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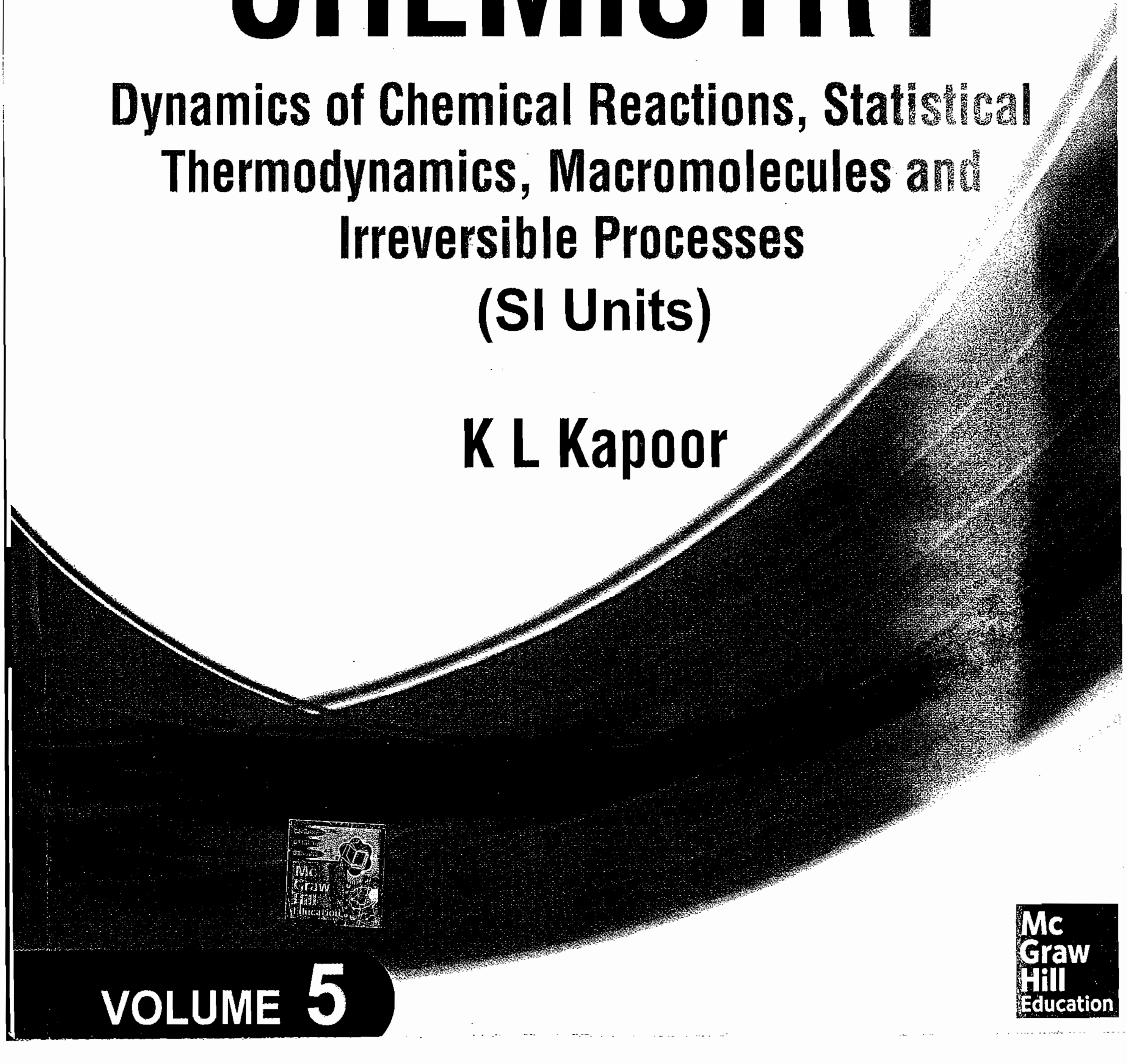
A Textbook of
PHYSICAL CHEMISTRY

Dynamics of Chemical Reactions, Statistical Thermodynamics, Macromolecules and Irreversible Processes

(SI Units)

K L Kapoor



VOLUME 5

Mc
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Education

A Textbook of Physical Chemistry

Volume V
(SI Units)

Dynamics of Chemical Reactions, Statistical Thermodynamics, Macromolecules and Irreversible Processes

Third Edition

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McGraw Hill Education (India) Private Limited
NEW DELHI

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McGraw Hill Education (India) Private Limited

Published by McGraw Hill Education (India) Private Limited,
P-24, Green Park Extension, New Delhi 110 016.

A Textbook of Physical Chemistry, Vol V

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This edition can be exported from India only by the publishers,
McGraw Hill Education (India) Private Limited.

Print Edition
ISBN (13): 978-93-39204-31-0
ISBN (10): 93-39204-31-X

E-book Edition
ISBN (13): 978-93-392-0432-7
ISBN (10): 93-392-0432-8

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Typeset at Script Makers, 19, A1-B, DDA Market, Paschim Vihar, New Delhi 110 063, and text printed at
Rajkamal Electric Press, Plot No. 2, Phase-IV, Kundli, Haryana.

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To the Memory of My Parnets

Preface

In recent years, the teaching curriculum of Physical Chemistry in many Indian universities has been restructured with a greater emphasis on a theoretical and conceptual methodology and the applications of the underlying basic concepts and principles. This shift in the emphasis, as I have observed, has unduly frightened undergraduates whose performance in Physical Chemistry has been otherwise generally far from satisfactory. This poor performance is partly because of the non-availability of a comprehensive textbook which also lays adequate stress on the logical deduction and solution of numericals and related problems. Naturally, the students find themselves unduly constrained when they are forced to refer to various books to collect the necessary reading material.

It is primarily to help these students that I have ventured to present a textbook which provides a systematic and comprehensive coverage of the theory as well as of the illustration of the applications thereof.

The present volumes grew out of more than a decade of classroom teaching through lecture notes and assignments prepared for my students of BSc (General) and BSc (Honours). The schematic structure of the book is assigned to cover the major topics of Physical Chemistry in six different volumes. **Volume I** discusses the states of matter and ions in solutions. It comprises five chapters on the gaseous state, physical properties of liquids, solid state, ionic equilibria and conductance. **Volume II** describes the basic principles of thermodynamics and chemical equilibrium in seven chapters, viz., introduction and mathematical background, zeroth and first laws of thermodynamics, thermochemistry, second law of thermodynamics, criteria for equilibrium and A and G functions, systems of variable composition, and thermodynamics of chemical reactions. **Volume III** seeks to present the applications of thermodynamics to the equilibria between phases, colligative properties, phase rule, solutions, phase diagrams of one-, two- and three-component systems, and electrochemical cells. **Volume IV** deals with quantum chemistry, molecular spectroscopy and applications of molecular symmetry. It focuses on atomic structure, chemical bonding, electrical and magnetic properties, molecular spectroscopy and applications of molecular symmetry. **Volume V** covers dynamics of chemical reactions, statistical and irreversible thermodynamics, and macromolecules in six chapters, viz., adsorption, chemical kinetics, photochemistry, statistical thermodynamics, macromolecules and introduction to irreversible processes. **Volume VI** describes computational aspects in physical chemistry in three chapters, viz., synopsis of commonly used statements in BASIC language, list of programs, and projects.

The study of Physical Chemistry is incomplete if students confine themselves to the ambit of theoretical discussions of the subject. They must grasp the practical significance of the basic theory in all its ramifications and develop a clear perspective to appreciate various problems and how they can be solved.

It is here that these volumes merit mention. Apart from having a lucid style and simplicity of expression, each has a wealth of carefully selected examples and solved illustrations. Further, three types of problems with different objectives in view are listed at the end of each chapter: (1) Revisionary Problems, (2) Try Yourself Problems, and (3) Numerical Problems. Under *Revisionary Problems*, only those problems pertaining to the text are included which should afford an opportunity to the students in self-evaluation. In *Try Yourself Problems*, the problems related to the text but not highlighted therein are provided. Such problems will help students extend their knowledge of the chapter to closely related problems. Finally, unsolved *Numerical Problems* are pieced together for students to practice.

Though the volumes are written on the basis of the syllabi prescribed for undergraduate courses of the University of Delhi, they will also prove useful to students of other universities, since the content of physical chemistry remains the same everywhere. In general, the SI units (*Systeme International d'unite's*), along with some of the common non-SI units such as atm, mmHg, etc., have been used in the books.

Salient Features

- Comprehensive coverage to adsorption, chemical kinetics, photochemistry, statistical thermodynamics, macromolecules
- Emphasis given to applications and principles
- Explanation of equations in the form of solved problems and numericals
- IUPAC recommendations and SI units have been adopted throughout.
- Rich and illustrious pedagogy

Acknowledgements

I wish to acknowledge my greatest indebtedness to my teacher, late Prof. R P Mitra, who instilled in me the spirit of scientific inquiry. I also record my sense of appreciation to my students and colleagues at Hindu College, University of Delhi, for their comments, constructive criticism and valuable suggestions towards improvement of the book. I am grateful to late Dr Mohan Katyal (St. Stephen's College), and late Prof. V R Shastri (Ujjain University) for the numerous suggestions in improving the book. I would like to thank Sh. M M Jain, Hans Raj College, for his encouragement during the course of publication of the book.

I wish to extend my appreciation to the students and teachers of Delhi University for the constructive suggestions in bringing out this edition of the book. I also wish to thank my children, Saurabh-Urvashi and Surabhi-Jugnu, for many useful suggestions in improving the presentation of the book.

Finally, my special thanks go to my wife, Pratima, for her encouragement, patience and understanding.

Feedback Request

The author takes the entire responsibility for any error or ambiguity, in fact or opinion, that may have found its way into this book. Comments and criticism from readers will, therefore, be highly appreciated and incorporated in subsequent editions.

K L Kapoor

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Contents

1 Adsorption

1.1 INTRODUCTION

The term adsorption implies the presence of excess concentration of any particular component at the surface of liquid or solid phase as compared to that present in the bulk of the material. This phenomenon of adsorption is basically due to the presence of residual forces at the surface of the body. These residual forces, in case of liquids, arise from the nonuniform distribution of molecules around the molecules at the surface. In solids, these residual forces are due to the presence of unsatisfied valence forces of atoms at the surface. The latter are created when some of the inter-atomic bonds are broken as a result of cleavage of a bigger crystal into the smaller units as shown by the dotted line in Fig. 1.1.1.

It is because of these residual forces that the substances stick to the surface and thus create an excessive concentration at the surface. The phenomenon of adsorption is a spontaneous process and hence, like any other spontaneous process, is attained by a decrease in free energy of the system, i.e. ΔG of the adsorption process has a negative value. Since $\Delta G = \Delta H - T\Delta S$ and that the entropy change ΔS for adsorption is necessarily a negative quantity (since the molecules at the surface are in more ordered state than in the solution), it may be concluded that the enthalpy change of the adsorption process must have a negative value and must satisfy the relation

$$|\Delta H| > |T\Delta S|$$

Hence, the process of adsorption is an exothermic process. This also follows directly from the fact that the adsorption process involves the forces of attraction between the adsorbate (the substance which is being adsorbed) and the adsorbent (the substance which adsorbed the absorbate) and hence on adsorption, there must be a release of energy.

The term adsorption must clearly be distinguished from the term absorption. The latter implies the presence of more or less uniform concentration throughout the substance.

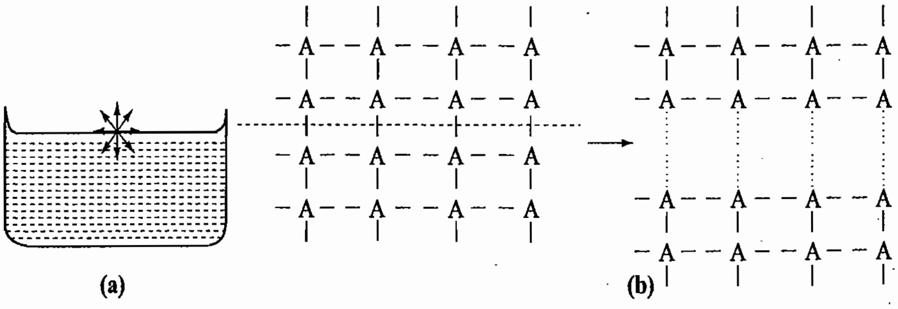


Fig. 1.1.1 Residual forces at (a) the liquid surface, and (b) the solid surface

1.2 ADSORPTION OF GASES BY SOLIDS

Preliminary Discussions

Adsorption of gases by solids is very common. The amount of a gas adsorbed, besides depending upon the nature of the gas and the surface involved, is highly dependent upon the surface area for a given mass of the adsorbent. The total surface area available in a given mass of the adsorbent depends upon its size. Take, for example, a cube of edge-length equal to 1 cm. It has a surface area of 6 cm^2. If this cube is divided into very small cublets of edge-length say of 10^{-3} cm, then the total surface area becomes equal to 6×10^3 cm^2. More and more of residual forces are created when a substance of bigger size is divided into the smaller units and hence causes more of adsorption. It is because of this reason, most of the adsorbents are available in the finely divided form. One of the extensively used adsorbents is the activated charcoal. The process of activation involves the heating of charcoal to a high temperature (ranging between 300 °C to 1000 °C) in vacuum or in the presence of an inert gas. This process removes the already adsorbed gases such as hydrocarbons and other impurities.

Effect of Temperature

As stated above, the process of adsorption is an exothermic process and thus, according to the Le-Chatelier's principle, a decrease in temperature of the system would result in an increase in adsorption. In fact, it is found to be so, as shown by the broken vertical line in Fig. 1.2.1. Qualitatively, the above effect of temperature can be understood on the basis of two parameters, namely, the thermal energy of gaseous molecules and the residual forces of the surface. These two parameters act in the opposite directions. If the temperature of the system is large, then because of the larger thermal energy, lesser number of molecules are held to the surface of the solid by the residual forces and hence lesser is the adsorption. At lower temperatures, the thermal energy is less and thus more number of molecules remain stick to the surface and hence larger is the adsorption.

Effect of Pressure

At a constant temperature, the extent of adsorption of gases increases with increase in pressure. This fact is in agreement with the Le-Chatelier principle. According to the latter, the system would move in a direction of lesser number of molecules with increase in external pressure. Since the process of adsorption decreases the

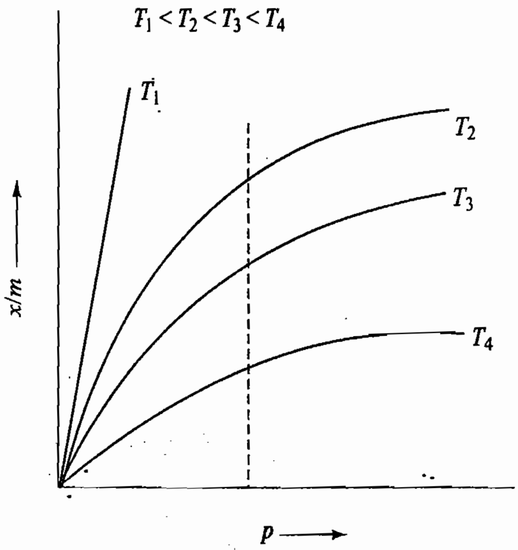


Fig. 1.2.1 Variation in the extent of adsorption with pressure at different temperatures. These are known as adsorption isotherms

number of molecules in the gaseous phase, it is expected that the extent of adsorption would increase with the increase in external pressure as it would result in the decrease of number of molecules in the gaseous phase.

Figure 1.2.1 displays qualitatively the variation in the extent of adsorption with pressure at different temperatures. The adsorption isotherm shown in Fig. 1.2.1 can be easily understood on the basis of a fixed number of adsorption sites at the surface of adsorbent where only gaseous molecules can be adsorbed. Initially as pressure is increased, the number of molecules which strike the unit area of the surface increases in proportion to the increase in pressure and hence adsorption increases almost linearly with pressure. Since a fixed number of adsorption sites are available, eventually at some high pressure a stage would be reached where all the sites are occupied and hence further increase in pressure would not cause any further increase in adsorption, i.e. the extent of adsorption becomes independent of pressure. In the intermediate range of pressure, the increase in adsorption is not as fast as the increase in pressure.

Explanation of Fig. 1.2.1

The facts shown in Fig. 1.2.1 can be explained on the basis of reversible nature of adsorption where adsorption and desorption processes proceed simultaneously. At equilibrium, both these processes proceed with equal speeds. This equilibrium process may be represented as follows:

$$\mathrm{G + S} \underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftharpoons}} \mathrm{GS} \qquad (1.2.1)$$

where G, S and GS represent, respectively, the unadsorbed gaseous molecule, adsorption site at the surface of the solid and the adsorbed gaseous molecule. Though the adsorption process increases in proportion to pressure but because of the reverse reaction (i.e. desorption), the increase in adsorption is not as fast as the increase in pressure.

Freundlich Adsorption Equation

An empirical expression representing the isothermal variation in the extent of adsorption over a limited range of pressure as suggested by Freundlich is

$$\left(\frac{x}{m}\right) = kp^{1/n} \qquad (1.2.2)$$

where x is the mass of gas adsorbed by the mass m of adsorbent at the pressure p, and k and n are constants for a given pair of adsorbent and adsorbate. The value of n is generally greater than one and thus its reciprocal is less than one. This accounts the fact that the increase in adsorption is not as fast as the increase in pressure.

The values of k and n for a given system can be determined by following the graphical method. If we take the logarithm of Eq. (1.2.2), we get

$$\log\left(\frac{x}{m}\right) = \log k' + \left(\frac{1}{n}\right)\log\left(\frac{p}{p^\circ}\right) \qquad (1.2.3)$$

where p° is the unit pressure. A plot of log (x/m) versus log (p/p°) would be a straight line with slope equal to $(1/n)$ and intercept equal to log k'. From these, the values of k and n can be determined. Equation (1, 2, 3) is applicable over a small range of pressure only. It may be mentioned that $n = 1$ at low pressures, $n = \infty$ at high pressures and $n > 1$ (from 2 to 10) for the intermediate range of pressures.

Langmuir Adsorption Equation

Langmuir derived an expression for the variation in the extent of adsorption with pressure on the basis of following approximations.

- The surface of solid consists of a fixed number of adsorption sites where only adsorption of gaseous molecules can take place.
- Each site can hold only one gaseous molecule and involves a constant heat of adsorption. The latter is identical for all adsorption sites.
- The adsorption is monolayer, i.e. only one layer of adsorption of gaseous molecules is formed.
- The gaseous molecules adsorbed at different sites do not interact with each other.
- The phenomenon of adsorption involves a dynamic equilibrium and can be represented as

$$\mathrm{G + S \rightleftharpoons GS}$$

where G, S, and GS represent, respectively the unadsorbed gaseous molecule, the vacant site on the surface of adsorbent and the adsorbed gaseous molecule.

Equilibrium Constant involving Adsorption

The above equilibrium process implies that the forward reaction (adsorption) and backward reaction (desorption) can take place simultaneously. At equilibrium, the rates of these two processes are identical. On equating these two rates, we get the equilibrium constant characterizing the given equilibrium reaction.

According to the law of mass action, we can write

$$\text{Rate of forward reaction} = k_{\mathrm{f}}\,[\mathrm{G}]\,[\mathrm{S}]$$

$$\text{Rate of backward reaction} = k_{\mathrm{b}}\,[\mathrm{GS}]$$

Therefore, at equilibrium,

$$\text{Rate of adsorption} = \text{Rate of desorption}$$

i.e. $k_{\mathrm{f}}\,[\mathrm{G}]\,[\mathrm{S}] = k_{\mathrm{b}}\,[\mathrm{GS}]$

or
$$K = \frac{k_{\mathrm{f}}}{k_{\mathrm{b}}} = \frac{[\mathrm{GS}]}{[\mathrm{G}][\mathrm{S}]} \qquad (1.2.4)$$

The constant K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

Derivation of Langmuir Equation

The concentration of adsorbed molecules GS depends only on one factor, namely, the number of occupied adsorption sites. The latter will be directly proportional to the fraction θ of the surface that is covered with gaseous molecules. Thus, we can write,

$$\text{Rate of desorption} \propto \theta$$

i.e. $\text{Rate of desorption} = k_{\mathrm{d}}\theta$

The concentration of unadsorbed gaseous molecules G will be directly proportional to the pressure of the gas.

The concentration of vacant sites on the surface of an adsorbent will be directly proportional to the fraction of the surface that remains uncovered and hence will be directly proportional to the factor $(1 - \theta)$. Thus we can write,

$$\text{Rate of adsorption} \propto p(1 - \theta)$$

i.e. $$\text{Rate of adsorption} = k_a\, p(1 - \theta)$$

Now since at equilibrium

Rate of adsorption = rate of desorption,

it follows that

$$k_a(1 - \theta)p = k_d\theta$$

i.e. $$\theta = \frac{k_a p}{k_d + k_a p} = \frac{(k_a/k_d)}{1 + (k_a/k_d)p} = \frac{K_1 p}{1 + K_1 p} \tag{1.2.5}$$

Equation (1.2.5) is known as *Langmuir adsorption equation*. The form of Langmuir isotherm for several values of K_1 is shown in Fig. 1.2.2. The surface coverage increases with pressure, and approaches unity only at very high pressures. Since the value of K_1 depends only on temperature, Fig. 1.2.2 also represents the form of Langmuir isotherm at various temperatures.

Physical Significance of the Constant K_1

The constant K_1, which is equal to k_a/k_d, is known as distribution coefficient. The constant K_1 is, in fact, an equilibrium constant for the distribution of adsorbate between the surface and the gas phase and is given by

$$K_1 = \frac{k_a}{k_d} = \frac{\theta}{1 - \theta}\,\frac{1}{p} \tag{1.2.6}$$

The equilibrium constant K_1, like any other equilibrium constant, depends only on the temperature of the system. Thus, for a given pressure p, different values of K_1 are obtained at different temperatures. The fraction θ of ~~the area~~ covered with gases is expected to increase with decrease in temperature. Thus, from Eq. (1.2.6) it follows that a given pressure, the equilibrium constant K_1 will increase with decrease in temperature, i.e. the equilibrium constant K_1 and temperature will have inverse relation with each other.

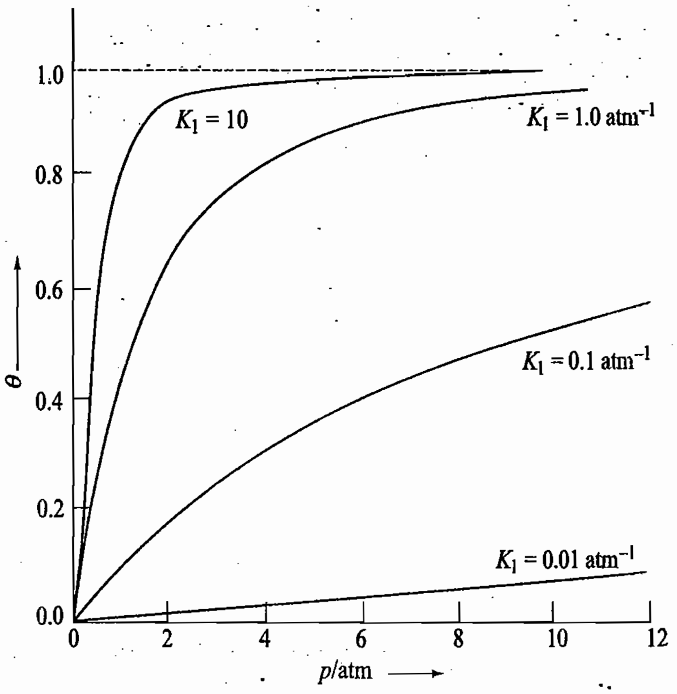


Fig. 1.2.2 The form of Langmuir isotherm at various values of K_1

The equilibrium constant K_1° can be utilized for calculating the change in standard free energy on adsorption by the relation

$$\Delta G^\circ = -RT \ln K_1^\circ \tag{1.2.7}$$

Explanation of Adsorption Isotherms of Fig. 1.2.1

Since the formation of a single layer of adsorbed gaseous molecules is assumed, it is obvious that the mass of gas adsorbed by the unit mass of adsorbent, will be directly proportional to the factor θ that is,

$$\left(\frac{x}{m}\right) \propto \theta \quad \text{i.e.} \quad \left(\frac{x}{m}\right) = k_2\theta \tag{1.2.8}$$

Substituting Eq. (1.2.8) in Eq. (1.2.5), we get

$$\left(\frac{x}{m}\right) = \frac{K_1k_2p}{1+K_1p} \tag{1.2.9}$$

Equation (1.2.9) can be used to correlate the following experimental facts regarding the adsorption of gases as shown in Fig. 1.2.1.

(i) At low pressure, the extent of adsorption is proportional to pressure.

At low pressure, the factor K_1p in Eq. (1.2.9) is much smaller than 1 and hence can be ignored. Thus, we have

$$\left(\frac{x}{m}\right) \simeq K_1k_2p \quad \text{or} \quad \left(\frac{x}{m}\right) \propto p$$

that is, the extent of adsorption is directly proportional to the pressure of the gas.

(ii) At high pressure, the extent of adsorption is independent of pressure.

Here K_1p will be much greater than 1 and hence the factor one can be ignored in comparison to K_1p. Thus, we have

$$\left(\frac{x}{m}\right) = \frac{K_1k_2p}{K_1p} = k_2$$

that is, the extent of adsorption is independent of pressure.

(iii) In the intermediate range of pressure, adsorption does not increase as fast as the increase in pressure.

This is due to the presence of p dependent term in the denominator of Eq. 1.2.9. On increasing pressure, the value of the denominator increases faster than that of the numerator.

Determination of the Constants in Eq. (1.2.9)

The values of the two constants K_1 and k_2 in Eq. (1.2.9) can be obtained by following the graphical method. Inverting Eq. (1.2.9), we get

$$\frac{1}{(x/m)} = \frac{1+K_1p}{K_1k_2p} = \frac{1}{K_1k_2}\frac{1}{p} + \frac{1}{k_2}$$

or

$$\frac{p}{(x/m)} = \frac{1}{K_1k_2} + \frac{p}{k_2} \tag{1.2.10}$$

Thus, a plot of $p/(x/m)$ versus p would yield a straight line with slope equal to $1/k_2$ and intercept equal to $1/K_1k_2$. From these, the values of K_1 and k_2 can be determined.

Alternative Form of Langmuir Equation

Equation (1.2.5) can be written in an alternative form involving the volume of the adsorbed gas. Since θ is the fraction of the surface covered, it will be given by

$$\theta = \frac{\upsilon}{\upsilon_{\text{mono}}}$$

where υ is the volume of gas adsorbed at the given conditions of pressure and temperature and υ_{mono} is that adsorbed at sufficiently high gas pressure so as to give a complete coverage of the surface with a single layer of gaseous molecules. These volumes are reduced to STP conditions and then substituted in Eq. (1.2.5). Thus, we have

$$\frac{\upsilon}{\upsilon_{\text{mono}}} = \frac{K_1 p}{1 + K_1 p} \tag{1.2.11}$$

Equation (1.2.11) can be written in a more suitable form by taking its reciprocal, i.e.

$$\frac{\upsilon_{\text{mono}}}{\upsilon} = \frac{1 + K_1 p}{K_1 p} \quad \text{or} \quad \frac{\upsilon_{\text{mono}}}{\upsilon} = \frac{1}{K_1}\frac{1}{p} + 1$$

or
$$\frac{p}{\upsilon} = \frac{1}{K_1 \upsilon_{\text{mono}}} + \frac{p}{\upsilon_{\text{mono}}} \tag{1.2.12}$$

Now, if a plot is made between p/υ and p, one would get a linear plot with slope equal to $1/\upsilon_{\text{mono}}$ and intercept $1/K_1\upsilon_{\text{mono}}$. From these, the values of υ_{mono} and K_1 can be determined.

Conditions for the Applicability of Langmuir Equation

It is worth pointing out the temperature and pressure conditions over which the Langmuir adsorption isotherm is expected to be applicable. While deriving the Langmuir adsorption isotherm, two important assumptions have been made. These are: (i) formation of monolayer adsorption, and (ii) adsorbed molecules do not interact with each other. These assumptions are expected to hold good at low gaseous pressure and moderately high temperature. Under these conditions, the forces of attraction between adsorbent and adsorbate will be effective only up to the short distances. The condition of low pressure implies that lesser number of molecules strike the surface per unit area per unit time. On the other hand, the condition of high temperature implies that molecules have sufficient high thermal energy to prevent the multilayer formation.

Example 1.2.1

The data below are for the adsorption of CO on charcoal at 273 K. Confirm that they fit the Langmuir isotherm, and find (i) the constant K_1 and volume corresponding to complete surface coverage, (ii) the fraction of surface covered at each pressure, and (iii) change of standard free energy on adsorption at STP.

p/mmHg	100	200	300	400	500	600	700
υ/cm^3	10.2	18.6	25.5	31.4	36.9	41.6	46.1

Mass of sample of charcoal = 3.022 g.

Solution

(i) The constants K_1 and υ_{max} can be determined from the slope and intercept of the graph between p/υ and p. Thus from given data, we have

p/mmHg	100	200	300	400	500	600	700
υ/cm^3	10.2	18.6	25.5	31.4	36.4	41.6	46.1
$\dfrac{p/\text{mmHg}}{\upsilon/\text{cm}^3}$	9.8	10.8	11.8	12.7	13.6	14.4	15.2

The graph between p/υ and p is shown in Fig. 1.2.3. The slope and intercept of the graph are 0.9×10^{-2} and 9.0, respectively, i.e.

$$\text{slope} = \frac{\Delta\{(p/\text{mmHg})/(\upsilon/\text{cm}^3)\}}{\Delta(p/\text{mmHg})} = 0.9 \times 10^{-2}$$

$$\text{intercept} = \Delta\{(p/\text{mmHg})/(\upsilon/\text{cm}^3)\} = 9.0$$

For the Langmuir equation, we will have

$$\text{slope} = \frac{1}{\upsilon_{\text{mono}}} = \frac{\Delta\{p/\upsilon\}}{\Delta p} = 0.9 \times 10^{-2}\ \text{cm}^{-3}$$

$$\text{intercept} = \frac{1}{K\upsilon_{\text{mono}}} = (p/\upsilon)_{p=0} = 9.0\ \text{mmHg cm}^{-3}$$

$$\text{Hence,}\quad \upsilon_{\text{mono}} = \frac{1}{\text{slope}} = \frac{1}{0.009\ \text{cm}^{-3}} = 111\ \text{cm}^3$$

$$K_1 = \frac{\text{slope}}{\text{intercept}} = \frac{0.009\ \text{cm}^{-3}}{9.0\,\text{mmHg cm}^{-3}} = 1.0 \times 10^{-3}\ \text{mmHg}^{-1} = 0.76\ \text{atm}^{-1}$$

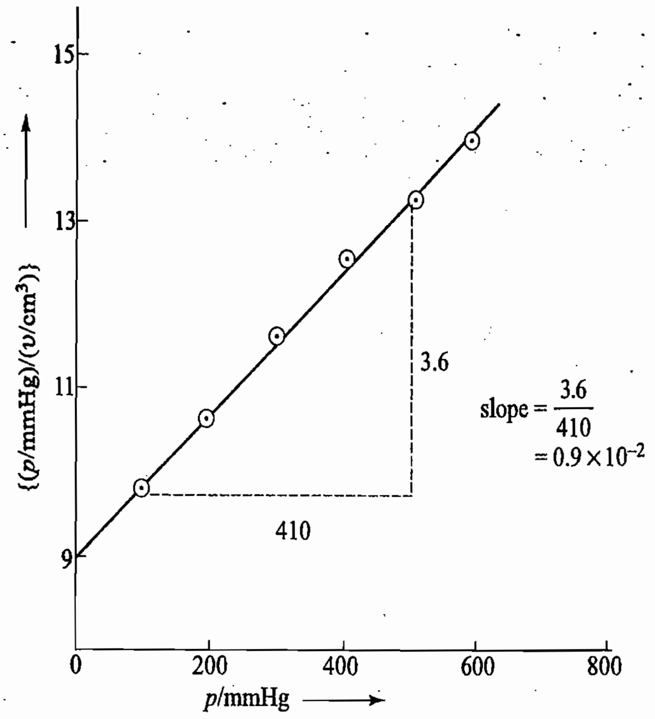


Fig. 1.2.3 The graph between p/υ and p from the given data

(ii) The fractions of surface covered at the given pressures are as follows.

p/mmHg	100	200	300	400	500	600	700
υ/cm^3	10.2	18.6	25.5	31.4	36.2	41.6	46.1
$\theta = \upsilon/\upsilon_{\text{mono}}$	0.092	0.168	0.230	0.283	0.332	0.375	0.415

(iii) The change of standard free energy on adsorption at 273 K will be given by

$$\Delta_{\text{ads}}G^\circ = -RT\ \ln\,(K_1/\text{atm}^{-1})$$

Substituting the value of K_1, we get

$$\Delta_{\text{ads}}\,G^\circ = -\,(8.314\ \text{J K}^{-J}\text{mol}^{-1})\ (273\ \text{K})\ (2.303)\ (\log 0.76)$$

$$= 622.9\ \text{J mol}^{-1} \simeq\ 0.62\ \text{kJ mol}^{-1}$$

Determination of Surface Area of the Adsorbent

Since the molar volume of an ideal gas at STP is 22.414 dm^3, the number of molecules N adsorbed corresponding to the volume υ_{mono} is

$$N = \left(\frac{\upsilon_{\text{mono}}}{22.414\text{dm}^3\,\text{mol}^{-1}}\right)\ (6.022 \times 10^{23}\ \text{mol}^{-1})$$

where 6.022×10^{23} mol^{-1} is Avogadro constant. Now if the area of cross-section of a single molecule is known, it can be multiplied by the above number to give the total surface area of the adsorbent.

The area of cross-section A of the molecule is usually determined from the density of the liquefied or solidified adsorbate. If ρ is the density, then the volume υ occupied by a single molecule (assuming the adsorbate to be highly packed with no void volume) is given by

$$\rho = \frac{M}{V_{\text{m}}} = \frac{M}{\upsilon N_{\text{A}}}$$

or $$\upsilon = \frac{M}{N_{\text{A}}\rho}$$

Assuming the molecule to be spherical, its cross-sectional area can be computed as follows.

