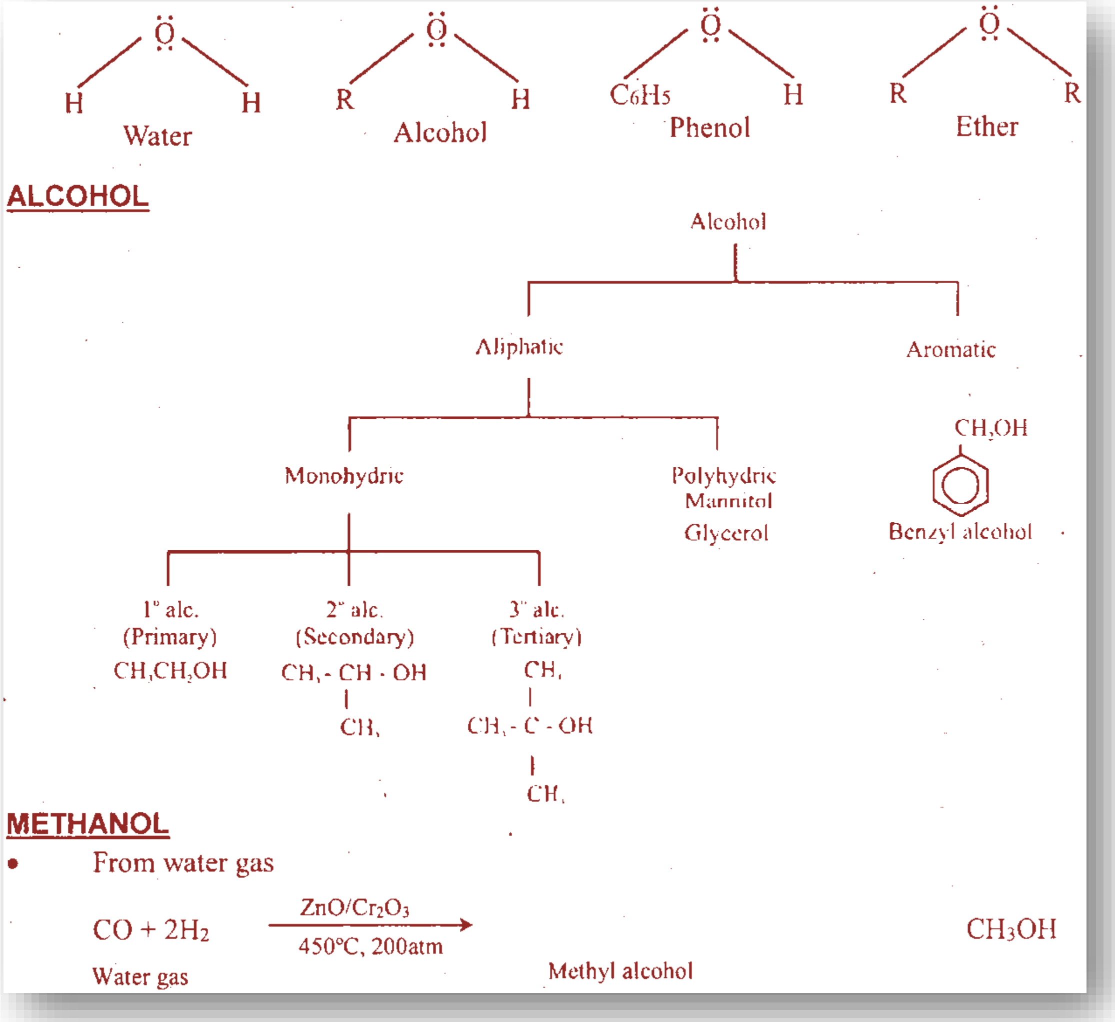
On boiling with water this produce alcohol.

$H_3C-CH_2-OSO_3H + H_2O \xrightarrow[\text{hydrolysis}]{100^\circ C} H_3C-CH_2-OH + H_2SO_4$

ethyl alcohol

INTRODUCTION:

- When H of alkane is replaced by – OH group, then it is called alcohol.
- When the H of benzene ring is replaced by – OH group, then it is called phenol.
- The linkage between two carbon atoms through oxygen atom is called ether.
- Alcohols, phenols and ethers are classes of organic compounds which are much closer to water in structure and hence considered as derivatives of water:



ALCOHOL

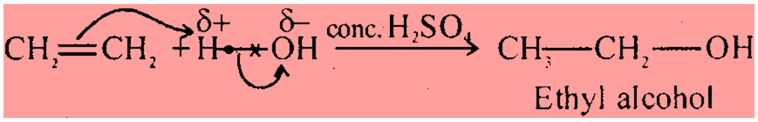
METHANOL

- From water gas

$$\underset{\text{Water gas}}{CO + 2H_2} \xrightarrow[450^\circ C,\ 200atm]{ZnO/Cr_2O_3} \underset{\text{Methyl alcohol}}{CH_3OH}$$

HYDRATION OF ALKENE

The overall reaction involves addition of water to an alkene to form alcohol in the presence of concentrated sulphuric acid or concentrated phosphoric acid. Therefore, this reaction is called as hydration reaction.

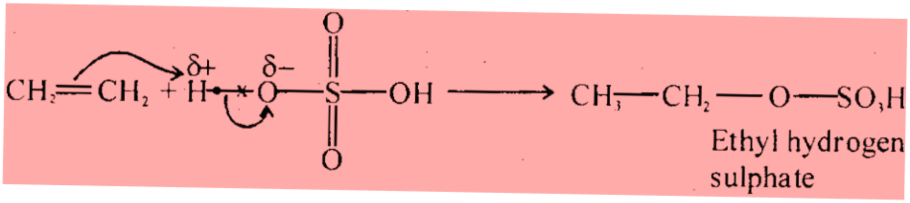


$$CH_2{=}CH_2 + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow{\text{conc. } H_2SO_4} CH_3-CH_2-OH$$

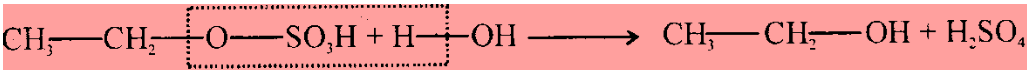
Ethyl alcohol

Mechanism:

Alkenes are dissolved in cold concentrated sulphuric acid and react with it to form alkyl hydrogen sulphate.



Alkyl hydrogen sulphate decomposes on boiling with water to form respective alcohol.



REACTIVITY OF – OH GROUP:

- Oxygen atom of the – OH group in alcohols is sp_3 hybridized
- The carbon oxygen bond (C –O) and hydrogen oxygen bond (O– H) are highly polarized.
- The negative charge is present on the oxygen atom of alcohol.

CHEMICAL PROPERTIES:

Alcohols react with other reagents in two ways

(i) Reactions in which C – O bond breaks

(ii) Reactions in which O – H bond breaks

The order of reactivity of alcohols when C – O bond breaks

Tertiary Alcohol > Secondary Alcohol > Primary alcohol

- The order of reactivity of alcohols when O – H bond breaks

  CH_3OH > Primary Alcohol > Secondary Alcohol > Tertiary Alcohol

- Nucleophile breaks C – O bond of alcohol
- Attacking electrophile breaks C – H bond of alcohol
- Catalytic oxidation of secondary alcohol in presence of K_2CrO_7 and H_2SO_4, converts it into ketones while same reaction of tertiary alcohol gives alkenes.
- On heating with conc. H_2SO_4, alcohol changes to alkene.

REACTIONS OF ALCOHOLS:

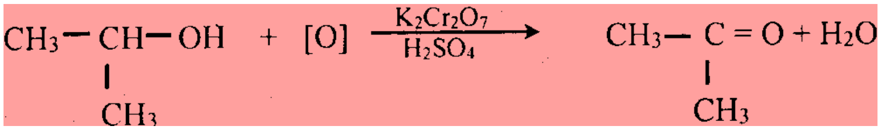
$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

Phosphorous acid

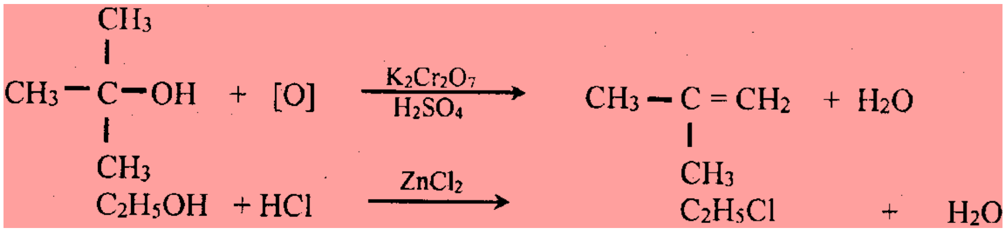
$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + HCl + POCl_3$$

Phosphorous oxytrichloride

$$C_2H_5OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 \cdot CHO + H_2O$$



$$\underset{\displaystyle CH_3}{CH_3-\overset{}{CH}-OH} + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\displaystyle CH_3}{CH_3-C}=O + H_2O$$



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\underset{\displaystyle CH_3}{C}=CH_2 + H_2O$$

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

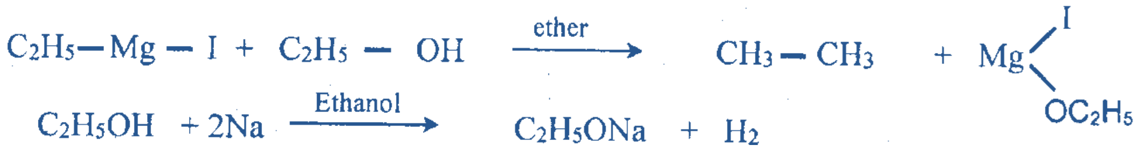
$$C_2H_5OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

$$C_2H_5OH \xrightarrow[180^\circ C]{\text{Conc. } H_2SO_4} CH_2=CH_2 + H_2O$$

$$2C_2H_5OH \xrightarrow[\text{Conc. } H_2SO_4]{140^\circ C} C_2H_5-O-C_2H_5 + H_2O$$

$$\underset{\text{Thionyl chloride}}{C_2H_5OH + SOCl_2} \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$$

$$C_2H_5OH + NH_3 \xrightarrow{ThO_2} C_2H_5NH_2 + H_2O$$



$$C_2H_5-Mg-I + C_2H_5-OH \xrightarrow{\text{ether}} CH_3-CH_3 + Mg\begin{cases} I \\ OC_2H_5 \end{cases}$$

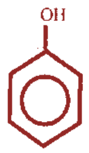
$$C_2H_5OH + 2Na \xrightarrow{\text{Ethanol}} C_2H_5ONa + H_2$$

PHENOL:

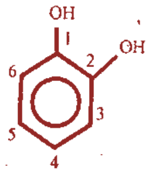
Aromatic compounds which contain one or more – OH groups directly attached with carbon of benzene ring are called phenols.

Simplest Phenol:

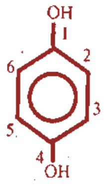
Carbolic acid (benzenol) (C_6H_5OH) is phenol. It was first obtained from coaltar by Runge in 1834.



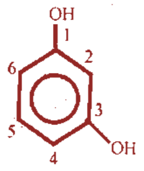
Phenol



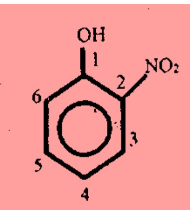
1,2-Dihydroxy benzene
o-Hydroxyl phenol
(catechol)



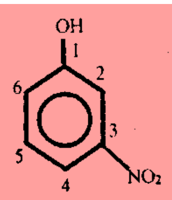
1,4-Dihydroxy benzene
p-hydroxy phenol
(hydroquinone)



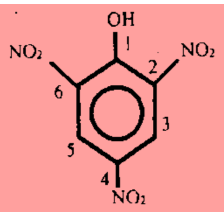
1,3-Dihydroxy benzene
m-dihydroxy phenol
(resorcinol)



2-Nitrophenol
o-Nitrophenol



3-Nitrophenol
m-Nitrophenol



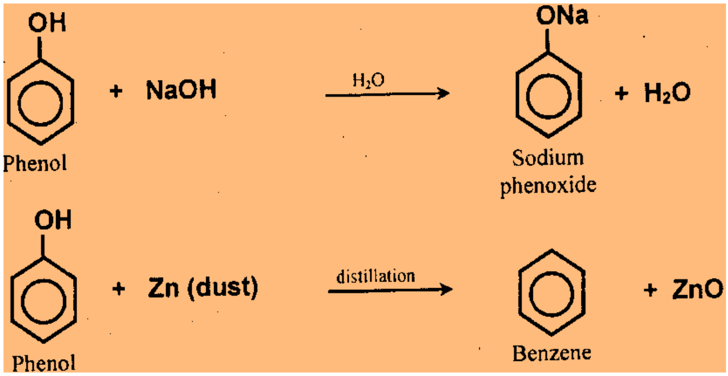
2,4,6- Trinitrophenol
Picric acid

REACTIONS OF PHENOL:

Phenol shows two types of-reactions

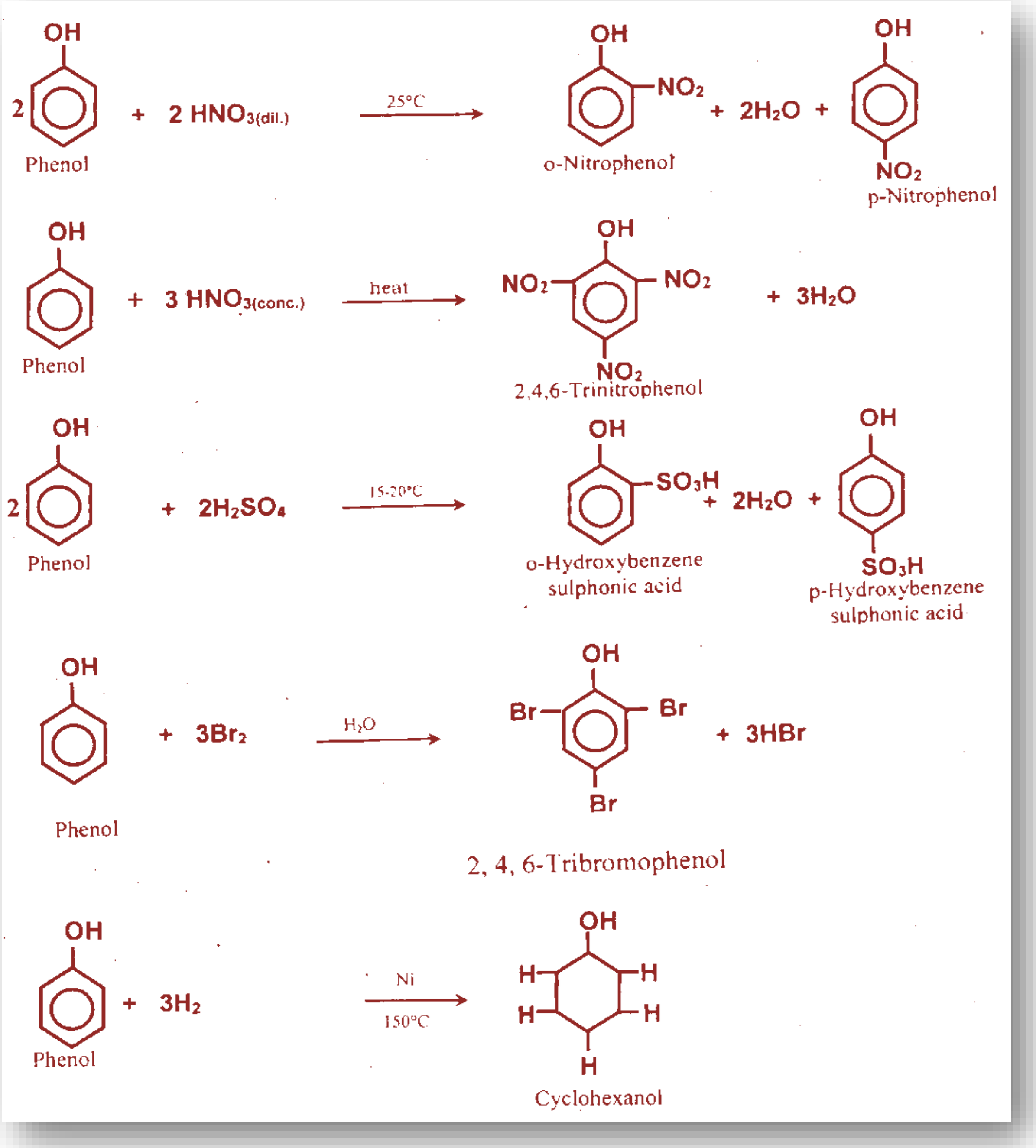
(i) Reaction of Phenol Due to – OH Group:

Nature of reaction	Remarks
Salt formation	Phenoxides are formed
Ester formation	Reaction takes place in basic media
Reduction with Zn	Benzene is obtained



Reaction of Phenol Due to Benzene Ring:

REACTION	REMARKS
Nitration	• At room temperature, the product is a mixture of ortho and p-nitrophenol with dil. HNO_3
	• At higher temperature with concentrated HNO_3 the product is picric acid.
Sulphonation	• Introduction of HSO_3^- is called sulphonation which give a mixture of ortho and para products at 15 to 20°C
Halogenation	• White ppt. of 2,4,6-tribromophenol is obtained
Hydrogenation	• Uni-saturation of ring is removed
Reaction with formaldehyde	• This is a condensation polymerization of phenol
	• Formaldehyde polymerizes with phenol produces bakelite
	• Bakelite is used for manufacturing of switch buttons


OH
2
Phenol
+ 2 HNO3(dil.)
25°C
OH
NO2
o-Nitrophenol
+ 2H2O +
OH
NO2
p-Nitrophenol
OH
Phenol
+ 3 HNO3(conc.)
heat
OH
NO2
NO2
NO2
2,4,6-Trinitrophenol
+ 3H2O
OH
2
Phenol
+ 2H2SO4
15-20°C
OH
SO3H
o-Hydroxybenzene sulphonic acid
+ 2H2O +
OH
SO3H
p-Hydroxybenzene sulphonic acid
OH
Phenol
+ 3Br2
H2O
OH
Br
Br
Br
+ 3HBr
2, 4, 6-Tribromophenol
OH
Phenol
+ 3H2
Ni
150°C
OH
H
H
H
H
H
Cyclohexanol

Reaction of Phenol Due to Benzene Ring:		
PROPERTY	ALCOHOL	PHENOL
Solubility in water	Soluble	Sparingly soluble at room temperature, soluble at 68.5° C
Volatile	Volatile	Almost non volatile
Hydrogen binding	Present	Present

EXCLUSIVE PRACTICE EXERCISE (UHS TOPIC ONLY)

1. **Which alcohol is most acidic?**

A) Methanol C) Ethanol

B) Isopropyl alcohol D) t-butyl alcohol

2. **Ethanol can be distinguished from methanol by the use of**

A) Tollen's reagent C) Fehling's solution

B) I_2 + NaOH D) $AgNO_3$(aq)