If r is the radius of the molecule, it follows that

$$\upsilon = \frac{4}{3}\pi r^3 = \frac{M}{N_{\text{A}}\rho}$$

or $$r = \left(\frac{3}{4\pi}\frac{M}{N_{\text{A}}\rho}\right)^{1/3}$$

Hence, $$A = \pi r^2 = \pi\left(\frac{3}{4\pi}\frac{M}{N_{\text{A}}\rho}\right)^{2/3} \tag{1.2.13}$$

The obtained value of r (or πr^2) is only an approximate one since it lacks the information regarding the exact nature of packing at the surface of the adsorbent. Even in the above method, the presence of void volume in the crystal lattice has been neglected. However, the latter can be accounted for provided the crystal lattice of the solidified adsorbate is known.

Emmett and Brunauer employed the following expression for the computation of area of cross-section A of the molecule on the assumption that the average cross-section of the adsorbed molecule is the same as that of the molecules in the corresponding plane of closest packing in the solidified gas.

$$A = (4)\,(0.866)\left(\frac{M}{4\sqrt{2}\,N_A\rho}\right)^{2/3} \qquad (1.2.14)$$

Table 1.2.1 records the values of A for some of the molecules calculated from Eq. (1.2.14).

Table 1.2.1 Area of Cross-section of Some of the Molecules

Substance	*Temperature* °C	*Liquid Density* g cm^{-3}	*Area of Cross-section* nm^2
N_2	− 183	0.751	0.171
N_2	− 195.8	0.808	0.162
O_2	−183	1.14	0.141
Ar	− 183	1.374	0.144
CO	− 183	0.763	0.168
CO_2	− 56.6	1.179	0.170
CH_4	− 140	0.392	0.181
NH_3	− 36	0.688	0.129

Example 1.2.2 In adsorption of hydrogen over a sample of copper, monolayer-formation volume per gram of powder was found to be 1.36 cm^3 measured at STP. Calculate the specific surface area of copper. Liquid hydrogen has a density of 0.07 g cm^{-3}.

Solution Number of molecules of hydrogen in 1.36 cm^3 at STP is

$$N' = \frac{(1.36\ \text{cm}^3)}{(22\ 414\ \text{cm}^3\,\text{mol}^{-1})}\,(6.022 \times 10^{23}\ \text{mol}^{-1}) = 3.6 \times 10^{19}$$

If liquid hydrogen is assumed to be closely packed (ignoring void volume), then the molar volume of hydrogen will be equal to $N_A v$, where N_A is Avogadro constant and v is the volume of one molecule. If ρ is the density of liquid hydrogen, it is obvious that

$$(N_A v)\,\rho = M(H_2) \qquad \text{or} \qquad v = \frac{M(H_2)}{N_A \rho}$$

Substituting the volumes of $M(H_2)$, N_A and ρ, we get

$$v = \frac{(2\ \text{g mol}^{-1})}{(6.022\times10^{23}\,\text{mol}^{-1})(0.07\ \text{g cm}^{-3})} = 4.742 \times 10^{-23}\ \text{cm}^3$$

Now $v = (4/3)\pi r^3$

Hence, $r = \left(\dfrac{3v}{4\pi}\right)^{1/3} = \left(\dfrac{3\times 4.742\times10^{-23}\,\text{cm}^3}{4\times3.14}\right)^{1/3} = 2.246 \times 10^{-8}\ \text{cm}$

Now the area of cross-section of hydrogen molecule will be

$$A = \pi r^2 = 3.14 \times (2.246 \times 10^{-8}\ \text{cm})^2 = 1.583 \times 10^{-15}\ \text{cm}^2$$

Finally,

Specific area of copper = $N'A = (3.6 \times 10^{19})\,(1.583 \times 10^{-15}\ \text{cm}^2) = 5.70 \times 10^4\ \text{cm}^2$

Example 1.2.3 A solution of palmitic acid ($M = 256\ \text{g mol}^{-1}$) in benzene contains 4.24 g of acid per dm^3. When this solution is dropped on a water surface the benzene evaporates and the palmitic acid forms a monomolecular film of the solid type. If we wish to cover an area of 500 cm^2 with a monolayer, what volume of solution should be used? The area covered by one palmitic acid molecule may be taken to be 0.21 nm^2.

Solution Let the volume υ of palmitic acid solution be required to cover the desired area of 500 cm^2. The number of molecules of palmitic acid in this volume is

$$\left(\frac{(4.24\ \text{g dm}^{-3})(\upsilon)}{256\ \text{g mol}^{-1}}\right)(6.022 \times 10^{23}\ \text{mol}^{-1})$$

$$= (9.976 \times 10^{21}) \times (\upsilon/\text{dm}^3)$$

The area covered by these molecules would be

$$\begin{aligned} &= (9.976 \times 10^{21})\,(\upsilon/\text{dm}^3)\,(0.21\ \text{nm}^2) \\ &= (9.976 \times 10^{21})\,(\upsilon/\text{dm}^3)\,(0.21 \times 10^{-14}\ \text{cm}^2) \\ &= 2.095 \times 10^{7}\,(\upsilon/\text{dm}^3)\ \text{cm}^2 \end{aligned}$$

and will be equal to the given area of 500 cm^2. Thus

$$2.095 \times 10^{7}\,(\upsilon/\text{dm}^3)\ \text{cm}^2 = 500\ \text{cm}^2 \quad \text{or} \quad \upsilon/\text{dm}^3 = 2.439 \times 10^{-5}$$

Multilayer Adsorption

The adsorption of gases on the surface of an adsorbent is no more monolayer at high pressures and low temperatures. At high pressure, the number of molecules striking per unit area of the surface per unit time is quite high. On the other hand, at low temperature the thermal energy of molecules is not sufficiently large to overcome the forces of attraction (van der Waals forces of attraction) between the adsorbed molecule and nearby unadsorbed molecule. This results into the multilayer adsorption, i.e. more than one layer of molecules is adsorbed at the surface. The formation of multilayer is very much enhanced as the pressure of the gas reaches near to the saturation vapour pressure of the liquefied adsorbent at the given experimental temperature. Consequently, the shape of adsorption isotherm is no more identical with that given in Fig. 1.2.1. In fact, four different types of isotherms are observed. These are shown in Fig. 1.2.4 along with the monolayer adsorption isotherm.

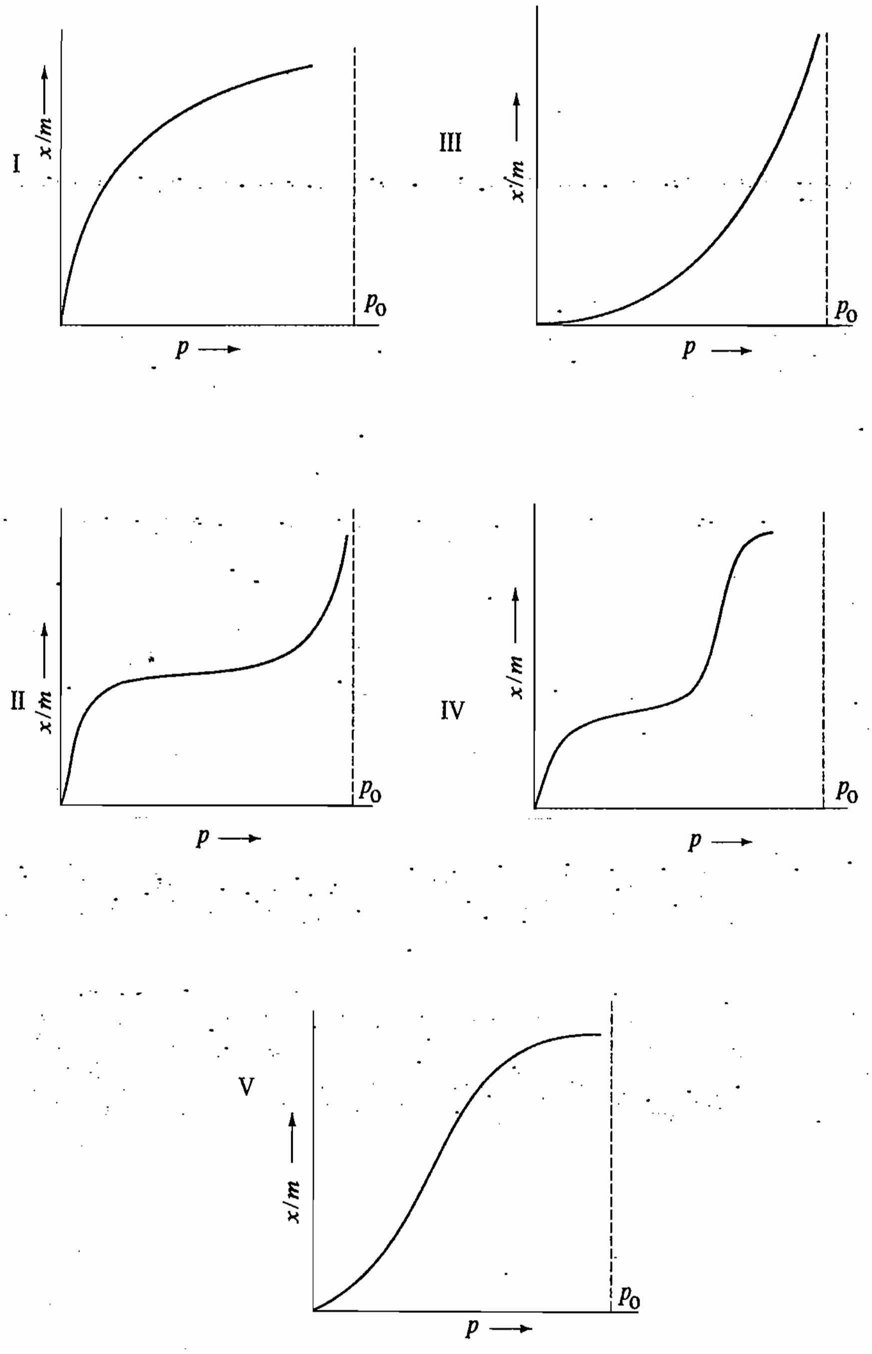
Derivation of BET Equation

The adsorption isotherms shown in Fig 1.2.4 have been interpreted by Brunauer, Emmett and Teller on the basis of formation of multilayer. They derived a theoretical expression, known as BET adsorption isotherm, on the lines very similar to those adopted by Langmuir. While deriving the expression, it was again assumed that interactions amongst the adsorbed molecules in the adsorption layer along the adsorbent surface are neglected.

The formation of multilayer may be represented by the following equilibria.

$$\left.\begin{aligned} &\text{G} + \text{S} \rightleftharpoons \text{GS} \\ &\text{G} + \text{GS} \rightleftharpoons \text{G}_2\text{S} \\ &\text{G} + \text{G}_2\text{S} \rightleftharpoons \text{G}_3\text{S} \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ &\text{G} + \text{G}_{n-1}\text{S} \rightleftharpoons \text{G}_n\text{S} \end{aligned}\right\} \tag{1.2.15}$$

where G, S, GS, G_2S, ···, represent, respectively, the unadsorbed gaseous molecule, the vacant site of the adsorbent surface, single molecule adsorbed per vacant site, two molecules adsorbed per vacant site and so on.



I Monolayer formation: Examples: N_2 at – 195 °C on charcoal and O_2 at – 183 °C on charcoal.

II Examples: N_2 at – 195 °C on Fe catalyst and N_2 at – 195 °C on silica gel.

III Examples: Br_2 at 79 °C on silica gel and I_2 at 79 °C on silica gel.

IV Example: Benzene on Fe_2O_3 at 50 °C.

V Example: Water vapour at 100 °C on charcoal.

Fig. 1.2.4 Five different types of adsorption isotherms

The various equilibria of Eq. (1.2.15) may be characterized by the equilibrium constants defined as follows.

$$\left.\begin{aligned} K_1' &= \frac{[\mathrm{GS}]}{[\mathrm{G}][\mathrm{S}]} \\ K_2' &= \frac{[\mathrm{G_2S}]}{[\mathrm{G}][\mathrm{GS}]} \\ K_3' &= \frac{[\mathrm{G_3S}]}{[\mathrm{G}][\mathrm{G_2S}]} \\ &\cdots\cdots\cdots\cdots, \text{and so on.} \end{aligned}\right\} \qquad (1.2.16)$$

Now, as usual, we will have:

(i) [G] ∝ pressure of the gas, that is,

$$[\mathrm{G}] \propto p$$

(ii) [S] ∝ the fraction of the free surface, that is,

$$[\mathrm{S}] \propto \theta_0$$

(iii) [GS] ∝ fraction of surface covered with single-molecule adsorption, that is,

$$[\mathrm{GS}] \propto \theta_1$$

(iv) $[\mathrm{G_2S}]$ ∝ fraction of surface covered with two-molecule adsorption, that is,

$$[\mathrm{G_2S}] \propto \theta_2$$

$$\cdots\cdots\cdots\cdots, \text{and so on.}$$

With the above relations, the expressions of equilibrium constants (Eqs 1.2.16) become

$$\left.\begin{aligned} K_1 &= \frac{\theta_1}{p\theta_0} \\ K_2 &= \frac{\theta_2}{p\theta_1} \\ K_3 &= \frac{\theta_3}{p\theta_2} \\ &\cdots\cdots\cdots\cdots, \text{and so on.} \end{aligned}\right\} \qquad (1.2.17)$$

The value of constant K_1 is usually very large as compared to the rest of the equilibrium constants. The reason for this is that the interaction between the adsorbate and the adsorbent decreases very rapidly as the distance from the surface is increased. The remaining constants $K_2, K_3, \ldots$, etc. though will not have the same values, but the difference between any two constants is generally much smaller than that between K_1 and K_2. It is for this reason, it can assumed that

$$K_2 \simeq K_3 \simeq K_4 \simeq \ldots \simeq K_\mathrm{L} \qquad (1.2.18)$$

where K_L is the equilibrium constant corresponding to the saturated vapour-liquid equilibrium and, by definition, is given as

$$\text{saturated vapour} \rightleftharpoons \text{liquid}$$

$$K_\mathrm{L} = \frac{1}{p_0} \qquad (1.2.19)$$

With the approximation given in Eq. (1.2.18), the various equilibrium constants of Eqs (1.2.17) are reduced to

$$\left.\begin{aligned}
&K_1 = \frac{\theta_1}{p\theta_0}\\
&K_2 \simeq K_L = \frac{\theta_2}{p\theta_1}\\
&K_3 \simeq K_L = \frac{\theta_3}{p\theta_2}\\
&\text{.............................., and so on.}
\end{aligned}\right\} \qquad (1.2.20)$$

Rearranging the above expressions and making use of Eq. (1.2.19), we get

$$\left.\begin{aligned}
&\theta_1 = K_1 p\theta_0\\
&\theta_2 = K_L p\theta_1 = \left(\frac{1}{p_0}\right)p(K_1 p\theta_0) = K_1 p\left(\frac{p}{p_0}\right)\theta_0\\
&\theta_3 = K_L p\theta_2 = \left(\frac{1}{p_0}\right)p\left(K_1 p\frac{p}{p_0}\theta_0\right) = K_1 p\left(\frac{p}{p_0}\right)^2\theta_0\\
&\text{.................................., and so on.}
\end{aligned}\right\} \qquad (1.2.21)$$

If we assume that the entire adsorbent surface is covered, then the total coverage of the first layer will be given by

$$\theta_{\text{total}} = \theta_0 + \theta_1 + \theta_2 + \cdots = 1 \qquad (1.2.22)$$

Substituting the values of θ_1, θ_2, $\cdots$ from Eqs (1.2.21), we have

$$\begin{aligned}
\theta_{\text{total}} &= \theta_0 + K_1 p\theta_0 + K_1 p\left(\frac{p}{p_0}\right)\theta_0 + K_1 p\left(\frac{p}{p_0}\right)^2\theta_0 + \cdots = 1\\
&= \theta_0\left[1 + K_1 p\left\{1 + \left(\frac{p}{p_0}\right) + \left(\frac{p}{p_0}\right)^2 + \cdots\right\}\right] = 1 \qquad (1.2.23)
\end{aligned}$$

Since $p/p_0 \leq 1$, the expression within the curly brackets of Eq. (1.2.23) can be written as

$$1 + \left(\frac{p}{p_0}\right) + \left(\frac{p}{p_0}\right)^2 + \cdots = \left[1 - \left(\frac{p}{p_0}\right)\right]^{-1} = \frac{1}{1-(p/p_0)} \qquad (1.2.24)$$

Substituting Eq. (1.2.24) in Eq. (1.2.23), we get

$$\theta_{\text{total}} = \theta_0\left[1 + \frac{K_1 p}{1-(p/p_0)}\right] = 1$$

or
$$\theta_0 = \frac{1}{1 + K_1 p/\{1-(p/p_0)\}} = \frac{1 - p/p_0}{1 + K_1 p - p/p_0} \qquad (1.2.25)$$

Now the total volume of the adsorbed gas (corrected to STP) will be given by

$$v_{\text{total}} = v_{\text{mono}}\,(\theta_1 + 2\theta_2 + 3\theta_3 + \cdots) \qquad (1.2.26)$$

where v_{mono} is the volume required for the monolayer adsorption. Substituting the values of θ_1, θ_2, θ_3, ... from Eqs (1.2.21), we get

$$v_{\text{total}} = v_{\text{mono}}\,K_1 p\theta_0 \left[1 + 2\left(\frac{p}{p_0}\right) + 3\left(\frac{p}{p_0}\right)^2 + \cdots\right] \qquad (1.2.27)$$

The expression within the bracket of Eq. (1.2.27) is simply a derivative of the expression within the curly bracket of Eq. (1.2.23). Thus in view of Eq. (1.2.24), we get

$$1 + 2\left(\frac{p}{p_0}\right) + 3\left(\frac{p}{p_0}\right)^2 + \cdots = \frac{1}{(1 - p/p_0)^2} \qquad (1.2.28)$$

Substituting Eq. (1.2.28) in Eq. (1.2.27), we get

$$v_{\text{total}} = v_{\text{mono}}\,\frac{K_1 p\theta_0}{(1 - p/p_0)^2} \qquad (1.2.29)$$

Substituting the expression of θ_0 from Eq. (1.2.25), we get

$$v_{\text{total}} = \frac{v_{\text{mono}} K_1 p}{(1 - p/p_0)(1 + K_1 p - p/p_0)} \qquad (1.2.30)$$

The pressure p in the above expression may be replaced in terms of relative pressure (p/p_0) as shown below.

$$p = p_0\,\frac{p}{p_0} = \frac{1}{K_{\text{L}}}\left(\frac{p}{p_0}\right) \qquad (1.2.31)$$

Thus, substitution of Eq. (1.2.31) in Eq. (1.2.30) gives

$$v_{\text{total}} = \frac{v_{\text{mono}}\,(K_1/K_{\text{L}})(p/p_0)}{(1 - p/p_0)\{1 + (K_1/K_{\text{L}})(p/p_0) - (p/p_0)\}} \qquad (1.2.32)$$

The ratio K_1/K_{L} is designated by the symbol C. Thus, we have

$$v_{\text{total}} = \frac{v_{\text{mono}}\,C(p/p_0)}{(1 - p/p_0)\{1 + C(p/p_0) - (p/p_0)\}} \qquad (1.2.33)$$

Equation (1.2.33) is the required Brunauer, Emmett and Teller equation for multilayer adsorption of gaseous molecules (written in short as BET equation).

Equation (1.2.33) may be written in the form

$$\frac{p}{v_{\text{total}}(p_0 - p)} = \frac{1}{v_{\text{mono}} C} + \frac{C - 1}{v_{\text{mono}} C}\,\frac{p}{p_0} \qquad (1.2.34)$$

Thus, a plot of $p/\{\upsilon_{\text{total}}(p_0 - p)\}$ against p/p_0 should give a straight line, whose intercept and slope are $1/(\upsilon_{\text{mono}} C)$ and $(C-1)/(\upsilon_{\text{mono}} C)$, respectively. The two constants υ_{mono} and C can thus be evaluated. Knowing υ_{mono}, the surface area of the adsorbent can be determined by following the method given earlier in this section (Eq. 1.2.13).

Physical Significance of the Constant *C* in BET Equation

The adsorption equilibrium constant K_1 is related to the standard change in the free energy ΔG° by the relation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_1^\circ \qquad ; \text{(where } K_1^\circ = K_1 p^\circ\text{)}$$

Therefore

$$K_1^\circ = \exp(\Delta_{\text{ads}} S_1^\circ/R)\exp(-\Delta_{\text{ads}} H_1^\circ/RT)$$

$$= g_1 \exp(\Delta_{\text{des}} H_1^\circ/RT)$$

where g_1 is the entropy factor and $\Delta_{\text{des}} H_1^\circ$ is the standard enthalpy of desorption of the monolayer formation. Similarly, for the equilibrium constant K_{L}, one can write

$$K_{\text{L}}^\circ = g_{\text{L}} \exp(\Delta_{\text{vap}} H_{\text{L}}^\circ/RT) \qquad ; \text{(where } K_{\text{L}}^\circ = K_{\text{L}} p^\circ\text{)}$$

where $\Delta_{\text{vap}} H_{\text{L}}^\circ$ is the standard enthalpy of vaporization of the liquid adsorbate.

The ratio of these two equilibrium constants, which is equal to C in BET equation, is given by

$$C = \frac{K_1^\circ}{K_{\text{L}}^\circ} = \frac{g_1 \exp(\Delta_{\text{des}} H_1^\circ/RT)}{g_{\text{L}} \exp(\Delta_{\text{vap}} H_{\text{L}}^\circ/RT)} \simeq \exp\left(\frac{\Delta_{\text{des}} H_1^\circ - \Delta_{\text{vap}} H_{\text{L}}^\circ}{RT}\right) \qquad (1.2.35)$$

Derivation of Langmuir Equation from BET Equation

Equation (1.2.34) may be written as

$$\frac{p\,p_0}{\upsilon_{\text{total}}(p_0 - p)} = \frac{1}{\upsilon_{\text{mono}}}\frac{p_0}{C} + \frac{1}{\upsilon_{\text{mono}}}\frac{C-1}{C}p \qquad (1.2.36)$$

Now $C = \dfrac{K_1}{K_{\text{L}}}$ and $K_{\text{L}} = \dfrac{1}{p_0}$

Thus $C = \dfrac{K_1}{K_{\text{L}}} = \dfrac{K_1}{(1/p_0)} = p_0 K_1$

or $K_1 = \dfrac{C}{p_0}$

Substituting the above relation in Eq. (1.2.36), we get

$$\frac{p\,p_0}{\upsilon_{\text{total}}(p_0 - p)} = \frac{1}{\upsilon_{\text{mono}} K_1} + \frac{1}{\upsilon_{\text{mono}}}\frac{C-1}{C}p \qquad (1.2.37)$$

Now if we assume that C is much greater than one and that p_0 is much greater than p, then Eq. (1.2.37) is modified to

$$\frac{p}{\upsilon_{\text{total}}} = \frac{1}{\upsilon_{\text{mono}}}\frac{1}{K_1} + \frac{p}{\upsilon_{\text{mono}}} \qquad (1.2.38)$$

which is, in fact, the Langmuir equation (1.2.12).

Explanation of Isotherms of Fig. 1.2.4

The five isotherms shown in Fig. 1.2.4 can be explained on the basis of BET equation as described below.

Type I This type of adsorption is obtained whenever $p/p_0 \ll 1$ and $C \gg 1$. Note that under these conditions, we have deduced above the Langmuir equation (1.2.38) and hence the adsorption in the present case is monolayer.

Type II This type of adsorption is observed when C is considerably greater than one or, in other words, $\Delta_{\text{des}}H_1^\circ$ is greater than $\Delta_{\text{vap}}H_L^\circ$. The intermediate flattish portion corresponds to the formation of monolayer.

Type III This type of adsorption is observed when C is considerably smaller than one, or in the other words, $\Delta_{\text{des}}H_1^\circ$ is less than $\Delta_{\text{vap}}H_L^\circ$. There is no intermediate flattish portion indicating that the formation of multilayer takes place from the very beginning.

Type IV In the lower pressure region, the shape of the adsorption is very similar to that observed in the type II indicating the formation of monolayer followed by the development of multilayer. The essential condition of $\Delta_{\text{des}}H_1^\circ$ being greater than $\Delta_{\text{vap}}H_L^\circ$ is still satisfied. However, the shape of the adsorption as $p \rightarrow p_0$ differs from that observed in type II. In the present case, the adsorption reaches a limit at pressures well below the saturation vapour pressure. This has been explained on the basis of multilayer formation along with the possibility of filling the capillary pores as a result of condensation of the adsorbate at pressures appreciably below the saturation vapour pressure.

Type V Again, the lower portion of the diagram in this case is very similar to that observed in the type III indicating that $\Delta_{\text{des}}H_1^\circ$ is less than $\Delta_{\text{vap}}H_L^\circ$. The higher portion is identical to that of type IV indicating the saturation in adsorption at pressures below the saturation vapour pressure. This has been again explained on the basis of filling the capillary pores as a result of condensation of the adsorbate at pressures appreciably below the saturation vapour pressure.

Example 1.2.4

In the adsorption of N_2 at 90.1 K on a certain solid, the following volumes of gas, reduced to standard conditions, were found to be adsorbed per gram of solid at the indicated relative pressures p/p_0, where p_0 is the saturated vapour pressure of liquid nitrogen.

p/p_0	0.05	0.10	0.15	0.20	0.25
υ/cm^3	51.3	58.8	64.0	68.9	74.2

Evaluate the constants υ_{mono} and C in the BET equation.

Solution

For testing BET equation, we plot a graph between $1/[\upsilon\{(p_0/p) - 1\}]$ and p/p_0 whose slope and intercept are equal to $(C - 1)/(\upsilon_{\text{mono}}\, C)$ and $1/(\upsilon_{\text{mono}}\, C)$, respectively. Thus from the given data, we have

p/p_0	υ/cm^3	p_0/p	$\dfrac{\text{cm}^3}{\upsilon\{(p_0/p)-1\}}$
0.05	51.3	20	$\dfrac{1}{51.3\times19}=0.001\,03$
0.10	58.8	10	$\dfrac{1}{58.8\times9}=0.001\,90$
0.15	64.0	6.67	$\dfrac{1}{64.0\times5.67}=0.002\,76$
0.20	68.9	5.0	$\dfrac{1}{68.9\times4}=0.003\,63$
0.25	74.2	4.0	$\dfrac{1}{74.2\times3}=0.004\,49$

The plot of $1/[\upsilon\{(p_0/p)-1\}]$ versus p/p_0 is shown in Fig. 1.2.5.

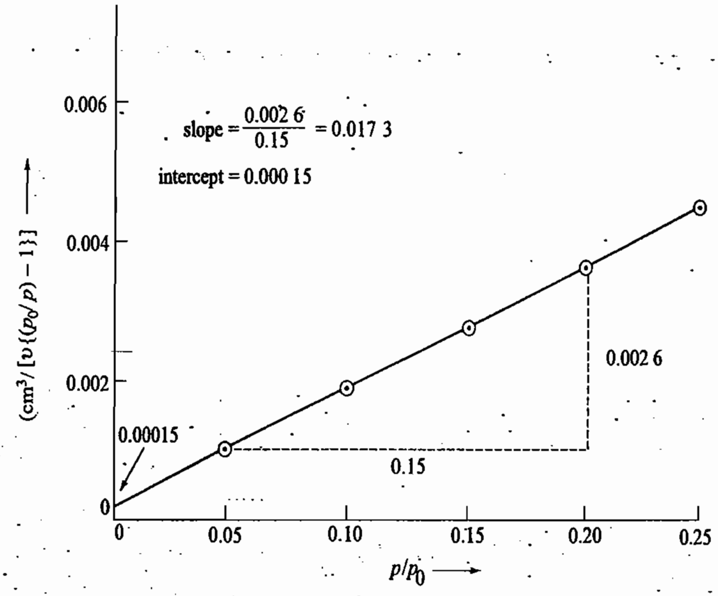


Fig. 1.2.5

The slope and intercept of the BET equation are;

$$\text{slope} = \left(\frac{1}{\upsilon_{\text{mono}}}\right)\frac{C-1}{C} = 0.017\ 3\ \text{cm}^{-3}$$

$$\text{intercept} = \frac{1}{\upsilon_{\text{mono}}C} = 0.000\ 15\ \text{cm}^{-3}$$

Thus $\dfrac{\text{slope}}{\text{intercept}} = C-1 = \dfrac{0.017\ 3\ \text{cm}^{-3}}{0.000\ 15\ \text{cm}^{-3}} = 115.3$

Hence, $C = 116.3$

From the intercept expression, we have

$$\upsilon_{\text{mono}} = \frac{1}{C\times(\text{intercept})}$$

Substituting the values of C and intercept, we get

$$\upsilon_{\text{mono}} = \frac{1}{(116.3)(0.000\ 15\ \text{cm}^{-3})} = 57.32\ \text{cm}^3$$

Example 1.2.5 From the answer of Example 1.2.4, find the area of the solid in square metres per gram, and the value of $\Delta_{\mathrm{des}}H_1^\circ - \Delta_{\mathrm{vap}}H_{\mathrm{L}}^\circ$. Given the area of nitrogen molecule equal to 0.162 nm^2.

Solution Number of molecules in the obtained value of v_{mono} in Example 1.2.4

$$= \left(\frac{v_{\mathrm{mono}}}{22\ 414\ \mathrm{cm^3\ mol^{-1}}}\right)(6.022 \times 10^{23}\ \mathrm{mol^{-1}})$$

$$= \left(\frac{(57.32\ \mathrm{cm^3})}{22\ 414\ \mathrm{cm^3\ mol^{-1}}}\right)(6.022 \times 10^{23}\ \mathrm{mol^{-1}}) = 1.540 \times 10^{21}$$

Thus Area/g of adsorbent = Area of nitrogen × Number of molecules adsorbed

$$= (0.162 \times 10^{-18}\ \mathrm{m^2})\,(1.540 \times 10^{21})$$

$$= 249.5\ \mathrm{m^2}$$

Now, the constant C is related to $\Delta_{\mathrm{des}}H_1^\circ - \Delta_{\mathrm{vap}}H_{\mathrm{L}}^\circ$ by the expression

$$C \simeq \exp\{(\Delta_{\mathrm{des}}H_1^\circ - \Delta_{\mathrm{vap}}H_{\mathrm{L}}^\circ)/RT\}$$

Hence, $\Delta_{\mathrm{des}}H_1^\circ - \Delta_{\mathrm{vap}}H_{\mathrm{L}}^\circ = RT \ln C$

$$= (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\,(90.1\ \mathrm{K})\,(2.303 \times \log 116.3)$$

$$= 3\ 563.5\ \mathrm{J\ mol^{-1}}$$

Thermodynamic Treatment of Adsorption

Jura and Harkins extended thermodynamically derived Gibbs equation (see Section 1.4) to the adsorption of gases on solids on the assumption that the adsorbed films of gases on solid surfaces are similar to those at liquid-vapour interfaces. The Gibbs equation is given by

$$\Gamma = -\frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln a} \tag{1.2.39}$$

where Γ is the excess concentration of solute per unit area at the surface.

For the adsorption of gases, Eq. (1.2.39) takes the form

$$\Gamma = -\frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln(p/p^\circ)} \tag{1.2.40}$$

where p is the pressure of the gas and p° is the standard-state unit pressure. Now the excess concentration of solute per unit area at the surface will be equal to concentration of adsorbed gas since the concentration of gas in the bulk of adsorbent is zero. If v is the volume of gas adsorbed per unit mass of solid and σ is the surface area of the solid per unit of mass, then

$$\text{Volume of gas adsorbed per unit surface area of adsorbent} = \frac{v}{\sigma}$$

Now, if V_{m} is the molar volume of the gas, we will have

$$\text{Amount of gas adsorbed per unit surface area of adsorbent} = \frac{1}{V_{\mathrm{m}}}\left(\frac{v}{\sigma}\right)$$

and this will be equal to surface excess concentration at the surface. Thus

$$\Gamma = \frac{1}{V_m}\left(\frac{\upsilon}{\sigma}\right) \tag{1.2.41}$$

Substituting Eq. (1.2.41) in Eq. (1.2.40), we get

$$\frac{\upsilon}{\sigma V_m} = -\frac{1}{RT}\,\frac{d\gamma}{d\ln(p/p^\circ)} \tag{1.2.42}$$

or
$$d\gamma = -\frac{\upsilon RT}{\sigma V_m}\, d\ln(p/p^\circ) \tag{1.2.43}$$

The change in surface tension $d\gamma$ of absorbent may be correlated with the area of cross-section of the absorbed molecules. Lesser the area, larger the number of molecules absorbed per unit area of the adsorbent and hence larger the decrease in the surface tension of the latter. The dependence of surface tension γ on the cross-sectional area A of the molecule of adsorbate may be represented as

$$\gamma_0 - \gamma = b - aA \tag{1.2.44}$$

where b and a are constants. From Eq. (1.2.44), we have

$$d\gamma = a\, dA \tag{1.2.45}$$

Now

Number of molecules of gas adsorbed per unit area of adsorbent

$$= N_A\Gamma = \frac{N_A\upsilon}{\sigma V_m}$$

Thus

Area of cross-section of a molecule of gas absorbed

$$A = \frac{1}{N_A\Gamma} = \frac{\sigma V_m}{N_A\upsilon}$$

Hence, $dA = -\dfrac{\sigma V_m}{N_A\upsilon^2}\, d\upsilon$

Substituting dA in Eq. (1.2.45), we get

$$d\gamma = a\, dA = -\frac{a\sigma V_m}{N_A\upsilon^2}\, d\upsilon \tag{1.2.46}$$

Substituting Eq. (1.2.46) in Eq. (1.2.43), we get

$$-\frac{a\sigma V_m}{N_A\upsilon^2}\, d\upsilon = -\frac{\upsilon RT}{\sigma V_m}\, d\ln(p/p^\circ)$$

or
$$\frac{a\sigma^2 V_m^2}{N_A RT}\,\frac{d\upsilon}{\upsilon^3} = d\ln(p/p^\circ)$$

Integrating the above expression, we have

$$-\frac{a\sigma^2 V_m^2}{2N_A RT}\,\frac{1}{\upsilon^2} + I = \ln(p/p^\circ) \tag{1.2.47}$$

where I is a constant of integration. Thus, if $\ln(p/p^\circ)$ is plotted against $1/\upsilon^2$, we get a straight line with slope equal to $(-a\sigma^2 V_m^2/2N_A RT)$.