3. **Number of isomers represented by molecular formula $C_4H_{10}O$ is**

A) 3 C) 7

B) 4 D) 10

4. **The order of reactivity of alcohols towards halogen acid is**

A) Primary > secondary > tertiary C) Primary = secondary = tertiary

B) Tertiary > secondary > primary D) Primary > secondary > tertiary

5. On treatment with Lucas reagent, there is appearance of an oily layer at once. This is a

A) Primary alcohol

C) Secondary alcohol

B) Tertiary alcohol

D) Isobutyl alcohol

6. Ethyl iodide on treatment with dry Ag_2O will yield

A) Ethyl alcohol

C) Diethyl ether

B) Ethyl methyl ether

D) Ethylene

7. Methanol and ethanol are soluble in water due to

A) Their acidic character

C) Hydrogen bonding

B) Dissociation in water

D) Alkyl groups

8. When CH_3MgI is to react with acetone and the addition product is hydrolysed we get

A) Primary alcohol

C) Secondary alcohol

B) Tertiary alcohol

D) and aldehyde

9. Which of the following type of alcohol is prepared from inorganic source

A) Methanol

C) Ethanol

B) 1-propenol

D) 1-butanol

10. Which of the following types of enzymes is required to convert starch into maltose

A) Invertase

C) Zymase

B) Diastase

D) Lipase

11. 100% alcohol is called

A) Rectified spirit

C) Absolute alcohol

B) Power alcohol D) Methylated spirit

12. Which of the following has more acidic character

A) Phenol C) Acetylene

B) Acetic acid D) Water

13. Which compound will have the maximum repulsion with H_2O

A) C_6H_6 C) C_2H_5OH

B) C_2H_6O D) CH_3OH

14. Which compound is called a universal solvent?

A) H_2O C) CH_3OH

B) C_2H_5OH D) CH_3OH_3

15. Consider the following structure CH_2-CH_2-CH_2-OH

|

CH_3

A) n-Butyl alcohol C) iso-Butyl alcohol

B) sec-Butyl alcohol D) ter-Butyl alcohol

16. Ethyl alcohol is made unfit for drinking by adding:

A) Methanol C) Pyridine

B) Acetone D) All of the above

17. Aldehydes after catalytic reduction change to:

(A) P° alcohol (B) S° alcohol

(C) T° alcohol (D) P° and S° alcohol

18. Which of the following alcohol is commonly used as anti-freeze:

(A) Methanol (B) Ethanol

(C) Ethylene glycol (D) propylene glycol

19. Which of the following will have the highest boiling point:

(A) Methanal (B) Ethanal

(C) Propanal (D) 2-hexanone

20. 95% ethanol is called:

(A) Absolute alcohol (B) Rectified spirit

(C) Methylated spirit (D) Wood spirit

21. Isopropyl alcohol an oxidation forms:

(A) Acetaldehyde (B) Acetone

(C) Propanoic acid (D) Propane

22. Methyl alcohol can be distinguished from ethyl alcohol by:

(A) Action of Cl_2 (B) Action of NH_3

(C) Dissolving in water (D) Iodofom test

23. What will be the product formed when 2-methyl-2-propanol reacts with $K_2Cr_2O_7/H_2SO_4$?

(A) Propanone (B) 2-methyl propanone

(C) 2-methyl propene (D) 2-methyl propanal

24. The conjugate base of which of the following is most stable:

(A) Phenol

(B) Acetic acid

(C) Formic acid

(D) Ethanol

25. $ROH + R'COOH \xrightleftharpoons{H_2SO_4} R'COOR + H_2O$

The order of reactivity of alcohols in the above case is:

(A) Ter-alcohol > Sec-alcohol > Primary alcohol

(B) Primary alcohol > Sec-alcohol > Ter-alcohol

(C) CH_3OH > Primary alcohol > Ter-alcohol > Sec-alcohol

(D) Sec-alcohol > Primary alcohol > Ter-alcohol

26. Which of the following give iodofom test?

(A) CH_3OH

(B) C_2H_5OH

(C) Methanal

(D) 1-propanol

27. Ethanol can be converted to ethanoic acid by:

(A) Hydrogenation

(B) Oxidation

(C) Fermentation

(D) Hydration

28. Which of the following is more reactive when O – H bond breaks?

(A) P° alcohol

(B) T° alcohol

(C) S° alcohol

(D) Cannot be predicted

29. Which of the following is the weakest acid?

(A) Phenol

(B) Alcohol

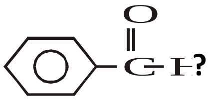
(C) Carboxylic acid (D) Water

30. Ka of phenol at normal temperature is:

(A) 10^{-14} (B) Less than that of alcohol

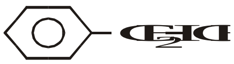
(C) More than carbonic acid (D) Less than carboxylic acids

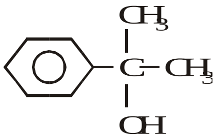
31. What is structure of alcohol which on reaction with $K_2Cr_2O_7$ and H_2SO_4 gives



(A) 

(B) 

(C) 

(D) 

32. Treatment of propene with cold concentrated H_2SO_4 followed by boiling water forms:

(A) Propyne (B) 1-propanol

(C) Propanal (D) 2-propanol

33. The alcohol which does not give a stable compound on dehydration is:

(A) Ethyl alcohol (B) Methyl alcohol

(C) n-propyl alcohol (D) n-butyl alcohol

34. The dehydration of alcohol in the presence of Con(C) H_2SO_4 at 170°C involves:

(A) Free radical intermediate (B) A carbonium ion intermediate

(C) Addition of OH^- ion (D) A carbanion intermediate

35. The reaction of phenol with conc. HNO_3 gives:

(A) Picric acid (B) Benzoic acid

(C) Adipic acid (D) Salicylic acid

36. By reacting phenol with bromine water, the product obtained is:

(A) O-bromophenol (B) m- bromophenol

(C) p- bromophenol (D) 2, 4, 6-tribromophenol

37. Electrophilic substitution in phenol generally occurs at:

(A) o- and p-position (B) m-position

(C) o-position only (D) p-position only

38. Alcohol is an organic compound that reacts with an acid to give

(A) an ester (B) an amine

(C) salt (D) an aldehyde

39. Phenol can be distinguished from benzene by:

(A) Nitration (B) Sulphonation

(C) Hydrogenation (D) Bromination

40. 2-butene on treatment with cold Con(C) H_2SO_4 will produce

(A) 1-Butanol (B) Butanoic acid

(C) Butanone (D) 2-Butanol

ANSWER KEY

1	**A**	**11**	**C**	**21**	**B**	**31**	**C**
2	**B**	**12**	**B**	**22**	**D**	**32**	**D**
3	**B**	**13**	**A**	**23**	**C**	**33**	**B**
4	**B**	**14**	**A**	**24**	**C**	**34**	**B**
5	**B**	**15**	**A**	**25**	**B**	**35**	**A**
6	**C**	**16**	**D**	**26**	**B**	**36**	**D**
7	**C**	**17**	**A**	**27**	**B**	**37**	**A**
8	**B**	**18**	**C**	**28**	**A**	**38**	**A**
9	**A**	**19**	**D**	**29**	**B**	**39**	**D**
10	**B**	**20**	**B**	**30**	**D**	**40**	**D**

UHS TOPIC 5 – C

ALDEHYDES AND KETONES

LEARNING OUTCOMES

In this topic, student should be able to:

a) Describe the structure of aldehyde and ketones.

b) Discuss preparation of aldehydes and ketones by oxidation of alcohols.

c) Discuss following reactions of aldehydes and ketones:

i) Common to both;

- 2,4-DNPH to detect the presence of carbonyl group
- HCN to show mechanism of nucleophilic addition reaction
- Reduction with $NaBH_4$ or $LiAlH_4$

ii) Reactions in which, Aldehydes differs, from ketones i.e. Oxidation with Tollen's reagent and Fehling's solution.

iii) Reaction which show presence of $CH_3CO–$ group in aldehydes and ketones Triiodomethane test (Iodo form test) using alkaline aqueous iodine.

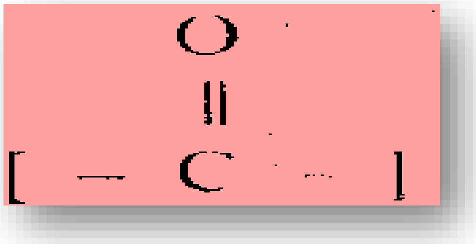
INTRODUCTION

:

Carbonyl Compounds:

The organic compounds which contain carbonyl functional group in their molecules are called carbonyl compounds.

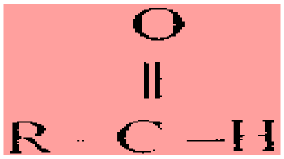
- In a carbonyl group, a carbon atom is bonded to oxygen with a double bond.
- The homologous series of both aldehydes and ketones have the general formula, $C_nH_{2n}O$
- Aldehydes and Ketones are carbonyl compounds



$[-\overset{\overset{O}{\|}}{C}-]$

Aldehydes:

- In aldehydes, the carbonyl group is bonded to at least one hydrogen atom and so it occurs at the end of the chain.



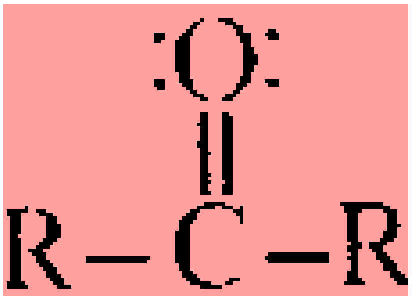
$R-\overset{\overset{O}{\|}}{C}-H$

- An aldehyde can be represented by the general formula.

Ketones:

In ketones, the carbonyl group is bonded to two carbon atoms and so it occurs within a chain.

- A ketone may be represented by the general formula



$R-\overset{\overset{:\ddot{O}:}{\|}}{C}-R$

PREPARATION OF ALDEHYDES

Formaldehyde:

INDUSTRIAL METHOD	LABORATORY METHOD
By passing methanol vapours and air over iron oxide-molybdenum oxide or silver catalyst at 500° C	By passing methanol vapours and air over platinized asbestos or copper or silver catalyst at 300° C

FORMALIN: A mixture of 40 % fromaldehyde, 8 % methyl alcohol and 52 % water.

- **Industrial Method**

$2CH_3OH + O_2$ $2CHHO + 2H_2O$

- **Laboratory Method**

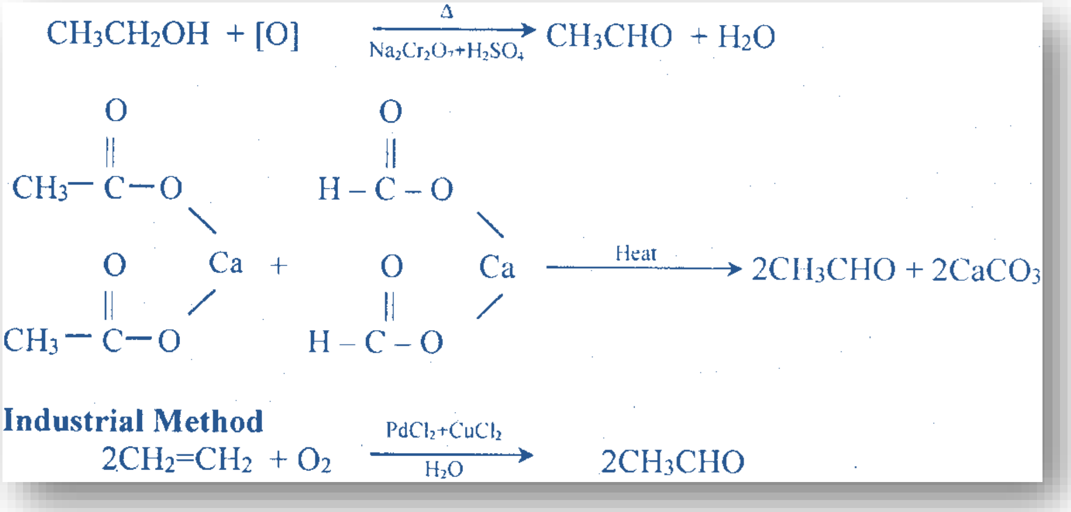
$2CH_3OH + O_2$ $2CHHO + 2H_2O$

$(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$

Acetaldehyde:

LABORATORY METHOD	INDUSTRIAL METHOD
•By oxidation of ethyl alcohol with acidified sodium dichromate •By dry distillation of mixture of calcium salt of promoter formic acid and acetic acid	By oxidation of ethylene using palladium chloride catalyst with cupric chloride as promoter

- **Laboratory Method:**



$$CH_3CH_2OH + [O] \xrightarrow[Na_2Cr_2O_7+H_2SO_4]{\Delta} CH_3CHO + H_2O$$

$$(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow{Heat} 2CH_3CHO + 2CaCO_3$$

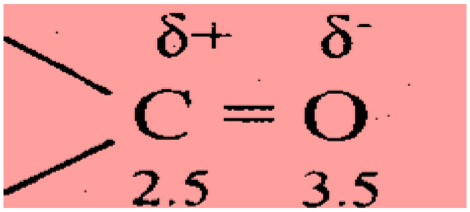
Industrial Method

$$2CH_2{=}CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2+CuCl_2} 2CH_3CHO$$

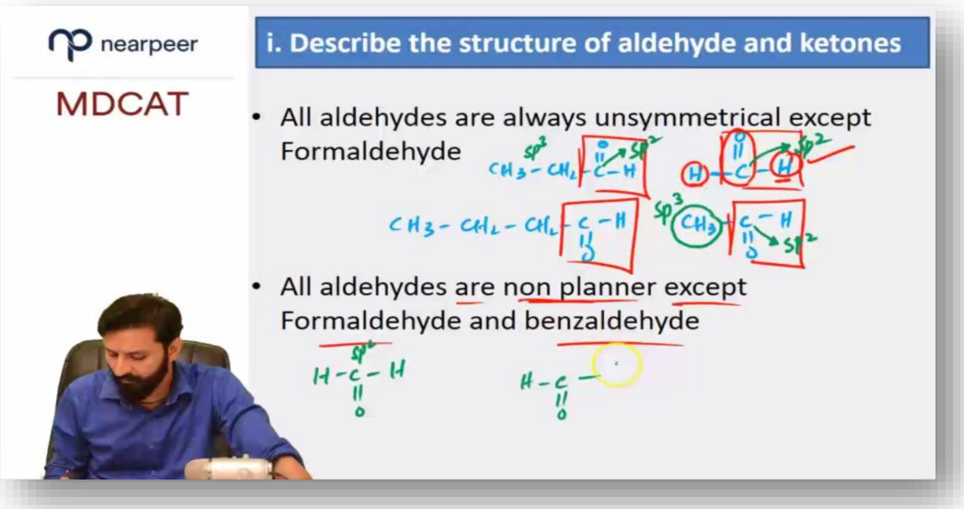
POINT TO PONDER: Hindrance by alkyl groups to nucleophile attack is called ……..

REACTIVITY OF CARBONYL GROUP

Both carbon and oxygen are sp^2 hybridized. Reactivity of carbonyl group is due to the polarity of carbon and oxygen.



E^+ Nü

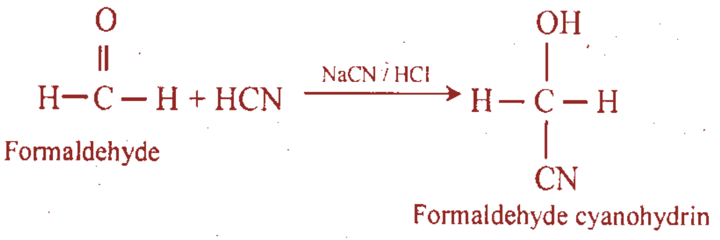


i. Describe the structure of aldehyde and ketones

- All aldehydes are always unsymmetrical except Formaldehyde
- All aldehydes are non planner except Formaldehyde and benzaldehyde

Sir Shoaib Anwar, explaining each and every equation in full details in his video lectures at www.nearpeer.org

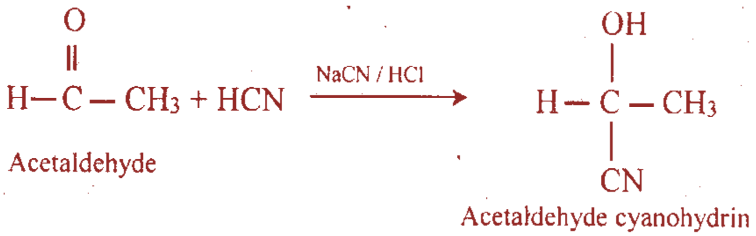
Addition of Hydrogen Cyanide:



$$H-\overset{\overset{O}{\|}}{C}-H + HCN \xrightarrow{NaCN / HCl} H-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

Formaldehyde

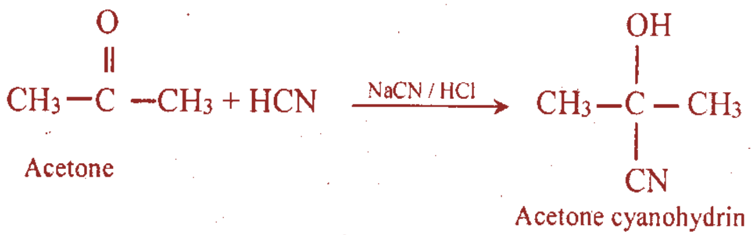
Formaldehyde cyanohydrin



$$H-\overset{\overset{O}{\|}}{C}-CH_3 + HCN \xrightarrow{NaCN / HCl} H-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

Acetaldehyde

Acetaldehyde cyanohydrin



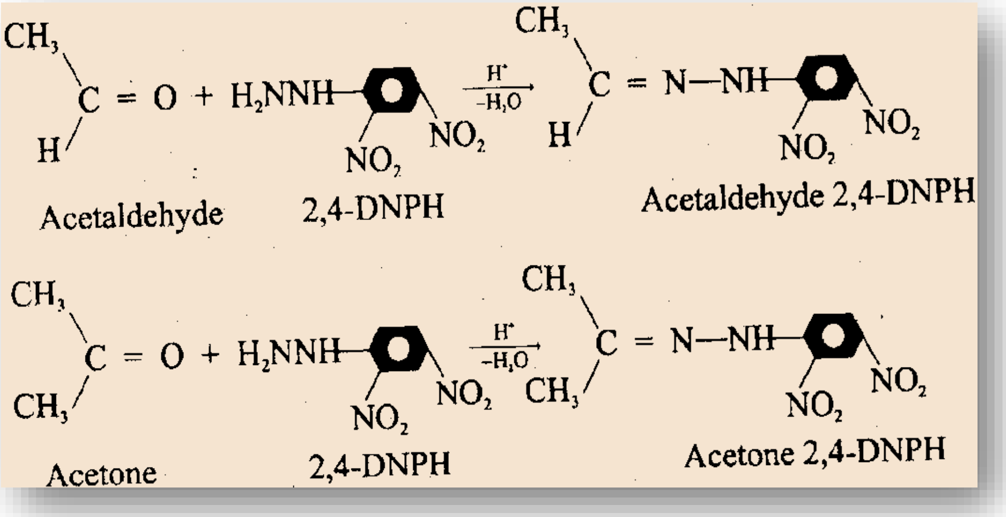
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + HCN \xrightarrow{NaCN / HCl} CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

Acetone

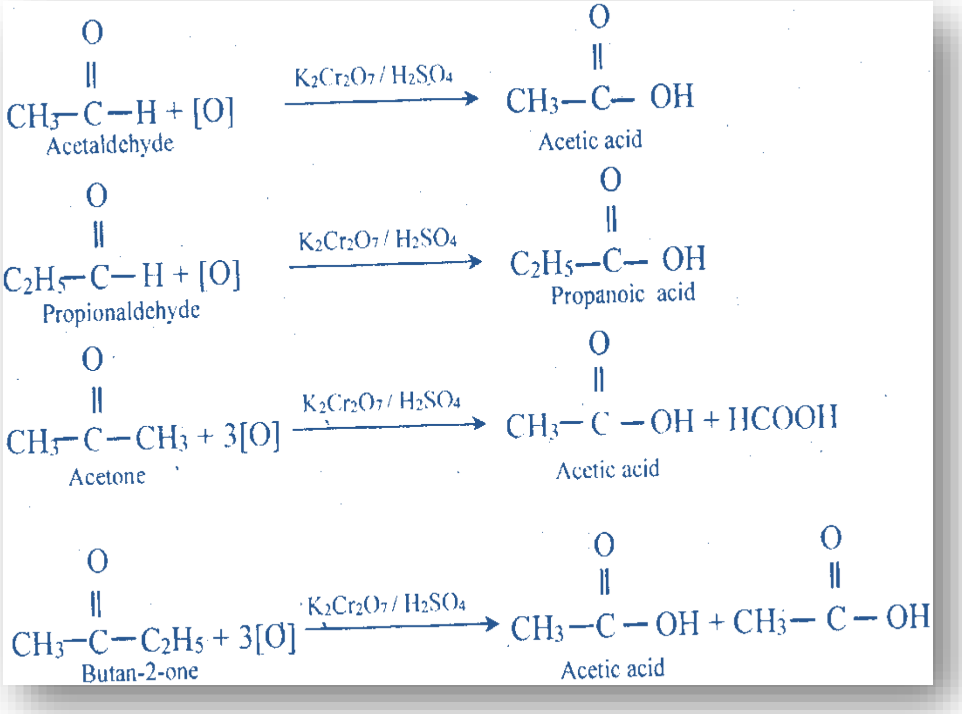
Acetone cyanohydrin

Addition of Ammonia Derivative:

(i) **Reaction with 2,4-Dinitrophenyl hydrazine [2, 4-DNPH]**



OXIDATION:



$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH}$$

$$\underset{\text{Propionaldehyde}}{C_2H_5-\overset{\overset{O}{\|}}{C}-H} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Propanoic acid}}{C_2H_5-\overset{\overset{O}{\|}}{C}-OH}$$

$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + 3[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + HCOOH$$

$$\underset{\text{Butan-2-one}}{CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5} + 3[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH + CH_3-\overset{\overset{O}{\|}}{C}-OH}$$

(ii) Tollen's Test [Silver Mirror Test]:

$AgNO_3 + 3NH_4OH \rightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + 2H_2O$

$R - CHO + 2[Ag(NH_3)_2]OH \rightarrow R - COONH_4 + 2Ag + 2NH_3 +$ H2O

Silver mirror

Note: Ketones do not give this test:

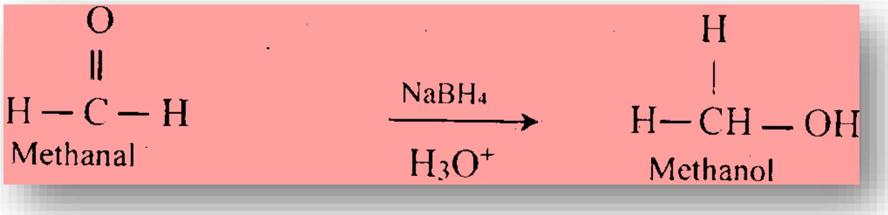
Fehling's Solution Test [an alkaline solution containing a cupric tarti-ate complex ion:

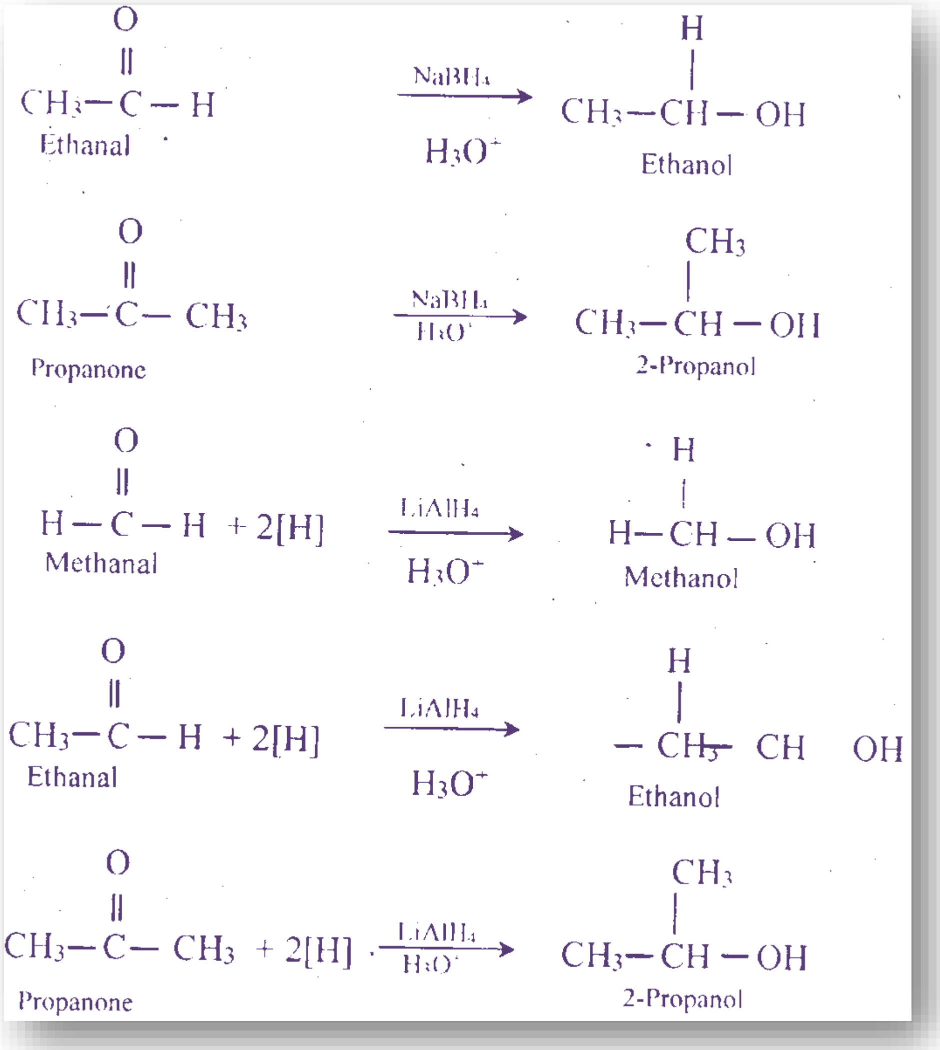
$R - CHO + 2Cu(OH)_2 + NaOH \rightarrow$ $R - COONa + Cu_2O + 2H_2O$

Brick red ppts.

Note: Ketones do not give this test.

Reduction





$$\underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow[H_3O^+]{NaBH_4} \underset{\text{Ethanol}}{CH_3-\overset{H}{\overset{|}{CH}}-OH}$$

$$\underset{\text{Propanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[H_3O^+]{NaBH_4} \underset{\text{2-Propanol}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-OH}$$

$$\underset{\text{Methanal}}{H-\overset{O}{\overset{\|}{C}}-H} + 2[H] \xrightarrow[H_3O^+]{LiAlH_4} \underset{\text{Methanol}}{H-\overset{H}{\overset{|}{CH}}-OH}$$

$$\underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + 2[H] \xrightarrow[H_3O^+]{LiAlH_4} \underset{\text{Ethanol}}{-\overset{H}{\overset{|}{\cancel{CH_3}}}\ CH\ \ OH}$$

$$\underset{\text{Propanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + 2[H] \xrightarrow[H_3O^+]{LiAlH_4} \underset{\text{2-Propanol}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-OH}$$

Reaction Showing the Presence OF CH_3CO Group (Haloform Reaction):

$CH_3CHO + 3I_2 + 4NaOH \rightarrow CHI_3 + HCOONa + 2NaI + 3H_2O$

Acetaldehyde Iodofrom

$CH_3OCH_3 + 3I_2 + 4NaOH \rightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$

Aceone Iodoform

EXCLUSIVE PRACTICE EXERCISE UHS TOPIC ONLY)

1. **Which ketone will yield tertiary butyl alcohol on treatment with CH_3MgBr following by hydrolysis**

A) 2-Butanone

B) Acetone

C) 3-Pentanone

D) 2-Pentanone

2. **Aldehydes are first oxidation product of:**

A) Primary alcohols

B) Tertiary alcohols

C) Secondary alcohol

D) Dihydric alcohol

3. **Both aldehydes and ketones can be represented by the general formula**

A) $C_nH_{2n}O$

B) C_nH_{2n+2}

C) $C_nH_{2n+1}O_2$

D) $C_nH_{2n}O_2$

4. **The oxidation product of ethanol / ($K_2Cr_2O_7$-H_2SO_4) is treated first with calcium and then subjected to distillation under dry conditions, the final product is**

A) Acetic acid

B) Ethanol

C) Propanone

D) acetone

5. **What is the correct order of increasing boiling points in the following series**

A) Acetone > Ethanal > Methanal > Propanal

B) Ethanal > Acetone > Propanal > Methanal

C) Methanal < Ethanal < Propanal < Acetone

D) Ethanal < Acetone < Propanal < Methanal

6. **The least reactive aldehyde towards nucleophilic addition reaction among the following is**

A) C_6H_5CHO

B) HCHO

C) CH_3CH_2CHO

D) CH_3CHO

7. Which of the following reagent can provide distinction between propionaldehyde and acetaldehyde?

A) Tollen’s reagent
B) benedict’s solution
C) Fehiling solution
D) I_2 + NaOH solution

8. Which of the following gives positive silver mirror test?

A) Ethanoic acid
B) Butanal
C) Butanoic acid
D) 2-Butanone

9. Which alkene on ozonolysis will give only acetaldehyde as a product?

A) Propend
B) 2-Butene
C) 1-Butene
D) Isobutylene

10. Which of the following tests is only shown by ketones?

A) Fehling solution test
B) Sodium Nitroprusside test
C) Benedict’s solution test
D) Tollen’s test

11. Which of the following types of aldehydes give cannizzaro reaction?

A) Formaldehyde
B) Propionaldehyde
C) Acetaldehyde
D) n-butyraldehyde

12. Which of the following is a example of acid catalyzed reaction

A) Aldol condensation
B) Reaction with HCN
C) cannizzoar reaction
D) Polymerization

13. Which of the following is strong oxidizing agent:

A) Fehiling solution
B) Benedict reagent
C) Tolen reagent
D) Acidified $K_2Cr_2O_7$

14. The formation of cyanohydrins from a ketones is an example of:

A) Electrophilic addition
C) Nucleophilic addition

B) Nucleophilic substiution D) Electrophilic substitution

15. When acetaldehyde is heated with Fehling's solution, it gives a red precipitate of:

A) Cu C) CuO

B) Cu + Cu_2O D) Cu_2O

16. A plastic Bakelite is a compound of HCHO with

A) Benzene C) Phenol

B) Ammonia D) Hydrocarbon

17. Methyl ketones are characterized through:

A) Tollen's reagent C) Iodoform test

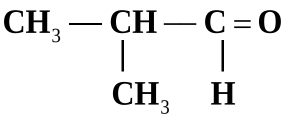
B) Fehling's solution D) Benedict's reagent

18. In order to obtain acetaldehyde from calcium acetate, it should be heated with

A) Calcium acetate C) Acetic acid

B) Calcium formate D) Formic acid

19. Consider the following structure, the name given to this structure is



$CH_3-\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle H}{C}=O$

A) n-butyr aldehyde C) Sec-butyr aldehyde

B) iso-butyr aldehyde D) ter-butyraldehyde

20. For the preparation of CH3CHO form calcium acetate, we need:

(A) 2 molecules of $Ca(CH_3COO)_2$

(B) 1 mole of $Ca(CH_3COO)_2$ and 1 molecule of $Ca(HCOO)_2$

(C) 2 molecules of $Ca(HCOO)_2$(D) None of these

21. Which of the following tests is shown by ketones?

(A) Fehling solution test (B) Tollen's reagent test

(C) Schiff reagent test (D) Sodium nitroprusside test

22. Fehling solution consists of two separate solutions. One solution contains $CuSO_4$. The other contains:

(A) $NaHCO_3$ (B) $H_2C_2O_4$

(C) K_2CO_3 (D) $Na_2C_4H_4O_6$

23. Isopropyl alcohol on passing over heating copper at 300°C gives:

(A) Propylene (B) Acetaldehyde

(C) Acetone (D) Propanal

24. One of an organic compound requires 0.5 mole of oxygen to produce on acid. The compound may be:

(A) Alcohol (B) Ether

(C) Ketone (D) Aldehyde

25. Compound 'A' $C_5H_{10}O$ forms a phenyl hydrazone and gives negative Tollen's and iodoform test:

(A) 2-pentanone (B) 3-pentanone

(C) Pentanal (D) n-pentane

26. The organic compounds 'A' and 'B' react with $NaHSO_3$ 'A' reacts with ammonical $AgNO_3$ but 'B' does not. The compound A and B are:

(A) ROR and RCHO (B) COR_2 and $R-NH_2$

(C) RNH_2 and RCHO (D) RCHO and RCOR

27. The molecular formula $C_5H_{10}O$ represents:

(A) 4 aldehydes and 3 ketones (B) 3 aldehydes and 4 ketones

(C) 5 aldehydes and 2-ketones (D) 5 ketones and 2-aldehydes

28. In ketones both sides of carbonyl group always contains:

(A) H-atom (B) O-atom

(C) C-atom (D) Both (b) and (c)

29. The carboxylic acid formed during haloform reaction contains carbon atoms:

(A) Same as in parent ketone (B) Two less then parent ketone

(C) One more then parent ketone (D) One less then parent ketone

30. The product of reduction of butanone with sodium borohydride is:

(A) Methanol (B) 2-propanol

(C) Ethanol (D) 2-butanol

31. Iodoform test can be used to identify:

(A) Methyl aldehydes (B) Methyl ethers

(C) Ethyl ketones (D) Alkan-2-ones

32. In this sequence what is B?

$$C_2H_5Br + KCN \longrightarrow A + H_2O/H_3O^+ \longrightarrow B$$

(A) Acetic acid (B) Propanal

(C) Propanoic acid (D) Ethyl alcohol

33. C-atom in a carbonyl group acts as a/an:

(A) Nucleophilic centre (B) Neutral atom

(C) Electrophilic centre (D) Chiral centre

34. 2-hydroxyl propanoic acid can be prepared in the following two steps starting from ethanal:

$$\mathbf{CH_3 - CHO \xrightarrow{Step\ 1} CH_3CHOHCN \xrightarrow{Step\ 2} CH_3CHOHCO_2^{-}}$$

a. What is the reagent and condition for the two steps?

(A) HCN, acid hydration (B) NaCN in alcohol, oxidation with H_2O_2

(C) HCN, acidic hydrolysis (D) NaCN in alcohol, reduction Sn + HCl

35. In iodoform test, how many moles of I_2 are used for each mole of reagent:

(A) 4 (B) 3

(C) Both (a), (B) (D) Depends upon reagent

36. Which of the following is correct conversion?

(A) CH_3CHO to $CH_3CHOHCN$ to lactic acid (B) HCHO to $CNCH_2OH$ to CH_3COOH

(C) CH_3CHO to $CH_3CHOHCN$ to butyric acid (D) HCHO to HCOHCN to HCOOH

37. The product of oxidation of 3-pentanone:

(A) Acetic acid (B) Propanoic acid

(C) Acetic acid + Formic acid (D) Both (a) and (b)

38. Which type of isomerism is shown by 3-pentanone and pentanal?

(A) No isomerism (B) Metamerism

(C) Cis-trans (D) Functional group

39. In base catalyzed reaction of aldehydes, an aldehyde acts as:

(A) Base (B) Acid

(C) Electrophile (D) Nucleophile

40. The product of reduction of propanone with sodium borohydride is:

(A) Methanol (B) 2-propanol

(C) Ethanol (D) 2-butanol

41. Which of the following reactions may associated with aldehyde and ketone in general?

(A) nucleophile addition (B) polymerization

(C) oxidation (D) all of the above

42. Ketones are comparatively less reactive than aldehdye. It is due to

(A) alkyl groups are electron donating (B) steric hindrance

(C) both (a) and (B) (D) none

43. Which of the following will not give addition reaction with $NaHSO_3$

(A) HCHO (B) CH3CHO

(C) CH_3-CH_2-CHO (D) CH_3-CH_2-OH

44. On heating aldehydes with Fehlings solution we get a precipitate whose colour is

(A) pink (B) black

(C) yellow (D) brick red

45. Aldehyde and ketone have same general formula for homologous series

(A) $C_nH_{2n}O_{2n}$ (B) C_nH_{2n}

(C) $C_nH_{2n}O$ (D) $C_nH_{2n}O_{n+1}$

ANSWER KEY

1	B	11	A	21	D	31	D	41	A
2	A	12	D	22	D	32	C	42	C
3	A	13	D	23	C	33	C	43	D
4	D	14	C	24	D	34	D	44	D
5	C	15	D	25	B	35	D	45	C
6	C	16	C	26	D	36	A	46	
7	D	17	C	27	A	37	D	47	
8	B	18	B	28	C	38	D	48	
9	B	19	B	29	D	39	C	49	
10	B	20	B	30	D	40	B	50	

UHS TOPIC 6 – C

CARBOXYLIC ACID

LEARNING OUTCOMES

In this topic, student should be able to:

a) Show preparation of ethanoic acid by oxidation of ethanol or by acidic hydrolysis of Ethane nitrile (CH_3CN)

b) Discuss the reactions of ethanoic acid with emphasis on:

  i) Salt formation.

  ii) Esterification.

  iii) Acid chloride formation (acyl chloride).

  iv) Amide formation.

c) Describe the strength of organic acids relative to chloro substituted acids.

d) Explain the relative acidic strength of carboxylic acids, phenols and alcohols.

CARBOXYLIC ACIDS:

Organic compounds containing – COOH as a functional group are called carboxylic acids (carb from carbonyl and oxyl from hydroxyl).

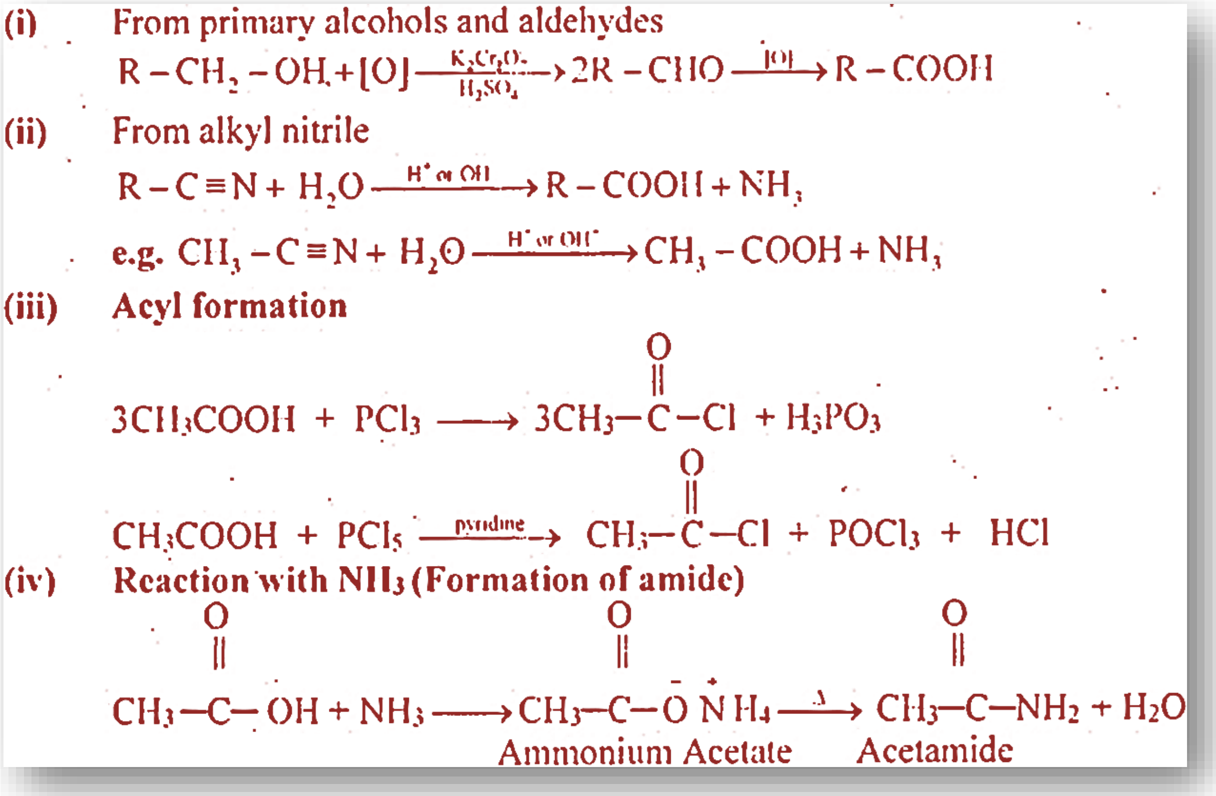
- Their general formula is R-COOH

Nomenclature:

STRUCTURAL FORMULA	COMMON NAME	IUPAC NAME
$H - COOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
$CH_3 - CH_2 - COOH$	Propanoic acid	Propanoic acid
$CH_3 - CH_2 - CH_2 - COOH$	Butyric acid	Butanoic acid
$CH_2 - CHCOOH$ | CH_3	Iso-butyric acid	2-methylpropanoic acid

Preparation of Carboxylic Acid:

DESCRIPTION OF REACTION	REMARKS
From primary alcohols and aldehydes	• In case of alcohol $K_2Cr_2O_7$ is used as oxidizing agent. • In case of aldehyde, Tollens reagent can also be used as oxidizing agent
By hydrolysis of ethyl nitrile	• Nitriles oxidize in acidic medium which gives free carboxylic acid nitrile(With HCl)



(i) From primary alcohols and aldehydes

$$R-CH_2-OH+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}2R-CHO\xrightarrow{[O]}R-COOH$$

(ii) From alkyl nitrile

$$R-C\equiv N+H_2O\xrightarrow{H^+ \text{ or } OH}R-COOH+NH_3$$

e.g. $CH_3-C\equiv N+H_2O\xrightarrow{H^+ \text{ or } OH^-}CH_3-COOH+NH_3$

(iii) **Acyl formation**

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_3PO_3$$

$$CH_3COOH + PCl_5 \xrightarrow{\text{pyridine}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + POCl_3 + HCl$$

(iv) **Reaction with NH₃ (Formation of amide)**

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{O}\,\overset{+}{N}H_4 \xrightarrow{\Delta} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + H_2O$$

Ammonium Acetate Acetamide

POINT TO PONDER: Ethanoic anhydride is used for the manufacture of ……

PHYSICAL PROPERTIES

:

Smell:

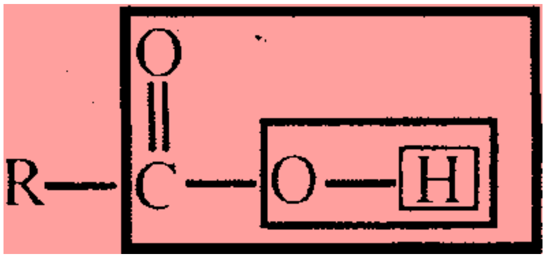
C_1 to C_4 have pungent smell and C_4 to C_6 have unpleasant smell.

Reactivity of Carboxyl Group:

- Carbonyl group is electron withdrawing it increases the polarity of – OH.
- The – OH group of carboxylic acid is more active in chemical reactions than those of alcohols.

Types of Reaction:

- Reaction in which H of carboxylic acid is replaced.
- Reaction in which – OH of carboxylic acid is replaced.
- Reaction involving carboxylic group as whole



CHEMICAL PROPERTIES OF CARBOXYLIC ACID

:

REACTIONS INVOLVING – H GROUP OF CARBOXYLIC ACID		
Salt formation	•	Alkalis form salt and replaces the H of carboxylic acid
	•	Carbonates give same result with effervescence of CO_2
	•	Metals form salt and H_2 with carboxylic acid
REACTIONS INVOLVING – H GROUP OF CARBOXYLIC ACID		
Formation of acid halide	•	OH group is replaced by X group
Ester formation RCOO – H + R $\overset{H}{\rightleftharpoons}$ RCOO R + H_2O	•	OH group is replaced by alkoxy radical
	•	Reaction is reversible
	•	Reaction is acid catalyzed

Formation of amide	• With NH_3 form ammonium salt on dehydration yield acid amide • Amides are very stable compound
Formation of acid anhydride	• P_2O_5 works as dehydrating agent
REACTIONS INVOLVING CARBOXYL GROUP	
Partial reduction of carboxylic acid to alcohol	• Reduction of carboxylic group is very difficult • Strong reducing agent like $LiAH_4$ is used • Reducing agents which are used in aldehydes or ketones cannot be used
Complete reduction of carboxylic acid to alkanes	• Reduction is carried out in the presence of red phosphorus and HI forms alkane

ACETIC ACID:

- Its dilute solution is called vinegar. (6 – 10 %)
- In combined form It IS present in the form of ester.
- It was first of all derived from vinegar.
- In free form it occurs in a number of fruit, juices, which have undergone fermentation

ESTER	FLAVOUR
Amylaceiate	Banana
Isobutyl formate	Rasberry
Benzylcetate	Jasmine
Ethyl butyrate	Pineapple
Amyl buryrate	Apricot
Octyl acetate	Orange

PREPARATION OF ACETIC ACID

LABORATORY SCALE	
Oxidation of C_2H_5OH	• Dilute H_2SO_4 is used
	• First acetaldeh de is formed which then convert into acetic acid
Hydrolysis of CH_3CN	• Dilute HCl is used
	• Acetamide is formed, which on hydrolysis gives CH_3COOH
INDUSTRIAL SCALE	
From Acetylene	• Best source to prepare CH_3COOH
	• Acetylene is bubbled in 20 % H_2SO_4 at 80° C and 1 % $HgSO_4$ acting as catalyst results in acetaldehyde
	• Acetaldehyde changes Into acetic acid on oxidation by using V_2O_5 as catalyst
	• 97 % pure acid is obtained
Oxidation of ethanol	• 12 % ethanol is obtained by fermentation of molasses
	• Oxidation of ethanolis done by $K_2Cr_2O_7$ and H_2SO_4

Laboratory preparation:

(i) By the oxidation of ethyl alcohol or acetaldehyde

$$CH_3-CH_2-OH+[O] \qquad C\xrightarrow[H_2SO_4]{K_2Cr_2O_7}\rightarrow CH_3-COOH$$

(ii) By the hydrolysis of methyl nitrile:

$$CH_3-CN \xrightarrow[H_2O]{\text{Dil HCl}} CH_3-CO-NH_2\xrightarrow[HO_2H^+]{} CH3-COOH+NH_4^+$$

PHYSICAL CHARACTERISTICS

PROPERTIES	DESCRIPTION
Colour, taste and odour	Colourless, sour taste, strong vinegar odour

Melting point, solidifying	16.5 °C is MP, below 16.5° C it solidify (called glacial acetic temperature acid)
Boiling point	118° C
Specific gravity	1.0 gm/cm^3
Solubility	Soluble in ether and alcohol
Existence	Dimer

USES	DESCRIPTION
Chemical industry	Dye stuffs, perfumes, rayon, rubber, copper acetate used in paint
Food industry	Ingredients of food pickles etc
Medical sciences	Preparation of lead acetate for fracture and burn sand aluminum acetate used as antiseptic

STRENGTH OF ORGANIC ACIDS

In each of the carboxylic acids, the H – O group is attached to a carbonyl C = O group which is in turn bonded to other atoms, The comparison we observe here is between carboxylic acid molecules, denoted as RCOOH, and other organic molecules containing the H – O group, such as alcohols denoted as ROH (R is simply an atom or group of atoms attached to the functional group). The former are obviously acids whereas the latter group contains molecules which are generally extremely weak acids. One interesting comparison is tor the acid and alcohol when R is the benzene ring (C_6H_5), benzoic acid (C_6H_5COOH), has pKa = 4.2, whereas phenol (C_6H_5OH) has pKa = 9.9. Thus, the presence of the doubly bonded oxygen atom on the carbon atom adjacent to the O – H clearly increases the acidity of the molecule, and thus increases ionization of the O – H bond.

Strength of Chloro-Substituted Acids:

Carboxylic acids are converted to acid chlorides by a range of reagents: $SOCl_2$, PCl_5 or PCl_3 are the usual reagents. Other products are HCl & SO_2, HCl & $POCl_3$ and H_3PO_3 respectively. The conditions must be dry, as water will hydrolyze the acid chloride in a vigorous reaction. Hydrolysis forms the original carboxylic acid.

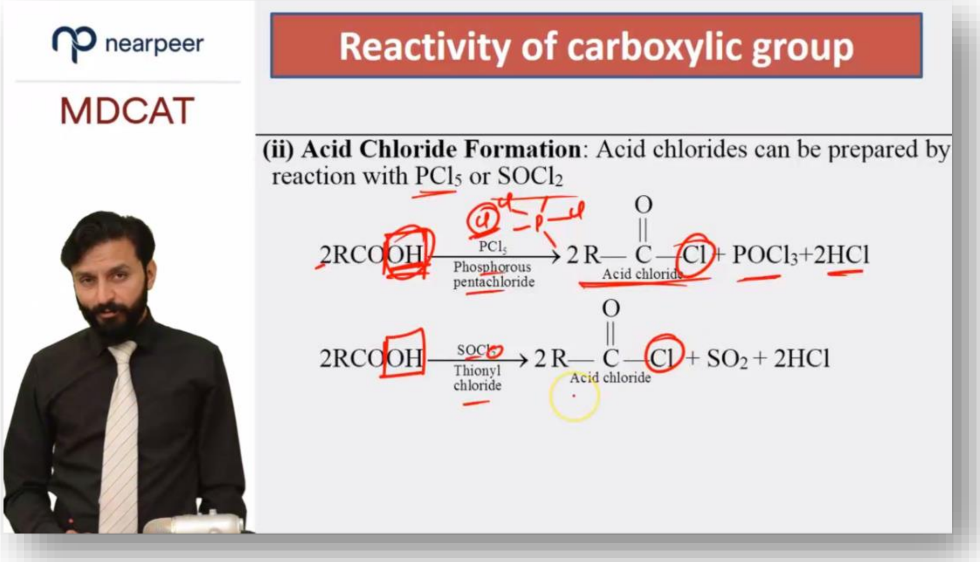
$CH_3COOH + SOCO_2 \rightarrow CH_3COCl + HCl + SO_2$

$C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl + HCl + POCl_3$

$3CH_3CH_2COOH + PCl_3 \rightarrow 3CH_3CH_2COCl + H_3PO_3$

Substituents of high electronegativity (especially – OB, – Cl and – NH_3^+) near the carboxyl group increase the acidity of carboxylic acids, often by several orders of magnitude compare, for example, the acidities of acetic acid and the chlorine-substituted acetic acids. Both dichloroacetic acid and trichloroacetic are stronger acids than acetic acid (pKa 4.75) and H_3PO_4(pKa 2.12).

Formula:	CH_3COOH	$ClCH_2COOH$	$Cl_2CHCOOH$	Cl_3CCOOH
Name:	acetic acid	chloroacctic acid	dichloroacetic acid	trichloroacetic acid
pKa:	4.76	2.86	1.48	0.70



Reactivity of carboxylic group

(ii) Acid Chloride Formation: Acid chlorides can be prepared by reaction with PCl_5 or $SOCl_2$

$$2RCOOH \xrightarrow[\text{Phosphorous pentachloride}]{PCl_5} 2R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + POCl_3 + 2HCl$$

Acid chloride

$$2RCOOH \xrightarrow[\text{Thionyl chloride}]{SOCl_2} 2R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + SO_2 + 2HCl$$

Acid chloride

Electronegative atoms on the carbon adjacent to a carboxyl group increase acidity because they pull electron density away from the O – H bond, thereby facilitating ionization of the carboxyl group and making it a stronger acid.

PRACTICE EXERCISE (FOR UHS TOPIC)

1. **The increasing order of acid strength is**

A) Phenol, Acetic Acid, Ethanol, Chloroacetic acid

B) Acetic acid, Ethanol, Phenol, Chloroacetic acid

C) Ethanol, Phenol, Acetic acid, Chloroacetic acid

D) Chloroacetic acid, Acetic acid, Ethanol, Phenol

2. **Which of the following is not a derivative of carboxylic acid**

A) Alkanyl chloride

C) Alkanamide

B) Alkanal

D) Alkyl alkanoate

3. Monocarboxylic acids shows functional group isomerism with

A) Esters

B) Ethers

C) Alcohols

D) Aldehydes

4. When sodium formate is heated with soda lime, it forms

A) H_2

B) C_2H_6

C) CH_4

D) $CH\equiv CH$

5. Which is used to removed ink and rust stains on cloth

A) Oxalic acid

B) Ether

C) Alcohol

D) Kerosene oil

6. The reaction between an alcohol and an acid is known as

A) Saponification

B) Hydrolysis

C) Esterfication

D) Hydrogenation

7. Lactic acid is:

A) Propionic acid

B) β-hydroxy proionic acid

C) α-hydroxy proionic acid

D) None of these

8. The compound which on reduction with $LiALH_4$ gives alcohols

A) CH_3COOH

B) CH_3COCH_3

C) $CH_3COOC_2H_5$

D) CH_3CHO

9. Carboxylic acids on reduction with HI and red phosphorous gives

A) Alkane

C) Benzene

B) Alkene D) Alkyne

10. Which of the following derivatives of carboxylic acid is not directly prepared

A) Acid halide C) ester

B) Acid amide D) acid anhydride

11. Which of the following reaction is given by carboxylic acid?

A) Acid base reaction C) Nucleophilic substitution reactions

B) Decarboxylation D) All of the above

12. Which of the following esters shows flavor of pineapple

A) Ethyl butyrate C) Amyl btyrate

B) Octyl acetate D) Amyl acetate

13. When carboxylic acid is dissolved in non polar solvent such as benzene it exist as cyclic dimmers and shows __________ membered ring

A) 6 C) 8

B) 10 D) 12

14. It has been observed that melting points of carboxylic acid increases irregularly with the increase in molecular mass. Which of the following carboxylic acid has the highest boiling point?

A) Ethanoic acid C) Propanoic acid

B) Butanoic acid D) Pentanoic acid

15. The name glacial acetic acid is given to pure acetic acid

A) Below 17 ^oC it is white liquid C) it forms ice like solid below 17 ^oC

B) It is mixed with mehtanol

D) Pure acetic acid above 17 °C

16. The peptide bond which is formed by the condensation of amino acids is what type of bond

A) ester

C) amide

B) ether

D) Anhydride

17. Which acid is used in the manufacture of synthetic fiber

A) Formic acid

C) oxalic acid

B) Carbonic acid

D) acetic acid

18. The solution of which acid is used for seasoning of food

A) Fumaric acid

C) Acetic acid

B) Benzoic acid

D) Butanoic acid

19. Slight oxidation of primary alcohol gives:

(A) Ketone

(B) Organic acid

(C) Aldehyde

(D) An ester

20. Which of the following is the strongest acid:

(A) $HCOOH$

(B) CH_3COOH

(C) $CH_3 - CH_2 - COOH$

(D) $Cl - CH_2 - COOH$

21. Which derivative cannot be prepared directly from acetic acid?

(A) Acetamide

(B) Acetyl chloride

(C) Acetic anhdride

(D) Ethyl acetate

22. Amyl butyrate has flavour of:

(A) Banana

(B) Apricot

(C) Jasmine

(D) Orange

23. Which of the following is formed when acetic acid reacts with $SOCl_2$?

(A) CH_3COCl

(B) SO_2

(C) HCl

(D) All

24. Which of the followings show maximum acidic character?

(A) Phenol

(B) Ethanol

(C) Ethanoic acid

(D) Methanoic acid

25. The solution of which is used for seasoning of food:

(A) Formic acid

(B) Acetic acid

(C) Benzoic acid

(D) Butanoic acid

26. Formic acid reduces Tollen's reagent because:

(A) It is very strong acid

(B) It has an aldehyde group in its structure

(C) It is carboxylic acid

(D) It cannot react with Tollen's reagent

27. Amides are:

(A) Acidic

(B) Basic

(C) Neutral

(D) Amphoteric

28. Toluene on oxidation with air in presence of V_2O_5 yields:

(A) Phenol

(B) Benzoic acid

(C) Benzaldehyde (D) Benzyl alcohol

29. The acidic nature of carboxylic acid is due to:

(A) Higher degree of ionization of the acid

(B) Greater resonance stabilization of the acid

(C) Greater resonance stabilisation of the carboxylate ion

(D) Lower degree of ionization

30. The organic compound A and B react with sodium metal and release H_2 gas. A and B react with each other to give ethyl acetate. The A and B are:

(A) CH_3COOH and C_2H_5OH (B) $HCOOH$ and C_2H_5OH

(C) CH_3COOH and CH_3OH (D) CH_3COOH and $HCOOH$

31. Which of the following would react faster with NH_3 to give acid amide?

(A) RCOCl (B) RCOOR

(C) RCOOH (D) $(RCO)_2O$

32. Reaction of acetic acid with $LiAlH_4$ gives:

(A) Ethanol (B) Ethane

(C) Ethanal (D) Ethyl acetate

33. The weakest carboxylic acid:

(A) HCOOH (B) CH_3CH_2COOH

(C) CH_3COOH (D) $ClCH_2COOH$

34. General formula of monocarboxylic acid:

(A) $C_nH_{2n}O$ (B) $C_nH_{2n+1}COOH$

(C) $C_nH_{2n}COOH$ (D) $C_nH_{2n-2}COOH$

35. Esterification is faster in case of:

(A) HCOOH (B) CH_3COOH

(C) $(CH_3)_2CHCOOH$ (D) All are equal

36. Which of the following will react with both ethanol and ethanoic acid at room temperature?

(A) $CaCO_3$ (B) CuO

(C) Na-metal (D) CH_3OH

37. Which product is not formed when acetic acid reacts with $SOCl_2$?

(A) CH_3Cl (B) CH_3COCl

(C) HCl (D) SO_2

38. Carboxylic acid can be changed to acid chloride by the treatment with:

(A) S_2Cl_2 (B) $SOCl_2$

(C) HCl (D) HOCl

39. Reaction of carboxylic acid with thionyl chloride gives:

(A) Acid halides (B) Acid amides

(C) Acid anhydrides (D) Ester

40. Which of the following is that carboxylic acid whose molecular formula in a non-polar solvent is $(CH_2)_6O_4$?

(A) Acetic acid (B) Hexanoic acid

(C) Propionic acid (D) Pentanoic acid

41. $2CH_3COOH + M \longrightarrow (CH_3COO)_2M + H_2$ what is M?