Surface Area of Adsorbent by Harkins and Jura Method

According to Eq. (1.2.47), the slope of the graph of log ($p/p°$) versus $1/v^2$ is given by

$$\text{slope} = -\frac{a\sigma^2 V_\text{m}^2}{2N_\text{A}RT}\,\frac{1}{2.303}$$

Hence, $$\sigma^2 = \left(\frac{2\times 2.303\times N_\text{A}RT}{aV_\text{m}^2}\right)(-\text{ slope})$$

or $$\sigma = \left(\frac{2\times 2.303\times N_\text{A}RT}{aV_\text{m}^2}\right)^{1/2}(-\text{ slope})^{1/2}$$

$$= k_1\,(-\text{ slope})^{1/2} \qquad (1.2.48)$$

where k_1 is a constant and is equal to $(2\times 2.303\times N_\text{A}RT/aV_\text{m}^2)^{1/2}$. For area in square metre per gram of adsorbent, k_1 is equal to $4.06\times 10^6\ \text{m}^{-1}$ for nitrogen at −195.8 °C.

Example 1.2.6

Using the data given in Example 1.2.4, determine the area per gram of the adsorbent.

Solution

Equation (1.2.47) is

$$-\frac{a\sigma^2 V_\text{m}^2}{2N_\text{A}RT}\,\frac{1}{v^2} + I = \ln\frac{p}{p_0}$$

or $$-\frac{a\sigma^2 V_\text{m}^2}{2N_\text{A}RT}\,\frac{1}{2.303}\,\frac{1}{v^2} + \frac{I}{2.303} = \log\frac{p}{p_0}$$

Thus, we may plot log (p/p_0) versus $1/v^2$ to determine the surface area. The slope of the line will be equal to ($-a\sigma^2V_\text{m}^2/4.606\,N_\text{A}RT$). From the given data, we have

p/p_0	v/cm^3	log(p/p_0)	$10^4(1/v^2)$ cm^6
0.05	51.3	$\bar{2}.699\,0$	3.80
0.10	58.3	$\bar{1}.000\,0$	2.89
0.15	64.0	$\bar{1}.176\,1$	2.44
0.20	68.9	$\bar{1}.301\,0$	2.17
0.25	74.2	$\bar{1}.397\,9$	1.87

The plot of log (p/p_0) versus $1/v^2$ is shown in Fig. 1.2.6.

The slope of the given equation will be -0.355×10^4 cm^6, i.e. -35.5×10^{-10} m^6.

Since

$$\sigma = k_1\,(-\text{ slope})^{1/2}$$

we have

$$\sigma = (4.06\times 10^6\ \text{m}^{-1})\,(35.50\times 10^{-10}\ \text{m}^6)^{1/2}$$
$$= (4.06\times 10^6\ \text{m}^{-1})\,(59.58\times 10^{-6}\ \text{m}^3)$$
$$= 241.8\ \text{m}^2/\text{g of adsorbent}$$

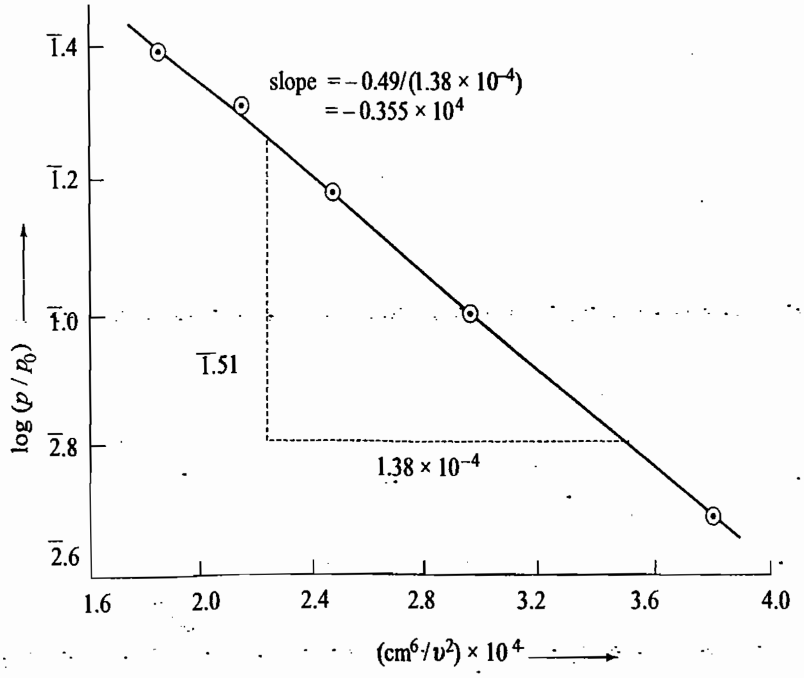


Fig. 1.2.6

Problem 1.2.1 The variation of surface tension of an adsorbent is related to the surface excess concentration of a gas by the relation

$$\gamma - \gamma_0 = a - b\Gamma$$

where a and b are constants. Show that the Gibbs adsorption equation when applied to gas adsorption leads to the Freundlich adsorption equation.

Solution The Gibbs equation when applied to gas adsorption has a form

$$\Gamma = -\frac{1}{RT}\,\frac{d\gamma}{d\ln(p/p^\circ)} \qquad \text{(Eq. 1.2.40)}$$

where the surface excess concentration of the gas at the surface is given by

$$\Gamma = \frac{v}{\sigma V_\mathrm{m}} \qquad \text{(Eq. 1.2.41)}$$

It is given that

$$\gamma - \gamma_0 = a - b\Gamma$$

Substituting the expression of Γ, we get

$$\gamma - \gamma_0 = a - b\,\frac{v}{\sigma V_\mathrm{m}}$$

Hence, $$d\gamma = -\frac{b}{\sigma V_\mathrm{m}}\,dv$$

Substituting $d\gamma$ from the above relation and Γ from Eq. (1.2.41) in Eq. (1.2.40), we get

$$\frac{v}{\sigma V_\mathrm{m}} = -\frac{1}{RT}\left(-\frac{b\,dv}{\sigma V_\mathrm{m}}\right)\frac{1}{d\ln(p/p^\circ)}$$

or $$\frac{dv}{v} = \left(\frac{RT}{b}\right) d\ln(p/p^\circ)$$

or $$\frac{\mathrm{d}v}{v} = \frac{1}{n}\,\mathrm{d}\ln(p/p^\circ) = \mathrm{d}\ln(p/p^\circ)^{1/n}$$

where $1/n = RT/b$. Integrating the above relation, we get

$$\ln(v/v^\circ) = \ln(p/p^\circ)^{1/n} + \ln k'$$

where $\ln k'$ is the constant of integration. The above expression may be written as

$$\ln(v/v^\circ) = \ln(kp^{1/n})$$

or $$v = kp^{1/n}$$

which is the required Freundlich adsorption equation.

Problem 1.2.2

The variation of surface tension of an adsorbent is related to the surface excess concentration of a gas by the relation

$$\gamma - \gamma_0 = a + \frac{RTv_{\mathrm{mono}}}{\sigma V_{\mathrm{m}}}\ln\left(1 - \frac{v}{v_{\mathrm{mono}}}\right)$$

where a is a constant and v_{mono} is the volume corresponding to the monolayer formation. Show that the Gibbs adsorption equation when applied to the gas adsorption leads to the Langmuir adsorption equation.

Solution

It is given that

$$\gamma - \gamma_0 = a + \frac{RTv_{\mathrm{mono}}}{\sigma V_{\mathrm{m}}}\ln\left(1 - \frac{v}{v_{\mathrm{mono}}}\right)$$

Hence, $$\mathrm{d}\gamma = \frac{RTv_{\mathrm{mono}}}{\sigma V_{\mathrm{m}}}\left(\frac{-1/v_{\mathrm{mono}}}{1 - v/v_{\mathrm{mono}}}\right)\mathrm{d}v$$

Substituting $\mathrm{d}\gamma$ from the above relation and Γ from Eq. (1.2.41) in Eq. (1.2.40), we get

$$\frac{v}{\sigma V_{\mathrm{m}}} = \left(-\frac{1}{RT}\right)\left(-\frac{RT}{\sigma V_{\mathrm{m}}}\frac{\mathrm{d}v}{1 - v/v_{\mathrm{mono}}}\right)\left(\frac{1}{\mathrm{d}\ln(p/p^\circ)}\right)$$

or $$v = \frac{\mathrm{d}v}{(1 - v/v_{\mathrm{mono}})}\left(\frac{1}{\mathrm{d}\ln(p/p^\circ)}\right)$$

or $$\frac{\mathrm{d}v}{v(1 - v/v_{\mathrm{mono}})} = \mathrm{d}\ln(p/p^\circ)$$

or $$\frac{\mathrm{d}v}{v} + \frac{\mathrm{d}v}{v_{\mathrm{mono}}(1 - v/v_{\mathrm{mono}})} = \mathrm{d}\ln(p/p^\circ)$$

or $$\mathrm{d}\ln(v/v^\circ) - \mathrm{d}\ln\{(v_{\mathrm{mono}}/v^\circ)(1 - v/v_{\mathrm{mono}})\} = \mathrm{d}\ln(p/p^\circ)$$

Integrating the above relation, we get

$$\ln(v/v^\circ) - \ln\{(v_{\mathrm{mono}}/v^\circ)(1 - v/v_{\mathrm{mono}})\} = \ln(p/p^\circ) + \ln K_1$$

where $\ln K_1$ is the constant of integration. The above relation may be rearranged as follows.

$$\ln\left(\frac{v}{v_{\mathrm{mono}}(1 - v/v_{\mathrm{mono}})}\right) = \ln(K_1'p)$$

or $$\frac{\upsilon}{\upsilon_{\text{mono}}(1-\upsilon/\upsilon_{\text{mono}})} = K_1'p$$

or $$\frac{1}{K_1'\upsilon_{\text{mono}}} = p\left(\frac{1-\upsilon/\upsilon_{\text{mono}}}{\upsilon}\right)$$

or $$\frac{1}{K_1'\upsilon_{\text{mono}}} = \frac{p}{\upsilon} - \frac{p}{\upsilon_{\text{mono}}}$$

or $$\frac{p}{\upsilon} = \frac{1}{K_1'\upsilon_{\text{mono}}} + \frac{p}{\upsilon_{\text{mono}}}$$

which is the required Langmuir adsorption equation (1.2.12).

Change in Enthalpy, Entropy and Free Energy on Adsorption

The enthalpy of adsorption can, in principle, be determined from the measurements of the pressures required to produce a given amount of adsorption at different temperatures. The equation used for this purpose has the same form as that of Clausius-Clapeyron equation and can be derived thermodynamically. Since there exists an equilibrium between the adsorbed gaseous molecules and unadsorbed gaseous molecules, the thermodynamic condition for the equilibrium requires that

$$\mu_{\text{g}} = \mu_{\text{s}} \tag{1.2.49}$$

where μ_{g} and μ_{s} are the chemical potentials of unadsorbed and adsorbed gaseous molecules, respectively. Now

$$\mu_{\text{g}} = f(T, p) \tag{1.2.50a}$$

and $$\mu_{\text{s}} = f(T, \theta) \tag{1.2.50b}$$

Now if the temperature and pressure are changed while keeping θ constant (i.e. the extent of a adsorption constant), the changes in chemical potentials are

$$\mathrm{d}\mu_{\text{g}} = -S_{\text{g}}\,\mathrm{d}T + V_{\text{g}}\,\mathrm{d}p \tag{1.2.51}$$

$$\mathrm{d}\mu_{\text{s}} = -S_{\text{s}}\,\mathrm{d}T \tag{1.2.52}$$

When a new equilibrium state is reached, these two changes are identical. Thus

$$\mathrm{d}\mu_{\text{g}} = \mathrm{d}\mu_{\text{s}}$$

Making use of Eqs (1.2.51) and (1.2.52), we get

$$-S_{\text{g}}\,\mathrm{d}T + V_{\text{g}}\,\mathrm{d}p = -S_{\text{s}}\,\mathrm{d}T$$

or $$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{-(S_{\text{s}} - S_{\text{g}})}{V_{\text{g}}} = -\frac{\Delta_{\text{ads}}S}{V_{\text{g}}} \tag{1.2.53}$$

where $\Delta_{\text{ads}}S$ is the change in the molar entropy on adsorption. Now

$$\Delta_{\text{ads}}S = \frac{\Delta_{\text{ads}}H}{T} \tag{1.2.54}$$

Thus, Eq. (1.2.53) becomes

$$\frac{\mathrm{d}p}{\mathrm{d}T} = -\frac{\Delta_{\text{ads}}H}{V_{\text{g}}T} \tag{1.2.55}$$

If the gas behaves ideally, then

$$\frac{\mathrm{d}p}{p} = -\frac{\Delta_{\mathrm{ads}}H}{RT^2}\,\mathrm{d}T \tag{1.2.56}$$

which on integration gives

$$\ln\left(\frac{p}{p^\circ}\right) = \frac{\Delta_{\mathrm{ads}}H}{R}\,\frac{1}{T} + \text{constant} \tag{1.2.57}$$

Thus, a plot $\ln(p/p^\circ)$ against $1/T$ at a fixed value of θ gives a straight line with slope equal to $\Delta_{\mathrm{ads}}H/R$ (Fig. 1.2.7).

From the slope, the value of $\Delta_{\mathrm{ads}}H$ can be determined. The curve showing the variation of the pressure with temperature is called *isostere* (constant volume) and the value of $\Delta_{\mathrm{ads}}H$ obtained from the slope is known as the *isosteric enthalpy of adsorption*. The slope of $\ln(p/p^\circ)$ versus $1/T$ is negative indicating that $\Delta_{\mathrm{ads}}H$ is negative (exothermic process).

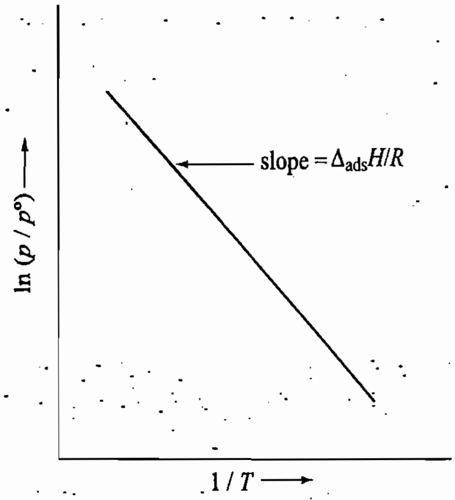


Fig. 1.2.7 Plot of $\ln(p/p^\circ)$ versus $1/T$ where p is the pressure required to produce a fixed amount of adsorption at temperature T

If Eq. (1.2.56) is integrated within the limits, we have

$$\int_{p_1}^{p_2}\frac{\mathrm{d}p}{p} = -\frac{\Delta_{\mathrm{ads}}H}{R}\int_{T_1}^{T_2}\frac{1}{T^2}\,\mathrm{d}T$$

$$\ln\frac{p_2}{p_1} = \frac{\Delta_{\mathrm{ads}}H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \tag{1.2.58}$$

Thus, knowing p_2, p_1, T_2 and T_1, $\Delta_{\mathrm{ads}}H$ can be determined from Eq. (1.2.58).

Derivation of Eq. (1.2.57) from Langmuir Equation

Equation (1.2.57) or (1.2.58) can also be derived directly from the Langmuir equation (1.2.6), according to which, we have

$$K_1 = \left(\frac{\theta}{1-\theta}\right)\frac{1}{p} \tag{1.2.59}$$

The equilibrium constant K_1 depends on temperature. Its temperature dependence will be given by the van't Hoff equation. According to the latter, we will have

$$\frac{\mathrm{d}\ln K_1^\circ}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2}$$

Substituting K_1 from Eq. (1.2.59), we get

$$\frac{\mathrm{d}\ln\left(\frac{\theta}{1-\theta}\frac{p^\circ}{p}\right)}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2} \tag{1.2.60}$$

where p° is the standard-state unit pressure. If the factor θ is kept constant, Eq. (1.2.60) gets modified to

$$\left[\frac{\partial\ln(p/p^\circ)}{\partial T}\right]_\theta = -\frac{\Delta_\theta H^\circ}{RT^2} \tag{1.2.61}$$

where $\Delta_\theta H^\circ$ will known as isosteric enthalpy of adsorption. Equation (1.2.61) may be written as

$$\mathrm{d}\ln(p/p^\circ) = -\frac{\Delta_\theta H^\circ}{RT^2}\,\mathrm{d}T \qquad (\theta \text{ is constant})$$

Integrating the above expression, we get

$$\ln(p/p^\circ) = \frac{\Delta_\theta H^\circ}{RT} + \text{constant} \qquad \text{(Eq. 1.2.57)}$$

The integration within the limits gives

$$\ln\frac{p_2}{p_1} = \frac{\Delta_\theta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{(Eq. 1.2.58)}$$

The change of ~~free~~ energy on adsorption can be calculated from the relation

$$\Delta_{\text{ads}}G^\circ = -RT\ln K_1^\circ \tag{1.2.62}$$

Finally, the entropy change on adsorption can be calculated from the relation

$$\Delta_{\text{ads}}S^\circ = \frac{\Delta_{\text{ads}}H^\circ - \Delta_{\text{ads}}G^\circ}{T} \tag{1.2.63}$$

Example 1.2.7

The data below show the pressure of CO required for the volume of adsorption to be 10.0 cm^3 at each temperature (all volumes corrected to 1 atm and 273 K). Determine (i) the enthalpy of adsorption at this coverage, (ii) change of free energy on adsorption at 230 K, and (iii) entropy change on adsorption at 230 K.

T/K	200	210	220	230	240	250
p/mmHg	30.0	37.1	45.2	54.0	63.5	73.9

Given also that $V_{\text{mono}} = 110\ \text{cm}^3$.

Solution

(i) Isosteric enthalpy of adsorption can be determined from the slope of the graph between log (p/p°) and $1/T$. The slope is equal to $\Delta_{\text{ads}}H/2.303R$. Thus from given data, we have

p/mmHg	30.0	37.1	45.2	54.0	63.5	73.9
log (p/mmHg)	1.4771	1.5694	1.6551	1.7324	1.8024	1.8680
T/K	200	210	220	230	240	250
K/T	5×10^{-3}	4.76×10^{-3}	4.55×10^{-3}	4.35×10^{-3}	4.17×10^{-3}	4.02×10^{-2}

The graph between log ($p/p°$) and $1/T$ is shown in Fig. 1.2.8. The slope of the graph is – 395 and thus the slope of Eq. (1.2.58) will be – 395 K. Hence

$$\frac{\Delta_{\text{ads}}H}{2.303R} = -\,395\ \text{K}$$

or

$$\Delta_{\text{ads}}H = (2.303)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\,(-\,395\ \text{K})$$

$$= -\,7\,563\ \text{J mol}^{-1}$$

(ii) At 230 K, the fraction of area covered will be given by

$$\theta = \frac{V}{V_{\text{mono}}} = \frac{10.0\ \text{cm}^3}{110.0\ \text{cm}^3} = 0.090\,9$$

Hence,

$$K_1 = \frac{\theta}{1-\theta}\,\frac{1}{p} = \left(\frac{0.090\,9}{1-0.090\,9}\right)\left(\frac{1}{(54.0/760)\ \text{atm}}\right)$$

$$= 1.4073\ \text{atm}^{-1}$$

$$\Delta_{\text{ads}}G° = -\,RT\ln K_1^\circ$$

$$= -\,(8.314\ \text{J K}^{-1}\,\text{mol}^{-1})\,(230\ \text{K})\,(2.303 \times \log 1.407\,3)$$

$$= -\,653.35\ \text{J mol}^{-1}$$

(iii) Now since

$$\Delta G° = \Delta H° - T\Delta S°$$

we have

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T}$$

Substituting the given data, we have

$$\Delta_{\text{ads}}S° = \frac{-7563\,\text{J mol}^{-1} - (-653.35\,\text{J})\,\text{mol}^{-1}}{230\,\text{K}} = -\,30.04\ \text{J K}^{-1}\ \text{mol}^{-1}$$

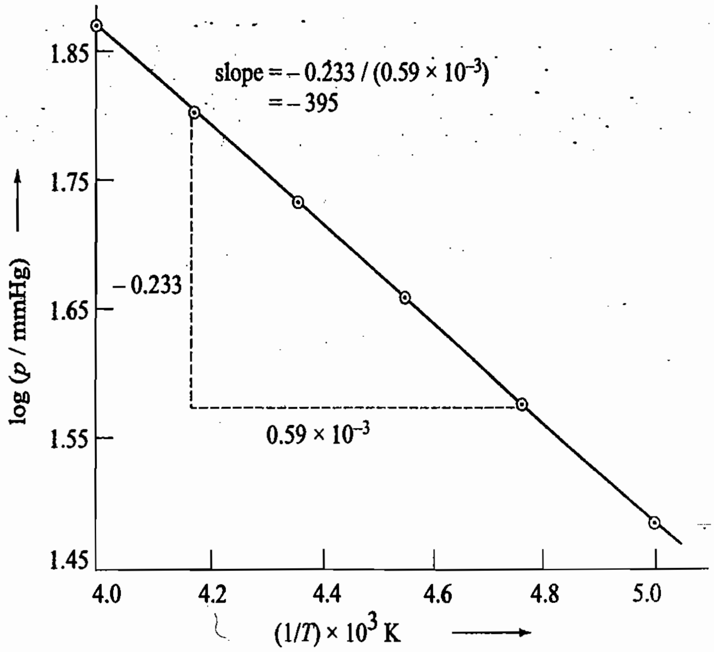


Fig. 1.2.8

Example 1.2.8 The ΔH of adsorption at constant amount of vapour adsorbed is called the isosteric enthalpy of adsorption, $\Delta_\theta H$. The adsorption of N_2 on charcoal amounted to 0.894 cm^3 (STP) g^{-1} at $p = 4.6$ atm and 194 K, and at 35.4 atm and 273 K. Calculate $\Delta_\theta H$.

Solution Employing the reaction

$$\ln \frac{p_2}{p_1} = \frac{\Delta_\theta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

we have

$$\ln\left(\frac{4.6\ \text{atm}}{35.4\ \text{atm}}\right) = \frac{\Delta_\theta H}{8.314\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}}\left(\frac{1}{194\text{K}} - \frac{1}{273\text{K}}\right)$$

$$\Delta_\theta H = (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\left(\frac{194\times 273}{79}\text{K}\right)\left(2.303\log\frac{4.6}{35.4}\right)$$

$$= -\,11376\ \text{J mol}^{-1} = -\,11.376\ \text{kJ mol}^{-1}$$

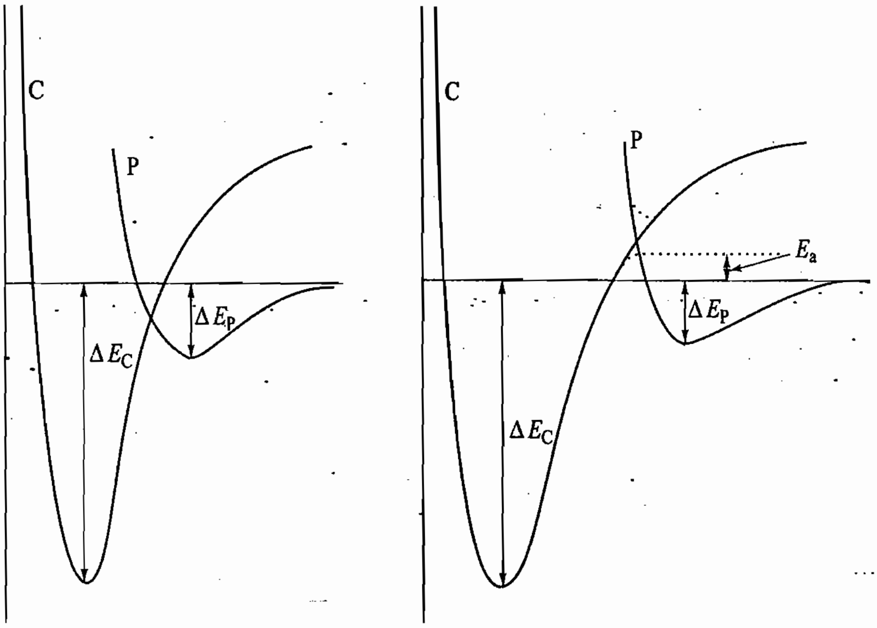
1.3 PHYSICAL ADSORPTION AND CHEMISORPTION

On the basis of forces of attraction between adsorbent and adsorbate, adsorption has been classified into two categories, namely, van der Waals adsorption (or physical adsorption) and chemisorption (or activated adsorption). The general characteristics of these adsorptions are described in Table 1.3.1.

Table 1.3.1 Characteristics of Physical Adsorption and Chemisorption

Physical Adsorption	*Chemisorption*
1. The forces of attraction between adsorbent and adsorbate are of van der Waals type (weak forces).	The forces of attraction between adsorbent and absorbate are of chemical nature (strong forces).
2. This predominates at low temperatures.	This usually occurs at high temperature.
3. Almost all gases show this type of adsorption at low temperatures.	It is highly specific in nature.
4. The enthalpy of adsorption is low and has a value of about 20 kJ mol^{-1} or less.	The enthalpy of adsorption is high and has a value of the order of 80 to 420 kJ mol^{-1}.
5. This type of adsorption attains equilibrium very rapidly on changing the temperature and pressure of the system.	This type of adsorption is relatively slower.
6. This is reversible in nature.	This is usually irreversible in nature. For example, O_2 adsorbed on charcoal, when desorbed also contains CO and CO_2.
7. The activation energy involved in this adsorption is small and is often less than 5 kJ mol^{-1}. It is for this reason, this is even attained at low temperatures.	The activation energy involved in this adsorption is high. It is for this reason this is attained only at high temperatures.
8. Adsorption in this case is often multilayer.	Adsorption in this case is monolayer and thus Langmuir adsorption isotherm is applicable.

Sometimes physical adsoprtion can pass over to chemisorption on increasing the temperature of system. For example, hydrogen shows physical adsorption on a nickel surface at 73 K. On increasing temperature, the extent of adsorption decreases sharply as is to be expected. But very soon, the extent of adsorption starts increasing and attains a maximum value at about 173 K. Beyond 173 K, the extent of adsorption again starts decreasing. Thus, the physical adsorption which predominates at 73 K is passed over to chemisorption at 173 K. This transformation can be explained on the basis of intersections of potential energy curves of physical adsorption and chemisorption as shown in Fig. 1.3.1.



(a) (b)

Fig. 1.3.1 Potential energy diagram for physical adsorption (P) and chemisorption (C); (a) with no activation energy, and (b) with an activation energy

The potential energy diagram of physical adsorption shows a shallow minimum at a relatively long distance from the surface as compared to the larger minimum observed in case of chemisorption. The depths of these minima are in agreement with the enthalpies of adsorption involved in these two cases. It may be seen that at a distance very large from the surface, the gaseous molecules have zero potential energy in case of physical adsorption while those in case of chemisorption have a positive value. These suggest that the molecules in physical adsorption are not very much perturbed as a result of weak forces of attraction while those involved in cheimsorption are very much perturbed. The perturbation may be present even up to the extent of excited electronic state or a dissociated state and thus the molecule in chemisorption is altogether different from the ground state of the molecule. The two potential energy curves may intersect each other and at the point of intersection, both of them have the same energy. As in the interaction of two atomic orbitals to form bonding and antibonding orbitals, we have two different states, one with higher and one with a lower energy, as shown by the dashed curves in Fig. 1.3.1b. At round about these intersection points, the physical adsorption can pass over to the chemisorption. Now this passing over may or may not require activation energy. In the latter, the intersection occurs on the negative side of the potential energy of physical adsorption while in the former, it takes place on the positive side of potential energy. These two cases are also shown in Fig. 1.3.1.

1.4 ADSORPTION AT THE SURFACE OF A LIQUID

Gibbs Adsorption Equation

The concentration of a solute at the surface of a solution may be different from that present in the bulk. While discussing the surface tension of a liquid, we have seen that the surface tends to decrease its surface area in order to obtain a minimum value of surface free energy. The latter arises because of the unbalanced molecular forces experienced by the molecules at the surface. It was also seen that the surface tension is numerically equal to the surface energy per unit area of the surface. Now if the added solute has a surface tension lower than that of the liquid, then it has a tendency to accumulate more at the surface of the liquid since this way the surface tension of the liquid (or the surface free energy per unit area of the surface) is decreased. A quantitative expression which relates the excessive concentration of the solute at the surface (or the extent of adsorption) and the change in surface tension of the liquid (solvent) due to the addition of the solute was derived by J.W. Gibbs and is thus known as Gibbs adsorption equation. The latter can be derived as follows.

Following the additivity rule, the free energy of a system consisting of two components is given by

$$G = n_1\mu_1 + n_2\mu_2 \qquad (1.4.1)$$

where n_1 and n_2 are the amounts and μ_1 and μ_2 are the chemical potentials of the two components, respectively.

Since in the present case we are dealing with the change in the surface free energy, we must also add a factor corresponding to surface energy in Eq. (1.4.1). If γ is the interfacial tension (or the interfacial energy per unit area) and s is the surface area, then the surface free energy is equal to γs. Thus, Eq. (1.4.1), in the present case, modifies to

$$G = n_1\mu_1 + n_2\mu_2 + \gamma s \qquad (1.4.2)$$

The complete differential of Eq. (1.4.2) is given by

$$\mathrm{d}G = n_1\mathrm{d}\mu_1 + \mu_1\mathrm{d}n_1 + n_2\mathrm{d}\mu_2 + \mu_2\mathrm{d}n_2 + \gamma\mathrm{d}s + s\mathrm{d}\gamma \qquad (1.4.3)$$

The function G will now depend on five independent variables, namely, T, p, n_1, n_2 and s, i.e.

$$G = f(T, p, n_1, n_2, s) \qquad (1.4.4)$$

The total differential of G will be given by

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,s}\mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2,s}\mathrm{d}p + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2,s}\mathrm{d}n_1$$

$$+ \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,s}\mathrm{d}n_2 + \left(\frac{\partial G}{\partial s}\right)_{T,p,n_1,n_2}\mathrm{d}s \qquad (1.4.5)$$

or $$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu_1\mathrm{d}n_1 + \mu_2\mathrm{d}n_2 + \gamma\,\mathrm{d}s \qquad (1.4.6)$$

At constant temperature and pressure, Eq. (1.4.6) reduces to

$$\mathrm{d}G_{T,p} = \mu_1\mathrm{d}n_1 + \mu_2\mathrm{d}n_2 + \gamma\,\mathrm{d}s \qquad (1.4.7)$$

From Eqs. (1.4.7) and (1.4.3), we get

$$n_1\,\mathrm{d}\mu_1 + n_2\mathrm{d}\mu_2 + s\mathrm{d}\gamma = 0 \qquad (1.4.8)$$

The corresponding expression for the bulk of the liquid is

$$n_1^0\,\mathrm{d}\mu_1 + n_2^0\,\mathrm{d}\mu_2 = 0 \qquad (1.4.9)$$

where n_1^0 and n_2^0 are the respective amounts of the liquid and solute in the bulk phase.

Now since the system is at equilibrium, the chemical potential of each of the components in both phases (surface and bulk) must be identical. When the system is slightly disturbed and it attains the new equilibrium, then the changes in chemical potentials must be identical in both the phases, i.e. the differentials $\mathrm{d}\mu_1$ and $\mathrm{d}\mu_2$ in Eqs (1.4.8) and (1.4.9) are identical. Eliminating $\mathrm{d}\mu_1$ from these two equations, we get

$$n_1\left(-\frac{n_2^0}{n_1^0}\,\mathrm{d}\mu_2\right) + n_2\mathrm{d}\mu_2 + s\mathrm{d}\gamma = 0$$

or

$$\left(n_2 - \frac{n_1 n_2^0}{n_1^0}\right)\mathrm{d}\mu_2 + s\,\mathrm{d}\gamma = 0$$

or

$$-\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_2} = \frac{n_2 - (n_1 n_2^0/n_1^0)}{s} \qquad (1.4.10)$$

The expression within the bracket of Eq. (1.4.10) gives the amount of solute that would be associated with the amount n_1 of the liquid in the bulk phase. Since n_2 is the amount of solute that is associated with the amount n_1 of the liquid at the surface, the numerator on the right-hand side of Eq. (1.4.10) gives the excessive amount of solute that is present in the surface of the liquid. Dividing this quantity with s gives the excessive concentration of solute per unit area of surface. This quantity is represented by the symbol Γ_2. Thus, we have

$$\Gamma_2 = -\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_2} \qquad (1.4.11)$$

Equation (1.4.11) is the required *Gibbs adsorption equation*. If we eliminate $\mathrm{d}\mu_2$ instead of $\mathrm{d}\mu_1$ from Eqs (1.4.8) and (1.4.9), we would have got the Gibbs adsorption equation as applicable to the solvent. It has a form

$$\Gamma_1 = -\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_1} \qquad (1.4.12)$$

where Γ_1 is the surface excessive concentration of the solvent at the surface of liquid.

The chemical potential of the solute is given by

$$\mu_2 = \mu_2^*(1) + RT\ln a_2$$

where $\mu_2^*(1)$ is the chemical potential of pure solute in liquid phase. Hence

$$\mathrm{d}\mu_2 = RT\,\mathrm{d}\ln a_2 \qquad (1.4.13)$$

Substituting Eq. (1.4.13) in Eq. (1.4.11), we get

$$\Gamma_2 = -\frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln a_2} = -\frac{a_2}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}a_2} \tag{1.4.14}$$

For a dilute solution, we have

$$\Gamma_2 = -\frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln(c_2/c^\circ)} = -\frac{c_2}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}c_2} \tag{1.4.15}$$

where c° is standard unit concentration.

Example 1.4.1 According to Szyszkowski, the surface tension of an aqueous solution of butyric acid is related at 291 K to the bulk concentration c by the empirical relation

$$\gamma^* - \gamma = (29.8\ \text{dyn cm}^{-1}) \log \{1 + (19.64\ \text{mol}^{-1}\ \text{dm}^3)c\}$$

where γ^* is the surface tension of pure water. Apply the Gibbs adsorption equation to calculate the excess concentration Γ of solute per square centimetre of surface when $c = 0.01\ \text{mol dm}^{-3}$. What would be the value of Γ when c becomes infinite?

Solution The Gibbs adsorption equation is

$$\Gamma = -\frac{c}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}c} \tag{1}$$

The expression of $\mathrm{d}\gamma/\mathrm{d}c$ can be determined from the given empirical relation

$$\gamma^* - \gamma = (29.8\ \text{dyn cm}^{-1}) \log \{1 + (19.64\ \text{mol}^{-1}\ \text{dm}^3)c\}$$

$$= \left(\frac{29.8}{2.303}\ \text{dyn cm}^{-1}\right) \ln \{1 + (19.64\ \text{mol}^{-1}\ \text{dm}^3)c\}$$

Thus, $$-\frac{\mathrm{d}\gamma}{\mathrm{d}c} = \left(\frac{29.8}{2.303}\ \text{dyn cm}^{-1}\right)\left(\frac{19.64\ \text{mol}^{-1}\ \text{dm}^3}{1+(19.64\ \text{mol}^{-1}\ \text{dm}^3)c}\right)$$

Hence, Eq. (1) becomes

$$\Gamma = \frac{c}{RT}\left(\frac{29.8}{2.303}\ \text{dyn cm}^{-1}\right)\left(\frac{19.64\ \text{mol}^{-1}\ \text{dm}^3}{1+(19.64\ \text{mol}^{-1}\ \text{dm}^3)c}\right)$$

Substituting the given data, we get

$$\Gamma = \frac{0.01\ \text{mol dm}^{-3}}{(8.314\times10^7\ \text{ergs K}^{-1}\ \text{mol}^{-1})(291\text{K})}\left(\frac{29.8}{2.303}\ \text{dyn cm}^{-1}\right)$$

$$\times\left(\frac{19.64\ \text{mol}^{-1}\ \text{dm}^3}{1+(19.64\ \text{mol}^{-1}\ \text{dm}^3)(0.01\ \text{mol dm}^{-3})}\right)$$

$$= 8.78 \times 10^{-11}\ \text{mol cm}^{-2}$$

The value of Γ when c becomes infinite will be given by

$$\lim_{c\to\infty}\Gamma = \lim_{c\to\infty}\left[\left(\frac{c}{RT}\right)\left(\frac{29.8}{2.303}\ \text{dyn cm}^{-1}\right)\left(\frac{19.64\ \text{mol}^{-1}\ \text{dm}^3}{1+(19.64\ \text{mol}^{-1}\ \text{dm}^3)c}\right)\right]$$

$$= \lim_{c\to\infty}\left[\frac{1}{RT}\left(\frac{29.8}{2.303}\,\text{dyn cm}^{-1}\right)\left(\frac{19.64\ \text{mol}^{-1}\,\text{dm}^3}{(1/c)+19.64\ \text{mol}^{-1}\,\text{dm}^3}\right)\right]$$

$$= \frac{1}{RT}\ \frac{29.8}{2.303}\ \text{dyn cm}^{-1}$$

Thus, we have

$$\lim_{c\to\infty} \varGamma = \frac{29.8\ \text{dyn cm}^{-1}}{(8.314\times10^{7}\ \text{ergs K}^{-1}\,\text{mol}^{-1})(291\ \text{K})(2.303)}$$

$$= 5.35\times10^{-10}\ \text{mol cm}^{-2}$$

Example 1.4.2

According to Szyszkowski, the surface tension of an aqueous solution of an acid is related at 291 K to the bulk concentration c by the empirical relation.

$$\gamma^* - \gamma = (0.030\,8\ \text{N m}^{-1})\log\{1 + (0.018\,64\ \text{mol}^{-1}\,\text{dm}^3)c\}$$

where γ^* is the surface tension of pure water. Apply the Gibbs adsorption equation to calculate the excess concentration $\varGamma$ of solute per square metre of surface when $c = 0.01$ mol dm^{-3}. What would be the value of $\varGamma$ when c becomes infinite?

Solution

The Gibbs adsorption equation is

$$\varGamma = -\frac{c}{RT}\frac{d\gamma}{dc} \qquad (1)$$

Now dγ/dc obtained from the given empirical expression is

$$-\frac{d\gamma}{dc} = \left(\frac{0.030\,8\ \text{N m}^{-1}}{2.303}\right)\left(\frac{0.018\,64\ \text{mol}^{-1}\,\text{dm}^3}{1+(0.018\,64\ \text{mol}^{-1}\,\text{dm}^3)c}\right)$$

Hence, Eq. (1) becomes

$$\varGamma = \frac{c}{RT}\left(\frac{0.030\,8\ \text{N m}^{-1}}{2.303}\right)\left(\frac{0.018\,64\ \text{mol}^{-1}\,\text{dm}^3}{1+(0.018\,64\ \text{mol}^{-1}\,\text{dm}^3)c}\right)$$

At the given value of c, we have

$$\varGamma = \left\{\frac{10\ \text{mol m}^{-3}}{(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})(291\,\text{K})}\right\}\left\{\frac{0.030\,8\ \text{N m}^{-1}}{2.303}\right\}$$

$$\times\left\{\frac{0.018\,64\ \text{mol}^{-1}(10^{-1}\ \text{m})^3}{1+(0.018\,64\ \text{mol}^{-1}\,\text{dm}^3)(0.01\ \text{mol dm}^{-3})}\right\}$$

$$= 1.030\times10^{-6}\ \text{mol m}^{-2}$$

The value of $\varGamma$ when c becomes infinite is

$$\lim_{c\to\infty}\varGamma = \lim_{c\to\infty}\left[\left(\frac{1}{RT}\right)\left(\frac{0.030\,8\ \text{N m}^{-1}}{2.303}\right)\left(\frac{0.018\,64\ \text{mol}^{-1}\,\text{dm}^3}{(1/c)+0.018\,64\ \text{mol}^{-1}\,\text{dm}^3}\right)\right]$$

$$= \frac{1}{RT}\left(\frac{0.030\,8\ \text{N m}^{-1}}{2.303}\right)$$

Thus, we have $\varGamma = \dfrac{1}{(8.314\ \text{J K}^{-1}\,\text{mol}^{-1})(291\,\text{K})}\left(\dfrac{0.030\,8\,\text{N m}^{-1}}{2.303}\right)$

$$= 5.53\times10^{-6}\ \text{mol m}^{-2}$$

Example 1.4.3

The surface tension of ethanol-water mixtures follows the equation

$$\gamma/(10^{-3}\ \mathrm{N\ m^{-1}}) = 72.0 - 0.5\ (c/\mathrm{mol\ dm^{-3}}) + 0.2\ (c/\mathrm{mol\ dm^{-3}})^2$$

where c is the molar concentration of ethanol. The temperature is 298 K. Calculate the surface excess of ethanol for a 0.5 mol dm^{-3} solution.

Solution

From the equation

$$\gamma/(10^{-3}\ \mathrm{N\ m^{-1}}) = 72.0 - 0.5\ (c/\mathrm{mol\ dm^{-3}}) + 0.2\ (c/\mathrm{mol\ dm^{-3}})^2$$

we get

$$\frac{\mathrm{d}(\gamma/10^{-3}\mathrm{N m^{-1}})}{\mathrm{d}(c/\mathrm{mol dm^{-3}})} = -0.5 + 0.4\ (c/\mathrm{mol\ dm^{-3}})$$

Thus, at $c = 0.5$ mol dm^{-3}, we have

$$\frac{\mathrm{d}\gamma}{\mathrm{d}c} = (-0.5 + 0.4 \times 0.5)\ (10^{-3}\ \mathrm{N\ m^{-1}\ mol^{-1}\ dm^{3}})$$
$$= -0.3 \times 10^{-3}\ \mathrm{N\ m^{-1}\ mol^{-1}\ dm^{3}} \equiv -0.3 \times 10^{-6}\ \mathrm{N\ m^{2}\ mol^{-1}}$$

Hence, $$\Gamma = \frac{c}{RT}\,\frac{\mathrm{d}\gamma}{\mathrm{d}c}$$

$$= -\frac{(0.5\ \mathrm{mol\ dm^{-3}})}{(8.314\mathrm{J K^{-1} mol^{-1}})(298\mathrm{K})}\ (-0.3 \times 10^{-6}\ \mathrm{N\ m^{2}\ mol^{-1}})$$
$$= 6.05 \times 10^{-11}\ \mathrm{mol\ dm^{-3}} \equiv 6.05 \times 10^{-12}\ \mathrm{mol\ cm^{-2}}$$

Surface-Active Substances

According to Eq. (1.4.15), Γ_2 is positive if $(\mathrm{d}\gamma/\mathrm{d}c_2)$ is negative. In other words, if the surface tension of a solvent is decreased as a result of adding a solute, then the latter has relatively more concentration at the surface than in the bulk of the solution. Substances which produce a marked reduction in surface tension are known as surface-active substances or *surfactants*. The limiting value of the decrease of surface tension with concentration, i.e. the quantity $-(\mathrm{d}\gamma/\mathrm{d}c_2)_{c_2 \to 0}$ is called the *surface activity*. Most of the organic compounds if added to water, decrease the surface tension of the latter, thus they are present in excess at surface of water. Soaps, detergents and dyestuffs also belong to the surface-active materials. The reason why the surface-active substances have a tendency to have more concentration at the surface of water can be easily understood in terms of solvent-solvent and solute-solvent interactions. In general, the interaction between surface-active solute and solvent are of weaker nature than those existing between solvent-solvent molecules. Because of the stronger interactions between the solvent and solvent molecules, the solute molecules are pushed up to the surface from the bulk of the solution and hence Γ_2 is positive. The presence of these substances at the surface markedly decreases the molecular interaction in the surface layer. Consequently, a sharp decrease in the surface tension is observed as more and more of solute is added to the solvent.

Orientations of Surfactants on the Surface of a Solution

In fact, any substance which exhibits positive deviations from Raoult's law is expected to have a positive value of Γ. Such a substance will be present in excess at the surface of the solution. The orientations of surface-active materials such as fatty acids and alcohols appear to be highly specific in nature, especially when the concentration of the solution is fairly large. The carboxylic group or —OH group points towards the surface of water and the hydrocarbon chain points vertically away from the solution. This conclusion has been derived from the following equation as proposed by B. Szyszkowski on the variation of the surface tension of relatively concentrated aqueous solutions of soluble fatty acids with concentration.

$$\frac{\gamma}{\gamma^*} = 1 - X \ln \frac{c}{Y} \tag{1.4.16}$$

where γ and γ^* are the surface tensions of solution of concentration c and of pure water, respectively, and X and Y are constants. The value of X is found to be constant for a series of fatty acids containing two to six carbon atoms whereas that of Y decreases with increasing length of the hydrocarbon chain. Rearranging Eq. (1.4.16), we have

$$\gamma = \gamma^* \{1 - X \ln (c/\text{mol dm}^{-3}) + X \ln (Y/\text{mol dm}^{-3})\}$$

Differentiating this, we have

$$\mathrm{d}\gamma = \gamma^* \{-X \,\mathrm{d} \ln (c/\text{mol dm}^{-3})\}$$

or
$$\frac{\mathrm{d}\gamma}{\mathrm{d} \ln (c/\text{mol dm}^{-3})} = -X\gamma^* \tag{1.4.17}$$

Substituting Eq. (1.4.17) in Eq. (1.4.15), we get

$$\Gamma_2 = -\frac{1}{RT}(-X\gamma^*) = X\frac{\gamma^*}{RT} \tag{1.4.18}$$

Since the right side of Eq. (1.4.18) involves only constant terms, it may be concluded that the surface excessive concentration attains a constant value and is independent of the length of the hydrocarbon chain of the fatty acid. This can be explained on the basis of forming a single layer of fatty acid molecules with CO_2H groups pointing toward the surface and hydrocarbon tails pointing vertically away from the solution. The concentration of the surface-adsorbed fatty acid increases as the concentration of the latter is increased until a complete unimolecular layer is formed. If the value of Γ in the latter stage is known, it can be used to calculate the area occupied by each molecule at the surface as shown in the following.

The quantity Γ represents the excessive concentration of solute at the surface, thus the area A occupied by a single molecule will be equal to

$$A = \frac{1}{N_A \Gamma} = \frac{1}{N_A}\frac{R\Gamma}{X\gamma^*} = \frac{k_B \Gamma}{X\gamma^*}$$

where k_B is Boltzmann constant. The reported value of X from the Szyszkowski work is equal to 0.179. With this, the value of A at 293 K is found to be

$$A = \frac{\{8.314\ \text{J K}^{-1}\text{mol}^{-1}/(6.022 \times 10^{23}\ \text{mol}^{-1})\}(293\ \text{K})}{0.179 \times (0.072\,75\ \text{N m}^{-1})}$$

$$= 3.10 \times 10^{-19}\ \text{m}^2$$

This value is slightly greater than the value obtained by other methods. This is probably due to the intrusion of water molecules into the surface layer.

Surface-Inactive Substances

For surface-inactive substances $\mathrm{d}\gamma/\mathrm{d}c$ is positive, i.e. an increase in the concentration of a surface-inactive substance in a solution causes an increase in the surface tension of the solution. From Gibbs equation, it follows that the value of Γ_2 in such cases is negative indicating that the substance has larger concentration in the bulk in comparison to that present at the surface. This type of behaviour is known as negative adsorption. Examples include most of inorganic salts, sugar, etc. With surface-inactive substances, the concentration of solvent in the surface layer changes very slightly and, it is for this reason, the increase in surface tension is usually very small.

The fact that surface-inactive substances have more concentration in the bulk in comparison to that present at the surface can be explained on the basis of solvent-solvent and solute-solvent interactions. In general, the interaction between solute and solvent are of stronger in nature than those existing between solvent-solvent molecules. In view of this, the concentration of the solute is larger in the bulk since it allows more interactions between solute and solvent and hence more stability. It may be pointed here that the above interaction conditions also lead to the negative deviations from Raoult's law.

Surface Pressure

Certain insoluble substances such as long chain fatty acids and alcohols form thin films on the surface of water. Many of the film forming substances are solids at ordinary temperatures, but they can be spread as thin films on a water surface by adding a small quantity of a solution of the substance in benzene on to the water and allowing the benzene to evaporate. The spreading film can be confined between glass barriers. It is observed that the force required to compress the film increases gradually up to a certain stage followed by a steep rise. Figure 1.4.1 displays a typical variation of force against the available area per molecule of the film forming substance. The graph shown in Fig. 1.4.1 is known as F–A isotherm and is a two-dimensional analogue of a p versus V isotherm. At large areas the pressure is small and it increases slowly with decreasing area until an area of A_m is reached. For further compression of the film, the force required increases very rapidly. It is reasonable to assume that at the area A_m, the molecules of film forming substance are closely packed.

It is found that for a series of long-chain compounds with polar end-groups, such as fatty acids, alcohols, amides and methyl ketone, the area A_m has a constant value of about 0.205 nm^2. Thus, the area A_m is independent of their chain length. The

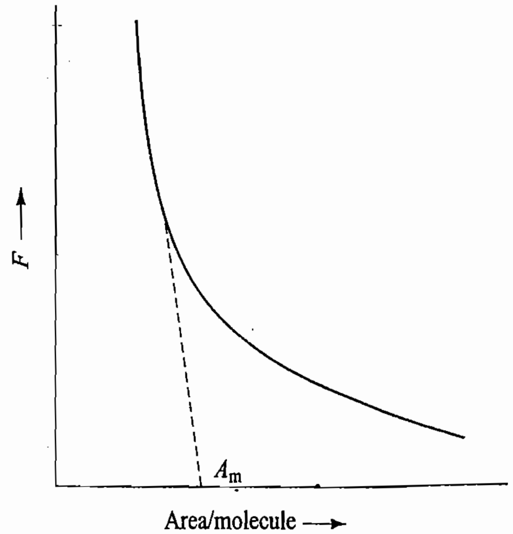


Fig. 1.4.1 F–A isotherm.

constant value of A_m can be explained on the basis that the molecules of these substances have specific orientation at the surface with the polar groups pointing towards water and the insoluble hydrocarbon chain projecting vertically away from water. At A_m, the molecules are closely packed forming a monolayer and thus represents the area of cross-section of the hydrocarbon chain. The value of A_m can be used to determine the length of the molecule. For example, the molecular volume of solid steric acid is 0.556 nm^3. If l is the length of the molecule, then it is obvious that

$$A_m \times l = 0.556 \text{ nm}^3$$

Therefore

$$l = \frac{(0.556 \text{ nm}^3)}{A_m} = \frac{(0.556 \text{ nm}^3)}{(0.205 \text{ nm}^2)} = 0.271 \text{ nm}$$

Since the surface excess concentration Γ is expressed in mol per unit area, it is obvious that the area occupied by 1 mol of the substance is

$$\sigma = \frac{1}{\Gamma} \tag{1.4.19}$$

The film is compressed between a floating barrier and one of the movable strips and the pressure of the film against the floating barrier is measured. The surface pressure π on the movable barrier is simply the difference between the surface tension of pure water and that of the film covered surface, i.e.

$$\pi = \gamma^* - \gamma \tag{1.4.20}$$

For dilute solutions, it is observed that the surface tension decreases linearly with the concentration such that

$$\gamma = \gamma^* - bc \tag{1.4.21}$$

where b is a constant. Combining Eqs (1.4.20) and (1.4.21), we get

$$\pi = bc \tag{1.4.22}$$

Now the Gibbs adsorption equation may be represented in terms of surface pressure. We have

$$\Gamma = -\frac{c}{RT}\frac{d\gamma}{dc}$$

From Eq. (1.4.21), we have

$$d\gamma = -b\,dc \tag{1.4.23}$$

Substituting Eq. (1.4.23) and c in terms of π from Eq. (1.4.22) in the Gibbs adsorption, we get

$$\Gamma = -\frac{(\pi/b)}{RT}\frac{(-b\,dc)}{dc}$$

$$\Gamma = \frac{\pi}{RT} \tag{1.4.24}$$

Substituting Γ from Eq. (1.4.19) in Eq. (1.4.24), we have

$$\frac{1}{\sigma} = \frac{\pi}{RT}$$

or $$\pi\sigma = RT \tag{1.4.25}$$

Equation (1.4.25) is known as the *two-dimensional ideal gas law* and is applicable to the monolayer film formed at the surface. Equation (1.4.25) may be employed to calculate either π (i.e. $-\mathrm{d}\gamma$, the change in surface tension on adsorption) or σ.

Example 1.4.4 A film containing 5.14×10^{-5} g of an alcohol X (molar mass 242 g mol^{-1}) spread on water was compressed into a monomolecular layer occupying an area 15.0×17.9 cm^2. The density of alcohol is 0.818 g cm^{-3}. Calculate: (a) the area of cross-section of the molecule, (b) its length, and (c) the decrease in surface tension of water at 298 K. Given $\gamma^* = 0.072$ N m^{-1}.

Solution **(a)** Number of molecules in the given mass of X

$$= \frac{(5.14 \times 10^{-5}\,\mathrm{g})}{(242\,\mathrm{g\,mol^{-1}})}(6.022 \times 10^{23}\,\mathrm{mol^{-1}}) = 1.279 \times 10^{17}$$

Area occupied by these molecules = 15.0×17.9 cm^2 = 268.5 cm^2

Hence, area occupied by a single molecule,

$$A = \frac{(268.5\,\mathrm{cm^2})}{(1.279 \times 10^{17})} = 2.09 \times 10^{-15}\,\mathrm{cm^2}$$

(b) Volume occupied by 1 g of X

$$= \frac{1}{\rho} = \frac{1}{(0.818\,\mathrm{g\,cm^{-3}})} = 1.223\,\mathrm{cm^3\,g^{-1}}$$

Volume occupied by 5.14×10^{-5} g of X

$$= (5.14 \times 10^{-5}\,\mathrm{g})(1.223\,\mathrm{cm^3\,g^{-1}}) = 6.284 \times 10^{-5}\,\mathrm{cm^3}$$

Volume occupied by 1 molecule of X

$$= \frac{(6.284 \times 10^{-5}\,\mathrm{cm^3})}{(1.279 \times 10^{17})} = 4.914 \times 10^{-22}\,\mathrm{cm^3}$$

Let l be the length of the given molecule. It is obvious that

$$A \times l = 4.914 \times 10^{-22}\,\mathrm{cm^3}$$

or $$l = \frac{4.914 \times 10^{-22}\,\mathrm{cm^3}}{A} = \frac{(4.914 \times 10^{-22}\,\mathrm{cm^3})}{(2.09 \times 10^{-15}\,\mathrm{cm^2})}$$

$$= 2.35 \times 10^{-7}\,\mathrm{cm} = 235\,\mathrm{nm}$$

(c) Amount of X,

$$n = \frac{(5.14 \times 10^{-5}\,\mathrm{g})}{(242\,\mathrm{g\,mol^{-1}})} = 2.124 \times 10^{-7}\,\mathrm{mol}$$

Area occupied by the amount n of X = 268.5 cm^2

Area occupied by 1 mol of X,

$$\sigma = \frac{(268.5\,\mathrm{cm^2})}{(2.124 \times 10^{-7}\,\mathrm{mol^{-1}})} = 1.264 \times 10^{9}\,\mathrm{cm^2\,mol^{-1}}$$

$$= 1.264 \times 10^{5}\,\mathrm{m^2\,mol^{-1}}$$

Using two-dimensional ideal gas law $\pi\sigma = RT$, we have

$$\pi = \frac{RT}{\sigma} = \frac{(8.314\,\mathrm{N\,m\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})}{(1.264\times10^{5}\,\mathrm{m^2\,mol^{-1}})} = 0.019\,6\ \mathrm{N\,m^{-1}}$$

Since $\pi = \gamma^* - \gamma$, therefore

$$\gamma = \gamma^* - \pi = 0.072\ \mathrm{N\,m^{-1}} - 0.019\,6\ \mathrm{N\,m^{-1}}$$

$$= 0.052\,4\ \mathrm{N\,m^{-1}}.$$

Example 1.4.5

An insoluble compound X spreads on water to give a gaseous type film at low concentrations. When 10^{-7} g of X is added to 200 cm^2 surface, the surface tension at 298 K is lowered by 0.20 dyn cm^{-1}. Calculate the molar mass of X.

Solution

Let M be the molar mass of X. Thus,

$$\text{Amount of X} = \frac{(10^{-7}\,\mathrm{g})}{M}$$

$$\pi = \gamma^* - \gamma = 0.20\ \mathrm{dyn\,cm^{-1}}$$

Using the two-dimensional ideal gas law, $\pi\sigma = RT$, we have

$$\sigma = \frac{RT}{\pi} = \frac{(8.314\times10^{7}\,\mathrm{dyn\,cm\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})}{0.20\ \mathrm{dyn\,cm^{-1}}}$$

$$= 1.239\times10^{11}\ \mathrm{cm^2\,mol^{-1}}.$$

Now for 200 cm^2 surface area, the amount of the compound X is

$$\frac{(200\,\mathrm{cm^2})}{(1.239\times10^{11}\,\mathrm{cm^2\,mol^{-1}})} = 1.614\times10^{-9}\ \mathrm{mol}$$

Hence, $\dfrac{(10^{-7}\,\mathrm{g})}{M} = 1.614\times10^{-9}\ \mathrm{mol}$

or $M = \dfrac{(10^{-7}\,\mathrm{g})}{(1.614\times10^{-9}\,\mathrm{mol})} = 61.94\ \mathrm{g\,mol^{-1}}$

Example 1.4.6

A protein with a molar mass of 60 000 g mol^{-1} forms an ideal gaseous film on water. What area of film per milligram of protein will produce a pressure of 0.005 N m^{-1} at 298 K?

Solution

From the two-dimensional ideal gas law $\pi\sigma = RT$, we have

$$\sigma = \frac{RT}{\pi} = \frac{(8.314\,\mathrm{N\,m\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})}{(0.005\,\mathrm{N\,m^{-1}})}$$

$$= 4.955\times10^{5}\ \mathrm{m^2\,mol^{-1}}$$

Amount of protein,

$$n = \frac{(0.001\,\mathrm{g})}{(60\,000\,\mathrm{g\,mol^{-1}})}$$

Area occupied by the amount n

$$= \left(\frac{0.001}{60\,000}\,\mathrm{mol}\right)(4.955\times10^{5}\ \mathrm{m^2\,mol^{-1}}) = 82.6\times10^{-4}\ \mathrm{m^2}$$

$$= 82.6\ \mathrm{cm^2}$$

REVISIONARY PROBLEMS

1.1 What do you understand by the terms (a) absorption, (b) adsorption, (c) adsorbent, and (d) adsorbate? Assuming adsorption to be a spontaneous process, show that it is always an exothermic process.

1.2 (a)Discuss how the extent of adsorption varies on,

(i) increasing the surface area per unit mass of adsorbent

(ii) increasing the temperature of the system, and

(iii) increasing the pressure of the gas.

(b) Show that the effects produced on the extent of adsorption by changing temperature and pressure are consistent with the Le-Chatelier's principle.

1.3 (a)What is an adsorption isotherm? Display qualitatively, how the extent of adsorption varies with pressure at a constant temperature and also display the effect of temperature on adsorption. Describe the five different types of adsorption which are observed at high pressures.

(b) The adsorption of gases on solids can be described by the Freundlich's empirical relation

$$\left(\frac{x}{m}\right) = kp^{1/n}$$

Explain, the terms involved in the above expression and also explain why the value of *n* should be equal to or greater than one.

(c) Outline the assumptions made during the derivation of Langmuir adsorption equation and hence derive this equation. Explain, how the variation of adsorption is accounted for (i) at lower pressure, (ii) at higher pressure, and (iii) in the intermediate range of pressure.

(d) Explain, how the surface area of an adsorbent can be determined with the help of Langmuir adsorption equation.

1.4 Adsorption of gases on the surface of adsorbent is no more monolayer at high pressures and low temperatures. Explain, why it is so.

1.5 Describe Jura and Harkins thermodynamic treatment of adsorption of gases on solids.

1.6 If in an adsorption of a gas, surface tension of the adsorbent varies as

$$\gamma - \gamma^* = a - b\Gamma$$

where *a* and *b* are constants, show that the Gibbs adsorption equation is reduced to the Freundlich adsorption equation.

1.7 If in an adsorption of a gas, surface tension of the adsorbent varies as

$$\gamma - \gamma^* = a + \frac{RT\upsilon_{\text{mono}}}{\sigma V_{\text{m}}} \ln\left(1 - \upsilon/\upsilon_{\text{mono}}\right)$$

where V_{m} is the molar volume of the gas and *a* is a constant, show that the Gibbs adsorption equation is reduced to the Langmuir adsorption equation.

1.8 (a) Derive the BET equation

$$\upsilon_{\text{total}} = \frac{\upsilon_{\text{mono}}\, C(p/p_0)}{\{1-(p/p_0)\}\{1+C(p/p_0)-(p/p_0)\}}$$

(b) What is the physical significance of the term C in the BET equation?

(c) Show qualitatively how the BET equation accounts for the explanation of five different types of observed adsorptions.

1.9 What do you understand by isosteric enthalpy of adsorption? Derive thermodynamically the following relation

$$\ln (p/p^\circ) = \frac{\Delta_{\text{ads}}H}{R} \cdot \frac{1}{T} + \text{constant}$$

What type of graph is expected between log (p/p°) and $1/T$? What will be its slope?

1.10 (a) Classify the adsorption of gases on solids on the basis of forces of interaction between adsorbent and adsorbate. What are their main characteristics?

(b) Sometimes physical adsorption can pass over to chemisorption as the temperature of the system is elevated. Explain, how this can be explained on the basis of intercrossing of potential energy diagrams of physical adsorption and chemisorption.

1.11 (a)Derive the Gibbs adsorption equation

$$\Gamma_2 = -\frac{c_2}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}c_2}$$

(b) What are surface-active substances? Explain, why the surface tension of a liquid is very much modified in the presence of surface-active substances.

(c) Explain how on the basis of Szyszkowski work (on the variation of the surface tension of relatively concentrated aqueous solution of fatty acids with concentration of the latter), the specific orientation of fatty acids on the surface of water can be derived. How does this help in determining the area occupied by a single molecule of the fatty acid?

(d) Explain, why the surface tension of a solvent is not modified to a large extent in the presence of surface-inactive substances.

(e) Justify the statement

"A Substance which exhibits positive deviation from Raoult's law must also exhibit a positive value of surface excessive concentration and if it exhibits negative deviation then it must also exhibit a negative value of surface excessive concentration."

1.12 Gibbs adsorption equation is given as

$$\Gamma = -\frac{c}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}c}$$

The change in surface tension is usually expressed as the surface pressure by the relation

$$\pi = \gamma^* - \gamma$$

For dilute solutions, π may be taken proportional to solute concentration, i.e.

$$\pi = k\,c$$

Show that for ideal solutions, the Gibbs adsorption equation may be written as

$$\Gamma_2 = \frac{c}{RT}\frac{\mathrm{d}\pi}{\mathrm{d}c} = \frac{\pi}{RT}$$

or $$\pi\frac{1}{\Gamma_2} = RT$$

or $$\pi\sigma = RT$$

where σ denotes the surface area per mole of solute. [**Note** that the equation $\pi\sigma = RT$ has the form of two-dimensional ideal gas law. Hence, it may be stated that the adsorbed film of gases (or any other adsorbate) follows two-dimensional ideal gas law.]

TRY YOURSELF PROBLEMS

1.1 By considering the derivation of the Langmuir isotherm on the basis of a reaction between the gas and the surface sites show that if a diatomic gas is adsorbed as atoms on the surface (i.e. the reaction is $A_2 + 2S \rightleftharpoons 2AS$), then

$$\theta = \frac{\sqrt{Kp}}{1+\sqrt{Kp}}$$

[*Hint:* $k_a p\,(1-\theta)^2 = k_d\,\theta^2$]

1.2 Two gases, A and B compete for the binding sites on the surface of an adsorbent. Show that the fraction of the surface covered by A molecules is

$$\theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B}$$

1.3 In an adsorption experiment, surface tension of the adsorbent follows the relation

$$\frac{\gamma}{\gamma_0} = 1 - B\ln\left(1+\frac{c}{a}\right)$$

where B and a are constants. Show that

$$\Gamma = \frac{B\gamma_0}{RT}\left(\frac{c/a}{1+c/a}\right)$$

If Γ is assumed to be proportional to θ, the fraction of area covered, show that the above expression may be written as

$$\theta = K_1\,\frac{K_2 c}{1+K_2 c}$$

[**Note** that the above relation is very similar to that of Langmuir adsorption equation $\theta = K_1p/(1+K_1p)$.]

1.4 For adsorption of gases, the concentration in Gibbs adsorption equation may be replaced by pressure, such that

$$\Gamma = -\frac{p}{RT}\frac{d\gamma}{dp} = -\frac{1}{RT}\frac{d\gamma}{d\ln(p/p^\circ)}$$

If the surface pressure π is given by

$$\pi = \gamma^* - \gamma$$

show that the film pressure may be determined from the expression

$$\pi = RT\int \Gamma\, d\ln(p/p^\circ)$$

1.5 The surface tension of solutions of a sulphonic acid in water is found to vary as

$$\gamma = \gamma^* - b\,c^2$$

Derive the relation connecting π and σ. [**Ans.** $\pi\sigma = RT/2$]

1.6 Show that at low surface coverage the Langmuir isotherm corresponds to the Freundlich expression with $n = 1$. Show also that at high surface coverage the Langmuir equation corresponds to the Freundlich expression with n equal to infinity.

NUMERICAL PROBLEMS

1.1 (a) What is the surface area of a cube having an edge-length of 1 cm?

(b) What would be the total surface area of the same material if it were subdivided into colloidal-size cubes, each having an edge-length of 10^{-7} cm?

[**Ans.** (a) 6 cm^2 (b) 6×10^7 cm^2]

Freundlich Isotherm

1.2 The Freundlich isotherm can be written as $V_a = kp^{1/n}$, where k and n are constants. The following data were obtained for the adsorption of methane on 10 g of carbon black at 0 °C. Show that the data follow Freundlich isotherm. Determine the values of constants k and n.

p/mmHg	100	200	300	400
V_a/cm^3	97.5	144	182	214

1.3 Predict whether following data on the adsorption of acetic acid on charcoal at 25 °C follow the Freundlich isotherm. If yes, what are the constants k' and n?

[acid]/mol dm^{-3}	0.05	0.10	0.50	1.0	1.5
m_a/g	0.04	0.06	0.12	0.16	0.19

where m_a is the mass adsorbed per unit mass of charcoal.

[**Ans.** $k' = 0.160$ and $n = 2.32$]

Langmuir Isotherm

1.4 (a) The following table gives the volume υ of nitrogen (reduced to 0 °C and 1 atm) adsorbed per gram of active charcoal at 0 °C at a series of pressures:

p/Torr	3.93	12.98	22.94	34.01	56.23
$\upsilon/(cm^3\ g^{-1})$	0.987	3.04	5.08	7.04	10.31

Plot the data according to the Langmuir isotherm and determine the constants.

[**Ans.** $k_1 = 156$ Torr, $\upsilon_{mono} = 40$ cm^3/g]

(b) If the area of nitrogen molecule is 0.162 nm^2, what will be the area of 1 g of charcoal in the above problem?

1.5 A study of adsorption of ethylene at –183 °C on a barium and stronium carbonate coated cathode yielded the results:

$\frac{p}{\text{mmHg}}$	p/p_0	$\frac{V/cm^3}{\text{gas at 1 mmHg and 25 °C}}$
0.030 60	1.00	22.50
0.030 35	0.992	15.22
0.022 30	0.729	10.34
0.012 70	0.415	7.85
0.007 30	0.239	6.42
0.004 48	0.146 4	5.52
0.002 74	0.089 6	4.98
0.001 85	0.060 5	4.60
0.001 32	0.043 1	4.33

Compare the values for the volume of gas adsorbed for monolayer coverage calculated from the Langmuir isotherm and the Brunauer-Emmett-Teller equation.

Surface Area and Surface Concentration

1.6 One gram of activated charcoal has a surface area of 1 000 m^2. If complete coverage is assumed, how much ammonia (in cm^3 at STP) could be adsorbed on the surface of 25 g of the charcoal? Given: diameter of NH_3 molecule = 0.3 nm.

1.7 Calculate the surface area of a catalyst that adsorbs 10^3 cm^3 of nitrogen reduced to STP per gram in order to form a monolayer. The effective area occupied by nitrogen molecule on the surface is 0.162 nm^2, i.e. 0.162×10^{-14} cm^2.