(A) Na
(B) K
(C) Mg
(D) NH_3

42. In preparation of acetic anhydride, P_2O_5 gets converted into:

(A) H_3PO_3
(B) H_3PO_4
(C) HPO_3
(D) $H_4P_2O_7$

43. Max. hydroxyl groups:

(A) Lactic acid
(B) Succinic acid
(C) Tartaric acid
(D) Glutamic acid

44. The final product formed when alkyl cyanide is boiled with dil. acid:

(A) An amine
(B) An acid + Ammonium salt
(C) An ester
(D) An amide

45. Which of the following does not give benzoic acid on oxidation?

(A) Benzaldehyde
(B) Benzyl alcohol
(C) Toluene
(D) All of these do give

46. Which of the following is hydroxy acid?

(A) Malic acid
(B) Adipic acid
(C) Lactic acid
(D) Succinic acid

47. Which acid do not contain –COOH groups?

(A) Ethanoic acid
(B) Lactic acid

(C) Picric acid (D) Palmitic acid

48. Which of the following compound will give effervescence of CO_2 on treatment with $NaHCO_3$?

(A) Phenol (B) Picric acid

(C) Acetic acid (D) None

49. Acetic acid exists as dimmer in benzene due to:

(A) Condensation reaction (B) Presence of H-atom at -carbon

(C) Presence of –COOH group (D) H-bonding

50. Which of the following derivatives of acid will form H-bond with each other?

(A) Acid chloride (B) Acid amide

(C) Acid anhydride (D) All

ANSWER KEY

1	**C**	**11**	**D**	**21**	**A**	**31**	**C**	**41**	**C**
2	**B**	**12**	**A**	**22**	**B**	**32**	**B**	**42**	**C**
3	**A**	**13**	**A**	**23**	**D**	**33**	**B**	**43**	**C**
4	**A**	**14**	**B**	**24**	**D**	**34**	**B**	**44**	**B**
5	**A**	**15**	**C**	**25**	**B**	**35**	**A**	**45**	**D**
6	**C**	**16**	**C**	**26**	**B**	**36**	**C**	**46**	**C**
7	**B**	**17**	**D**	**27**	**C**	**37**	**A**	**47**	**C**
8	**A**	**18**	**C**	**28**	**B**	**38**	**B**	**48**	**C**
9	**A**	**19**	**C**	**29**	**C**	**39**	**A**	**49**	**D**
10	**B**	**20**	**D**	**30**	**A**	**40**	**C**	**50**	**B**

UHS TOPIC 7 – C

AMINO ACIDS

LEARNING OUTCOMES

In this topic, student should be able to:

a) Describe the general structure of α- amino acids found in proteins

b) Classify the amino acids on the basis of nature of R-group

c) Describe Acid base properties of amino acids and formation of Zwitter ions

d) Understand peptide bond formation

AMINO ACIDS:

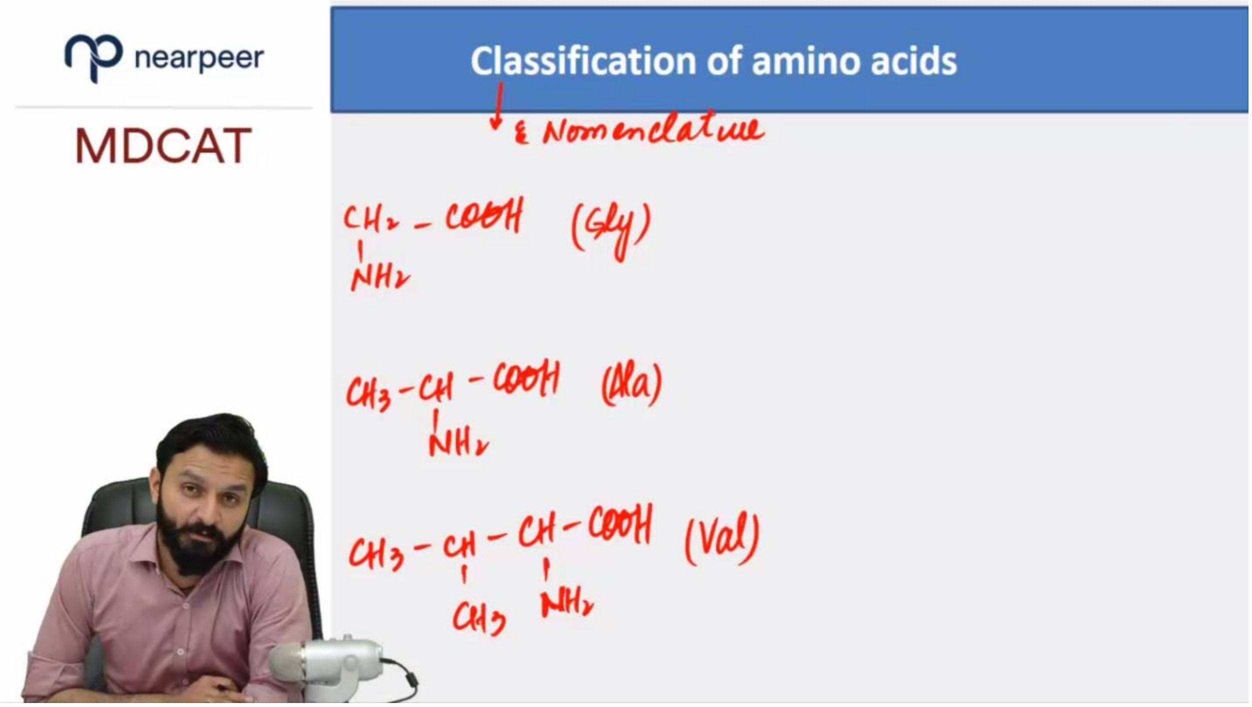
The compounds containing both amino group arid carboxylic groups are called amino acids

→ α-carbon ⇒ to which carboxyl group is attached

→ β-carbon ⇒ to which α-carbon is attached

→ γ-carbon ⇒ to which β-carbon is attached

- Those that cannot he synthesized in our body are called essential amino acid
- Those that can be synthesized in our body arc called non-essential amino acid



Classification of amino acids

& Nomenclature

$\underset{NH_2}{CH_2}-COOH$ (Gly)

$CH_3-\underset{NH_2}{CH}-COOH$ (Ala)

$CH_3-\underset{CH_3}{CH}-\underset{NH_2}{CH}-COOH$ (Val)

Comprehensive video lectures of Unit 7C available at www.nearpeer.org

Types of Amino Acid:

On basis of position of amino group:

α-AMINO ACID	β-AMINO ACID	γ-AMINO ACID
Ammo group is attached to α-carbon e.g. glycine, alanine	Amino group is attached to β-carbon e.g. 3-aminopropionic acid	Amino group is attached to γ-carbon e.g. 4-aminobutyric acid

No.	NAME	NATURE	ABBREVIATION	STRUCTURAL FORMULA
1	Glycine	Neutral	Gly	CH_2 – COOH | NH_2
2	Alanine	Neutral	Ala	CH3 – CH – COOH | NH_2
3	Valine	Neutral	Val	CH3 – CH – CH – COOH | | CH_3NH_2
4	Proline	Neutral	Pro	H_2C – CH_2 \ / NH
5	Aspartic acid	Acidic	Asp	HOOC – CH_2 – CH – COOH | NH_2
6	Glutamic acid	Acidic	Gla	HOOC – CH_3 – CH_2 – CH – COOH | NH_2
7	Lysine	Basic	Lys	CH2 – $(CH_2)_3$ – CH – COOH | | NH_2 NH_2
8	Histdine	Basic	His	CH = C – CH_2 – CH – COOH | | | N $NHNH_3$

				\\ / CH

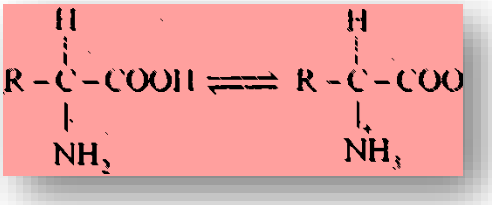
ESSENTIAL AMINO ACID:

An essential amino acid or indispensable amino acid is an amino acid that cannot be synthesized by the organism (usually referring to humans) and therefore must be supplied in the diet. These include phenylalanine. valine, threonine, tryptoplene, isoleucine, methionine, leucine, lysine and histidine additionally cysteine (or sulphur) containing amino acids), tyrosine (or aromatic amino acids) and arginine are required by infants and growing children.

Zwitter Ion:

The ions which contain positive and negative charge on same molecule is called Zwitter ions.

- Amino acids give zwitter ions.
- On addition of H$^+$,– COO$^+$ pan of amino acid accepts If' so acts as base
- On addition of OH$^+$,– NH_1^+, part liberates H$^+$ so acts as acid



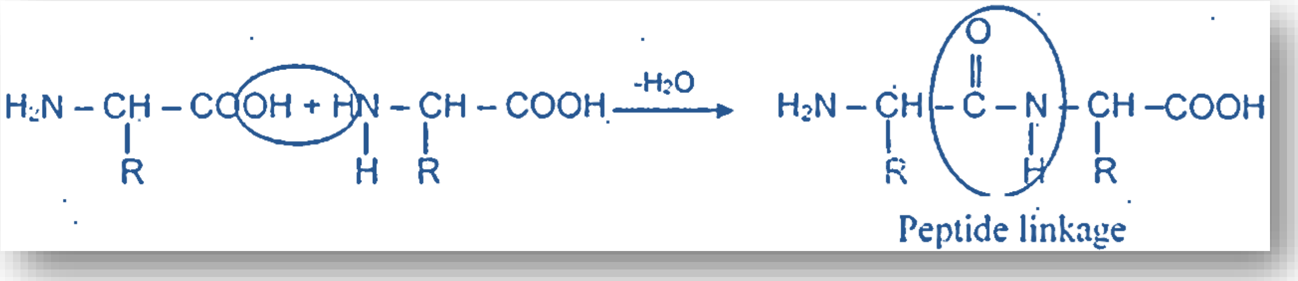
$$R-\underset{NH_2}{\overset{H}{C}}-COOH \rightleftharpoons R-\underset{NH_3^+}{\overset{H}{C}}-COO$$

Neutral, Acidic and Basic Amino Acids:

- Amino acid having equal number of amino and carboxylic groups are neutral e.g. glycine
- Amino acid having more amino groups than carboxylic group are basic e.g. Lysine; Arginine. histidine etc.
- Amino acid haying more carboxylic groups than amino groups are acidic e.g. aspartic acid. glutamic acid.

Proteins and Peptides:

- Peptides are produced, by condensation of amino acids
- The carboxyl group of one amino acid and amino group of another amino acid gets condensed with elimination of water. The resulting – CO – NH – linkage is called a peptide linkage
- Peptide bond depends upon the number of amino acids per molecule therefore there are dipeptidestripeptides, polypeptide, etc.
- When a large number of amino acids are joined by peptide bonds in a chain then it is called polypeptide chain.
- Polypeptide having more than 10,000 molar mass is called protein, while if less than 10,000 molar mass then it is polypeptide.



$$H_2N-\underset{R}{\underset{|}{CH}}-COOH + \underset{H}{\underset{|}{HN}}-\underset{R}{\underset{|}{CH}}-COOH \xrightarrow{-H_2O} H_2N-\underset{R}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-\underset{R}{\underset{|}{CH}}-COOH$$

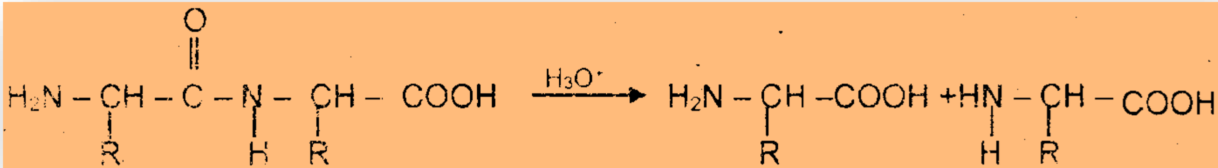
HYDROLYSIS OF POLYPEPTIDES/PROTEINS:

Peptide linkage

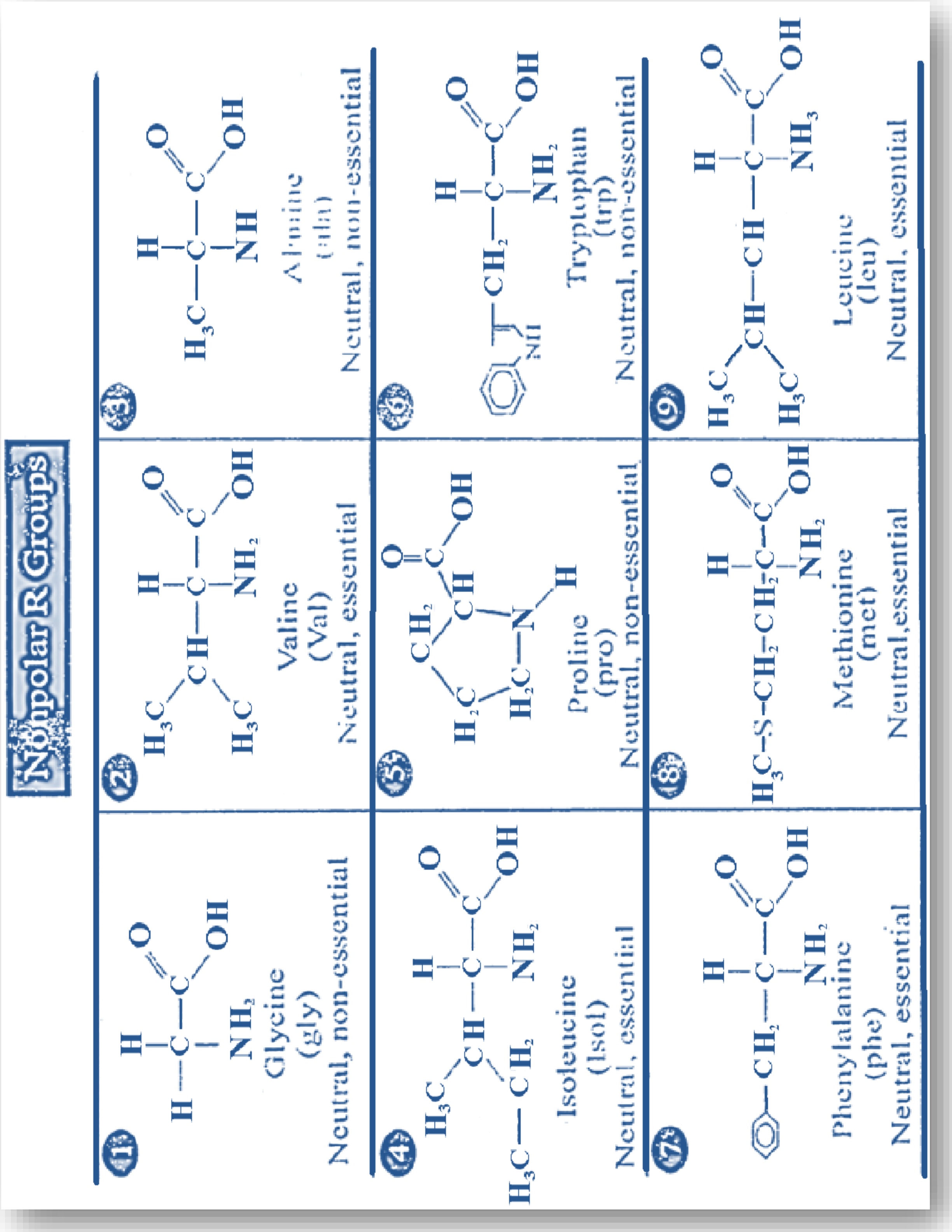
Polypeptides/proteins on hydrolysis with water is presence of NaOH or $Ba(OH)_2$, or proteolytic enzymes give α-amino acids. Hydrolysis occurs at the peptide linkage

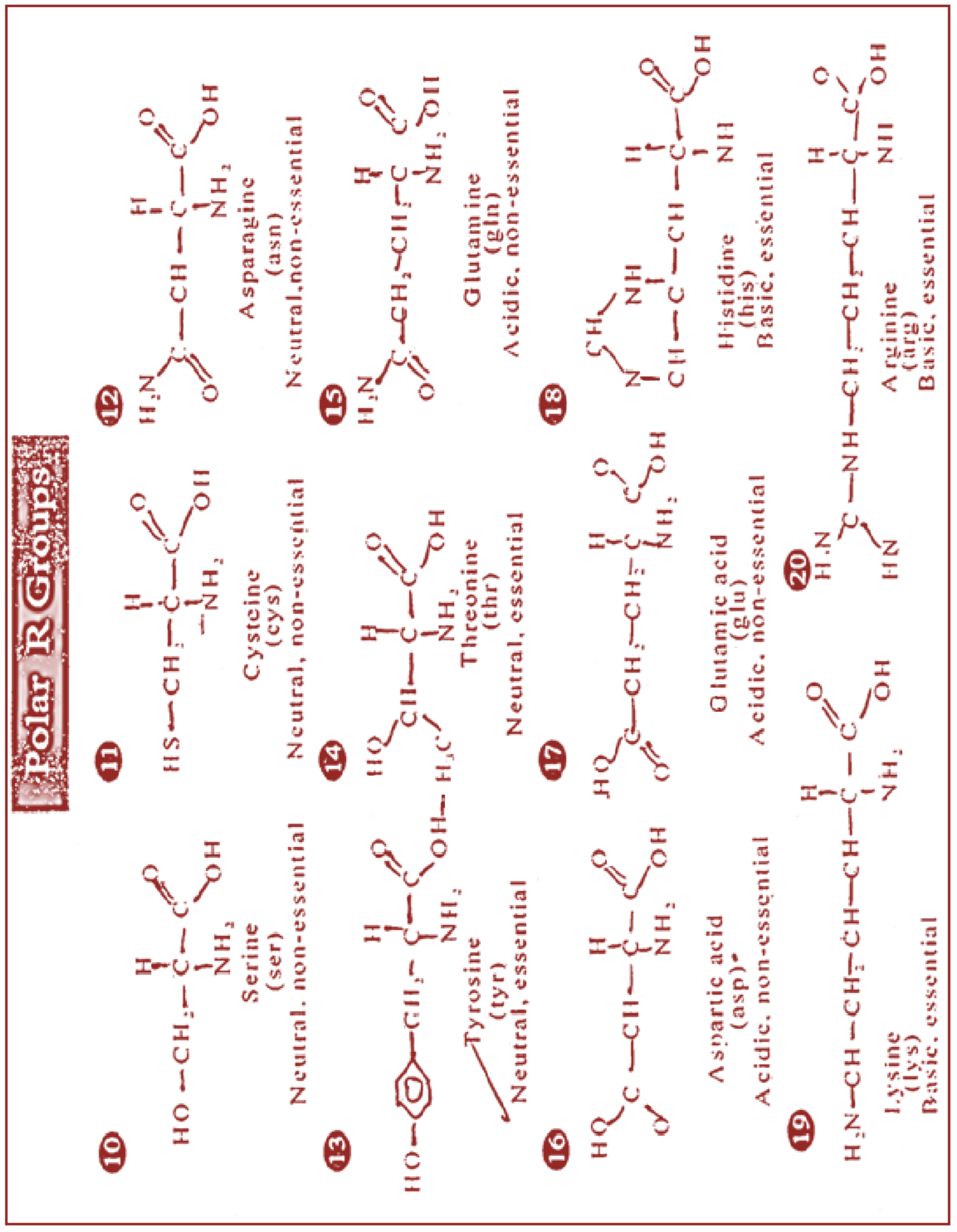
(– CO.NH –) in steps.