[**Ans.** 449 m^2]

BET Isotherm

1.8 The adsorption of water by a high polymer varies with the relative pressure of H_2O as follows:

p/p_0	0.05	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.8	0.9	0.95
n/mol of H_2O on 100 g polymer	0.040	0.070	0.125	0.180	0.2450	0.340	0.485	0.740	1.345	2.350	3.010

From a BET plot of $p/n\ (p_0 - p)$ against p/p_0, obtain the amount of water adsorbed when the surface is covered by a monolayer.

1.9 Show that the data given in Problem 1.3 follow the BET and Jura and Harkins equations. Calculate the area of the solid by each of the above two methods.

Enthalpy of Adsorption

1.10 Nitrogen gas adsorbed on charcoal to the extent of 0.921 $cm^3\ g^{-1}$ at a pressure 4.8 atm and at temperature of 190 K, but at 250 K the same amount of adsorption was achieved only when the pressure was increased to 32 atm. What is the molar enthalpy of adsorption of nitrogen on charcoal?

[**Ans.** – 12.7 kJ mol^{-1}]

Excess Surface Concentration

1.11 (i) At 19 °C, the surface tensions, γ, of solutions of butyric acid in water can be represented accurately by the equation

$$\gamma = \gamma^* - a \ln (1 + b\,c)$$

where γ^* is the surface tension of water, while a and b are constants. Set up the expression for the excess surface concentration Γ as a function of c.

(ii) For butyric acid, the constants a and b in the preceding problem are a = 13.1 and b = 19.62 $mol^{-1}\ dm^3$. Calculate Γ at a concentration of 0.20 mol dm^{-3}. [**Ans.** 4.32×10^{-10} mol cm^{-2}]

(iii) Calculate the limiting value of Γ as c becomes large.

(***Hint:*** Assume $bc \gg 1$)

(iv) Assuming that the only molecules present in the surface are those corresponding to the excess, calculate from the result of part (iii) the area occupied by a molecule of butyric acid in the solution surface.

[**Ans.** 0.305 nm^2]

1.12 The surface tensions of dilute solutions of phenol in water at 303 K were

mass % phenol	0.024	0.047	0.118	0.471
$\gamma/10^{-3}$ N m^{-1}	72.6	72.2	71.3	66.5

Calculate Γ_2 from the Gibbs adsorption isotherm for a 0.01 mass % solution.

1.13 The surface excess concentration of surface active reagent is found to be 3×10^{-10} mol cm^{-2} at 25 °C. Using the two-dimensional ideal gas law $\pi\,\sigma = RT$, calculate the surface tension of the solution. The surface tension of pure solvent is 0.072 N m^{-1}. [**Ans.** 0.064 5 N m^{-1}]

1.14 The surface tension of an aqueous solution of a surfactant decreases linearly with increase in concentration of the surfactant. If the surface tension of 2% solution of the surfactant is 0.068 N m^{-1} at 25 °C and the surface excess

concentration at this concentration is 20×10^{-9} g cm^{-2}, calculate the molar mass of the surfactant. Given: $\gamma^* = 0.072$ N m^{-1}. [**Ans.** 129 g mol^{-1}]
(***Hint:*** Use the relation $\pi/\Gamma = RT$)

1.15 A certain substance forms a surface film that obeys the ideal two-dimensional gas law. Calculate the excess surface concentration required to cause a surface tension lowering of 0.01 N m^{-1} at 25 °C. [**Ans.** 4.04×10^{-6} mol m^{-2}]

1.16 An organic acid of molar mass 242 g mol^{-1} forms a linearly ideal gaseous monolayer on water at 25 °C. Calculate the mass of acid per 100 cm^2 required to produce a film pressure of 1 N m^{-1}. [**Ans.** 9.77×10^{-7} g]

2

Chemical Kinetics

2.1 INTRODUCTION

The feasibility of a given reaction can be predicted with the help of thermodynamic principles. Besides this, the relative amounts of reactants and products at equilibrium position of the reaction can also be predicted. In addition, we can predict whether changes in the experimental conditions will increase or decrease the amount of a product at equilibrium. However, thermodynamic principles do not provide any information regarding the speed of the given reaction, i.e. how much time a given feasible reaction will take for its completion. Moreover, it is not possible to predict how the speed of a given reaction gets affected by changing the concentrations of various participants of the reaction or by changing the experimental conditions. The study of rate of reactions including its dependence on the concentrations of reacting species and the experimental conditions constitutes one of the topics of physical chemistry and is known as chemical kinetics. The important application of the study of rate of reaction is to use the kinetic data in establishing the molecular pathway or mechanism by which the reaction takes place.

2.2 RATE OF REACTION AND RATE OF REACTION DIVIDED BY CONSTANT VOLUME

Average Rate of Change of the Amount of a Reactant or a Product

Reactions with wide difference in speeds are known. On one extreme, we have reactions which proceed at very fast speeds. In some cases, the speed is so fast that the reaction appears to be instantaneous, e.g. reaction between a strong acid and a strong base. On the other extreme, reactions are known which proceed at very slow speeds. In some cases, the speed is so slow that virtually no visible results are observed. Examples include the reactions

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g); \qquad \text{(in dark)}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$$

Between these two extremes, we have reactions which proceed with measurable speeds. Examples include the decomposition of dinitrogenpentoxide dissolved in carbon tetrachloride, the hydrolysis of an ester, the reaction between persulphate and iodide ions, and the hydrolysis of sugars.

By the term rate of change of amount of a reactant or a product, we mean the disappearance of the amount of a reactant or appearance of the amount of a product occurring in a unit interval of time. Its SI unit is mol s^{-1}.

Illustration of A → B

Consider, for example, the simplest reaction

$$A \rightarrow B \qquad (2.2.1)$$

It is obvious that the amount of A will decrease whereas that of B will increase as the reaction proceeds. Figure 2.2.1 displays a typical behaviour of the changes in the amounts of reactant and product as the chemical reaction shown above progresses.

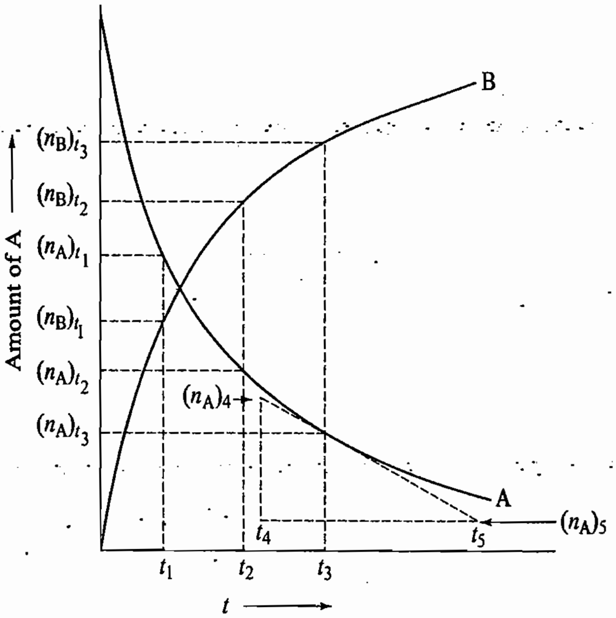


Fig. 2.2.1 The variations of amounts of A and B with time for the reaction A → B

Let $(n_A)_{t_1}$ and $(n_A)_{t_2}$ be the amounts of A at times t_1 and t_2, respectively (Fig. 2.2.1). The decrease in the amount of A (which we represent by $-\Delta n_A$, note the negative sign as the amount of A decreases with time) in the time interval $t_2 - t_1$ (which we represent by Δt) is equal to $(n_A)_{t_2} - (n_A)_{t_1}$. Hence, the decrease in the amount of reactant A in a unit time interval becomes

$$r_{av} = \frac{-\Delta n_A}{\Delta t} = -\frac{(n_A)_{t_2} - (n_A)_{t_1}}{t_2 - t_1} \qquad (2.2.2)$$

$r_{av} = \frac{c_2 - c_1}{t_2 - t_1}$

We will see shortly that the rate expressed by Eq. (2.2.2) changes during the course of a reaction. In general, the rate in the beginning is fast and it decreases as the reaction proceeds. Hence, the rate represented by Eq. (2.2.2) is an average rate over the time interval $t_2 - t_1$. It is for this reason, the subscript av has been added to the symbol r. Note that r_{av} is a positive quantity.

If $(n_B)_{t_1}$ and $(n_B)_{t_2}$ are the amounts of B at times t_1 and t_2, respectively, the increase in the amount of B (which we represent by Δn_B, note the positive sign as the amount of B increases with time) in the time interval $t_2 - t_1$ ($\equiv \Delta t$) is equal to $(n_B)_{t_2} - (n_B)_{t_1}$. Hence, the average rate of increase in the amount of B over the time interval t_1 to t_2 is

$$r'_{av} = \frac{\Delta n_B}{\Delta t} = \frac{(n_B)_{t_2} - (n_B)_{t_1}}{t_2 - t_1} \qquad (2.2.3)$$

From Eq. (2.2.1), it follows that the decrease in the amount of A will be equal to the increase in the amount of B and thus, we have

$$r_{av} = r'_{av} \qquad (2.2.4)$$

The average rate of appearance of a product or disappearance of a reactant decreases with time. For example, in the time interval $t_2 - t_3$ (Fig. 2.2.1), which is equal to time interval $t_1 - t_2$, the average rate is given by

$$r_{\text{av}} = -\frac{\Delta n_{\text{A}}}{\Delta t} = -\frac{(n_{\text{A}})_{t_3} - (n_{\text{A}})_{t_2}}{t_3 - t_2} \tag{2.2.5}$$

which is about 0.53 of that of Eq. (2.2.2).

Instantaneous Rate of Change of the Amount of a Reactant and a Product

In chemical kinetics, the rate at any particular instant rather than the average rate over a time interval has much more practical application and importance. This rate is known as the instantaneous rate r_{ins} and is defined as

$$r_{\text{ins}} = \lim_{\Delta t \to 0}\left(-\frac{\Delta n_{\text{A}}}{\Delta t}\right) = -\frac{\mathrm{d}n_{\text{A}}}{\mathrm{d}t} \tag{2.2.6}$$

or

$$r_{\text{ins}} = \lim_{\Delta t \to 0}\left(\frac{\Delta n_{\text{B}}}{\Delta t}\right) = \frac{\mathrm{d}n_{\text{B}}}{\mathrm{d}t} \tag{2.2.7}$$

Hence, the instantaneous rate at a given time may be determined by finding out the slope of either reactant or product curve at the given time. For example, at time t_3, r_{ins} of disappearance of A as determined from Fig. 2.2.1 is given by

$$r_{\text{ins},t_3} = -\left(\frac{\mathrm{d}n_{\text{A}}}{\mathrm{d}t}\right)_{t_3} = -\frac{(n_{\text{A}})_4 - (n_{\text{A}})_5}{t_4 - t_5} \tag{2.2.8}$$

Illustration of A → 2B

Consider now the reaction

$$\text{A} \rightarrow 2\text{B}$$

where 1 mol of A on disappearing produces 2 mol of B, i.e. the amount of B will increase twice as fast as the decrease in amount of A. Hence, the quantity $\mathrm{d}n_{\text{B}}/\mathrm{d}t$ will be twice as large as $-\mathrm{d}n_{\text{A}}/\mathrm{d}t$. Obviously, we cannot write

$$-\frac{\mathrm{d}n_{\text{A}}}{\mathrm{d}t} = \frac{\mathrm{d}n_{\text{B}}}{\mathrm{d}t} \tag{2.2.9}$$

but write either as

$$-\frac{\mathrm{d}n_{\text{A}}}{\mathrm{d}t} = \frac{1}{2}\frac{\mathrm{d}n_{\text{B}}}{\mathrm{d}t} \tag{2.2.10}$$

or as

$$-2\frac{\mathrm{d}n_{\text{A}}}{\mathrm{d}t} = \frac{\mathrm{d}n_{\text{B}}}{\mathrm{d}t} \tag{2.2.11}$$

In Fig. 2.2.2 where the changes in amounts of A and B during the course of reaction are displayed, the above expressions may be verified. For example, for the indicated slope, we find that the slopes of A and B curves are $-0.5\ \text{mol s}^{-1}$ and $1.0\ \text{mol s}^{-1}$, respectively, and hence

$$-\frac{\mathrm{d}n_{\text{A}}}{\mathrm{d}t} = \frac{1}{2}\frac{\mathrm{d}n_{\text{B}}}{\mathrm{d}t} = 0.5\ \text{mol s}^{-1}$$

and

$$-2\frac{\mathrm{d}n_{\text{A}}}{\mathrm{d}t} = \frac{\mathrm{d}n_{\text{B}}}{\mathrm{d}t} = 1.0\ \text{mol s}^{-1}$$

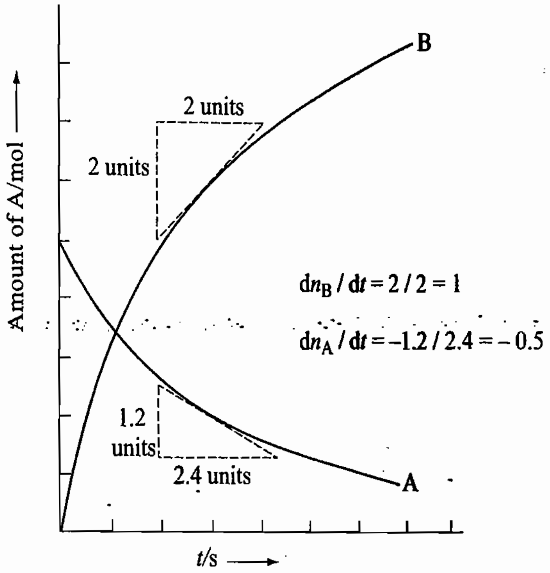


Fig. 2.2.2 The variation in the amounts of A and B with time for the reaction A → 2B

A Generalized Expression of Rate of Reaction

A chemical reaction may, in general, be represented as

$$0 = \sum_i \nu_i A_i \tag{2.2.12}$$

where ν_i has a positive value for a product and has a negative value for a reactant.

The change in the amount of a reactant or a product during the course of a reaction may be represented in terms of the extent of the reaction (ξ) defined as

$$n_t(A_i) = n_0(A_i) + \nu_i \xi \tag{2.2.13}$$

where $n_0(A_i)$ is the amount of A_i at $t = 0$. The unit of ξ is that of the amount of the substance, i.e. mol.

The rate of change of the amount of A_i during the course of a reaction is obtained by differentiating Eq. (2.2.13) with respect to time, such that

$$\frac{dn_t(A_i)}{dt} = \nu_i \frac{d\xi}{dt} \tag{2.2.14}$$

Thus, the change in extent of reaction with time is given as

$$\frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{dn_t(A_i)}{dt} \tag{2.2.15}$$

Note that ν_i as well as $dn_t(A_i)/dt$ have positive values for a product and have negative values for a reactant and thus the product of these two is always positive, i.e. the rate of change in extent of reaction is always a positive quantity.

If we write a reaction in a conventional form, such as

$$\nu_1 A_1 + \nu_2 A_2 = \nu_3 A_3 + \nu_4 A_4 \tag{2.2.16}$$

all the stoichiometric coefficients νs have positive values. If ξ is the extent of reaction at time t, we will have

Reaction:	$\nu_1 A_1$	+	$\nu_2 A_2$	=	$\nu_3 A_3$	+	$\nu_4 A_4$
Initial amount:	$n_0(A_1)$		$n_0(A_2)$		$n_0(A_3)$		$n_0(A_4)$
Amount at time t:	$n_0(A_1) - \nu_1 \xi$		$n_0(A_2) - \nu_2 \xi$		$n_0(A_3) + \nu_3 \xi$		$n_0(A_4) + \nu_4 \xi$

The disappearance of amounts of reactants and appearance of amounts of products will be given by

$$-\frac{\mathrm{d}n(\mathrm{A}_1)}{\mathrm{d}t} = -\frac{\mathrm{d}\{n_0(\mathrm{A}_1) - \nu_1\xi\}}{\mathrm{d}t} = \nu_1 \frac{\mathrm{d}\xi}{\mathrm{d}t}$$

$$-\frac{\mathrm{d}n(\mathrm{A}_2)}{\mathrm{d}t} = -\frac{\mathrm{d}\{n_0(\mathrm{A}_2) - \nu_2\xi\}}{\mathrm{d}t} = \nu_2 \frac{\mathrm{d}\xi}{\mathrm{d}t}$$

$$\frac{\mathrm{d}n(\mathrm{A}_3)}{\mathrm{d}t} = \frac{\mathrm{d}\{n_0(\mathrm{A}_3) + \nu_3\xi\}}{\mathrm{d}t} = \nu_3 \frac{\mathrm{d}\xi}{\mathrm{d}t}$$

$$\frac{\mathrm{d}n(\mathrm{A}_4)}{\mathrm{d}t} = \frac{\mathrm{d}\{n_0(\mathrm{A}_4) + \nu_4\xi\}}{\mathrm{d}t} = \nu_4 \frac{\mathrm{d}\xi}{\mathrm{d}t}$$

From the above expressions, it follows that

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = -\frac{1}{\nu_1}\frac{\mathrm{d}n(\mathrm{A}_1)}{\mathrm{d}t} = -\frac{1}{\nu_2}\frac{\mathrm{d}n(\mathrm{A}_2)}{\mathrm{d}t} = \frac{1}{\nu_3}\frac{\mathrm{d}n(\mathrm{A}_3)}{\mathrm{d}t} = \frac{1}{\nu_4}\frac{\mathrm{d}n(\mathrm{A}_4)}{\mathrm{d}t} \tag{2.2.17}$$

Defining Rate of Reaction

In view of the equality shown above, *the rate of reaction* is defined as *the rate of change of extent of the reaction.* It has the unit of mol s^{-1} and is represented by the symbol $\dot{\xi}$. It may be emphasized here that the rate of a reaction and rate of change of amount of a reactant or a product are two different things except when each of the involved stoichiometric coefficients is equal to unity. In other cases the rate of change of amount of a reactant or a product is to be divided by the corresponding stoichiometric coefficient to convert it into the rate of reaction. The above definition of rate of reaction is independent of the choice of reactant and product and is valid regardless of the conditions under which a reaction is carried out, e.g. it is valid for a reaction in which the volume varies with time or for a reaction involving two or more phases.

Rate of Reaction Divided by Volume

In chemical kinetics, it is more useful to use the term rate of reaction divided by any specified volume. This volume may be dependent or independent of time and may or may not be that of a single phase in which the reaction is taking place. For this, Eq. (2.2.15) becomes

$$r = \frac{\dot{\xi}}{V} = \frac{1}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{1}{V}\frac{1}{\nu_i}\frac{\mathrm{d}n_i}{\mathrm{d}t} \tag{2.2.18}$$

If the specified volume V is independent of time, then

$$r = \frac{\dot{\xi}}{V} = \frac{\mathrm{d}(\xi/V)}{\mathrm{d}t} = \frac{1}{\nu_i}\frac{\mathrm{d}(n_i/V)}{\mathrm{d}t} \tag{2.2.19}$$

If the specified volume V is such that

$$\frac{n_i}{V} = c_i$$

where c_i is the concentration of ith species, then

$$r = \frac{\dot{\xi}}{V} = \frac{\mathrm{d}(\xi/V)}{\mathrm{d}t} = \frac{1}{\nu_i}\frac{\mathrm{d}c_i}{\mathrm{d}t} \tag{2.2.20}$$

For the specific reaction shown in Eq. (2.2.16), we write the rate of reaction divided by constant volume as

$$r = \frac{1}{V}\left\{-\frac{1}{\nu_1}\frac{\mathrm{d}n(\mathrm{A}_1)}{\mathrm{d}t}\right\} = -\frac{1}{\nu_1}\frac{\mathrm{d}\{n(\mathrm{A}_1)/V\}}{\mathrm{d}t} = -\frac{1}{\nu_1}\frac{\mathrm{d}[\mathrm{A}_1]}{\mathrm{d}t}$$

$$r = \frac{1}{V}\left\{-\frac{1}{\nu_2}\frac{\mathrm{d}n(\mathrm{A}_2)}{\mathrm{d}t}\right\} = -\frac{1}{\nu_2}\frac{\mathrm{d}\{n(\mathrm{A}_2)/V\}}{\mathrm{d}t} = -\frac{1}{\nu_2}\frac{\mathrm{d}[\mathrm{A}_2]}{\mathrm{d}t}$$

$$r = \frac{1}{V}\left\{\frac{1}{\nu_3}\frac{\mathrm{d}n(\mathrm{A}_3)}{\mathrm{d}t}\right\} = \frac{1}{\nu_3}\frac{\mathrm{d}\{n(\mathrm{A}_3)/V\}}{\mathrm{d}t} = \frac{1}{\nu_3}\frac{\mathrm{d}[\mathrm{A}_3]}{\mathrm{d}t}$$

$$r = \frac{1}{V}\left\{\frac{1}{\nu_4}\frac{\mathrm{d}n(\mathrm{A}_4)}{\mathrm{d}t}\right\} = \frac{1}{\nu_4}\frac{\mathrm{d}\{n(\mathrm{A}_4)/V\}}{\mathrm{d}t} = \frac{1}{\nu_4}\frac{\mathrm{d}[\mathrm{A}_4]}{\mathrm{d}t}$$

The extent of reaction divided by constant volume is commonly abbreviated as x. Thus

$$r = \frac{\dot{\xi}}{V} = \frac{1}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{\mathrm{d}(\xi/V)}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t}$$

2.3 ORDER OF A REACTION

Law of Mass Action

The speed of a chemical reaction, in general, depends on the concentrations of reacting species of the reaction. An early generalization in this regard is due to Gulberg and Waage. This generalization is known as *law of mass action* and is stated as follows.

The rate of a reaction is proportional to the product of effective concentrations of the reacting species, each raised to a power which is equal to the corresponding stoichiometric number of the substance in the chemical equation.

Thus, for a general reaction

$$\nu_1\mathrm{A}_1 + \nu_2\mathrm{A}_2 \rightleftharpoons \nu_3\mathrm{A}_3 + \nu_4\mathrm{A}_4 \qquad (2.3.1)$$

we have

$$r \propto [\mathrm{A}_1]^{\nu_1}\,[\mathrm{A}_2]^{\nu_2}\,\ldots$$

or

$$r = k\,[\mathrm{A}_1]^{\nu_1}\,[\mathrm{A}_2]^{\nu_2}\,\ldots \qquad (2.3.2)$$

where k is a constant of proportionality

Defining Order of a Reaction

If the rate of a reaction divided by volume is determined experimentally, it is found that Eq. (2.3.2) is not always applicable. However, the experimental results can be fitted to satisfy a relation of the type of Eq. (2.3.2) where the exponents may or may not be equal to the respective stoichiometric coefficients. In general, we may write the rate as

$$r = k[\mathrm{A}_1]^a\,[\mathrm{A}_2]^b\,\ldots \qquad (2.3.3)$$

where the dimensionless exponents $a, b, \ldots$ may or may not be equal to $\nu_1, \nu_2, \ldots$, respectively. The constants $a, b, \ldots$ may have positive or negative integral values, fractional values or zero values. The constant a is known as the partial order of the reaction with respect to A, b as the partial order of the reaction with respect to B, and so on. The sum $a + b + \cdots$ is known as the overall order of the reaction. If $a + b + \cdots = 1$, the reaction is said to be of first-order; if $a + b + \cdots = 2$, the reaction is of second-order, and so on. The dependence of reaction rate on concentration is of great use as it helps proposing the mechanism of a reaction.

The constant k which appears in Eq. (2.3.3) is known as the *rate constant*, since it is numerically equal to the rate the reaction would have if all concentrations were set equal to unity. Each reaction is characterized by its own reaction rate constant. From Eq. (2.3.3), we find that the unit of k is $(\text{mol dm}^{-3})^n\ \text{s}^{-1}$ where $n = 1 - (a + b + \cdots)$.

The expression of Eq. (2.3.3) which relates the rate of reaction with the concentrations of reacting species is known as the *differential rate law*.

Comment about Rate Law

It may be emphasized once again here that *the rate equation with its rate constant and order of various reacting species is an experimental finding, and cannot be predicted from the stoichiometry of the balanced-reaction equation.*

Although a great many reactions obey Eq. (2.3.3), there are numerous other whose rate expressions are not of such simple form. A few such reactions are listed in Table 2.3.1.

Table 2.3.1 Examples of Reactions Obeying Complicated Rate Laws

Overall Reaction	*Experimentally Determined Rate Law*
$H_2 + I_2 = 2HI$	$\frac{1}{2}\frac{d[HI]}{dt} = k_1[H_2][I_2] - k_{-1}[HI]^2$
$H_2 + Br_2 = 2HBr$	$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}$
$OCl^- + I^- \xrightleftharpoons{OH^-} OI^- + Cl^-$	$\frac{d[Cl^-]}{dt} = \frac{k[OCl^-][I^-]}{[OH^-]}$
$CH_3COCH_3 + I_2 \xrightleftharpoons{H^+} CH_3COCH_2I + HI$	$-\frac{d[I_2]}{dt} = k[CH_3COCH_3][H^+]$

Table 2.3.1 reveals the following facts.

- The rate law may not bear a simple relationship to the stoichiometric equation.
- The rate law may not depend on the concentrations of every reactant or product of the reaction.
- The rate law may depend on the concentrations of species (e.g. catalysts) which do not appear in the equation for the overall reaction.

These facts clearly indicate that the rate equation cannot be predicted from the form of the stoichiometric equation for the overall reaction. Hence, the rate equation must be determined experimentally. In some cases, the order of the reaction is meaningless. For example, for the hydrogen-bromine reaction, the reaction is of first-order with respect to hydrogen gas but it would be impossible to assign the order with respect to bromine and to hydrogen bromide. Thus, the concept of order of reaction has no meaning if a rate law does not have the form as given in Eq. (2.3.3).

In the reaction between hypochloride and iodide ions, though OH^- does not appear in the overall reaction, yet it appears in the denominator of the rate law. This indicates that the OH^- acts as an inhibitor. Similarly, the reaction between acetone and iodine does not involve H^+ in the overall reaction, but it appears in the numerator of the rate law. This shows that H^+ acts as an accelerator or a catalyst.

Comment on Rate Constant

Since the expression of rate *r* in terms of rate of change of concentration of a reactant or product depends on the way the chemical equation is formulated, it follows that the value of *k* in the differential rate law also depends on the way the chemical equation is formulated. For example, the decomposition of N_2O_5 is experimentally found to be first order with respect to N_2O_5. Hence, for two ways of writing the chemical equations, we will have

$$2N_2O_5 \rightarrow 4NO_2 + O_2 \qquad r = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2 \qquad r' = -\frac{d[N_2O_5]}{dt} = k'[N_2O_5]$$

Since the rate at which a reactant consumed or product formed does not depend upon the way the chemical equation is formulated, it follows that

$$2r = r' \quad \text{and} \quad 2k = k'$$

Note that the rate of reaction refers to a time-independent stoichiometry, i.e. for a specified chemical equation and, therefore, it must be stated along with rate of reaction.

2.4 ELEMENTARY REACTION AND ITS MOLECULARITY

Most chemical reactions proceed through a series of elementary reactions. An elementary reaction is one which is proposed to take place in a single step. These elementary steps are classified according to the number of molecules which they involve. A process in which only one molecule is involved is known as unimolecular process. One involving two molecules is called bimolecular and so on. It is well known that in ~~elementary~~ reactions the products ~~are~~ formed when ~~the~~ reactant molecules come close and collide together at one and the same time. Since the collisions in which more than three particles come together simultaneously are very rare, the elementary process with molecularity greater than three are not known.

If a reaction involves more than one step, the overall reaction is obtained by adding these elementary steps. In such a case, it is wrong to decide the molecularity of the overall reaction on the basis of its stoichiometric and rate equation.

It was stated earlier that the order of a reaction, in general, cannot be predicted from the stoichiometry of the overall reaction. However, the order of an elementary step can be predicted from its molecularity. In fact, the order of an elementary step is always equal to its molecularity. This follows from the following analysis.

Unimolecular Elementary Reaction

In this process, a single activated molecule rearranges or decomposes independently of the others. It is obvious that the number of activated molecules that decompose in a given time interval will depend upon its total number; larger the number or concentration of molecules, larger the number of molecules that decompose to give product. Thus, for the unimolecular reaction.

$$A \rightarrow B$$

the rate of reaction will be given by

$$r = -\frac{d[A]}{dt} = k\,[A]$$

Hence, the unimolecular elementary process is necessarily a first-order process.

Bimolecular Elementary Reaction

Let the elementary process be represented as

$$A + B \rightarrow \text{products}$$

For a molecule of A to react with a molecule of B, the molecule A has to come close to B and collide with it. The rate at which collisions between A and B molecules occur is directly proportional to the concentrations of A and B. Thus, the rate of the reaction will be given as

$$r = k\,[A]\,[B]$$

which is the expression of the second-order process. Hence, a bimolecular elementary process is necessarily a second-order process.

The above arguments can be extended to a termolecular reaction. Hence a termolecular elementary process will follow third-order rate law.

It may be emphasized here that if the order of a reaction is known, it is not possible to predict its molecularity. This follows immediately from the fact that the order of a reaction is referred to the overall reaction whereas the molecularity is referred to an elementary step. A given overall reaction may involve more than one elementary step of different molecularities. For example, the decomposition of N_2O_5 is a first-order reaction, but it proceeds through the following four elementary processes.

$$N_2O_5 + N_2O_5 \rightarrow N_2O_5^{*} + N_2O_5$$

$$N_2O_5^{*} \rightarrow NO_2 + NO_3$$

$$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$$

$$NO + NO_3 \rightarrow 2NO_2$$

Here $N_2O_5^{*}$ stands for an energized molecule capable of dissociating.

Sometimes, a reaction follows a complicated rate expression. For example, the complex nature of the rate expression of $H_2(g)$ and $Br_2(g)$ shown in Table 2.3.1 is due to the fact that the said reaction involves more than one elementary step and the rate of the overall reaction is obtained by combining the rates of all these individual elementary reactions, which of course, follow the simple expressions as given by Eq. (2.3.3).

2.5 THE INTEGRATED RATE LAWS

The differential rate law shows how the rate of a reaction depends on the concentrations of reacting species. It is also worthwhile to know how the concentrations of these species change with time. This information can be obtained by integrating the differential rate law. In this section, we derive the integrated rate laws for the reactions having zero-, first-, second-, and third-order, respectively, and also derive their main characteristics.

ZERO-ORDER REACTIONS

Differential Rate Law

In zero-order reaction, the rate of reaction

$$\nu_1 A \rightarrow \text{product} \tag{2.5.1}$$

will be given by

$$r = -\frac{1}{\nu_1}\frac{d[A]}{dt} = k_0\,[A]^0 = k_0 \tag{2.5.2}$$

that is, the reaction proceeds at a constant rate and does not depend on the concentration of A.

Integrated Rate Law

Let $[A]_0$ be the concentration of A at $t = 0$ and $[A]_t$ be the concentration at time t. Equation (2.5.2) may be integrated within these limits. Thus, we have

$$\int_{[A]_0}^{[A]_t} \mathrm{d}[A] = -\nu_1 k_0 \int_{t=0}^{t=t} \mathrm{d}t$$

or $$[A]_0 - [A]_t = \nu_1 k_0 t \tag{2.5.3a}$$

From Eq. (2.5.1), it is obvious that

$$[A]_t = [A]_0 - \nu_1 x$$

where x is the extent of reaction divided by volume that occurs at time t. Substitution of the above relation in Eq. (2.5.3a) gives

$$[A]_0 - ([A]_0 - \nu_1 x) = \nu_1 k_0 t$$

or $$x = k_0 t \tag{2.5.3b}$$

The unit of k_0 is mol dm^{-3} s^{-1}.

Characteristics of Zero-Order Reactions

From Eq. (2.5.3), it is obvious that the concentration of the reactant decreases whereas that of the product increases linearly with time. If a plot is made between x and t, one would get a straight line passing through the origin (Fig. 2.5.3). Equation (2.5.3) can be used to determine the time required for the reaction to be completed, i.e. time at which $[A]_t$ is zero. Substituting the latter in Eq. (2.5.3a), we have

$$t_{\text{completion}} = \frac{[A]_0}{\nu_1 k_0}$$

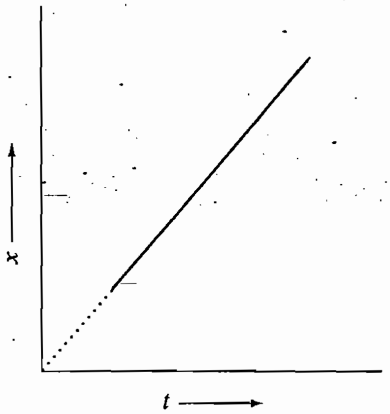


Fig. 2.5.1 Variation of x versus t for a reaction exhibiting zero-order kinetics

Examples of Zero-Order Reactions

Although reactions which have an overall order of zero are rare, it is not unusual to find the reactions in which order of reaction with respect to one of the reactants is zero. One of the well-known examples of this type is the enzyme-catalyzed reactions, which we write as

$$\text{substrate} \xrightarrow{\text{enzyme}} \text{product}$$

The rate expression follows the relation

$$r = k\,[\text{enzyme}]^1\,[\text{substrate}]^0$$

that is, the reaction is first-order with respect to the enzyme concentration and zero-order with respect to the substrate concentration.

The decomposition of various gases on the surface of metallic catalysts, such as decomposition of HI on gold surface also exhibits zero-order kinetics.

FIRST-ORDER REACTIONS

Differential Rate Law

In first-order reactions, the rate expression depends on the concentration of one species only. Thus, if the reaction

$$\nu_1 \mathrm{A} + \nu_2 \mathrm{B} \rightarrow \text{products}$$

is first-order with respect to A and zero-order with respect to B, we have

$$r = -\frac{1}{\nu_1}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_1\,[\mathrm{A}]$$

or

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{A}} = -\,\nu_1 k_1 \mathrm{d}t \tag{2.5.4}$$

Integrated Rate Law

Integrating Eq. (2.5.4) within the limits, we have

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -\,\nu_1 k_1 \int_0^t \mathrm{d}t$$

or

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}\right) = \nu_1 k_1 t \tag{2.5.5a}$$

or

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - \nu_1 x}\right) = \nu_1 k_1 t \tag{2.5.5b}$$

For most of first-order reactions, $\nu_1 = 1$ and thus Eq. (2.5.5b) is given as

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x}\right) = k_1 t \tag{2.5.6}$$

From Eq. (2.5.6), it follows that

$$\ln\left(\frac{[\mathrm{A}]_0 - x_{t_1}}{[\mathrm{A}]_0 - x_{t_2}}\right) = k_1(t_2 - t_1) \tag{2.5.7}$$

Since the left side of Eq. (2.5.6) or (2.5.7) is a pure number, it follows that unit of k_1 is s^{-1}.