Proteins → Polypeptides → simple peptides → Amino acids



$$H_2N-\underset{R}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-\underset{R}{\underset{|}{CH}}-COOH \xrightarrow{H_3O^+} H_2N-\underset{R}{\underset{|}{CH}}-COOH + \underset{H}{\underset{|}{HN}}-\underset{R}{\underset{|}{CH}}-COOH$$


Nonpolar R Groups
1
Glycine
(gly)
Neutral, non-essential
2
Valine
(Val)
Neutral, essential
3
Alanine
(ala)
Neutral, non-essential
4
Isoleucine
(Isol)
Neutral, essential
5
Proline
(pro)
Neutral, non-essential
6
Tryptophan
(trp)
Neutral, non-essential
7
Phenylalanine
(phe)
Neutral, essential
8
Methionine
(met)
Neutral,essential
9
Leucine
(leu)
Neutral, essential


Polar R Groups
10
Serine
(ser)
Neutral, non-essential
11
Cysteine
(cys)
Neutral, non-essential
12
Asparagine
(asn)
Neutral, non-essential
13
Tyrosine
(tyr)
Neutral, essential
14
Threonine
(thr)
Neutral, essential
15
Glutamine
(gln)
Acidic, non-essential
16
Aspartic acid
(asp)*
Acidic, non-essential
17
Glutamic acid
(glu)
Acidic, non-essential
18
Histidine
(his)
Basic, essential
19
Lysine
(lys)
Basic, essential
20
Arginine
(arg)
Basic, essential

EXCLUSIVE PRACTICE EXERCISE (UHS TOPIC ONLY)

1. **Some amino acids are most important because they are the final product of hydrolysis of peptide and proteins and they are**

A) (**α** -amino acid C) β -amino acids

B) (γ -amino acids D) All of the above

2. **The peptide bond which is formed by the condensation of amino acids is what type of bond**

A) ester C) amide

B) ether D) Anhydride

3. **Ninhydrin reacts with amino acid to form product which has colour:**

A) Blue C) purple

B) Bluish violet D) Red

4. **In amino acid proton is transferred from one point to the other point and this dipolar ion is called:**

A) Oxonium ion C) Carbonium ion

B) Zwitter ion D) Carbanion

5. **Which of the following is neutral amino acid:**

A) Glycine C) Histidine

B) Lysine D) Aspartic acid

6. **By convention a peptide having molecular mass upto 10,000 is called:**

A) Peptide C) Polypeptide

B) Protein D) Dipeptide

7. Which of following when treated with a mixture of $NaNO_2$ and HCl produces lactic acid:

A) Glycine C) Alanine

B) Lysine D) Valine

8. Amino acids are identified in paper chromatography by:

A) Nitroprusside test C) Iodoform test

B) Tollen's test D) Ninhydrin tests

9. The amino acid which was first isolated from cheese is:

A) Glycine C) Tyrosine

B) Lysine D) Valine

10. The amino acid containing sulphur is:

A) Glycine C) Cysteine

B) Methionine D) Both "B" and "C"

11. The pH at which concentration of Zwitter ion is maximal in solution is:

A) Optimum pH C) Isotonic point

B) Isoelectric point D) Azeotropic point

12. All the amino acids are asymmetric and show optical isomerism except:

A) Valine C) Tyrosine

B) Glycine D) Alanine

13. Which of the following is basic amino acid:

A) Glycine

B) Histidine

C) Valine

D) Proline

14. The amino acids exert buffer action as:

A) They have achiral alpha carbon center

B) They form peptide linkage with each other

C) They can combine with both H^+ and OH^- ions

D) They form proteins on polymerization

15. The amino acids which can be prepared by human body itself are:

A) Essential

B) Non-essential

C) Acidic

D) Basic

16. The amino acid which is basic as well as olefinic in nature:

A) Valine

B) Histidine

C) Arginine

D) All of these

17. The most common amino acids in nature are:

A) α-amino acids

B) γ-amino acids

C) β-amino acids

D) All of these

18. The amino acids are different from each other due to:

A) Arrangement of amino and carboxylic group with respect to each other

B) Number of amino and carboxylic group with respect to each other

C) Number of Nitrogen atoms in each amino acid

D) Structure of alkyl group

19. A dipeptide contains __________ amino acid

A) Three C) Five

B) Four D) Two

20. The amino acid which contains aromatic ring in its structure is

A) Lysine C) Tyrosine

B) Cystien D) Glycine

21. Which one of the following is not an amino acid?

(A) Alanine (B) Glycine

(C) Aspartic acid (D) Aniline

22. The simplest of all amino acids:

(A) Lysine (B) Glycine

(C) Alanine (D) Aspartic acid

23. Which of the following is neutral amino acids?

(A) Glycine (B) Histidine

(C) Lysine (D) Asparticacid

24. Which statement is incorrect about Zwitter ion?

(A) It is double ion (B) It is a salt

(C) It is internal salt (D) It can be precipitated

25. IUPAC name of glycine is:

(A) Amino acetic acid

(B) 2-Amino ethanoic acid

(C) Amino propionic acid

(D) Imino acetic acid

26. Peptide bond formation is accompanied by:

(A) Removal of water molecule

(B) Formation of C-N bond between two amino acids

(C) Formation of peptide chain

(D) All of the above is correct

27. -amino nitrile upon acidic hydrolysis yields:

(A) -carboxylic acid

(B) -amino acid

(C) -hydroxy carboxylic acid

(D) Acetic acid

28. In basic medium proton is released by the Zwitter ion from:

(A) –COOH

(B) $-NH_2$

(C) NH_3^+

(D) NH_3

29. When an alkali is added to the aqueous solution of an amino acid, net charge on a molecule of amino acid is:

(A) +ve

(B) Zero

(C) –ve

(D) May be +ve or –ve

30. Neutral amino acids contain:

(A) One amino group and one carboxyl group

(B) Two amino group and one-carboxyl groups

(C) Two carboxyl groups and one amino group

(D) none of these

31. During the formation of peptide bond, which substance is released as a byproduct?

(A) NH_3

(B) H_2O

(C) N_2

(D) CO_2

32. Amino acids are organic compounds containing both

(A) Amino and aldehydic group

(B) Amino and Carboxylic group

(C) Amino and ketonic group

(D) Amino and hydroxyl group

33. Amino acids exist as

(A) Polar ion

(B) non polar ion

(C) Dipolar ion

(D) Tripolar ion

34. The common name of, 2-amino Propanoic acid is

(A) Lysine

(B) Alanin

(C) Asparagine

(D) Glutamine

35. Example of amino acids with a non-polar R – Group are

(A) Glycine and serine

(B) Lysine and Orginine

(C) Tyrosine and Cystein

(D) Alanine and valine

36. All α – amino acids exist largely in

(A) Polar ionic from (B) Dipolar ionic form

(C) Ionic form (D) Non polar form

37. Which one of the following amino acids has the cyclic structure?

(A) Proline (B) Valine

(C) Glutamic acid (D) Alanine

38. The IUPAC name of Valine is

(A) 2 – Amino butyric acid

(B) 2 – Amino Pentanoic acid

(C) 3 – Amino , 2 – Methyl butanoic acid

(D) 2 – Amino 3 – methyl butanoic acid

39. α – Bromo Propionic acid reacts with ammonia to give

(A) α – Amino Propionic acid (B) β– amino propionic

(C) β – amono acid (D) β– Amino butanoic acid

40. Aldehydes react with ammonia in presence of HCN to give α - amino nitrile which on hydrolysis gives.

(A) α– Amino acid (B) α- Carboxylic acid

(C) B – amino acid (D) Di-carboxylic aicd

ANSWER KEY

1	D	11	D	21	D	31	B
2	**C**	**12**	**C**	**22**	**B**	**32**	**B**
3	**C**	**13**	**D**	**23**	**A**	**33**	**C**
4	**C**	**14**	**A**	**24**	**B**	**34**	**D**
5	**A**	**15**	**A**	**25**	**B**	**35**	**D**
6	**B**	**16**	**A**	**26**	**D**	**36**	**B**
7	**D**	**17**	**A**	**27**	**B**	**37**	**A**
8	**A**	**18**	**D**	**28**	**B**	**38**	**D**
9	**C**	**19**	**C**	**29**	**C**	**39**	**A**
10	**D**	**20**	**C**	**30**	**A**	**40**	**A**

UHS TOPIC 8 – C

HEXOMOLECULES

LEARNING OUTCOMES

In this topic, student should be able to describe and explain:

a) Formation and uses of Addition polymers such as polyethene, polystyrene and polyvinylchloride (PVC)

b) Formation and uses of Condensation polymers such as polyesters (terylene), polyamide (Nylon-6,6)

c) Structure of proteins i.e. primary and-secondary structures

d) Structure and function of nucleic acid (DNA)

POINT TO PONDER: Elastomers return to their original shapes after being deformed?

In thermosetting plastics, polymer chains are cross-linked to form a?

Addition polymerization involves the formation of?

Vulcanization creates cross-links and reduces?

MACROMOLECULE

:

A giant molecule which is often a polymer is called macromolecule.

POLYMER

:

A large molecule build up by the repetition of small and simple chemical units is called polymer.

MONOMER:

Small unit or simple molecule from which a macromolecule is formed is called monomers.

POLYMERIZATION:

In 1929 W.H. Carothers suggested a classification of the polymerization process into two types depending upon the way the polymers are formed.

(i) Addition polymerization

(ii) Condensation polymerization

ADDITION POLYMERIZATION	CONDENSATION POLYMERIZATION
Empirical formula of monomer and polymer is same	Empirical formula of polymer and monomer is different
No by-product is produced	By-products are produced like water or methanol
Reaction takes place in main chain through free radical mechanism	Reaction takes place through functional groups
Covalent in nature	Tonic in nature
It involves initiation propagation and termination steps	It involves only single step

Example: Polyethylene. PVc. Polystyrene. etc.	**Example:** Bakelite, Nylon, Polyester, etc

IMPORTANT SYNTHETIC POLYMER:

Name of polymer	Polymerization type	Monomers present	Uses
Polyvinyl chloride	Addition	Vinyl chloride (52° C and 9 atm) $CH_2 = CH - Cl$	• used in floor covering • Manufacturing in pipe • Manufacturing in gramophone records
Polystyrene	Addition	Styrene $CH2 = CH - C_6H_5$	Food container, cosmetics, bottles, toys, packing material, plastic cups, etc.
Polyethene	Addition	Ethylene $CH_2 = CH_2$	• Used as plastic bags
Poly propene	Addition	Propylene $CH2 = CH - CH_3$	• Used in plastic
Polyamide resin	Condensation	Ethane-1, 2-idol $HO - CH_2 - CH_2 - OH$ And benzene-1, 4-dicarboxylix acid 	Clothing and water tank

Polyamide resin (Nylon)	Condensation	Diamines (hexamethylenediamine) $H_2N(CH_2)_6NH_2$ and aliphatic dicarboxylic acid (adipic acid) $HOOC(CH_2)_4COOH$	Textile fibre

PROTEINS:

- The name protein is derived from the Greek word “PROTEINS” meaning of prime importance.
- Proteins are polymer of amino acids.
- Proteins may be defined as the high molecular weight organic materials which upon complete hydrolysis yield amino acids

TYPES OF PROTEINS:

Particular	Simple protein	Conjugated protein	Derived protein
Definitions	Gives only amino acid and its derivatives	Gives only amino acid Prosthetic group	Contains amino acids and substance derived from conjugated protein
Examples	Globulins, albumins collagens	Lipoproteins, Phosphor protein	Peptones, oligopeptides, enzymes, proteoses, polypeptide

POINT TO PONDER: Fibrous proteins have linear molecules, globular proteins have a….

Hair protein can be permanently ………….

STRUCTURE OF PROTEINS:

- The bond in which amino group and carboxylic group reacts and form bond with elimination of water molecule is called peptide bond.
- Protein molecule contains large number of peptide bonds called polypeptide bonds.

THREE DIFFERENT STRUCTURES OF PROTEINS:

(i) Primary structure (sequence of amino acid in peptide chain)

(ii) Secondary structure(regular coilingorzigzagging of polypeptide chain) caused by hydrogen bonding.

(iii) Tertiary structure (three dimensional twisting and folding of polypeptide chain)

DENATURATION OF PROTEINS:

Denaturation of proteins can be done by:

(a) Heat: albumin of egg white changes into solid

(b) Change in pH: each enzyme has its own particular pH for action

(c) Oxidizing or reducing conditions

NUCLEIC ACID:

- In puscellnucleic acid was discovered in 1868 and in 1872, in sperm head by Fredrick Mieschcr.
- It is present in Nucleus animals, plants and virus cells.
- Nucleic acid helpsin transmission of genetic information and mutation.

TYPES OF NUCLEIC ACID:

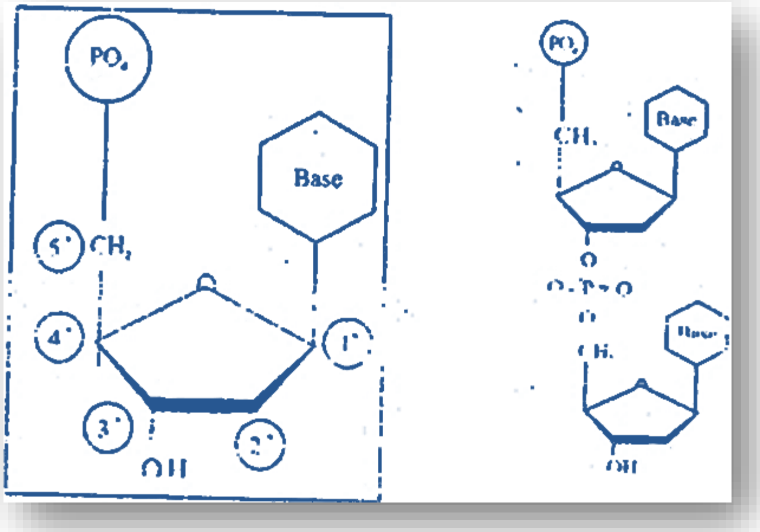
RNA	DNA

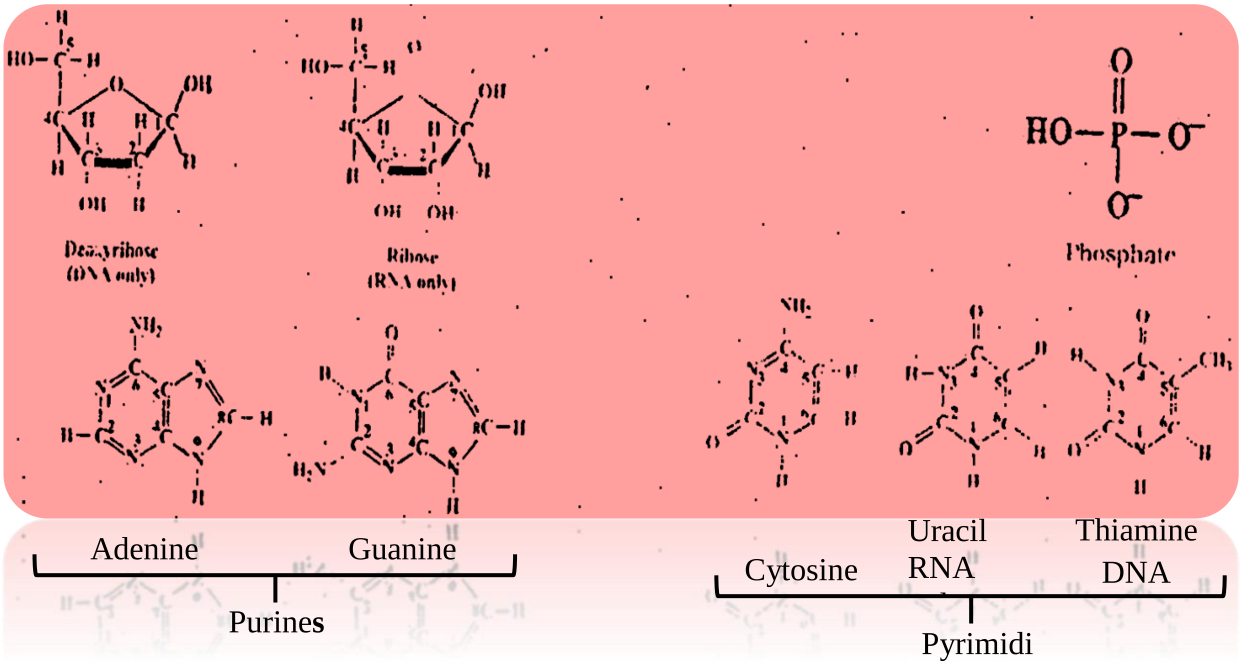
Oxyribose nucleic acid	Dexoyribose nucleic acid
Mostly present in cytoplasm	Present in DNA
Help in protein synthesis	Help in genetic transmission
Molecule contains single strand	Molecule contains double helical structure
Uracil nitrogenous base is present	Thiamine is present
Hydrogen bonding is absent	Hydrogen bonding is present
Ribose sugar is present	Dexoyribose sugar is present
it does not replicate	it replicates

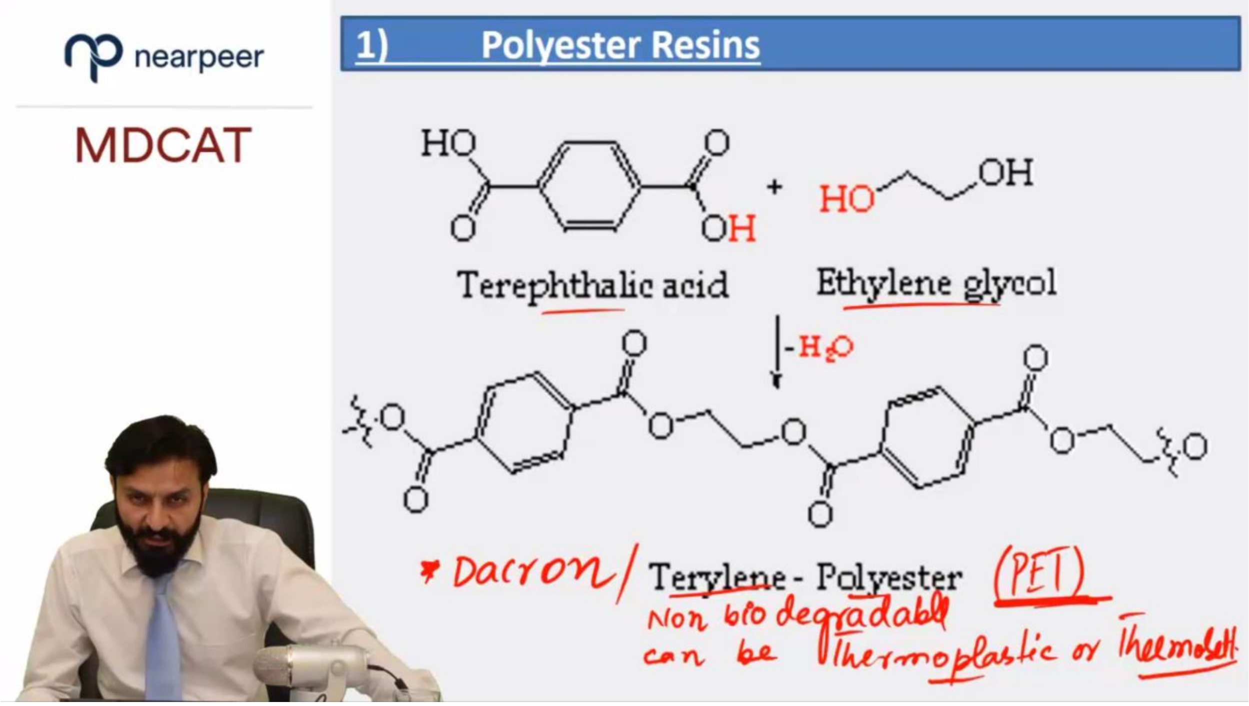
COMPOSITION OF DNA:

Each nucleotide of DNA contains:

- Sugar (pentose sugar)
- Phosphoric acid
- Nitrogen bases
  - » Purine based: adenine guanine
  - » Pyrimidine bases: cytosine, uracil and thiamine


PO4
Base
5'
CH2
4'
1'
3'
2'
OH
PO4
Base
CH2
O
O-P=O
O
CH2
Base
OH


Deoxyribose (DNA only)
Ribose (RNA only)
HO—P—O⁻
Phosphate
Adenine
Guanine
Purines
Cytosine
Uracil
RNA
Thiamine
DNA
Pyrimidi



1) Polyester Resins

* Dacron / Terylene - Polyester (PET)
Non bio degradable
can be Thermoplastic or Thermosett

A better and clear view of this topic is explained in the video lectures at www.nearpeer.org

EXCLUSIVE PRATICE EXERCISE (UHS TOPIC ONLY)

1. **In which of these processes are small organic molecules made into macromolecules**

A) The cracking of petroleum fractions
C) The polymerization of ethene
B) The fractional distillation of crude oil
D) The hydrolysis of proteins

2. **Which of these polymers is an addition polymer**

A) Nylon-6,6
C) Polystyrene

B) Terylene D) Epoxy resin

3. **Watson and crick noticed that the double strand structure provides a mechanism where by genetic information can be duplicated and the process is called**

A) Duplication C) Reproduction

B) Replication D) Evolution

4. **A polymeric substance that is formed in the liquid state and then hardened to a rigid solid is called**

A) Fiber C) Plastic

B) Varnish D) Polyamide resin

5. **Which of the following is an example of conjugated protein?**

A) Collagen C) Oligopeptide

B) Lecithin D) Globulin

6. **Which one of the following is inorganic polymer:**

A) Graphite (C) Rubber

B) DNA (D) Protein

7. **Formation of Terylene and Nylon both are examples of:**

A) Addition reaction (C) Elimination reaction

B) Condensation reaction (D) Hydrogenation reaction

8. **The idea of polymerization was given by:**

(A) Carothers (B) Staudinger

(C) Waston (D) Crick

9. The number of pi-electrons in styrene are:

(A) 3 (B) 6

(C) 8 (D) 10

10. A polymer which is not a condensation polymer:

(A) Polyester (B) Acrylic resin

(C) Nylon-6-6 (D) Polyamide

11. Which of the following is a simple protein?

(A) Proteoses (B) Peptones

(C) Collagen (D) Phosphosprotein

12. Which of the following is an addition homopolymer?

(A) Polythene (B) Teflon

(C) PVC (D) All

13. Which is not a polymer?

(A) Protein (B) Fructose

(C) Nylon-66 (D) Cellulose

14. Nylon-66 is made from hexamethylene diammine and:

(A) Sulphurous acid (B) Adipic acid

(C) Nitric acid (D) Phthalic acid

15. It is a fully fluorinated polymer:

(A) PVC (B) Nylon-66

(C) Teflon (D) Neoprene

16. Chloroethene, $CH_2 = CHCl$, is the monomer of PVC. What are the C – C – Cl bond angles along the polymeric chain in PVC?