Characteristics of First-Order Reactions

Equation (2.5.6) may be written as

$$\ln\left(\frac{[\mathrm{A}]_0}{c^\circ}\right) - \ln\left(\frac{[\mathrm{A}]_0 - x}{c^\circ}\right) = k_1 t$$

or

$$\ln\left(\frac{[\mathrm{A}]_0 - x}{c^\circ}\right) = \log\left(\frac{[\mathrm{A}]_0}{c^\circ}\right) - \frac{k_1}{2.303}\,t \tag{2.5.8}$$

where c° is the standard unit concentration.

If a plot is made between log $\{([A]_0 - x)/c^{\circ}\}$ and t, one would get a straight line of slope equal to $-k_1/2.303$ (Fig. 2.5.2).

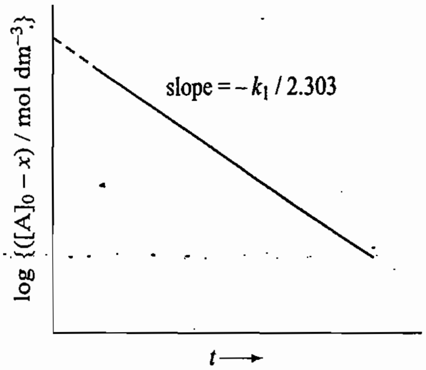


Fig. 2.5.2 Variation of log $\{([A]_0 - x)/c^{\circ}\}$ with time for a reaction exhibiting first-order kinetics

Equation (2.5.6) may also be written as

$$[A]_t = [A]_0 \exp(-k_1 t) \tag{2.5.9}$$

Equation (2.5.9), which is known as *Wilhelmy's equation*, indicates that the concentration of A decreases exponentially with time. The decrease is such that the time required for a definite fraction of the reaction (i.e. $[A]_t/[A]_0$ is constant) to occur is independent of the initial concentration of the reactant.

Half-Life

Half-life $t_{\frac{1}{2}}$ of a reaction is the time required for the concentration of reactant to decrease by half, i.e.

$$[A]_{t_{\frac{1}{2}}} = \frac{1}{2}[A]_0$$

Substituting the above relation in Eq. (2.5.6), we get

$$\ln\left(\frac{[A]_0}{[A]_0/2}\right) = k_1 t_{\frac{1}{2}}$$

or $\quad 2.303 \log 2 = k_1 t_{\frac{1}{2}}$

or $$t_{\frac{1}{2}} = \frac{2.303 \log 2}{k_1} = \frac{2.303 \times 0.301}{k_1} = \frac{0.693}{k_1} \tag{2.5.10}$$

that is, $t_{\frac{1}{2}}$ is independent of initial concentration.

Figure 2.5.3 displays the typical variation of concentration of reactant exhibiting first-order kinetics. It may be noted that though the major portion of the first-order kinetics may be over in a finite time, but the reaction will never cease as the concentration of reactant will be zero only at infinite time.

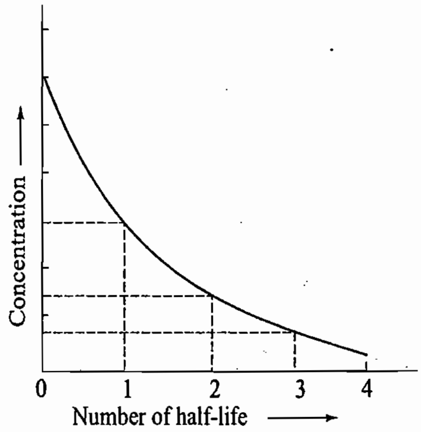


Fig. 2.5.3 Variation of concentration of reactant exhibiting first-order kinetics

Examples of First-Order Reactions

A large number of reactions exhibiting first-order kinetics are known. A few examples are listed below.

Decomposition of di-tert-butyl peroxide:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2\ CH_3COCH_3 + C_2H_6$$

Decomposition of dinitrogenpentoxide:

$$N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

Decomposition of azoisopropane:

$$(CH_3)_2CHN{=}NCH(CH_3)_2 \rightarrow N_2 + C_6H_{14}$$

Decomposition of thionyl chloride:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Decomposition of 2,4,6-trinitrobenzoic acid:

$$\text{2,4,6-trinitrobenzoic acid} \rightarrow \text{Trinitrobenzene} + CO_2(g)$$

Decomposition of hydrogen peroxide:

$$H_2O_2(aq) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

All radioactive decays:

There are reactions in which more than one species is involved in the rate determining step, but the order of the reaction is one. Such reactions are known as *pseudo-unimolecular reactions* and they involve solvent molecule or a catalyst as one of the reacting species. Examples of this type of reactions are:

Acid hydrolysis of an ester:

$$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{H^+} CH_3COOH + C_2H_5OH$$

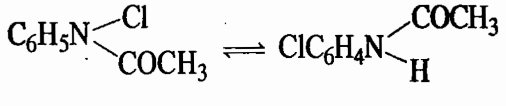
Inversion of cane sugar:

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightleftharpoons{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Decomposition of benzenediazonium chloride:

$$C_6H_5N{=}NCl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

Isomeric change of N-chloroacetanillide to p-chloroacetanilide:



$$C_6H_5N\begin{matrix}\diagup Cl\\ \diagdown COCH_3\end{matrix} \rightleftharpoons ClC_6H_4N\begin{matrix}\diagup COCH_3\\ \diagdown H\end{matrix}$$

Alternative Forms of Rate Equation of First-Order Reaction

It is evident from Eqs (2.5.6) and (2.5.7) that to determine the rate constant for a first-order reaction, it is only necessary to determine the ratio of the concentrations at two times. Quantities proportional to the concentration terms may be substituted in these equations, since the proportionality constants cancel. We describe below a few typical cases where concentration terms are replaced by other easily measurable quantities.

Concentrations Replaced in Terms of Pressure

In a reaction, if there occurs a change in the number of gaseous molecules, then the concentration terms in Eq. (2.5.6) may be replaced in terms of pressures provided the volume of the system is held constant.

Let Δv_g be the change in the number of gaseous molecules in going from reactants to products and let p_0 and p_t be the pressure of the system at $t = 0$ and $t = t$, respectively. If at time t, the concentration of A decreases by x, we will have

$$p_0 \propto [\mathrm{A}]_0 \quad \text{and} \quad p_t \propto [\mathrm{A}]_0 + (\Delta v_g)x$$

Hence $\quad [\mathrm{A}]_0 \propto p_0 \quad$ and $\quad x \propto (p_t - p_0)/\Delta v_g$

Thus $\quad [\mathrm{A}]_t = [\mathrm{A}]_0 - x \propto p_0 - \dfrac{p_t - p_0}{\Delta v_g} = \dfrac{(\Delta v_g + 1)p_0 - p_t}{\Delta v_g}$

With these Eq. (2.5.6) becomes

$$\ln\left(\frac{p_0}{[(\Delta v_g + 1)p_0 - p_t]/\Delta v_g}\right) = kt$$

or

$$\ln\left(\frac{\Delta v_g\, p_0}{(\Delta v_g + 1)p_0 - p_t}\right) = kt \qquad (2.5.11)$$

If p_∞ is the pressure of the system at infinite time (where the reaction is assumed to be completed), we will have

$$p_\infty = (\Delta v_g + 1)p_0 .$$

Hence, Eq. (2.5.11) may be written as

$$\ln\left(\frac{p_\infty - p_0}{p_\infty - p_t}\right) = kt \qquad (2.5.12)$$

Amounts Replaced in Terms of Volumes

Equation (2.5.6) if derived in terms of amounts of reactant will take the form

$$\ln\frac{(n_\mathrm{A})_0}{(n_\mathrm{A})_t} = kt \qquad (2.5.13)$$

For a constant pressure, we may write

$$V_0 \propto (n_\mathrm{A})_0 \quad \text{and} \quad V_t \propto (n_\mathrm{A})_0 + (\Delta v_g)\,\xi$$

Hence $\quad \xi \propto (V_t - V_0)/\Delta v_g$

Now $\quad (n_\mathrm{A})_0 \propto V_0$

$$(n_\mathrm{A})_t = (n_\mathrm{A})_0 - \xi \propto V_0 - \frac{V_t - V_0}{\Delta v_g} = \frac{(\Delta v_g + 1)V_0 - V_t}{\Delta v_g}$$

Hence, Eq. (2.5.13) becomes

$$\ln\left(\frac{V_0}{[(\Delta v_g + 1)V_0 - V_t]/\Delta v_g}\right) = kt$$

or

$$\ln\left(\frac{(\Delta v_g)V_0}{(\Delta v_g + 1)V_0 - V_t}\right) = kt \qquad (2.5.14)$$

If V_∞ is the volume of the system at infinite time (where the reaction is assumed to be completed), we will have

$$V_\infty = (\Delta v_g + 1)\,V_0$$

Hence, Eq. (2.5.14) may be written as

$$\ln\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right) = kt \qquad (2.5.15)$$

For a reaction in which reactant is present in the condensed form (i.e. liquid or solid) and products involve one or more gaseous species, we will have $V_0 \ll V_\infty$. Hence, Eq. (2.5.15) will modify to

$$\ln\left(\frac{V_\infty}{V_\infty - V_t}\right) = kt$$

Concentration Replaced in Terms of Volume of Titrant

Reactions such as the acid hydrolysis of an ester (e.g. reaction vii) can be studied by replacing the concentration of ester in terms of volume of alkali solution required to neutralize the produced acid. Let V_t and V_∞ be the respective volumes of alkali solution required to neutralize the acid produced at time t and at the end when the reaction has gone to completion. It is obvious that

$$[\text{Ester}]_0 \propto V_\infty$$

$$[\text{Ester}]_t \propto V_\infty - V_t$$

Hence, Eq. (2.5.6) in the present case becomes

$$\ln\left(\frac{V_\infty}{V_\infty - V_t}\right) = kt$$

$$\text{or} \qquad \log\left(\frac{V_\infty - V_t}{V^\circ}\right) = \log\left(\frac{V_\infty}{V^\circ}\right) - \frac{k}{2.303}t \qquad (2.5.16)$$

where V° is the standard unit volume. A plot of $\log\{(V_\infty - V_t)/V^\circ\}$ versus t will produce a straight line of slope equal to $-k/2.303$.

Comment on Acid-Catalyzed Hydrolysis of an Ester

It is worthwhile to mention here that the value of rate constant k of acid-catalyzed hydrolysis of an ester is found to be directly proportional to the concentration of H^+ ion (i.e. catalyst) in the solution. Thus, the rate of hydrolysis besides depending on the ester concentration, also depends on the concentration of H^+ ion. Truly speaking, the acid hydrolysis of an ester is a third-order reaction which follows the differential rate law given below.

$$\frac{dx}{dt} = k'\,[\text{ester}]\,[H^+]\,[H_2O] \qquad (2.5.17)$$

Since, the concentration of H^+ ion in the solution remains constant and H_2O is present in large amount, Eq. (2.5.17) is reduced to

$$\frac{dx}{dt} = k\,[\text{ester}] \qquad (2.5.18)$$

In fact, it is the constant k of Eq. (2.5.18) that is determined experimentally. Hence, the obtained value of reaction rate constant k is given by

$$k = k'\,[H^+]\,[H_2O] \qquad (2.5.19)$$

where k' is the actual reaction rate constant of the acid hydrolysis of an ester. Equation (2.5.19) has been utilized in comparing the acid strengths of two different acids of equal normalities (acids having the same amount of total hydrogen ions).

For example, if the hydrolysis of the same concentration of ester is carried out separately with equal normalities of HCl and H_2SO_4, then it follows that

$$\frac{[H^+]_{HCl}}{[H^+]_{H_2SO_4}} = \frac{k_{HCl}}{k_{H_2SO_4}} \tag{2.5.20}$$

Experimentally, $k_{HCl}/k_{H_2SO_4}$ is found to be greater than one indicating that the hydrochloric acid is a stronger acid than the sulphuric acid. This fact can be explained on the basis that in dilute solutions, hydrochloric acid is completely ionized whereas sulphuric acid dissociates in steps; the first dissociation is complete and the second one incomplete, i.e.

$$HCl \longrightarrow H^+ + Cl^-$$

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

Equation (2.5.19) has also been utilized in determining the concentration of H^+ ion in an acid solution, say that of hydrochloric acid. Acid hydrolysis of the same quantity of ester is repeated with different known concentrations of hydrochloric acid solutions. The experiment is repeated with the given solution of hydrochloric acid. A graph between k and the concentration of hydrochloric acid is drawn and from the straight-line plot, the concentration of the given solution of hydrochloric acid is determined.

Concentration Replaced in Terms of Rotation of the Polarized Light

Inversion of cane sugar can be followed by measuring the rotation of the angle of polarization of light during the experiment, since cane sugar is dextrorotatory, while the mixture of glucose and fructose is leavo-rotatory. Let θ_t and θ_∞ be the respective angles of rotation at time t and at the end when the reaction has gone to completion. It is obvious that

$$[\text{Cane sugar}]_0 \propto \theta_\infty$$

$$[\text{Cane sugar}]_t \propto \theta_\infty - \theta_t$$

Hence, Eq. (2.5.6) in this case becomes

$$\ln\left(\frac{\theta_\infty}{\theta_\infty - \theta_t}\right) = kt$$

or
$$\log\left(\frac{\theta_\infty - \theta_t}{\theta^\circ}\right) = \log\left(\frac{\theta_\infty}{\theta^\circ}\right) - \frac{k}{2.303}t \tag{2.5.21}$$

where θ° represent the unit of measuring angle . A graph between log $\{(\theta_\infty - \theta_t)/\theta^\circ\}$ and t would yield a straight line of slope $-k/2.303$.

Problem 2.5.1

The gaseous reaction

$$\nu_1 A(g) \rightarrow \nu_2 B(g)$$

is first order with respect to A. It is studied at a constant pressure with a_0 as the initial amount of A. Show that the volume of the system and the concentration of A at time t are given by the expressions

$$V = V_0\left[\left(\frac{\nu_2}{\nu_1}\right)-\left(\frac{\nu_2}{\nu_1}-1\right)\exp(-\nu_1 kt)\right]$$

and $$[\text{A}]_t = [\text{A}]_0\left[\frac{\exp(-\nu_1 kt)}{(\nu_2/\nu_1)-\{(\nu_2/\nu_1)-1\}\exp(-\nu_1 kt)}\right]$$

where V_0 is the volume of the system at $t = 0$. Assume ideal behaviour for the gases. Derive the expressions for V and [A] for the systems where $\nu_1 = \nu_2 = 1$ and $\nu_1 = 1$ and $\nu_2 = 2$.

Solution Let ξ be the extent of reaction at time t. We will have

$$\begin{array}{cc} \nu_1\text{A} \rightarrow & \nu_2\text{B} \\ a_0 - \nu_1\xi & \nu_2\xi \end{array}$$

Total amount of the substances at time $t = a_0 + (\nu_2 - \nu_1)\,\xi$

The kinetic expression of the reaction is

$$\frac{d\xi}{dt} = k(a_0 - \nu_1\xi) \qquad (2.5.22)$$

Since the gases are assumed to be ideal, we will have

$$pV_0 = a_0RT \qquad (2.5.23)$$

and $$\begin{aligned} pV &= [a_0 + (\nu_2 - \nu_1)\,\xi]\,RT \\ &= pV_0 + (\nu_2 - \nu_1)\,\xi\,RT \end{aligned} \qquad (2.5.24)$$

Hence, $$\xi = \frac{p(V - V_0)}{(\nu_2 - \nu_1)RT} \qquad (2.5.25)$$

and $$d\xi = \frac{p}{(\nu_2 - \nu_1)RT}\,dV \qquad (2.5.26)$$

Substituting Eqs (2.5.23), (2.5.25) and (2.5.26) in Eq. (2.5.22), we get

$$\frac{p}{(\nu_2 - \nu_1)RT}\frac{dV}{dt} = k\left[\frac{pV_0}{RT} - \nu_1\frac{p(V - V_0)}{(\nu_2 - \nu_1)RT}\right]$$

or $$\frac{dV}{dt} = k(\nu_2V_0 - \nu_1V)$$

or $$\frac{dV}{\nu_2V_0 - \nu_1V} = k\,dt$$

Integrating within the limits, we get

$$\int_{V_0}^{V}\frac{dV}{\nu_2V_0 - \nu_1V} = k\int_0^t dt$$

or $$\ln\frac{\nu_2V_0 - \nu_1V}{V_0(\nu_2 - \nu_1)} = -\nu_1kt$$

i.e. $$V = V_0\left[\left(\frac{\nu_2}{\nu_1}\right)-\left(\frac{\nu_2}{\nu_1}-1\right)\exp(-\nu_1 kt)\right]$$

The variation of amount A with time can be determined by integrating Eq. (2.5.22), such that

$$\int_0^\xi \frac{d\xi}{a_0 - \nu_1\xi} = k\int_0^t dt$$

or $$\ln \frac{a_0 - \nu_1\xi}{a_0} = -\,\nu_1 kt$$

i.e. $$a_0 - \nu_1\xi = a_0 \exp(-\nu_1 kt)$$

The variation of the concentration of A will be given by

$$\left(\frac{a_0 - \nu_1\xi}{V}\right)_t = \frac{a_0 \exp(-\nu_1 kt)}{V_0[(\nu_2/\nu_1) - \{(\nu_2/\nu_1) - 1\}\exp(-\nu_1 kt)]}$$

or $$[\mathrm{A}]_t = [\mathrm{A}]_0 \left[\frac{\exp(-\nu_1 kt)}{(\nu_2/\nu_1) - \{(\nu_2/\nu_1) - 1\}\exp(-\nu_1 kt)}\right]$$

For a case where $\nu_1 = \nu_2 = 1$, we get

$$V = V_0$$

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \exp(-kt)$$

For $\nu_1 = 1$ and $\nu_2 = 2$, we get

$$V = V_0\,[2 - \exp(-kt)]$$

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \left[\frac{\exp(-kt)}{2 - \exp(-kt)}\right]$$

The factor $\exp(-kt)/\{2 - \exp(-kt)\}$ is smaller than $\exp(-kt)$ as the value of $\exp(-kt)$ is always less than one. This means that at constant p condition, the concentration of A decreases more rapidly as compared to that in the constant volume condition. This is due to the fact that the decrease in the concentration of A in the former is due to two factors, viz. reaction in progress and increase in volume, whereas in the latter it is only due to the reaction in progress.

SECOND-ORDER REACTIONS

In second-order reactions, the rate expression depends on the two concentration terms. These concentration terms may refer to either the same species or different species. Thus, two cases may be distinguished. These are:

(i) *Both the concentration terms referred to the same species* The general expression for the reaction is

$$\nu\mathrm{A} \rightarrow \text{products}$$

The stoichiometric coefficient ν in most of cases may be made equal to 1.

(ii) *The concentration terms referred to the different species* The general expression for the reaction is

$$\nu_1\mathrm{A} + \nu_2\mathrm{B} \rightarrow \text{products}$$

In most common cases, the coefficients ν_1 and ν_2 are equal to unity.

The integrated rate equations for the above two cases can be derived as follows.

Rate Equation for $\nu A \rightarrow$ products

The reaction is

$$\nu \mathrm{A} \rightarrow \text{products}$$

The differential rate law is

$$-\frac{1}{\nu}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_2\,[\mathrm{A}]^2 \tag{2.5.27}$$

Let x be the extent of reaction divided by volume at time t. We will have

$$[\mathrm{A}] = [\mathrm{A}]_0 - \nu x \tag{2.5.28}$$

Substituting Eq. (2.5.28) in Eq. (2.5.27), we have

$$-\frac{1}{\nu}\frac{\mathrm{d}([\mathrm{A}]_0 - \nu x)}{\mathrm{d}t} = k_2\,([\mathrm{A}]_0 - \nu x)^2 \tag{2.5.29}$$

or $$\frac{\mathrm{d}x}{\mathrm{d}t} = k_2\,([\mathrm{A}]_0 - \nu x)^2$$

or $$\frac{\mathrm{d}x}{([\mathrm{A}]_0 - \nu x)^2} = k_2\,\mathrm{d}t$$

Integrating the above expression, we have

$$\int_0^x \frac{\mathrm{d}x}{([\mathrm{A}]_0 - \nu x)^2} = k_2 \int_0^t \mathrm{d}t$$

i.e. $$\frac{1}{\nu}\left(\frac{1}{[\mathrm{A}]_0 - \nu x} - \frac{1}{[\mathrm{A}]_0}\right) = k_2 t \tag{2.5.30}$$

The unit of k_2 is $\mathrm{mol^{-1}\ dm^3\ s^{-1}}$. Since $\nu = 1$ for most of reactions, Eq. (2.5.30) reduces to

$$\frac{1}{[\mathrm{A}]_0 - x} - \frac{1}{[\mathrm{A}]_0} = k_2 t \tag{2.5.31}$$

Rate Equation for $\nu_1 A + \nu_2 B \rightarrow$ products

The reaction is

$$\nu_1 \mathrm{A} + \nu_2 \mathrm{B} \rightarrow \text{products}$$

The differential rate law is

$$-\frac{1}{\nu_1}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_2\,[\mathrm{A}]\,[\mathrm{B}] \tag{2.5.32}$$

Let x be the extent of reaction divided by volume at time t. We will have

$$\left.\begin{aligned}[\mathrm{A}] &= [\mathrm{A}]_0 - \nu_1 x\\ [\mathrm{B}] &= [\mathrm{B}]_0 - \nu_2 x\end{aligned}\right\} \tag{2.5.33}$$

Substituting Eqs (2.5.33) in Eq. (2.5.32), we get

$$-\frac{1}{\nu_1}\frac{\mathrm{d}([\mathrm{A}]_0 - \nu_1 x)}{\mathrm{d}t} = k_2\,([\mathrm{A}]_0 - \nu_1 x)\,([\mathrm{B}]_0 - \nu_2 x)$$

or $$\frac{\mathrm{d}x}{\mathrm{d}t} = k_2\,([\mathrm{A}]_0 - \nu_1 x)\,([\mathrm{B}]_0 - \nu_2 x)$$

or $$\frac{\mathrm{d}x}{([\mathrm{A}]_0 - \nu_1 x)\,([\mathrm{B}]_0 - \nu_2 x)} = k_2\,\mathrm{d}t$$

or
$$\frac{1}{\nu_1[\mathrm{B}]_0-\nu_2[\mathrm{A}]_0}\left[\frac{\nu_1}{[\mathrm{A}]_0-\nu_1x}-\frac{\nu_2}{[\mathrm{B}]_0-\nu_2x}\right]\mathrm{d}x = k_2\,\mathrm{d}t$$

Integrating the above expression, we have

$$\frac{1}{\nu_1[\mathrm{B}]_0-\nu_2[\mathrm{A}]_0}\left[\int_0^x\frac{\nu_1\mathrm{d}x}{[\mathrm{A}]_0-\nu_1x}-\int_0^x\frac{\nu_2\mathrm{d}x}{[\mathrm{B}]_0-\nu_2x}\right]=k_2\int_0^t\mathrm{d}t$$

$$\frac{1}{\nu_1[\mathrm{B}]_0-\nu_2[\mathrm{A}]_0}\left[\ln\left(\frac{[\mathrm{B}]_0-\nu_2x}{[\mathrm{A}]_0-\nu_1x}\right)+\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{B}]_0}\right)\right]=k_2\,t$$

or
$$\log\left(\frac{[\mathrm{B}]_0-\nu_2x}{[\mathrm{A}]_0-\nu_1x}\right)=\log\left(\frac{[\mathrm{B}]_0}{[\mathrm{A}]_0}\right)+\left(\frac{(\nu_1[\mathrm{B}]_0-\nu_2[\mathrm{A}]_0)}{2.303}\right)k_2t \qquad (2.5.34)$$

Since $\nu_1 = \nu_2 = 1$ for most of reactions, Eq. (2.5.34) reduces to

$$\log\left(\frac{[\mathrm{B}]_0-x}{[\mathrm{A}]_0-x}\right)=\log\left(\frac{[\mathrm{B}]_0}{[\mathrm{A}]_0}\right)+\left(\frac{[\mathrm{B}]_0-[\mathrm{A}]_0}{2.303}\right)k_2\,t \qquad (2.5.35)$$

Special Cases of Eq. (2.5.35)

Two special cases where Eq. (2.5.34) is not applicable may be mentioned here. These are:

1. Same stoichiometric coefficient and identical concentrations of A and B.

Let $\nu_1 = \nu_2 = \nu$ and $[\mathrm{B}]_0 = [\mathrm{A}]_0$. The differential rate law will be given by

$$-\frac{1}{\nu}\,\frac{\mathrm{d}\{[\mathrm{A}]_0-\nu x\}}{\mathrm{d}x}=k_2\,([\mathrm{A}]_0-\nu x)^2$$

which is identical to Eq. (2.5.29). The integrated rate expression for this case is given by Eq. (2.5.30).

2. Different stoichiometric coefficients and the concentration of each reactant is directly proportional to its stoichiometric coefficient.

Thus, we have

$$\frac{[\mathrm{A}]_0}{\nu_1}=\frac{[\mathrm{B}]_0}{\nu_2}$$

The differential rate law in this case is

$$\begin{aligned}-\frac{1}{\nu_1}\,\frac{\mathrm{d}\{[\mathrm{A}]_0-\nu_1x\}}{\mathrm{d}t}&=k_2([\mathrm{A}]_0-\nu_1x)\,([\mathrm{B}]_0-\nu_2x)\\&=k_2([\mathrm{A}]_0-\nu_1x)\left(\frac{\nu_2}{\nu_1}[\mathrm{A}]_0-\nu_2x\right)\\&=k_2\,\frac{\nu_2}{\nu_1}\,([\mathrm{A}]_0-\nu_1x)^2\end{aligned}$$

The integrated rate law is given by

$$\frac{1}{[\mathrm{A}]_0-\nu_1x}-\frac{1}{[\mathrm{A}]_0}=k_2\nu_2t \qquad (2.5.36)$$

Characteristics of Second-Order Reactions

For reactions belonging to the case (i) discussed above, we have the following main characteristics.

(i) The plot of $1/([A]_0 - x)$ versus t will be a straight line of slope equal to k_2 (Eq. 2.5.31).

(ii) For half-life, we will have

$$[A]_{t_{\frac{1}{2}}} = [A]_0 - x = \frac{[A]_0}{2}$$

Substitution of the above relation in Eq. (2.5.31) gives

$$\frac{1}{[A]_0/2} - \frac{1}{[A]_0} = k_2\, t_{\frac{1}{2}}$$

or $$t_{\frac{1}{2}} = \frac{1}{k_2[A]_0} \quad \text{that is} \quad t_{\frac{1}{2}} \propto \frac{1}{[A]_0}$$

Hence, for the second-order reactions involving either only one species with $\nu = 1$ or two species with $[A]_0 = [B]_0$ and $\nu_1 = \nu_2 = 1$, (or $[A]_0 \propto \nu_1$ and $[B]_0 \propto \nu_2$) half-life is inversely proportional to the initial concentration of the reactant(s).

For reactions belonging to case (ii) discussed above, the plot of $\log [([B]_0 - x)/([A]_0 - x)]$ versus t will be a straight line of slope equal to $([B]_0 - [A]_0)k_2/2.303$ (Eq. 2.5.35).

Examples of Second-Order Reactions

Examples of reactions obeying second-order kinetics are numerous. A few of them are listed below.

Thermal dissociation of acetaldehyde

$$2CH_3CHO \rightarrow 2CH_4 + 2CO$$

Saponification of an ester

$$CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$$

Reaction between persulphate and iodide ions

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

Problem 2.5.2

The gaseous reaction

$$\nu_1 A(g) \rightarrow \nu_2 B(g)$$

is second-order with respect to A. It is carried out at a constant pressure with a_0 as the initial amount of A. Show that the volume of the system and the concentration of A at time t are given by the expressions

$$V = V_0\left(\frac{1+\nu_2 k a_0 t}{1+\nu_1 k a_0 t}\right)$$

$$\frac{1}{[A]_t} = \left(\frac{1}{[A]_0} + \nu_1 V_0 k t\right)\left(\frac{1+\nu_2 k a_0 t}{1+\nu_1 k a_0 t}\right)$$

where V_0 is the volume of the system at $t = 0$. Assume ideal behaviour for the gases. Derive the expressions of V and [A] for the systems where $\nu_1 = \nu_2 = 1$ and $\nu_1 = 1$ and $\nu_2 = 2$.

Solution Let ξ be the extent of the reaction at time t. We will have

$$\begin{array}{cc} \nu_1\mathrm{A} \rightarrow & \nu_2\mathrm{B} \\ a_0 - \nu_1\xi & \nu_2\xi \end{array}$$

Total amount of the substance at time $t = a_0 + (\nu_2 - \nu_1)\xi$

The kinetic expression of the reaction is

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = k\,(a_0 - \nu_1\xi)^2 \tag{2.5.37}$$

Since the gases are assumed to be ideal, we will have

$$pV_0 = a_0RT \tag{2.5.38}$$

and $$pV = [a_0 + (\nu_2 - \nu_1)\xi]\,RT = pV_0 + (\nu_2 - \nu_1)\,\xi\,RT$$

Hence, $$\xi = \frac{p(V - V_0)}{(\nu_2 - \nu_1)RT} \tag{2.5.39}$$

and $$\mathrm{d}\xi = \frac{p}{(\nu_2 - \nu_1)RT}\,\mathrm{d}V \tag{2.5.40}$$

Substituting Eqs (2.5.38), (2.5.39) and (2.5.40) in Eq. (2.5.37), we get

$$\frac{p}{(\nu_2 - \nu_1)RT}\,\frac{\mathrm{d}V}{\mathrm{d}t} = k\left[a_0 - \frac{\nu_1 p(V - V_0)}{(\nu_2 - \nu_1)RT}\right]^2$$

Replacing a_0 by pV_0/RT and rearranging, we get

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{pk}{(\nu_2 - \nu_1)RT}(\nu_2V_0 - \nu_1V)^2$$

or $$\frac{\mathrm{d}V}{(\nu_2V_0 - \nu_1V)^2} = \frac{pk}{(\nu_2 - \nu_1)RT}\,\mathrm{d}t$$

Integrating within the limits, we get

$$\frac{1}{\nu_1}\left[\frac{1}{\nu_2V_0 - \nu_1V} - \frac{1}{\nu_2V_0 - \nu_1V_0}\right] = \frac{pk}{(\nu_2 - \nu_1)RT}\,t$$

Rearranging the above expression for V, we get

$$V = V_0\left(\frac{1 + \nu_2kta_0}{1 + \nu_1kta_0}\right) \tag{2.5.41}$$

Equation (2.5.37) on integrating gives

$$\frac{1}{a_0 - \nu_1\xi} - \frac{1}{a_0} = \nu_1kt$$

Multiplying throughout by V, we get

$$\frac{V}{a_0 - \nu_1\xi} - \frac{V}{V_0}\,\frac{V_0}{a_0} = V\,\nu_1kt$$

$$\frac{1}{[\mathrm{A}]_t} - \frac{V}{V_0}\,\frac{1}{[\mathrm{A}]_0} = V\,\nu_1kt$$

Substituting V in term of V_0 from Eq. (2.5.41), we get

$$\frac{1}{[\mathrm{A}]_t} = \left(\frac{1}{[\mathrm{A}]_0} + V_0 \nu_1 kt\right)\left(\frac{1+\nu_2 kta_0}{1+\nu_1 kta_0}\right)$$

For a case where $\nu_1 = \nu_2 = 1$, we get

$$\frac{1}{[\mathrm{A}]_t} = \frac{1}{[\mathrm{A}]_0} + V_0 kt$$

$$V = V_0$$

For $\nu_1 = 1$ and $\nu_2 = 2$, we get

$$\frac{1}{[\mathrm{A}]_t} = \left(\frac{1}{[\mathrm{A}]_0} + V_0 kt\right)\left(\frac{1+2kta_0}{1+kta_0}\right)$$

$$V = V_0\left(\frac{1+2kta_0}{1+kta_0}\right)$$

THIRD-ORDER REACTIONS

Expression of Rate Equation

Third-order reactions known so far fall into the category

$$2\mathrm{A} + \mathrm{B} \rightarrow \text{products}$$

The differential rate law is

$$-\frac{1}{2}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_3[\mathrm{A}]^2[\mathrm{B}] \qquad (2.5.42)$$

Let x be the extent of reaction divided by volume at time t. We will have

$$[\mathrm{A}]_t = [\mathrm{A}]_0 - 2x$$

$$[\mathrm{B}]_t = [\mathrm{B}]_0 - x$$

Hence, Eq. (2.5.42) becomes

$$-\frac{1}{2}\frac{\mathrm{d}([\mathrm{A}]_0 - 2x)}{\mathrm{d}t} = k_3([\mathrm{A}]_0 - 2x)^2\,([\mathrm{B}]_0 - x)$$

or

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_3([\mathrm{A}]_0 - 2x)^2\,([\mathrm{B}]_0 - x)$$

On separating the variables and integrating, we get

$$k_3 = \frac{1}{t(2[\mathrm{B}]_0 - [\mathrm{A}]_0)^2}\left[\frac{2x(2[\mathrm{B}]_0 - [\mathrm{A}]_0)}{[\mathrm{B}]_0([\mathrm{A}]_0 - 2x)} + \ln\frac{[\mathrm{B}]_0([\mathrm{A}]_0 - 2x)}{[\mathrm{A}]_0([\mathrm{B}]_0 - x)}\right] \qquad (2.5.43)$$

Simplest Example

The simplest case is a reaction of the type

$$\nu\mathrm{A} \rightarrow \text{products}$$

for which, the differential rate law is

$$-\frac{1}{\nu}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_3\,[\mathrm{A}]^3 \qquad (2.5.44)$$

Let x be the extent of reaction divided by volume at time t. We will have

$$[\mathrm{A}] = [\mathrm{A}]_0 - \nu x$$

With this, Eq. (2.5.43) becomes

$$-\frac{1}{\nu}\,\frac{\mathrm{d}([\mathrm{A}]_0 - \nu x)}{\mathrm{d}t} = k_3\,([\mathrm{A}]_0 - \nu x)^3$$

or $$\frac{\mathrm{d}x}{\mathrm{d}t} = k_3([\mathrm{A}]_0 - \nu x)^3$$

or $$\frac{\mathrm{d}x}{([\mathrm{A}]_0 - \nu x)^3} = k_3\,\mathrm{d}t$$

Integrating the above expression, we get

$$\frac{1}{2\nu}\left[\frac{1}{([\mathrm{A}]_0 - \nu x)^2} - \frac{1}{[\mathrm{A}]_0^2}\right] = k_3 t \qquad (2.5.45)$$

For a special case, where $\nu = 1$, we will have

$$\frac{1}{2}\left[\frac{1}{([\mathrm{A}]_0 - x)^2} - \frac{1}{[\mathrm{A}]_0^2}\right] = k_3 t$$

The unit of the k_3 is $\mathrm{mol^{-2}\ dm^{6}\ s^{-1}}$.

Characteristics of Third-Order Reactions

We will discuss here only the characteristics of the reaction

$$\mathrm{A} \rightarrow \text{products}$$

According to Eq. (2.5.45), if a plot is made between $1/([\mathrm{A}]_0 - x)^2$ and t, we would get a straight line of slope equal to $2k_3$.

Half-life as calculated from Eq. (2.5.45) will be

$$t_{\frac{1}{2}} = \frac{1}{2k_3}\left[\frac{1}{([\mathrm{A}]_0/2)^2} - \frac{1}{[\mathrm{A}]_0^2}\right]$$

or $$t_{\frac{1}{2}} = \frac{3}{2k_3[\mathrm{A}]_0^2} \quad \text{that is} \quad t_{0.5} \propto \frac{1}{[\mathrm{A}]_0^2}$$

Examples of Third-Order Reactions

Only five homogeneous gas reactions of third-order are known. In these reactions, one of the reactants is nitric oxide. These are

$$2\mathrm{NO} + \mathrm{Cl_2} \rightarrow 2\mathrm{NOCl}$$

$$2\mathrm{NO} + \mathrm{Br_2} \rightarrow 2\mathrm{NOBr}$$

$$2\mathrm{NO} + \mathrm{O_2} \rightarrow 2\mathrm{NO_2}$$

$$2\mathrm{NO} + \mathrm{H_2} \rightarrow \mathrm{N_2O} + \mathrm{H_2O}$$

$$2\mathrm{NO} + \mathrm{D_2} \rightarrow \mathrm{N_2O} + \mathrm{D_2O}$$

Reactions in aqueous solution which appear to be third-order are the oxidation of ferrous sulphate, the reaction between iodide and ferric ions and the reduction of $\mathrm{FeCl_3}$ with $\mathrm{SnCl_2}$.

General Expression of Integrated Rate Law of a Reaction Involving Only One Concentration Term

It is possible to derive a general expression of integrated rate law for a reaction whose rate depends either on the concentration of only one reactant or on different reactants having same stoichiometric coefficients and identical concentrations. If all stoichiometric coefficients are assumed to be unity, we may write the general differential rate law as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_n([\mathrm{A}]_0 - x)^n \tag{2.5.46}$$

where n is the overall order of the reaction. On separating the variables and integrating, we get the general expression as

$$\frac{1}{(n-1)}\left\{\frac{1}{([\mathrm{A}]_0 - x)^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right\} = k_n t \tag{2.5.47}$$

Equation (2.5.47) is not applicable for $n = 1$. The units k_n is $\mathrm{mol}^{1-n}\ \mathrm{dm}^{3(n-1)}\ \mathrm{s}^{-1}$.

Half-life of the reaction can be determined by replacing $[\mathrm{A}]_0 - x$ in Eq. (2.5.47) by $[\mathrm{A}]_0/2$. Thus, we have

$$\frac{1}{n-1}\left[\frac{1}{([\mathrm{A}]_0/2)^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right] = k_n t_{\frac{1}{2}}$$

or
$$\frac{1}{n-1}\,\frac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}} = k_n t_{\frac{1}{2}}$$

or
$$t_{\frac{1}{2}} = \frac{1}{k_n(n-1)}\,\frac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}} \tag{2.5.48}$$

The form of rate law as given by Eq. (2.5.46) is also obtained for a reaction involving different stoichiometric coefficients provided the concentration of each of reactants is proportional to its stoichiometric coefficient. For example, for a reaction

$$a\mathrm{A} + b\mathrm{B} + c\mathrm{C} \rightarrow \text{products} \tag{2.5.49}$$

if we have

$$\frac{[\mathrm{A}]_0}{a} = \frac{[\mathrm{B}]_0}{b} = \frac{[\mathrm{C}]_0}{c} \tag{2.5.50}$$

then the differential rate law

$$-\frac{1}{a}\,\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k\,[\mathrm{A}]^{\alpha}\,[\mathrm{B}]^{\beta}\,[\mathrm{C}]^{\gamma} \tag{2.5.51}$$

will becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k([\mathrm{A}]_0 - ax)^{\alpha}\,([\mathrm{B}]_0 - bx)^{\beta}\,([\mathrm{C}]_0 - cx)^{\gamma} \tag{2.5.52}$$

where x is the extent of reaction per unit volume, Making use of Eq. (2.5.50) in Eq. (2.5.52), we have

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k([\mathrm{A}]_0 - ax)^{\alpha}\left(\frac{b}{a}[\mathrm{A}]_0 - bx\right)^{\beta}\left(\frac{c}{a}[\mathrm{A}]_0 - cx\right)^{\gamma}$$

i.e.
$$\frac{dx}{dt} = \frac{k b^{\beta} c^{\gamma}}{a^{\beta+\gamma}} ([A]_0 - ax)^{\alpha+\beta+\gamma}$$
$$= \frac{k b^{\beta} c^{\gamma}}{a^{n-\alpha}} ([A]_0 - ax)^{n}$$

where *n* is the overall order of the reaction.

The integrated rate law is given by

$$\frac{1}{(n-1)} \left\{ \frac{1}{([A]_0 - ax)^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\} = k \frac{b^{\beta} c^{\gamma}}{a^{n-\alpha-1}} t \qquad (2.5.53)$$

The half-life of the reaction will be given by

$$t_{\frac{1}{2}} = \frac{1}{k(n-1)} \frac{a^{n-\alpha-1}}{b^{\beta} c^{\gamma}} \frac{2^{n-1}-1}{[A]_0^{n-1}} \qquad (2.5.54)$$

FRACTIONAL-ORDER REACTIONS

Examples

In many reactions, the order of the reaction with respect to one of the reactants is found to be nonintegral. Examples include:

(i) The reaction between H_2 and D_2 follows the differential rate law

$$\frac{dx}{dt} = k\, p_{H_2} (p_{D_2})^{1/2}$$

(ii) The conversion of *para* hydrogen to *ortho* hydrogen at high temperature follows the rate law

$$\frac{dx}{dt} = k\, (p_{H_2})^{1.5}$$

(iii) The reaction

$$CH_3CHO \rightarrow CH_4 + CO$$

follows the expression

$$-\frac{d[CH_3CHO]}{dt} = k\, [CH_3CHO]^{3/2}$$

Noninteger orders are generally due to the complex nature of reactions which involve more than one elementary step. The overall rate law is obtained by combining the rates of individual elementary steps.

Rate Law and its Characteristics

For reactions following the differential rate equation

$$\frac{d[A]}{dt} = k_{p+1/2}\, [A]^{p+1/2}; \qquad (p \text{ is an integer}) \qquad (2.5.55)$$

the integrated rate law can be obtained from Eq. (2.5.47) by replacing *n* by $p + 1/2$. Thus, we have

$$\frac{1}{p-1/2} \left\{ \frac{1}{([A]_0 - x)^{p-1/2}} - \frac{1}{[A]_0^{p-1/2}} \right\} = k_{p+1/2} t \qquad (2.5.56)$$

Half-life of the reaction will be given by

$$t_{\frac{1}{2}} = \frac{1}{k_{p+1/2}(p-1/2)} \frac{2^{p-1/2}-1}{[\mathrm{A}]_0^{p-1/2}} \qquad (2.5.57)$$

NEGATIVE-ORDER REACTIONS

Sometimes, the rate of reaction decreases as the concentration of one of its constituents is increased. For example, the transformation of ozone into oxygen, i.e.

$$2\mathrm{O_3} \rightarrow 3\mathrm{O_2}$$

follows the rate law

$$-\frac{1}{2}\frac{\mathrm{d}[\mathrm{O_3}]}{\mathrm{d}t} = k\frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]} = k\,[\mathrm{O_3}]^2\,[\mathrm{O_2}]^{-1}$$

Thus, the order of the reaction with respect to O_2 is – 1.

It may be pointed out here again that negative orders like zero and fractional orders are obtained whenever the desired reaction does not occur as written (i.e. in a single step conversion) but involves more complicated reaction mechanism consisting of more than one elementary step. We will see in Section 2.12 how these orders result from more complex mechanism.

2.6 DETERMINATION OF ORDER OF A REACTION

As stated earlier, the order of a reaction is always determined experimentally on the basis of the dependence of the rate of reaction on the concentrations of reacting substances. To determine this dependence, we have to find out how the concentration of reacting species or products vary during the course of the reaction.

To determine the concentration of a particular substance at different time intervals, a known volume of reacting mixture is extracted at different time intervals. It is cooled so as to decrease the speed of the reaction and the concentration of the substance in this volume is determined by titration or by employing any other analytical technique. For example, in the acid-catalyzed reaction

$$\mathrm{CH_3COOC_2H_5 + H_2O \xrightleftharpoons{H^+} CH_3COOH + C_2H_5OH}$$

the concentration of acetic acid produced at different time intervals may be determined by the above method. A known volume of the reacting mixture is extracted, cooled and then titrated quickly against the standard sodium hydroxide solution. In the reaction

$$\mathrm{S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2}$$

the concentration of iodine produced at different time intervals may be determined by titrating a known volume of reacting mixture against the standard solution of sodium thiosulphate.

In many reactions, the concentration of the substance can be determined without disturbing the reaction mixture. This is accomplished by measuring a suitable property of the mixture which changes due to the change in concentration of a reactant or a product. We cite below a few typical examples.

1. If in a reaction there occurs a change in the amount of gaseous species, then the concentration of various species at various time intervals may be determined from the change in pressure of a constant-volume reaction vessel or the change in volume of a constant-pressure reaction vessel. The method of correlating the pressure or volume of the vessel with the concentration of the reactant of the reaction has been outlined in Section 2.5.
2. Reactions such as the inversion of cane sugar can be followed polarimetrically without disturbing the reaction mixture (Section 2.5).
3. If in a reaction, ions are consumed or produced, or one ion is replaced by the other, the concentration of reaction species at different time intervals may be determined conductometrically. For example, in the saponification of ethyl acetate, the fast conducting OH^- ions are replaced by acetate anions. The change in conductivity will be directly proportional to the amount of OH^- ions consumed or acetate ions produced. Let κ_0, κ_t and κ_∞ be the conductivities of the reaction mixture at the start of the reaction, at time t after the reaction has started and at the end of the reaction, respectively. We may write

$$[OH^-]_0 \propto \kappa_0 - \kappa_\infty$$

$$[OH^-]_t \propto \kappa_t - \kappa_\infty$$

and $$x \propto \kappa_0 - \kappa_t$$

where x is the extent of reaction per unit volume at time t.

In order to relate conductivity directly to concentration, a graph or table of conductivity may be constructed using solutions with known concentrations of the ions of interest. For first-order reactions, we may substitute

$$[A]_0 \propto \kappa_0 - \kappa_\infty$$

$$[A]_0 - x \propto \kappa_t - \kappa_\infty$$

Thus $$\ln \frac{[A]_0}{[A]_t} = \ln\left(\frac{\kappa_0 - \kappa_\infty}{\kappa_t - \kappa_\infty}\right) = k_1 t$$

4. Other analytical techniques such as potentiometry, polarography and spectrophotometry may be employed to determine the concentration of a reactant or product at different time intervals. Out of these, spectrophotometry constitutes one of the common methods for determining concentration of a substance of the reacting mixture. The principle underlying the method is Beer's law, according to which, we have

$$\log \frac{I_0}{I} = \varepsilon b c$$

where I_0 is the intensity of incident radiation, I is the intensity of the radiation after passing through the solution of concentration c of a light absorbing substance,

b is thickness of the cell in which the solution is placed and ε is the molar absorptivity. The latter is a function of the wavelength of the radiation and the absorbing material. Thus, if we choose a wavelength for which ε is larger for the chemical species of interest, log (I_0/I) will be directly proportional to the concentration of that material. If the substance is either a reactant or product, we can determine how its concentration varies from the plot of log (I_0/I) versus time.

Once the data on concentration versus time is available, the order of the reaction and its reaction rate constant may be determined by following the methods described below.

Integration Method

In this method, the data is substituted into the integrated rate equations for different order reactions. The equation which gives almost a constant value of k decides the order of the reaction. We can start fitting data in the order given in Table 2.6.1.

Table 2.6.1 Order of Fitting Integrated Rate Equations

Kinetics	*Equations to be Fitted*
(i) First-order	$k_1 = \frac{1}{t}\ln\left(\frac{[A]_0}{[A]_t}\right)$
(ii) Second-order with equal concentrations of reactants	$k_2 = \frac{1}{t}\left[\frac{1}{[A]_t} - \frac{1}{[A]_0}\right]$
(iii) Second-order with different concentrations of reactants	$k_2 = \frac{1}{t}\left[\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[A]_0([B]_0 - x)}{[B]_0([A]_0 - x)}\right)\right]$
(iv) Third-order with equal concentrations of reactants	$k_3 = \frac{1}{2t}\left[\frac{1}{[A]_t^2} - \frac{1}{[A]_0^2}\right]$
(v) Third-order with equal concentrations of two of the reactants	$k_3 = \frac{1}{t(2[B]_0 - [A]_0)^2}\left[\frac{2x(2[B]_0 - [A]_0)}{[A]_0([A]_0 - 2x)} + \ln\left(\frac{[B]_0([A]_0 - 2x)}{[A]_0([B]_0 - x)}\right)\right]$

Graphical Method

In this method, the data are plotted according to the different integrated rate equations so as to yield a straight-line. The rate constant of the reaction can be calculated from the slope of the resultant straight-line plot. We may start plotting the data in the order given in Table 2.6.2.

Table 2.6.2 Order of Plotting the Straight-Line Plot

Kinetics	*Straight-line Plot*	*Slope of the Plot*
(i) First-order	$\log [A]_t$ versus t	$-\frac{k_1}{2.303}$
(ii) Second-order with equal concentrations of reactants	$\frac{1}{[A]_t}$ versus t	k_2
(iii) Second-order with different concentrations of reactants	$\log\left(\frac{[B]_0-x}{[A]_0-x}\right)$ versus t	$\frac{([B]_0-[A]_0k}{2.303}$
(iv) Third-order with equal concentrations of reactants	$\frac{1}{[A]_t^2}$ versus t	$2k_3$
(v) Third-order with equal concentrations of two of reactants	$\frac{2x(2[B]_0-[A]_0)}{[A]_0([A]_0-2x)}$ $+\ln\frac{[B]_0([A]_0-2x)}{[A]_0([B]_0-x)}$ versus t	$k_3(2[B]_0-[A]_0)^2$

Half-Life Method This method can be employed only when the rate law involves only one concentration term. According to Eq. (2.5.48), we have

$$t_{\frac{1}{2}} = \frac{1}{k_n(n-1)}\frac{2^{n-1}-1}{[A]_0^{n-1}} \qquad \text{(Eq. 2.5.48)}$$

where n is the order of the reaction. If the measurements are done with two different initial concentrations, then, we will have

$$\frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2} = \left(\frac{[A]_{02}}{[A]_{01}}\right)^{n-1}$$

or
$$\log\frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2} = (n-1)\log\left(\frac{[A]_{02}}{[A]_{01}}\right) \qquad (2.6.1)$$

Hence
$$n = \frac{\log[(t_{\frac{1}{2}})_1/(t_{\frac{1}{2}})_2]}{\log([A]_{02}/[A]_{01})} + 1$$

Knowing n, the value of k can be computed from Eq. (2.5.48).

The value of n can also be determined graphically. Taking logarithm of Eq. (2.5.48), we get

$$\log\left(\frac{t_{\frac{1}{2}}}{\mathrm{s}}\right) = \log\left(\frac{2^{n-1}-1}{k'_n\,(n-1)}\right) + (1-n)\log\left(\frac{[A]_0}{\mathrm{mol\ dm^{-3}}}\right)$$

Thus, a plot of $\log(t_{\frac{1}{2}}/\mathrm{s})$ versus $\log([A]_0/\mathrm{mol\ dm^{-3}})$ will have a slope of $(1-n)$, from where the value of n can be determined.

The above method can be equally applied by using a fraction other than one half. Thus, equations can be obtained for $t_{1/y}$ where $1/y$ represents the fraction of the initial concentration of reactant that has converted to products. It can be shown that

$$t_{1/y} \propto \frac{1}{[\mathrm{A}]_0^{n-1}}$$

Thus, a plot of log $(t_{1/y}/\mathrm{s})$ versus log $([\mathrm{A}]_0/\mathrm{mol\ dm^{-3}})$ will have a slope of $(1 - n)$ irrespective of the value of the fraction.

It is not necessary to find the fractional life times in separate runs with different initial concentrations. A single run where the time taken for successive fractions to react is determined will suffice as the concentration at the end of one time period may be regarded as the initial concentration for the next interval and so on.

Van't Hoff's Differential Method

In this method, the order of a reaction with respect to each of its reactants can be determined. Consider, for example, a general reaction

$$\nu_1\mathrm{A} + \nu_2\mathrm{B} \rightarrow \text{products}$$

Let m and n be the orders of the reaction with respect to A and B, respectively. The differential rate law can be written as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\,[\mathrm{A}]^m\,[\mathrm{B}]^n \tag{2.6.2}$$

Let a number of kinetic experiments be carried out with different initial concentrations of A but with a constant concentration of B. Equation (2.6.2) in such conditions may be written as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k'\,[\mathrm{A}]^m \tag{2.6.3}$$

where k' is a constant and is equal to $k\,[\mathrm{B}]^n$. The concentration of A at various time intervals are determined and are plotted as shown in Fig. 2.6.1.

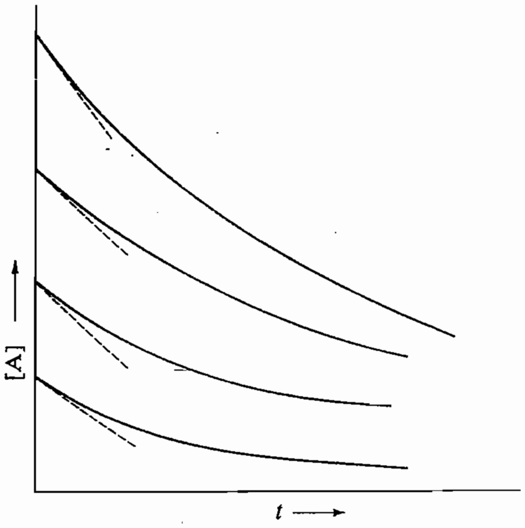


Fig. 2.6.1 Concentration of A versus time for various initial concentrations of A

The initial rates of the reaction are determined from the initial slopes of the curves of Fig. 2.6.1. Let $(\mathrm{d}x/\mathrm{d}t)_{01}$ and $(\mathrm{d}x/\mathrm{d}t)_{02}$ be the initial rates of the reaction when the initial concentrations of A are $[\mathrm{A}]_{01}$ and $[\mathrm{A}]_{02}$, respectively. From Eq. (2.6.3), we have

$$\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{01} = k'[\mathrm{A}]_{01}^{m} \tag{2.6.4a}$$

$$\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{02} = k'[\mathrm{A}]_{02}^{m} \tag{2.6.4b}$$

Dividing Eq. (2.6.4a) by Eq. (2.6.4b), we get

$$\frac{(\mathrm{d}x/\mathrm{d}t)_{01}}{(\mathrm{d}x/\mathrm{d}t)_{02}} = \frac{[\mathrm{A}]_{01}^{m}}{[\mathrm{A}]_{02}^{m}} \tag{2.6.5}$$

On taking logarithm of Eq. (2.6.5), we get

$$\log \frac{(\mathrm{d}x/\mathrm{d}t)_{01}}{(\mathrm{d}x/\mathrm{d}t)_{02}} = m \log \frac{[\mathrm{A}]_{01}}{[\mathrm{A}]_{02}}$$

or

$$m = \frac{\log\{(\mathrm{d}x/\mathrm{d}t)_{01}/(\mathrm{d}x/\mathrm{d}t)_{02}\}}{\log\{[\mathrm{A}]_{01}/[\mathrm{A}]_{02}\}} \tag{2.6.6}$$

Hence, the order of the reaction with respect to A can be determined from Eq. (2.6.6). Alternatively, the graphical method may be employed to determine the value of m. From Eq. (2.6.2), we get

$$\log\left\{\frac{(\mathrm{d}x/\mathrm{d}t)}{\mathrm{mol\ dm^{-3}\ s^{-1}}}\right\}_0 = \log k'' + m \log ([\mathrm{A}]_0/\mathrm{mol\ dm^{-3}}) \tag{2.6.7}$$

Hence, a plot of $\log \{(\mathrm{d}x/\mathrm{d}t)_0 / \mathrm{mol.dm^{-3}\ s^{-1}}\}$ versus $\log \{[\mathrm{A}]_0/\mathrm{mol\ dm^{-3}}\}$ will yield a straight line of slope equal to m (Fig. 2.6.2).

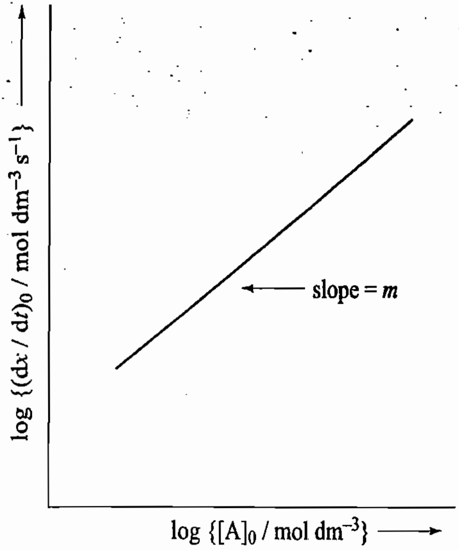


Fig. 2.6.2 A plot of $\log \{(\mathrm{d}x/\mathrm{d}t)_0 / \mathrm{mol\ dm^{-3}\ s^{-1}}\}$ versus $\log ([\mathrm{A}]_0 / \mathrm{mol\ dm^{-3}})$

Now the experiments are repeated keeping the concentration of A constant and varying the initial concentrations of B. Following the method described above, we can determine the order n of the reaction with respect to B.

In many cases, $(dx/dt)_0$ may be replaced by $(\Delta x/\Delta t)_0$ where Δt is the time required to change the initial concentration of the reactant by a small amount Δx. One of the reactions where such a replacement can be conveniently done is the reaction between persulphate and iodide ions. The experiment is known as *iodine-clock experiment.* The involved reaction is

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

The reacting mixture besides containing $S_2O_8^{2-}$ and I^-, also contains the known volumes of very dilute solutions of sodium thiosulphate and starch. Initially, the generated iodine reacts with $Na_2S_2O_3$ present in the solution. When the entire $Na_2S_2O_3$ is consumed, the generated iodine gives blue colour with starch. The strength of hypo solution is so adjusted that the blue colour appears in a very small interval of time (say, within 30 to 40 s) when the experiment is done with the largest concentrations of $S_2O_8^{2-}$ and I^- ions. Now, the different sets of solutions may be prepared according to the scheme given in Table 2.6.3.

Table 2.6.3 Different Sets of Solutions for Iodine-Clock Experiment*

	Flask 1		*Flask 2*			
	Volume of 0.1 M $S_2O_8^{2-}$ *V*/cm^3	*Volume of Water V*/cm^3	*Volume of* 0.1 M I^- *V*/cm^3	*Volume of Water V*/cm^3	*Volume of* $Na_2S_2O_3$ *Solution V*/cm^3	*Volume of Starch Solution V*/cm^3
Set 1	10.0	0.0	10.0	0	5.0	2.0
	8.0	2.0	10.0	0	5.0	2.0
	6.0	4.0	10.0	0	5.0	2.0
	4.0	6.0	10.0	0	5.0	2.0
Set 2	10.0	0.0	8.0	2.0	5.0	2.0
	10.0	0.0	6.0	4.0	5.0	2.0
	10.0	0.0	4.0	6.0	5.0	2.0

*For more accurate work, salt effect should also be taken into account (*see* Section 2.19).

In set 1, the volume of $S_2O_8^{2-}$ is varied keeping the volume of I^- constant and in set 2, the volume of I^- is varied keeping the volume of $S_2O_8^{2-}$ constant. This provides us different initial concentrations of $S_2O_8^{2-}$ and I^-. The two flasks are mixed and the times are recorded till the blue colour appears. The various times obtained may be analyzed as follows.

The rate expression of $S_2O_8^{2-}-I^-$ reaction may be written as

$$\frac{dx}{dt} = k\,[S_2O_8^{2-}]^m\,[I^-]^n \tag{2.6.8}$$

For set 1, Eq. (2.6.8) reduces to

$$\frac{dx}{dt} = k'\,[S_2O_8^{2-}]^m$$

Now $(dx/dt)_0$ may be replaced by $(\Delta x)_0/(\Delta t)_0$, where $(\Delta x)_0$ represents the small amount of iodine generated in the small interval of time $(\Delta t)_0$. Thus, we have

$$\left(\frac{\Delta x}{\Delta t}\right)_0 = k'[S_2O_8^{2-}]_0^m$$

or

$$\frac{1}{(\Delta t)_0} = \frac{k'}{(\Delta x)_0}[S_2O_8^{2-}]_0^m$$

Now since $[S_2O_8^{2-}]_0^m$ will be proportional to its volume, we may write the above expression as

$$\frac{1}{(\Delta t)_0} = k''\{V(S_2O_8^{2-})\}_0^m$$

Taking logarithm, we get

$$\log\{(\Delta t)_0/s\} = -\log k''' - m\log\{V(S_2O_8^{2-})/dm^3\}_0 \qquad (2.6.9)$$

where $k''' = k''\,(s\,dm^{3m})$. Hence, a plot of $\log\{(\Delta t)_0/s\}$ versus $\log\{V(S_2O_8^{2-})/dm^3\}_0$ will yield a straight line of slope equal to $-m$. For set 2, Eq. (2.6.9) will be given as

$$\log\{(\Delta t)_0/s\} = -\log k''' - n\log\{V(I^-)/dm^3\}_0 \qquad (2.6.10)$$

where $k''' = k''\,(s\,dm^{3n})$. Hence, the order n with respect to I^- can be determined from the plot of $\log\{(\Delta t)_0/s\}$ versus $\log\{V(I^-)/dm^3\}_0$.

Ratio Variation Method

The principle of this method is essentially the same as that of van't Hoff's differential method. The concentration of one of the reactants is varied by a known factor and its effect on the initial rate of the reaction is studied. Say, for example, the order of the reaction with respect to one of its constituents is one and if its concentration is doubled, it is obvious that the initial rate of the reaction will also be doubled. If the order is two, then the rate will increase four times and so on. This way, by changing the concentrations of all reactants one by one, we can find the order of the reaction with respect to each of the reacting species. Mathematically, for the reaction

$$\nu_1A + \nu_2B \rightarrow \text{products}$$

we may write

$$\left(\frac{dx}{dt}\right)_{01} = k[A]_0^m[B]_0^n \qquad (2.6.11)$$

Now let the concentration of A be changed to $j[A]_0$, where j is a constant, may be integral or nonintegral, and let the concentration of B remain unchanged. We will have

$$\left(\frac{dx}{dt}\right)_{02} = k(j[A]_0)^m[B]_0^n \qquad (2.6.12)$$

Dividing Eq. (2.6.12) by Eq. (2.6.11), we get

$$\frac{(dx/dt)_{02}}{(dx/dt)_{01}} = j^m$$

or

$$m = \frac{1}{(\log j)}\left[\log\left(\frac{dx/dt}{mol\,dm^{-3}\,s^{-1}}\right)_{02} - \log\left(\frac{dx/dt}{mol\,dm^{-3}\,s^{-1}}\right)_{01}\right] \qquad (2.6.13)$$

Similarly, the order n with respect to B can be determined.

Ostwald Isolation Method

This method is based on the fact that the concentration terms of reactants except one if present in excess remain virtually unchanged and thus can be merged with the rate constant. In this case, the rate of the reaction depends only on the concentration of that reactant which is not present in excess. Thus, in the rate expression

$$r = k\,[\mathrm{A}]^{\alpha}\,[\mathrm{B}]^{\beta}\,[\mathrm{C}]^{\gamma}$$

if B and C are present in large excess, we will have

$$r = k'\,[\mathrm{A}]^{\alpha}$$

where $k' = k\,[\mathrm{B}]^{\beta}\,[\mathrm{C}]^{\gamma}$.

The reaction is known to be pseudo α-order. Hence, we can study the kinetics of the reaction by taking all reacting species except one (say A) in large excess. The obtained order of the reaction will be equal to the order with respect to the species A. This way, we can proceed for different reacting species and the order with respect to each of them can be determined.

2.7 SOLVED NUMERICALS

1. The half-life of a first-order chemical reaction A → B is 10 min. What per cent of A remains after 1 h?

Solution

Since $t_{\frac{1}{2}} = 0.693/k$, we have

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{10 \times 60\,\mathrm{s}} = 0.001\,155\ \mathrm{s}^{-1}$$

The integrated rate expression for first-order kinetics is

$$\ln\left(\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0}\right) = -kt$$

Thus, after one hour we will have

$$\ln\left(\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0}\right) = -(0.001\,155\ \mathrm{s}^{-1})\,(60 \times 60\ \mathrm{s}) = -4.158$$

or

$$\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = \mathrm{e}^{-4.158} = 0.015\,63$$

Hence, per cent of A remaining is 1.563.

2. In the decomposition of N_2O_5 at 318 K according to the equation

$$\mathrm{N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)}$$

the following concentration data were obtained.

t/s	$\dfrac{[\mathrm{N_2O_5}]}{\mathrm{mol\ dm^{-3}}}$	t/s	$\dfrac{[\mathrm{N_2O_5}]}{\mathrm{mol\ dm^{-3}}}$
0	0.250	800	0.152
200	0.223	1 000	0.134
400	0.198	1 200	0.120
600	0.174		

Answer the following:

(i) What is the order of the reaction? (ii) What is the rate constant of the reaction? (iii) What is the rate of reaction at $t = 500$ s? (iv) What will be the concentration of N_2O_5 at 2 000 s? (v) What is the average rate over the period 0 to 200 s?

Solution

(i) To determine the order of the reaction in the present case, we may adopt the graphical method. For the first-order kinetics, the graph between log ($[A]_t$ /mol dm^{-3}) and t should be a straight line. Thus, we have

t/s	0	200	400	600	800	1 000	1 200
$[N_2O_5]$/mol dm^{-3}	0.250	0.223	0.198	0.174	0.152	0.134	0.120
log$\{[N_2O_5]$/mol dm$^{-3}\}$	$\bar{1}.398$	$\bar{1}.348$	$\bar{1}.297$	$\bar{1}.241$	$\bar{1}.182$	$\bar{1}.127$	$\bar{1}.079$

The graph between log (N_2O_5]/mol dm^{-3}) and t is shown in Fig. 2.7.1. Since the graph shown in Fig. 2.7.1 is a straight-line, the order of the decomposition of N_2O_5 is first-order.

(ii) The rate constant of the reaction can be obtained from the slope of the straight-line plot shown in Fig. 2.7.1.