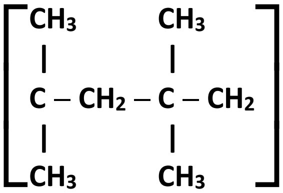
(A) They are all 120° (B) They are all 180°

(C) They are all 109° (D) Half are 109° and half are 120°

17. Which of the following can form hydrogen bonds between adjacent polymer molecules?

(A) Polychloroethene (B) Polythene

(C) Nylon-66 (D) Polyphenylethene

18. Drugs can be administered in patches made from 'pressure-sensitive adehesives' that stick to the skin but are easy to remove. One such pressure-sensitive adhesire has the following structure  $\left[\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}} - CH_2 - \overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}} - CH_2 \right]$ **which monomer could be used to make this polymer?**

(A) $CH_3 - CH = CH - CH_3$ (B) $(H_3C)_2C = CH_2$

(C) $(CH_3)_2C = CHC(CH_3)_3$ (D) $(CH_3)_2CHCH_2C(CH_3)_2CH_2OH$

19. In many countries plastic waste is collected separately and stored. Some of this is incinerated to provide heat for power stations. Why is PVC, polyvinyl chloride, removed from any waste that is to be incinerated?

(A) It can be melted down and re-used (B) Its combustion products are harmful

(C) It does not burn easily (D) It destroys the ozone layer

20. Soft drinks and baby feeding bottles are made of:

(A) Polyester (B) Polystyrene

(C) Urea (D) Polyamide

21. Which one of the following is purine?

(A) Cytosine (B) Uracil

(C) Adenine (D) Thyamine

22. The proteins present in the connective tissue throughout the body are:

(A) Globulins (B) Legumin and collagen

(C) Lactoglobulin (D) Glycogen

23. Monomers phenol + Formaldehyde = Polymer namely

(A) Nylon 6, 6 (B) Bakelite

(C) Terylene (D) Polyethylene

24. Non-stick cookwares generally have a coating of a polymer, whose monomer is:

(A) $H_2C = CH_2$ (B) $CH_2 = CH - CN$

(C) $CH_2 = CHCl$ (D) $F_2C = CF_2$

25. Which is not true for high-density polythene?

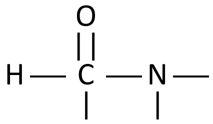
(A) Melting point higher than LDPE

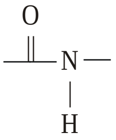
(B) Tensile strength higher than LDPE

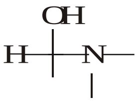
(C) Prepared in the presences of traces of O_2

(D) Linear molecules closely packed in space

26. Which one is the correct representation of peptide bond?

(A) 
$H-\overset{\overset{O}{||}}{\underset{|}{C}}-\underset{|}{N}-$

(B) 
$-\overset{\overset{O}{||}}{}-\underset{\underset{H}{|}}{N}-$

(C) 
$H-\overset{OH}{\underset{|}{}}-\underset{|}{N}-$

(D) None of these

27. Which of the following is not a pyrimidine?

(A) Uracil

(B) Guanine

(C) Cytosine

(D) Thymine

28. A long thread like structure is called:

(A) Fibre

(B) Plastic

(C) Pain

(D) Varnish

29. Terylene is another name of:

(A) Dacron

(B) Polyethene

(C) PVA

(D) Nylon

30. Monomers ethylene glycol + Phthalic acid = Polymer namely

(A) Nylon 6, 6

(B) Bakelite

(C) Terylene

(D) Polyethylene

31. Nylon is obtained by heating

(A) Acrylic acid

(B) Epichlorohydrin

(C) Vinyl chloride (D) Adipic acid with hexamethylene diamine

32. Industrial materials and thermal power stations are coated with

(A) Polyester resins (B) Epoxy paints

(C) Polyamide resins (D) Polyvinyl chloride

33. Polyester resins are the product of the reaction of

(A) Dihydric alcohol and dicarboxylic aromatic acids

(B) Polyamines with aliphatic dicarboxylic acids

(C) Styrene in the presence of catalyst

(D) Epichlorohydrin with diphenylol propane

34. The important monomers of acryclic resins is

(A) Vinyl chloride (B) Styrene

(C) Methylmethacrylate (D) Hexamethylenediamine

35. Regular coiling or zigzagging of polypeptide through hydrogen bonding is its.

(A) Quantum structure (B) Secondary structure

(C) Tertiary structure (D) Primary structure

36. All proteins yield upon complete hydrolysis.

(A) Nitrogen (B) Amino acids

(C) Carbon and hydrogen (D) Sulphur

37. Nucleic acids direct the synthesis of

(A) Glucose (B) Triglycerides

(C) Proteins (D) All

38. The mechanism by which the genetic information can be duplicated is called

(A) Duplication (B) Transcription

(C) Replication (D) Mutation

39. Nucleic acids were first demonstrated in

(A) Pus cells (B) Sperm heads

(C) 1872 (D) all of the above

40. The nitrogenous base different in RNA as compared to DNA is

(A) Cytosine (B) Thymine

(C) Adenine (D) Guanine

ANSWER KEY

1	C	11	A	21	C	31	D
2	C	12	D	22	B	32	B
3	B	13	B	23	B	33	A
4	C	14	B	24	D	34	C
5	C	15	C	25	C	35	B
6	A	16	A	26	B	36	B
7	B	17	C	27	B	37	C
8	A	18	B	28	A	38	C
9	C	19	B	29	A	39	A
10	B	20	D	30	C	40	B

UHS TOPIC 9 – C

ENVIRONMENTAL CHEMISTRY

LEARNING OUTCOMES

In this topic, student should be able to:

a) Describe air pollutants.

b) Understand the chemistry and cause of Acid Rain.

c) Depletion of Ozone layer by chlorofluorocarbons (CFCs).

ENVIRONMENTAL CHEMISTRY:

The branch of chemistry that deals with the abnormalities in the environment and their adverse effects on human beings is called environmental chemistry.

This branch is related to the other sciences like physics, medicine, biology agriculture, public health and sanitary engineering etc.

COMPONENTS OF THE ENVIRONMENT:

(i) Atmosphere

(ii) Hydrosphere

(iii) Lithosphere

(iv) Biosphere (Ecosphere)

IMPORTANCE OF PURE WATER:

Pure water is essential for life. A healthy man uses average 1.5 dm^3 of free drinking water per day. All living organism contain water e.g. an adult 60 and child 70 of the bodyweight. Marine life is impossible without water.

Air Pollution:

The mixing of harmful substances in the atmosphere which damage the environment, human health and quality of life is called air pollution.

Main sources of air pollution:

The main sources of air pollution are as follows:

Primary Pollutants:

(a) The waste products given out from chimneys of industrial units

(b) Exhaust of automobiles which may contain gases like

i) Sulphur dioxide

ii) Sulphur trioxide

iii) Oxides of nitrogen

  iv) Carbon monoxide

  v) Hydrocarbons

  vi) Ammonia

vii) Compounds of fluorine

viii) Radioactive materials

Secondary Pollutants:

The primary pollutants in the atmosphere produce secondary pollutants through various reactions. These are follows:

i) Sulphuric acid

ii) Nitrogen monoxide (N_2O)

iii) Carbonic acid

iv) Hydrofluoric acid

v) Peroxyacetyl nitrate (PAN)

vi) Ozone

vii) Aldehydes

viii) Ketones

ix) Peroxybenzol

All these compounds are toxic and their concentration in the atmosphere must becontrolled.

Some primary pollutants like carbon monoxide, oxides of nitrogen, oxides of sulphur and hydrocarbons along with their sources and adverse effects on living things have been discussed below.

Carbon monoxide:

SOURCES

(a) Natural:

Natural sources of carbon monoxide are:

i) Volcanic eruption

ii) Natural gas emission

iii) Oxidation of methane in the atmosphere

(b) Human Activities:

(i) Fuel burns in various types of transportations i.e. motor vehicles, railways and aircrafts.

These sources release 75 % of total carbon monoxide in the atmosphere.

(ii) Carbon monoxide is emitted from forest fires combustion of fossil fuel and agricultural products

(iii) Carbon monoxide is also emitted from industries in which any type of fuel is burnt in air. These industries' included iron and steel, petroleum, cement, brick kilns, paper and pulp etc.

(iv) Incomplete combustion and dissociation of CO_2 at high temperature also produces CO.

Properties:

i) It is a colourless, cdourless gas

ii) It is soluble in water

iii) It is three times lighter than air iv) It is a highly toxic gas

v) It causes suffocation if inhaled

Poisoning effect of CO:

During breathing we inhale oxygen which hinds with Haemoglobin to form oxyhaernoglobin. Oxyhaemoglobin being unstable complex decomposes to release oxygen which is used in cell activities. When CO is inhaled, it binds with haemoglobin to form carboxyhacmoglobin which is a stable complex. As a result, haemoglobin will not be available to transport oxygen for normal respiration.

Harmful effect of CO:

Exposure to high concentration of CO results in:

i) headache

ii) fatigue

iii) unconsciousness

Exposure to CO for longer period eventually leads to death.

Reversal of CO Poisoning:

The CO poisoning can he reversed by giving' high pressure oxygen.

Nitrogen oxides (NO_x):

Nitrogen gives live oxides: The gases nitric oxide, NO and nitrogen dioxide, NO_2 arc frequently produced in the atmosphere. They are represented by NO_x.

Sources:

(a) Natural:

Bacterial action produces NO_x mainly NO.

(b) Human Activities:

Nitrogen oxides are generally produced by combustion of fossil fuel i.e

i) Coal

ii) Oil

iii) Natural gas

ii) During the burning of oil in internal combustion engine, nitrogen and oxygen of air react to form NO.

$$N_2 + O_2 \xrightarrow{\text{High Temperature}} 2NO$$

Nitrogen dioxide, NO_2 is produced when nitric oxide, NO reacts with oxygen.

$$2NO + O_2 \rightarrow 2NO$$

How do the oxides of nitrogen reach the earth?

The residence time of NO and NO_2 in the atmosphere varies from 3 – 4days. Due to photochemical reactions, NO_x are converted to HNO_3 which is carried down in either rain fall or dust.

Sulphur oxides (SO_x):

Sources:

The oxides of sulphur are sulphur dioxide SO_2 and sulphur trioxide SO_3. They are represented by SOx.

(a) Natural:

Most of SO_2 is produced by

i) Volcanoes (67 %)

ii) Oxidation of sulphur containing gases produced by decomposition of organic matter

(b) Human Activities:

i) Combustion of coal which contains 1 – 9 % sulphur

ii) Burning of crude oil

iii) Burning of fossil fuel in power plants and petroleum industry.

The reactions are as follows:

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Properties of SO_2 and SO_3:

i) These gases have pungent odour

ii) These gases are very irritant and suffocating

Adverse Effects:

i) SO_2 and SO_3 through various reactions in the atmosphere form sulphate aerosols.

These aerosols cause Severe respiratory troubles particularly among older people.

ii) SO_2 is the major source of acid deposition in the atmosphere.

Hydrocarbons Sources:

(a) Natural:

i) Large quantities of hydrocarbons are emitted by different trees and plants in the atmosphere.

ii) Paddy fields produce a significant amount of methane in the atmosphere.

iii) Anaerobic decomposition of organic matter by bacteria in water sediments and in soils.

$$2CH_2O \xrightarrow{\text{Bacteria}} CO_2 + CH_4$$

Residence time of methane:

The mean residence time of methane is about 3-7 years in the atmosphere.

(b) Human Activities:

Hydrocarbons are dispersed in the atmosphere due to:

i) Automobiles, major source of hydrocarbons

ii) Coal

iii) Wood

iv) Incinerator

v) Refuse burning

vi) Solvent evaporators

POINT TO PONDER: A photochemical smog of oxidants and oxidation products are formed. It includes …….

Effect of Air Pollutants/Polluted Air on Environment:

It has two types

(i) Reducing smoke:

- Contain higher concentration of SO_2
- It is mainly produced by combustion of coal

(ii) Oxidizing or photochemical smog:

- Contain higher concentration of oxidants (e.g. O_3 etc.)
- It is produced in the presence of water droplets and chemical reactions of pollutants in the air.

Characteristics:

- It is a yellowish brownish grey haze
- It has unpleasant odour because of its gaseous component
- The yellow colour in photochemical smog is due to the presence of nitrogen dioxide

The following conditions are required for the formation of smog:

(i) There must be sufficient NO, hydrocarbons and volatile organic compounds (VOC) emitted by the vehicular traffic.

(ii) Sunlight, so that some of the chemical reactions may occur at a rapid rate

(iii) The movement of air mass must be little so that reactions are not disturbed

The overall result of photochemical smog in afternoon is the built up of oxidizing agents. Such as H_2O_2, HNO_3, peroxyacetyl nitrate (PAN) and ozone in the air. PAN is an eye irritant and is also toxic to plants.

ACID RAIN

:

Discovered by Angus Smith 1650, a serious environment problem in 1950's, initially referred as precipitation, which IS more acidic than natural rain.

- The pH of unpolluted rain water should be 5.6 the rain water having pH less than 5 is considered truly acidic:

$H_2O_{(l)} + CO_{2(g)} \rightarrow H_2CO_{3(aq)}$

$SO_2 + 1/2O_2 + H_2O \rightarrow H_2SO_4$

$2NO_2 + H_2O + ½O_2 \rightarrow 2HNO_3$

- The acid deposition includes both wet (rain. snow. fog) and dry acidic deposition.
- In some countries due to release of HCl by volcanic eruption there is temporary acid rain.

Harmful effects:

Rock Al These heavy metal are accumulated in the

Hg fishes

ACIDIFICATION

Soil Pb The increased concentration of Al clogs

Buildings Ca The gills of fishes and cause suffocation

Acidification of Soil Leaves

Can l each nutrients Plants

Damaging Growth of forest

Damaging Building Materials:

Such as

→ Steel

→ Paint

→ Plastic

→ Cement

→ Masonry work

→ Sculptural work especially marble and lime stone

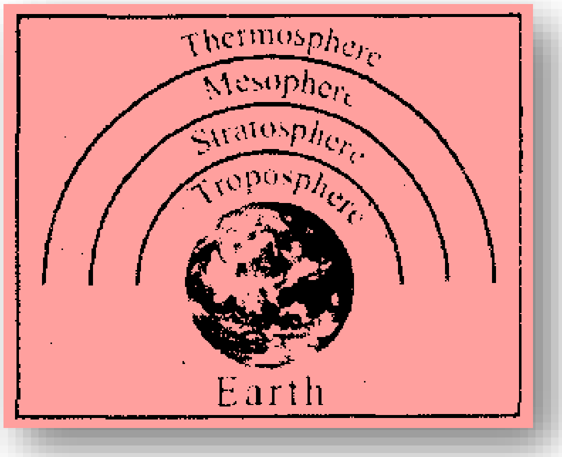
OZONE:

Atmosphere:

- Ozone is low boiling point gas and an allotrope of oxygen

Presence:

- The main ozone layer exists in the stratosphere which is approximately between 15 to 40 kilometers from the earth.
- It is just above the troposphere which exists up to 15 kilometer from the earth.



Amount of Ozone in atmosphere:

- It is present in small concentrations throughout the atmosphere.
- The amount of ozone in the atmosphere is expressed in Dobson units (DU)
- The normal amount of ozone in stratosphere is about 350 DU.

Production:

In tropical region usually in mesosphere:

O2 $\xrightarrow{Dissociates} O^{\bullet} + O^{\bullet}$

$O + O_2 \rightarrow O_3$

That diffuse down in stratosphere from mesosphere.

Function:

Filter the harmful radiation of sunlight like UV.

Depletion of Ozone:

- In 1980's a large hole in the ozone layer over Antarctic was discovered.
- Since mid-1970's the thickness of the ozone layer has been decreasing over Antarctic during the spring time.

- By the mid-1980’s loss in ozone at some places over Antarctica reaches to about 50 % of the total overhead amount.

- The region in which ozone depletes substantially in every year during Sep-Nov is now termed as "ozone hole".

Role of CFCs in Destroying Ozone:

CFCs used as refrigerants in air conditioners or in aerosol sprays. CFC’s diffuse from troposphere to stratosphere and form free radical due to UV radiations.

$CFCl_3 \xrightarrow{UV} CFCl_2^{\bullet} + Cl^{\bullet}$

$Cl^{\bullet} + O_2 \rightarrow ClO^{\bullet} + O_2$

$ClO^{\bullet} + O \rightarrow Cl^{\bullet} + O_2$

→ A single chloride free radical can destroy up to 100.000 ozone molecules.

Effect of O_3 as Pollutant:

- Health problems
- Damages eyes
- Decreases the elasticity of lung tissues
- Aggravates Asthma. Coughing and Chest Discomfort
- Paints and other materials

POINT TO PONDER: The structure of ozone

There is a layer of ozone in the stratosphere (upper atmosphere), the first step in the formation of ozone in the stratosphere is the ….

Paints and Other Material:

- Attacks rubber
- Reduces

→ Durability

→ Appearance of paint

- Causes

→ Fabric dyes to fade

PRACTICE EXERCISE (FOR UHS ONLY)

1. **The pH range of acid rain is**

A) 6.5 - 6

C) 8-7.5

B) less than 5

D) 7-6.5

2. **Why is CO called as pollutant? Reason is**

A) If combines with oxygen

C) It inactivates glycolysis

B) it combines with hemoglobin

D) inactivates nerves

3. **Choose the chief air pollutant among the following which depletes ozone player**

A) CO

C) CFCs

B) CO_2

D) SO_2

4. **CFCs destroy ozone layer. How many ozone molecule a chlorine free radical can destroy?**

A) 50000

C) 20000

B) 100000

D) 10000

5. **The thickness of ozone layer is**

A) 25-50km

C) 3km only

B) 25-28km

D) 1km only

6. **Which adversely affects the human health is**

A) Ecosystem

C) Ecosphere

B) atmosphere D) pollutant

7. Primary pollutant is that

A) waste product of an industry C) which causes cancer

B) Whose concentration cannot be controlled D) which corrode the metal only

8. Which of the following is considered as cause of pollution:

(A) Rapid increase in population (C) Industrialization

(B) Transportation (D) All of the above

9. In which of the following layer of atmosphere, there is more thickness of ozone:

(A) Troposphere (C) Stratosphere

(B) Mesosphere (D) Thermosphere

10. Which of the following air pollutants is quiet killer:

(A) CO_2 (C) CO

(B) NO_2 (D) N_2O_4

11. Ecosystem is a smaller unit of:

(A) Lithosphere (C) Hydrosphere

(B) Biosphere (D) Atmospheric

12. The major component of environment where life can exist is called:

(A) Atmosphere (B) Hydrosphere

(C) Lithosphere (D) Biosphere

13. The third major component of atmosphere is:

(A) N_2 (B) O_2

(C) Ar (D) CO_2

14. The type of contaminants present in leachate is:

(A)Dissolved (B)Suspended

(C)Microbial (D)All

15. Which of the following is a primary pollutant?

(A) H_2SO_4 (B) CO

(C) H_2CO_3 (D) PAN

16. Identify the wrong statement:

(A) Chlorofluorocarbons are responsible for ozone layer depletion

(B) Greenhouse effect is responsible for global warming

(C) Ozone layer filter out the infrared radiations

(D) Acid rain causes NO_x and SO_z

17. Ozone is mostly concentrated in:

(A) Troposphere (B) Stratosphere

(C) Mesosphere (D) Thermosphere

18. Which component of atmosphere is far away from earth surface?

(a)Thermosphere (B) Mesosphere

(c)Troposphere (D) Stratosphere

19. The one which react with hemoglobin of blood and produce toxic effect:

(a)Carbon monoxide (B) Carbon dioxide

(c)Oxygen (D) Sulphur trioxide

20. Peroxyacetyl nitrate is an irritant to human beings and it affects human:

(A) Eyes (B) Nose

(C) Ears (D) Stomach

21. The agriculture field that produces maximum methane gas into the atmosphere:

(A) Wheat field (B) Paddy rice field

(C) Cotton field (D) Groundnut field

22. Carbon dioxide contents in atmosphere is:

(A) 0.0034% (B) 0.034%

(C) 0.34% (D) 3.4%

23. Which of the following is main component of temporary acid rain?

(A) Sulphuric acid (B) Nitric acid

(C) Carbonic acid (D) Hydrochloric acid

24. Select the one which is non-physical and non-chemical pollutant:

(A) Radiations (B) Noise

(C) Insecticides (D) Ozone

25. Green chemistry refers to:

(A) Chemistry of plants

(B) Chemistry of green pigments

(C) Chemistry of development of chemical products and processes less harmful to humans

(D) Chemistry of greenhouse effect

26. Total thickness of atmosphere is:

(A) 5.6 km (B) 100 km

(C) 1000 km (D) 1500 km

27. Eutrophication is a process which involves:

(A) Depletion of ozone layer

(B) Increase in concentration of ozone in water

(C) Decrease in concentration of D.O in water by algae

(D) Decrease in the level of SO_2 in air

28. The source of energy that does not cause pollution:

(A) Gasoline
(B) Nuclear power plant
(C) Fossil fuels
(D) Sun

29. Which is not correct about greenhouse effect?

(A) It results in global warming
(B) CO_2 is one of the main chemical specie responsible for it
(C) It results in lowering of levels of oceans over the years
(D) CH_4, O_3, CFCs also contribute to greenhouse effect

30. Increasing skin cancer and high mutation rate are due to:

(A) Acid rain
(B) Ozone depletion
(C) CO pollution
(D) CO_2 pollution

31. Flue gases are generally made free from NO_x by:

(A) Mixing them with oxygen
(B) Scrubbing them with H_2SO_4
(C) Passing them through heated platinum plates
(D) Passing them through water

32. Which one is not a secondary pollutant?

(A) Ozone
(B) Aldehyde
(C) Peroxybenzol
(D) Radioactive materials

33. Major cause of SO_2 on global scale is:

(A) Volcanoes
(B) Combustion of coal
(C) Fossil fuels in power plants
(D) Chemical industries

34. SO_2 and SO_3 through various reactions in the atmosphere form:

(A) Sulphur
(B) CFCs

(C) Ozone

(D) Sulphate aerosols

35. Which statement is not correct?

(A) The amount of ozone is greater in the equator regions

(B) Ozone acts as filter for UV radiations

(C) Ozone acts as pollutant in polar regions

(D) CFCs play effective role in removing O_3 in the stratosphere

36. Ozone is

(A) a gas having high boiling point

(B) a liquid having low boiling point

(C) a solid having high boiling point

(D) a gas having low boiling point

37. The normal amount of overhead ozone is about

(A) 250DU

(B) 350DU

(C) 200DU

(D) 150DU

38. The range of atmosphere from 25-28km above the head level is called as

(A) Atmosphere

(B) Stratosphere

(C) Toposphere

(D) None of these

39. The residence time of NO gas in atmosphere is

(A) 3 days

(B) 4 days

(C) 3-4 days

(D) 3-7 years

40. The residence time of CH_4 gas in atmosphere is

(A) 3 days

(B) 4 days

(C) 3-4 days

(D) 3-7 years

ANSWER KEY

1	**B**	**11**	**B**	**21**	**B**	**31**	**A**
2	**B**	**12**	**D**	**22**	**B**	**32**	**D**
3	**C**	**13**	**C**	**23**	**D**	**33**	**A**
4	**B**	**14**	**D**	**24**	**B**	**34**	**D**
5	**B**	**15**	**B**	**25**	**C**	**35**	**C**
6	**D**	**16**	**C**	**26**	**C**	**36**	**D**
7	**A**	**17**	**B**	**27**	**C**	**37**	**B**
8	**D**	**18**	**A**	**28**	**D**	**38**	**B**
9	**C**	**19**	**A**	**29**	**D**	**39**	**B**
10	**C**	**20**	**A**	**30**	**B**	**40**	**D**

SAMPLE PAPER (MCAT)

SAMPLE (MCAT)

Note: Chemistry paper of MCAT contains 58 questions.

1. The compound which does not have empirical formula (CH_2O):

a) acetic acid
b) methanol
c) lactic acid
d) methanol

2. If 56 g Fe and 24 g O_2 reacts completely to produce Fe_2O_3, which of them is limiting reactant:

a) Fe
b) O_2
c) both of these
d) none of these

3. The number of moles of solute arc present in 500 cm^3 0.2 M solution of NaOH is:

a) 0.1 moles
b) 1 moles
c) 0.5 moles
d) 0.2 moles

4. A solution of glucose is 10 % the volume in which 1 g mole of it will be dissolved is:

a) 1 dm^3
b) 1.8 dm^3
c) 200 dm^3
d) 180 dm^3

5. Which of following has highest vapour pressure at 20° C?

a) isopentane
b) chloroform
c) mercury
d) glycerol

6. The solids which conduct electricity only in fused state are:

a) ionic solids
b) covalent solids
c) molecular solids
d) metallic solids

7. The shape of P_y atomic orbital is:

a) spherical
b) dumb-bell
c) dumb-bell with collar
d) sausage shaped

8. The sub-shell with lowest energy is:

a) 7s b) 6p

c) 5d d) 4f

9. The molecule in which carbon-carbon bond length is minimum:

a) ethane b) ethane

c) ethyne d) benzene

10. The hybridization which imparts non-coplanar geometry in a molecule:

a) sp b) sp^2

c) sp^3 d) dsp^2

11. The enthalpy change in Bomb calorimeter is measured at constant:

a) temperature b) pressure

c) volume d) all of these

12. Enthalpy of neutralization of all strong acids and strong bases has the same value because:

a) neutralization leads to the formation of salt and Water

b) strong acids and strong bases are ionic substances

c) acid always give rise to h" ions and base always furnish oil ions .

d) the net chemical change involve the combination of h+ and oh- ions to form water

13. The electrolysis of one of the following solution gives different products:

a) $CaSO_4$ b) $PbSO_4$

c) $CuSO_4$ d) $MgSO_4$

14. Stronger the oxidizing agent, then at standard condition higher is:

a) redox potential b) reduction potential

c) standard reduction potential d) oxidation potential

15. Which of the following mathematical relationship is incorrect?

a) $[H^-]\ [OH^-] = k_w$

b) $pK_a - pK_b = pK_w$

c) pH + pOH = 14

d) $K_a + K_b = K_w$

16. In case when $[OH^-] > [H^+]$ the solution is:

a) acidic

b) basic

c) neutral

d) unpredictable

17. In which one of the following the half-life is directly proportional to initial concentration:

a) zero order reaction

b) 2nd order reaction

c) 1st order reaction

d) 3rd order reaction

18. The rate of reaction involving ions can be studied by _________ method.

a) dilatometric

b) refractometric

c) electrical conductivity

d) optical rotation

19. The element with highest ionization energy:

a) boron

b) carbon

c) nitrogen

d) oxygen

20. The property which decreases across the periods:

a) ionization energy

b) acidic character

c) atomic size

d) electronegativity

21. The alkaline earth metal which is non-reactive with cold water is:

a) Be

b) Ba

c) Mg

d) both "A" and "B"

22. The gas used to predict earthquake:

a) helium

b) neon

c) krypton d) radon

23. What is the colour of $[Ti(H_2O)_6]^{3+}$?

a) yellow b) green

c) violet d) orange

24. In which of the following complex the metal exhibit highest oxidation state:

a) $[Cu(NH_3)_6]SO_4$ b) $[Ni(CO)_4]$

c) $K_3[Fe(CN)_6]$ d) $[Pt(NH_3)_2Cl_2]SO_4$

25. Urea is produced by the reaction of liquid ammonia with:

a) CO b) CO_2

c) CaO d) C

26. ___________ is used as catalyst-in Haber's process for NH_3 gas manufacture:

a) iron b) carbon

c) copper d) silver

27. The fertilizer which cannot be used in paddy rice field:

a) NH_4NO_3 b) $(NH_4)_2HPO_4$

c) $(NH_2)_2CO$ d) NH_3

28. The raw material which can be used for synthesis of HNO_3:

a) ammonia b) air

c) Chile salt peter d) all of these

29. All among the following are electrophiles except:

a) CO_2 b) SO_2

c) BF_3 d) SO_3

30. The compound $C_4H_{10}O$ can show:

a) functional group isomerism b) metamerism

c) positional isomerism d) all of them

31. Geometric isomerism is shown by:

a) alkanes b) alkenes

c) carbonyl compounds d) arenes

32. Hydration of alkenes can be done in the presence of:

a) cold $KMnO_4$ b) Ag_2O

c) H_2SO_4 d) Raney nickel

33. The more reactive compound towards nitration:

a) aniline b) chlorobenzene

c) phenol d) benzene

34. Every carbon atom in polyethylene is _________ hybridized.

a) sp b) sp^3

c) sp^2 d) dsp^2

35. The reagent which can be used to distinguish between ethane and ethane:

a) bromine water b) Bayer's reagent

c) Tollen's reagent d) both a and b

36. The molecular formula of halothane is:

a) $Cl_3CHBrCl$ b) CHF_2CBrCl_2

c) $CF_3CHBrCl$ d) CF_3CHBrI

37. Which one of the following cannot give β-elimination reaction?

a) CH_3CH_2Br b) $(CH_3)_3CBr$

c) $(CH_3)_2CHBr$ d) $(CH_3)_3CCH_2Br$

38. The CH_3CH_2Br with Aq. KOH gives __________ reaction:

a) nucleophilic substitution bimolecular

b) β-elimination bimolecular

c) nucleophilic substitution uni-molecular

d) β-elimination uni-molecular

39. The alkyl halide which is most reactive:

a) CH_3Cl

b) C_2H_5Cl

c) C_3H_7Cl

d) C_4H_9Cl

40. Rectified spirit contains __________ of ethanol.

a) 80 %

b) 85 %

c) 90 %

d) 95 %

41. The alcohol which is a dihydric but not a glycol:

a) ethane-l, 2-diol

b) propane-1, 2-diol

c) butane-2, 3-diol

d) butane-1, 3-diol

42. Phenol can be prepared by:

a) C_6H_5Cl

b) $C_6H_5SO_3Na$

c) C_6H_6

d) both A and B

43. Neopentylalcohol is _________ alcohol:

a) primary

b) tertiary

c) secondary

d) quaternary

44. Aldehydes and ketones react with 2,4-DNPH to give _________ precipitate.

a) yellow or blue

b) yellow or-green

c) yellow or red

d) yellow or violet

45. The statement which is correct:

a) formaldehyde is used in silvering of mirrors

b) propanal and propanone behave similarly in Tollen' s reagent

c) acetone on reduction gives primary alcohols

d) ketones give brick red colour with Fehling's solution

46. The oxidation of _________ always gives carboxylic acids:

a) aldehydes b) benzene

c) phenols d) esters

47. The pair of compounds which can be distinguished by iodoform test:

a) ethanol and ethanol b) propanone arid ethanol

c) methanol and 3-pentanone d) propanone and propanal

48. The stronger acid is:

a) acetic acid b) dichloroacetic acid

c) chloroacetic acid d) trichloroacetic acid

49. The esterification reactions of carboxylic acid is:

a) electrophilic substitution reaction b) nucleophilic addition reaction

c) nucleophilic substitution reaction d) eliminaiton reaction

50. Hydrolysis of cyano group by an aqueous acid results into formation of:

a) acid amide b) carboxylic acid

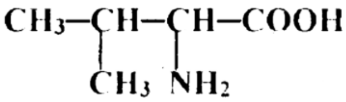
c) cyanohydrin d) formaldehyde

51. Which one of the following reagent is usually used for the manufacture of acetic acid?

a) ethane b) ethane nitrile

c) ethyne d) ethanol

52. A formula .of an amino acid is shown below:



$CH_3-\underset{|}{\underset{CH_3}{CH}}-\underset{|}{\underset{NH_2}{CH}}-COOH$

The name of this amino add is:

a) valine b) glycine

c) lysine d) proline

53. Which one is a sulphur containing amino acid?

a) proline b) histidine

c) cysteine d) serine

54. Polymer which can form hydrogen bonds between adjacent macromolecule:

a) polyethene b) nylon

c) terylene d) polyphenylethene

55. Major function of DNA is:

a) to control metabolism

b) to transfer genetic information from one generation to another

c) to control synthesis of protein

d) to catalyze biochemical reactions

56. Which of the following is a natural polymer?

a) polyethene b) nylon

c) polysaccharide d) terylene

57. Which among the following is eye irritant?

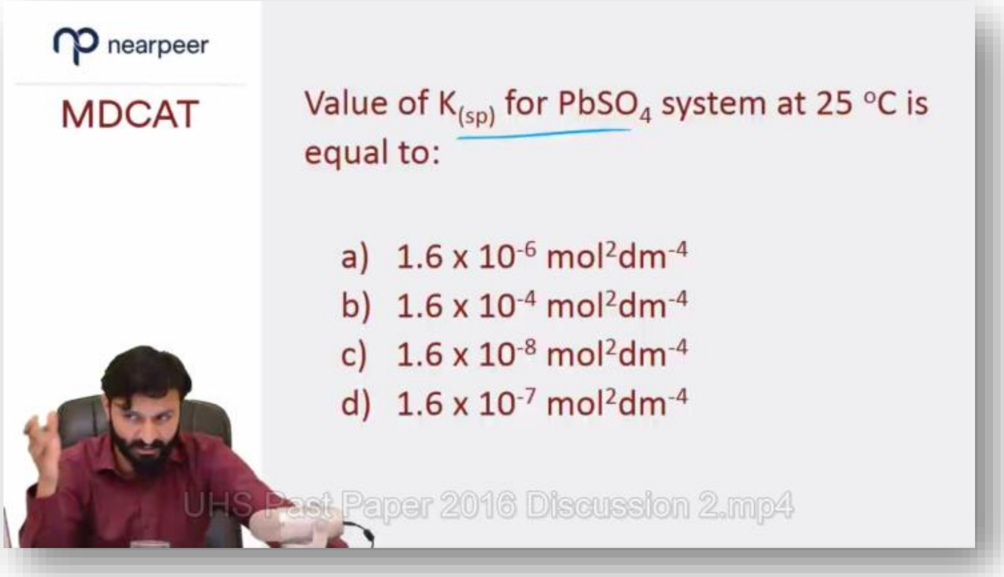
a) PAN b) O_3

c) CO_2　　　　d) both "A" and "B"

58.　Ozone layer is mostly affected by:

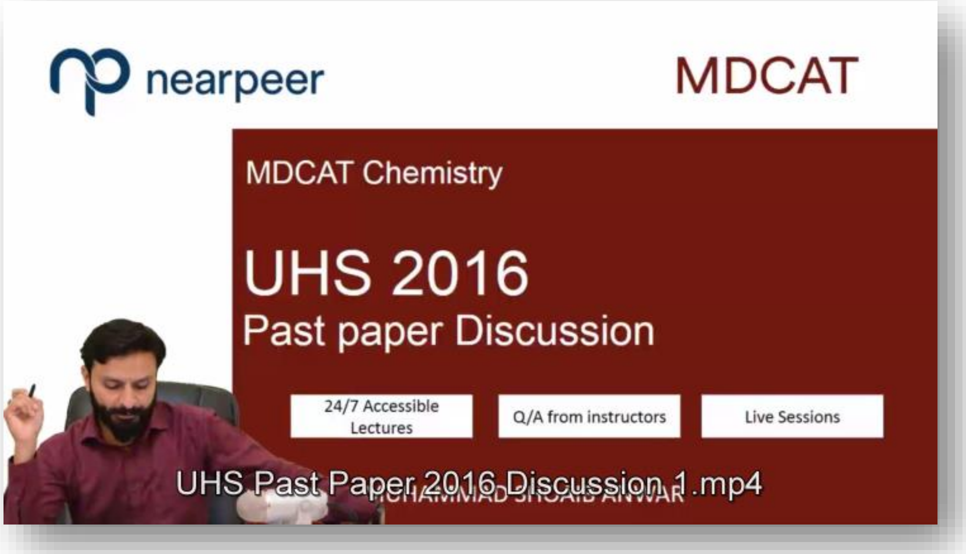
a) PAN　　　　b) CFC’s

c) NO_x　　　　d) hydrocarbon



Value of $K_{(sp)}$ for $PbSO_4$ system at 25 °C is equal to:

a) 1.6×10^{-6} mol^2dm^{-4}
b) 1.6×10^{-4} mol^2dm^{-4}
c) 1.6×10^{-8} mol^2dm^{-4}
d) 1.6×10^{-7} mol^2dm^{-4}

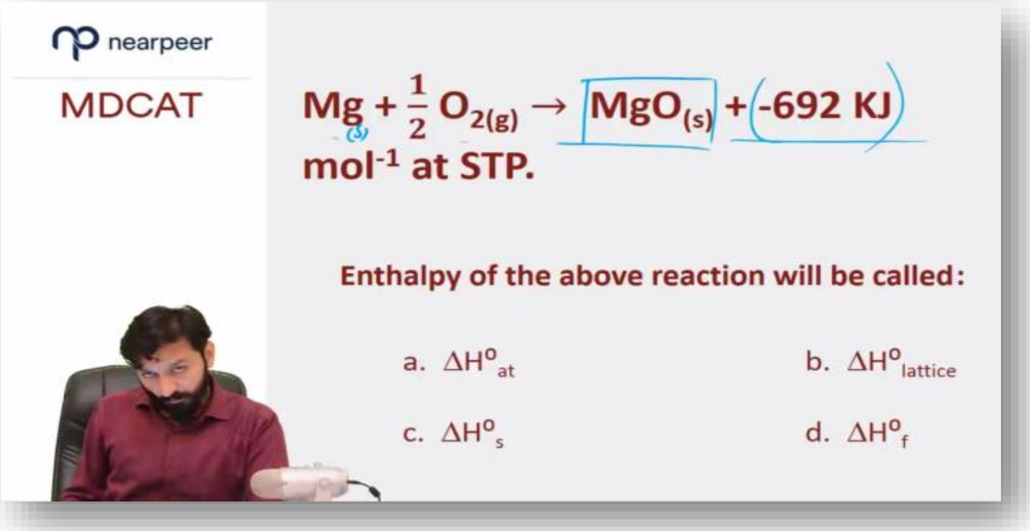


MDCAT Chemistry

UHS 2016

Past paper Discussion

UHS Past Paper 2016 Discussion 1.mp4



$\underset{(s)}{Mg} + \frac{1}{2} O_{2(g)} \rightarrow \boxed{MgO_{(s)}} + (-692\ KJ)$ mol^{-1} at STP.

Enthalpy of the above reaction will be called:

a. ΔH^{o}_{at}

b. $\Delta H^{o}_{lattice}$

c. ΔH^{o}_{s}

d. ΔH^{o}_{f}