We have $$\frac{\Delta\{\log[N_2O_5]/\mathrm{mol\,dm^{-3}}\}}{\Delta(t/\mathrm{s})} = 0.000\ 282\,6$$

Hence, $$\frac{\Delta\{\log[N_2O_5]/\mathrm{mol\,dm^{-3}}\}}{\Delta t} = -\ 0.000\ 282\,6\ \mathrm{s^{-1}}$$

From the rate expression, we have

$$\text{slope} = -\frac{k}{2.303} = -\ 0.000\ 282\,6\ \mathrm{s^{-1}}$$

Hence, $k = (-\,2.303)\,(-\,0.000\ 282\,6\ \mathrm{s^{-1}}) = 0.000\ 650\ 8\ \mathrm{s^{-1}}$

(iii) To determine the rate of reaction at 500 s, we determine first of all the concentration of A at 500 s and then multiply this concentration by the rate constant k. Thus, we have

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -\,kt\,.$$

$$= -\ (0.000\ 650\,8\ \mathrm{s^{-1}})(500\ \mathrm{s}) = -\ 0.325\ 4$$

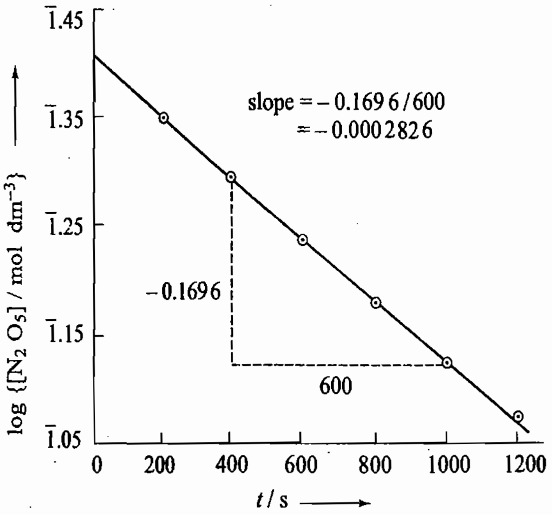


Fig. 2.7.1

Hence, $[\mathrm{A}]_t = [\mathrm{A}]_0\, \mathrm{e}^{-0.325\,4}$

$$= (0.250 \text{ mol dm}^{-3})(0.722\,3) = 0.180\,6 \text{ mol dm}^{-3}$$

Hence, Rate at 500 s $= k\,[\mathrm{A}]_t = (0.000\,650\,8 \text{ s}^{-1})\,(0.180\,6 \text{ mol dm}^{-3})$

$$= 0.000\,117\,5 \text{ mol dm}^{-3} \text{ s}^{-1}$$

(iv) The concentration at 2 000 s will be

$$[\mathrm{A}]_t = [\mathrm{A}]_0\, \mathrm{e}^{-kt} = (0.25 \text{ mol dm}^{-3}) \exp(-\,0.000\,6508 \times 2\,000)$$

$$= (0.25 \text{ mol dm}^{-3})\,(0.272\,1) = 0.068 \text{ mol dm}^{-3}$$

(v) Average rate over the period of 0 to 200 s will be

$$r_{\text{av}} = \frac{-(\Delta[\mathrm{A}])_{0-200\text{s}}}{200\,\text{s}} = \frac{(0.250\,\text{mol dm}^{-3} - 0.223\,\text{mol dm}^{-3})}{200\,\text{s}}$$

$$= 0.000\,135 \text{ mol dm}^{-3}\text{ s}^{-1}$$

3. Calculate the value of rate constant and the time (minutes) required for the solution to become optically inactive from the following data.

t/min	0.0	7.2	36.8	46.0	68.0	∞
Rotation of polarized light/degree	24.1	21.4	12.4	10.0	5.5	− 10.7

Solution

First of all, the order of the reaction is to be determined. We may adopt graphical method for this purpose. Trying for the first-order kinetics, we have

$$\ln \frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -\,kt$$

Now $[\mathrm{A}]_t \propto \theta_\infty - \theta_t$ and $[\mathrm{A}]_0 \propto \theta_\infty - \theta_0$

Hence, $\ln\left(\dfrac{\theta_\infty - \theta_t}{\theta_\infty - \theta_0}\right) = -\,kt$

Thus, the graph of log $\{(\theta_\infty - \theta_t)/(\theta_\infty - \theta_0)\}$ is made against t. From the given data, we have

t/min	0	7.2	36.8	45.0	66.8	∞
θ/degree	24.1	21.4	12.4	10.0	5.5	− 10.7
$(\theta_\infty - \theta_t)$/degree	− 34.8	− 32.1	− 23.1	− 20.7	− 16.2	
$\dfrac{\theta_\infty - \theta_t}{\theta_\infty - \theta_0}$	1	0.922	0.664	0.595	0.466	
$\log\left(\dfrac{\theta_\infty - \theta_t}{\theta_\infty - \theta_0}\right)$	0	$\bar{1}.965$	$\bar{1}.822$	$\bar{1}.774$	$\bar{1}.668$	

The graph between log $\{(\theta_\infty - \theta_t)/(\theta_\infty - \theta_0)\}$ and t is shown in Fig. 2.7.2.

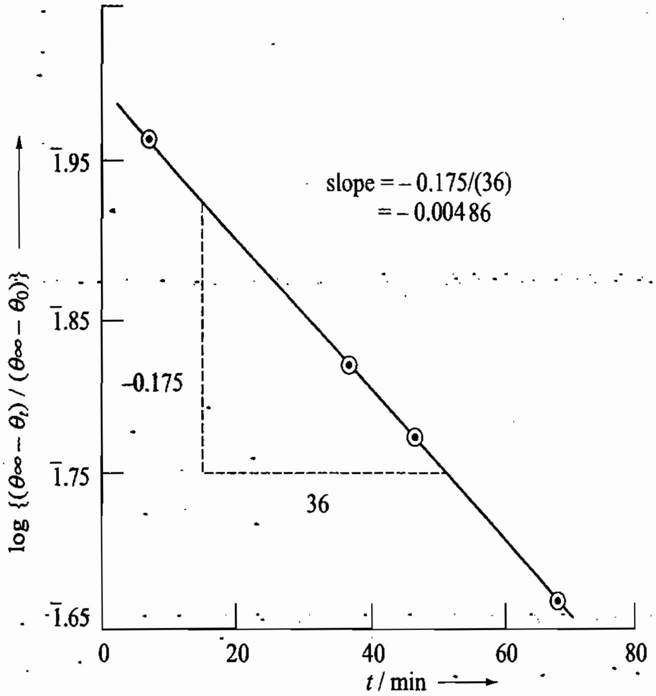


Fig. 2.7.2

Since the plot obtained is a straight line, the reaction is first-order. Its rate constant can be obtained from the slope of the straight-line plot. For the rate expression, we will have

$$\text{slope} = -\frac{k}{2.303} = -0.004\,86\ \text{min}^{-1}$$

$$k = (0.004\,86\ \text{min}^{-1}) \times 2.303 = 0.011\,19\ \text{min}^{-1}$$

For the solution to become optically inactive, we will have $\theta_t = 0$.

$$\text{Thus}\quad \frac{\theta_\infty - \theta_t}{\theta_\infty - \theta_0} = \frac{-10.7}{-34.8} = 0.307\,5$$

$$\log\left(\frac{\theta_\infty - \theta_t}{\theta_\infty - \theta_0}\right) = \bar{1}.487\,8$$

The time corresponding to the above value of log$\{(\theta_\infty - \theta_t)/(\theta_\infty - \theta_0)\}$ can be obtained from the rate expression

$$\log\left(\frac{\theta_\infty - \theta_t}{\theta_\infty - \theta_0}\right) = -\frac{k}{2.303}t$$

$$\text{Hence,}\quad t = -\frac{2.303 \times \bar{1}.487\,8}{0.011\,19\ \text{min}^{-1}} = 105.4\ \text{min}$$

4. The following data were obtained at a constant volume for the decomposition of di-tertiarybutyl peroxide in the gas phase at 427.7 K.

t/min	0	3	6	9	12	15	18	21
p/Torr	169.3	189.2	207.1	224.4	240.2	256.0	265.7	282.6

The reaction is

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2CH_3COCH_3 + C_2H_6$$

Show that the reaction is of the first-order and calculate its rate constant.

Solution

For the decomposition reaction

$$\underset{\textbf{(A)}}{(CH_3)_3COOC(CH_3)_3} \rightarrow 2CH_3COCH_3 + C_2H_6$$

we will have

$$[A]_0 \propto p_0$$

$$[A]_t \propto p_t = \left\{\frac{(\Delta \nu_g + 1)p_0 - p}{\Delta \nu_g}\right\} = \left\{\frac{3p_0 - p}{2}\right\}$$

Thus from the given data, we have

t/min	0	3	6	9	12	15	18	21
p/Torr	169.3	189.2	207.1	224.4	240.2	255.0	269.7	282.6
p_t/Torr	169.3	159.35	150.4	141.75	133.85	126.45	119.1	112.65
log(p_t/Torr)	2.229	2.202	2.177	2.152	2.126	2.102	2.076	2.052

To show that the reaction is first-order, we make a plot of log (p/Torr) versus t (Fig. 2.7.3). Since the plot is a straight line, the decomposition reaction is first order.

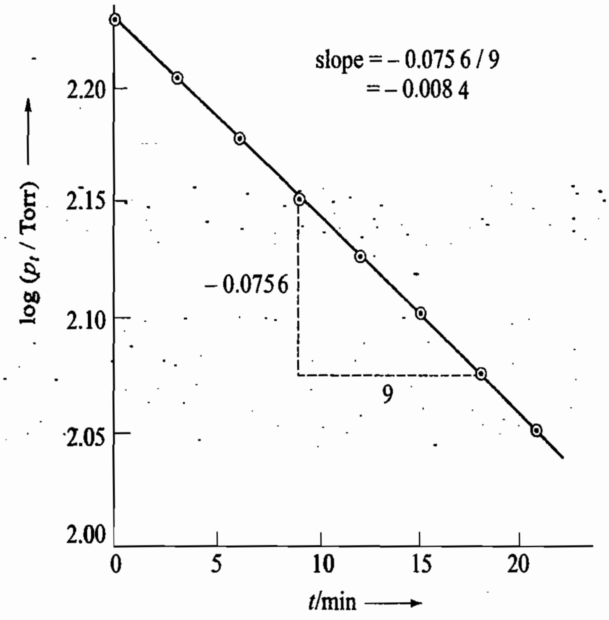


Fig. 2.7.3

We have $$\frac{\Delta\{\log(p_t/\text{Torr})\}}{\Delta(t/\text{min})} = 0.008\ 4$$

Hence, $$\frac{\Delta\{\log(p_t/\text{Torr})\}}{\Delta t} = -\ 0.008\ 4\ \text{min}^{-1}$$

For the rate expression, we will have

$$\text{slope} = -\frac{k}{2.303} = -\ 0.008\ 4\ \text{min}^{-1}$$

Hence, $$k = (2.303)\ (0.008\ 4\ \text{min}^{-1})$$
$$= 0.019\ 3\ \text{min}^{-1} = 3.217 \times 10^{-4}\ \text{s}^{-1}$$

5. The following data were obtained for the dimerization of butadiene according to the equation

$$C_4H_6 \rightarrow \tfrac{1}{2} C_8H_{12}$$

t/min	p_t/Torr	t/min	p_t/Torr
0	632.0	42.50	509.3
6.12	606.6	60.87	482.8
12.18	584.2	90.05	453.3
17.30	567.3	119.00	432.8
29.18	535.4	176.67	405.3

Calculate (i) the average rate over the period 0 to 12.18 minutes, and (ii) the order of the reaction and its rate constant.

Solution **(i)** The average rate of the reaction over the time period 0 to 12.18 minutes is given by

$$r_{\text{av}} = \frac{-\Delta p}{\Delta t} = \frac{-(584.2\,\text{Torr} - 632.0\,\text{Torr})}{12.18\,\text{min}} = 3.924\ \text{Torr/min}$$

(ii) For the reaction

$$\underset{(\text{A})}{C_4H_6} \rightarrow \tfrac{1}{2}\underset{(\text{B})}{C_8H_{12}}$$

we will have

$$[\text{A}]_0 \propto p_0$$

Let x be the amount of C_4H_6 that dimerizes in time t. We will have

$$[\text{A}]_t = [\text{A}]_0 - x \quad \text{and} \quad [\text{B}]_t = x/2$$

$$[\text{A}]_t + [\text{B}]_t = [\text{A}]_0 - x + \frac{x}{2} = [\text{A}]_0 - \frac{x}{2}$$

Now $\quad p_t \propto ([\text{A}]_t + [\text{B}]_t)$

i.e. $\quad p_t \propto \left([\text{A}]_0 - \dfrac{x}{2}\right)$

The change in pressure is due to the change in the amount of gaseous species which is $-x/2$. Hence

$$p_t - p_0 \propto -\frac{x}{2}$$

or $\quad x \propto 2(p_0 - p_t)$

Hence, $\quad [\text{A}]_t = \{[\text{A}] - x\} \propto \{p_0 - 2(p_0 - p_t)\} = (2p_t - p_0) \equiv y_t$

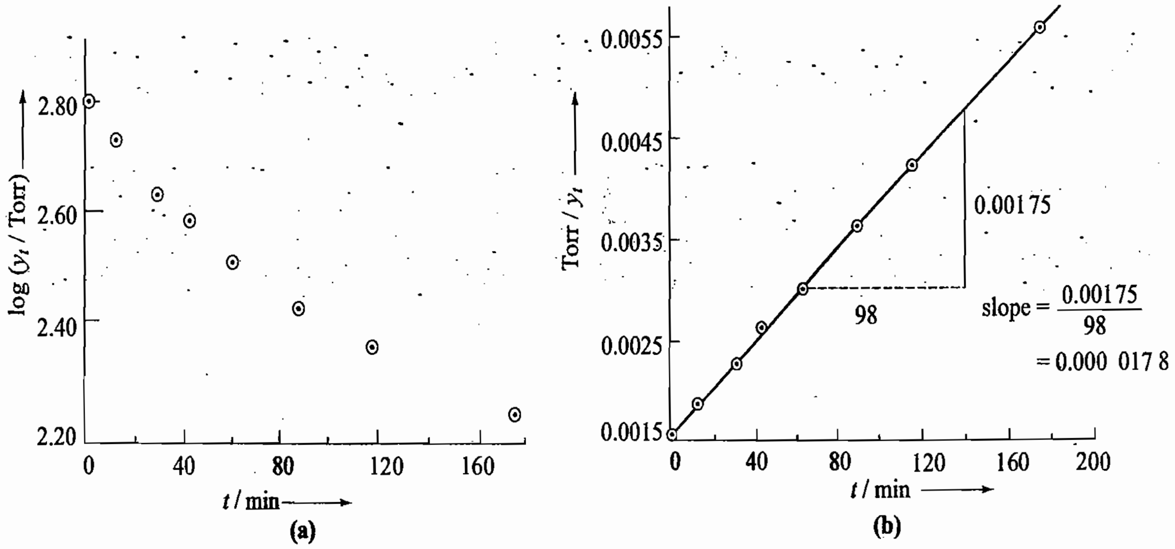
To determine the order of the reaction, we follow the graphical method. For the first-order kinetics, we should get a straight-line plot between log (y_t/Torr) and t. If a straight-line plot is not obtained, we try for the second-order kinetics and thus plot a graph between $1/y_t$ and t and so on. We tabulate below the values of log (y_t/Torr) and $1/y_t$.

t/min	p_t/Torr	$[A]_t \propto y_t$ $= (2p_t - p_0)$/Torr	$\log (y_t/\text{Torr})$	$(1/y_t)$ Torr
0	632.0	632	2.801	0.001 58
6.12	606.6	581.2	2.764	0.001 72
12.18	584.2	536.4	2.730	0.001 86
17.30	567.3	502.6	2.701	0.001 99
29.18	535.4	438.8	2.642	0.002 28
42.50	509.3	386.6	2.587	0.002 59
60.87	482.8	333.6	2.523	0.003 00
90.05	453.3	274.6	2.439	0.004 64
119.00	432.8	233.6	2.369	0.004 28
176.67	405.3	178.6	2.252	0.005 60

The graph between $\log (y_t/\text{Torr})$ and t is not a straight line (Fig. 2.7.4a) and hence the dimerization reaction does not follow the first-order kinetics. The graph between $1/y_t$ and t is a straight-line plot (Fig. 2.7.4b). Hence the given reaction follows the second-order kinetics. The slope of the line shown in Fig. 2.7.4b is 1.78×10^{-5}, that is

$$\frac{\Delta(\text{Torr}/y_t)}{\Delta(t/\text{min})} = 0.000\,0178 \quad \text{or} \quad \frac{\Delta(1/y_t)}{\Delta t} = 0.000\,0178\ \text{Torr}^{-1}\ \text{min}^{-1}$$

Hence, $k = 1.78 \times 10^{-5}\ \text{Torr}^{-1}\ \text{min}^{-1}$



(a) (b)

Fig. 2.7.4

6. For the reaction

$$2NO + H_2 \rightarrow N_2O + H_2O$$

the value of $-\,dp/dt$ was found to be 1.50 Torr s^{-1} for a pressure of 359 Torr of NO and 0.25 Torr s^{-1} for a pressure of 152 Torr, the pressure of H_2 being constant. On the other hand, when the pressure of NO was kept constant, $-\,dp/dt$ was 1.60 Torr s^{-1} for a hydrogen pressure of 289 Torr and 0.79 Torr s^{-1} for a pressure of 147 Torr. Determine the order of the reaction.

Solution

For the given reaction, we write

$$-\frac{\mathrm{d}p}{\mathrm{d}t} = k\,p_{\mathrm{NO}}^{m}\,p_{\mathrm{H}_2}^{n}$$

For the constant hydrogen pressure, we may write

$$\left(-\frac{\mathrm{d}p}{\mathrm{d}t}\right)_0 = k'\,p_{\mathrm{NO}}^{m}$$

Substituting the given two sets of readings, we have

$$1.50\ \mathrm{Torr\ s^{-1}} = k'\,(359\ \mathrm{Torr})^m$$

$$0.25\ \mathrm{Torr\ s^{-1}} = k'\,(152\ \mathrm{Torr})^m$$

On dividing, we get

$$\frac{1.50}{0.25} = \left(\frac{359}{152}\right)^m$$

or $$m = \frac{\log(1.50/0.25)}{\log(359/152)} = \frac{0.7782}{0.3773} \simeq 2$$

Similarly for the constant nitric oxide pressure, we get

$$n = \frac{\log(1.60/0.79)}{\log(289/147)} = \frac{0.3065}{0.2935} \simeq 1$$

Thus, the overall order of the reaction = $m + n = 3$.

7. For the reaction

$$\mathrm{I^- + OCl^- \rightarrow OI^- + Cl^-}$$

in basic aqueous medium, the following data were obtained.

(a) $[\mathrm{OCl^-}]_0 = [\mathrm{OH^-}]_0 = 0.1\ \mathrm{mol\ dm^{-3}}$					
$[\mathrm{I^-}]_0/\mathrm{mol\ dm^{-3}}$:	0.01	0.03	0.05	0.07	0.10
Initial rate/mol $\mathrm{dm^{-3}\ s^{-1}}$:	0.6	1.8	3.0	4.2	6.0
(b) $[\mathrm{I^-}]_0 = [\mathrm{OH^-}]_0 = 0.1\ \mathrm{mol\ dm^{-3}}$					
$[\mathrm{OCl^-}]_0/\mathrm{mol\ dm^{-3}}$:	0.01	0.03	0.05	0.07	0.10
Initial rate/mol $\mathrm{dm^{-3}\ s^{-1}}$:	0.6	1.8	3.0	4.2	6.0
(c) $[\mathrm{I^-}]_0 = [\mathrm{OCl^-}]_0 = 0.1\ \mathrm{mol\ dm^{-3}}$					
$[\mathrm{OH^-}]/\mathrm{mol\ dm^{-3}}$;	0.01	0.03	0.05	0.07	0.10
Initial rate/mol $\mathrm{dm^{-3}\ s^{-1}}$	60.0	20.0	12.0	8.6	6.0

Find (i) the orders of the reaction with respect to $\mathrm{I^-}$, $\mathrm{OCl^-}$ and $\mathrm{OH^-}$, and (ii) the reaction rate constant of the reaction.

Solution

(i) The orders of the reaction with respect to $\mathrm{I^-}$, $\mathrm{OCl^-}$ and $\mathrm{OH^-}$ in the present case can be determined from the inspection of the given data. In the set (a), we observe that the initial rate of the reaction increases as fast as the increase in concentration of $\mathrm{I^-}$. For example, if the concentration of $\mathrm{I^-}$ is increased three times from 0.01 to 0.03 mol $\mathrm{dm^{-3}}$, the initial rate also increases three times, i.e. from 0.6 to 1.8 mol $\mathrm{dm^{-3}\ s^{-1}}$. Thus, it follows that the order of the reaction with respect to $\mathrm{I^-}$ is one. From the data of set (b), we conclude that the order of the reaction with respect to $\mathrm{OCl^-}$ is also one. However, in the set (c) where the concentration of $\mathrm{OH^-}$ is varied, the rate decreases as fast as the concentration of OH^- is increased. Thus, we conclude that the order of the reaction with respect to OH^- is –1.

To be more quantitative, we may follow graphical method to determine the order of the reaction. We write the differential rate law as

$$\left(\frac{dx}{dt}\right)_0 = k\,[I^-]_0^{\alpha}\,[OCl^-]_0^{\beta}\,[OH^-]_0^{\gamma}$$

For set (a), since $[OCl^-]$ and $[OH^-]$ are held constant, the above expression becomes

$$\left(\frac{dx}{dt}\right)_0 = k'\,[I^-]_0^{\alpha}$$

or $$\{\log (dx/dt)/\text{mol dm}^{-3}\,\text{s}^{-1}\} = \log k'' + \alpha \log ([I^-]_0/\text{mol dm}^{-3})$$

Thus, a plot between $\log\{(dx/dt)_0/\text{mol dm}^{-3}\,\text{s}^{-1}\}$ and $\log\{[I^-]_0/\text{mol dm}^{-3}\}$ should yield a straight line of slope equal to α. Similarly, for other sets, we may write

Set (*b*): $\{\log (dx/dt)_0/\text{mol dm}^{-3}\,\text{s}^{-1}\} = \log k'' + \beta \log \{[OCl^-]_0/\text{mol dm}^{-3}\}$

Set (*c*): $\{\log (dx/dt)_0/\text{mol dm}^{-3}\,\text{s}^{-1}\} = \log k'' + \gamma \log \{[OH^-]_0/\text{mol dm}^{-3}\}$

The following are the logarithm values of the given data.

Set (*a*):					
$[I^-]_0/\text{mol dm}^{-3}$	0.01	0.03	0.05	0.07	0.10
$\log\{[I^-]_0/\text{mol dm}^{-3}\}$	$\bar{2}.000$	$\bar{2}.477$	$\bar{2}.699$	$\bar{2}.845$	$\bar{1}.000$
$(dx/dt)_0/\text{mol dm}^{-3}\,\text{s}^{-1}$	0.6	1.8	3.0	4.2	6.0
$\log\{(dx/dt)_0/\text{mol dm}^{-3}\,\text{s}^{-1}\}$	$\bar{1}.778$	0.225	0.477	0.623	0.778
Set (*b*):					
$[OCl^-]_0/\text{mol dm}^{-3}$	0.01	0.03	0.05	0.07	0.10
$\log\{[OCl^-]_0/\text{mol dm}^{-3}\}$	$\bar{2}.000$	$\bar{2}.477$	$\bar{2}.699$	$\bar{2}.845$	$\bar{1}.000$
$(dx/dt)_0/\text{mol dm}^{-3}\,\text{s}^{-1}$	0.6	1.8	3.0	4.2	6.0
$\log\{(dx/dt)_0/\text{mol dm}^{-3}\,\text{s}^{-1}\}$	$\bar{1}.778$	0.255	0.477	0.623	0.778
Set (*c*):					
$[OH^-]_0/\text{mol dm}^{-3}$	0.01	0.03	0.05	0.07	0.10
$\log\{[OH^-]_0/\text{mol dm}^{-3}\}$	$\bar{2}.000$	$\bar{2}.477$	$\bar{2}.699$	$\bar{2}.845$	$\bar{1}.000$
$(dx/dt)_0/\text{mol dm}^{-3}\,\text{s}^{-1}$	60.0	20.0	12.0	8.6	6.0
$\log\{(dx/dt)_0/\text{mol dm}^{-3}\,\text{s}^{-1}\}$	1.778	1.301	1.079	0.935	0.778

Figure 2.7.5 depicts the required plots. The slopes are +1, +1 and –1, respectively. Thus, the order of the reaction with respect to I^-, OCl^- and OH^- are +1, +1 and –1, respectively.

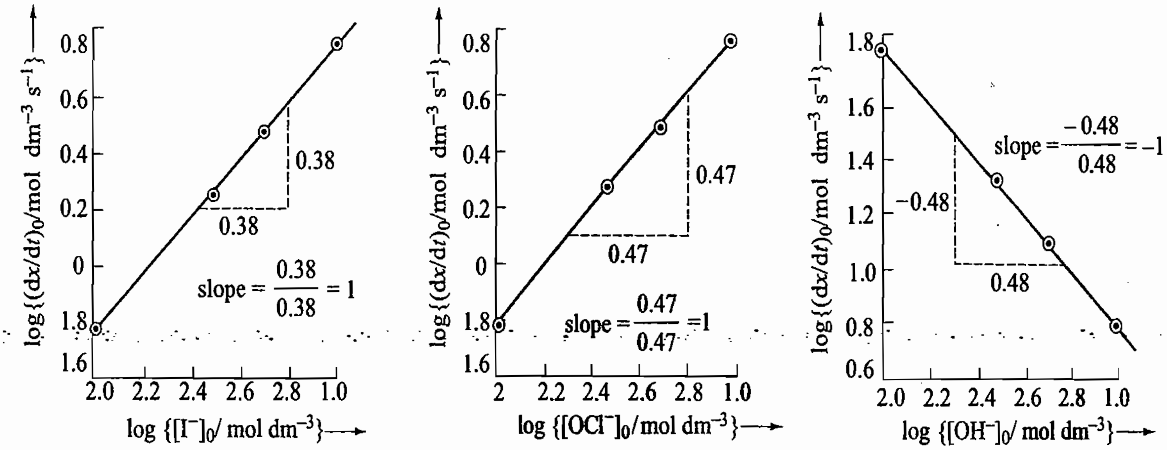


Fig. 2.7.5

(ii) The reaction rate constant can be determined by substituting the data in the rate law:

$$\left(\frac{dx}{dt}\right)_0 = \frac{k[I^-][OCl^-]}{[OH^-]}$$

Substitution of each data gives the same value of k equal to 60 s^{-1}. Alternatively, the graphical methods may be employed to determine the value of k.

8. (a) Using the following data, obtain the differential rate expression and the value of the rate constant for the following reaction–

$$CO + Cl_2 \rightarrow COCl_2$$

Experiment number	1	2	3	4
$[CO]_0$/mol dm^{-3}	0.10	0.10	0.05	0.05
$[Cl_2]_0$/mol dm^{-3}	0.10	0.05	0.10	0.05
r_0/mol dm^{-3} s^{-1}	1.2×10^{-2}	4.26×10^{-3}	6.0×10^{-3}	2.13×10^{-3}

(b) Using the following data, obtain the differential rate expression and the value of the rate constant for the following reaction

$$COCl_2 \rightarrow CO + Cl_2.$$

Experiment number	1	2	3	4
$[COCl_2]_0$/mol dm^{-3}	0.16	0.16	0.04	0.04
$[Cl_2]_0$/mol dm^{-3}	0.16	0.04	0.16	0.04
r_0/mol dm^{-3} s^{-1}	1.9×10^{-2}	9.6×10^{-3}	4.8×10^{-3}	2.4×10^{-3}

Solution

(a) We write the rate expression as

$$\left(\frac{dx}{dt}\right)_0 = k[CO]_0^m\,[Cl_2]_0^n$$

For the constant initial concentration of Cl_2, we have

$$\left(\frac{dx}{dt}\right)_0 = k'[CO]_0^m$$

or $$\log\{(\mathrm{d}x/\mathrm{d}t)_0/\mathrm{mol\ dm^{-3}\ s^{-1}}\} = \log k'' + m \log\{[\mathrm{CO}]_0/\mathrm{mol\ dm^{-3}}\}$$

For the two sets of data, we have

$$m = \frac{\log\{(\mathrm{d}x/\mathrm{d}t)_{01}/\mathrm{mol\ dm^{-3}\ s^{-1}}\} - \log\{(\mathrm{d}x/\mathrm{d}t)_{02}/\mathrm{mol\ dm^{-3}\ s^{-1}}\}}{\log\{[\mathrm{CO}]_{01}/\mathrm{mol\ dm^{-3}}\} - \log\{[\mathrm{CO}]_{02}/\mathrm{mol\ dm^{-3}}\}}$$

Substitution of the data from the first and third experiments (or we may equally use the data of the second and fourth experiments), we get

$$m = \frac{\log(1.2\times10^{-2}) - \log(6.0\times10^{-3})}{\log(0.1) - \log(0.05)} = \frac{\bar{2}.0792 - \bar{3}.7782}{\bar{1}.0000 - \bar{2}.6090} = \frac{0.3000}{0.3000} = 1$$

Similarly for the constant initial concentration of CO, we may write

$$n = \frac{\log\{(\mathrm{d}x/\mathrm{d}t)_{01}/\mathrm{mol\ dm^{-3}\ s^{-1}}\} - \log\{(\mathrm{d}x/\mathrm{d}t)_{02}/\mathrm{mol\ dm^{-3}\ s^{-1}}\}}{\log\{[\mathrm{Cl_2}]_{01}/\mathrm{mol\ dm^{-3}}\} - \log\{[\mathrm{Cl_2}]_{02}/\mathrm{mol\ dm^{-3}}\}}$$

Thus, employing the data from the first and second experiments (or we may equally use the data of third and fourth experiments), we get

$$n = \frac{\log(1.2\times10^{-2}) - \log(4.26\times10^{-3})}{\log(0.10) - \log(0.05)} = \frac{\bar{2}.0792 - \bar{3}.6294}{\bar{1}.0000 - \bar{2}.6990} = \frac{0.4498}{0.3010}$$

$$= 1.494 = 3/2$$

Thus, the differential rate expression for the given reaction is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k[\mathrm{CO}][\mathrm{Cl_2}]^{3/2}$$

The value of rate constant can be obtained by using any one of the given data points. Making use of the data of the first experiment, we get

$$1.2\times10^{-2}\ \mathrm{mol\ dm^{-3}\ s^{-1}} = k\,(0.1\ \mathrm{mol\ dm^{-3}})(0.1\ \mathrm{mol\ dm^{-3}})^{3/2}$$

$$k = \frac{1.2\times10^{-2}\ \mathrm{mol\ dm^{-3}\ s^{-1}}}{(0.1\,\mathrm{mol\ dm^{-3}})(0.1\,\mathrm{mol\ dm^{-3}})^{3/2}} = 3.795\ (\mathrm{mol/dm^3})^{-3/2}\ \mathrm{s^{-1}}$$

(b) We may write the rate expression as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\,[\mathrm{COCl_2}]^m\,[\mathrm{Cl_2}]^n$$

Proceeding similarly as in part (a), we will get

$$m = \frac{\log\{(\mathrm{d}x/\mathrm{d}t)_{01}/\mathrm{mol\ dm^{-3}\ s^{-1}}\} - \log\{(\mathrm{d}x/\mathrm{d}t)_{02}/\mathrm{mol\ dm^{-3}\ s^{-1}}\}}{\log\{[\mathrm{COCl_2}]_{01}/\mathrm{mol\ dm^{-3}}\} - \log\{[\mathrm{COCl_2}]_{02}/\mathrm{mol\ dm^{-3}}\}}$$

$$n = \frac{\log\{(\mathrm{d}x/\mathrm{d}t)_{01}/\mathrm{mol\ dm^{-3}\ s^{-1}}\} - \log\{(\mathrm{d}x/\mathrm{d}t)_{02}/\mathrm{mol\ dm^{-3}\ s^{-1}}\}}{\log\{[\mathrm{Cl_2}]_{01}/\mathrm{mol\ dm^{-3}}\} - \log\{[\mathrm{Cl_2}]_{02}/\mathrm{mol\ dm^{-3}}\}}$$

Thus from the first and third, and first and second experiments, we get

$$m = \frac{\log(1.9\times10^{-2})-\log(4.8\times10^{-3})}{\log(0.16)-\log(0.04)} = \frac{\bar{2}.2788-\bar{3}.6812}{\bar{1}.2041-\bar{2}.6021} = \frac{0.5976}{0.6020}$$

$$\simeq 1$$

$$n = \frac{\log(1.9\times10^{-2})-\log(9.6\times10^{-3})}{\log(0.16)-\log(0.04)} = \frac{\bar{2}.2788-\bar{3}.9823}{\bar{1}.2041-\bar{2}.6021} = \frac{0.2965}{0.6020}$$

$$= 1/2$$

Hence, the rate expression is

$$\frac{dx}{dt} = k[COCl_2][Cl_2]^{1/2}$$

For the value of k, we get from the first experiment

$$1.9 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1} = k\,(0.16 \text{ mol dm}^{-3})(0.16 \text{ mol dm}^{-3})^{1/2}$$

$$k = \frac{1.9\times10^{-2}\text{ mol dm}^{-3}\text{ s}^{-1}}{(0.16\text{ mol dm}^{-3})(0.16\text{ mol dm}^{-3})^{1/2}} = 0.297\ (\text{mol/dm}^3)^{-1/2}\ \text{s}^{-1}$$

9. For the bromination of acetone

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + H^+ + Br^-$$

the following data were obtained.

Experiment Number	$[CH_3COCH_3]$ / mol dm^{-3}	$[Br_2]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$-d[Br_2]/dt$ / mol dm^{-3} s^{-1}
1	0.30	0.05	0.05	5.7×10^{-5}
2	0.30	0.10	0.05	5.7×10^{-5}
3	0.30	0.05	0.10	1.14×10^{-4}
4	0.40	0.05	0.20	3.04×10^{-4}
5	0.40	0.05	0.05	7.6×10^{-5}

Calculate the rate constant for the reaction.

Solution

We may write the rate expression as

$$-\frac{d[Br_2]}{dt} = k\,[CH_3COCH_3]^{\alpha}\,[Br_2]^{\beta}\,[H^+]^{\gamma}$$

Proceeding similarly as in Q. 8, we have

$$\alpha = \frac{\log\{(-d[Br_2]/dt)_{01}/\text{mol dm}^{-3}\text{ s}^{-1}\}-\log\{(-d[Br_2]/dt)_{05}/\text{mol dm}^{-3}\text{ s}^{-1}\}}{\log\{[CH_3COCH_3]_{01}/\text{mol dm}^{-3}\}-\log\{[CH_3COCH_3]_{05}/\text{mol dm}^{-3}\}}$$

$$\beta = \frac{\log\{(-d[Br_2]/dt)_{01}/\text{mol dm}^{-3}\text{ s}^{-1}\}-\log\{(-d[Br_2]/dt)_{02}/\text{mol dm}^{-3}\text{ s}^{-1}\}}{\log\{[Br_2]_{01}/\text{mol dm}^{-3}\}-\log\{[Br_2]_{02}/\text{mol dm}^{-3}\}}$$

$$\gamma = \frac{\log\{(-d[Br_2]/dt)_{01}/\text{mol dm}^{-3}\text{ s}^{-1}\}-\log\{(-d[Br_2]/dt)_{03}/\text{mol dm}^{-3}\text{ s}^{-1}\}}{\log\{[H^+]_{01}/\text{mol dm}^{-3}\}-\log\{[H^+]_{03}/\text{mol dm}^{-3}\}}$$

Thus, making use of experiments 1 and 5, 1 and 2, and 1 and 3, respectively, we get

$$\alpha = \frac{\log(5.7\times10^{-5}) - \log(7.6\times10^{-5})}{\log(0.30) - \log(0.40)} = \frac{\bar{5}.7559 - \bar{5}.8808}{\bar{1}.4771 - \bar{1}.6021} = \frac{1.8751}{1.8750} = 1$$

$$\beta = \frac{\log(5.7\times10^{-5}) - \log(5.7\times10^{-5})}{\log(0.05) - \log(0.1)} = 0$$

$$\gamma = \frac{\log(5.7\times10^{-5}) - \log(1.14\times10^{-4})}{\log(0.05) - \log(0.10)} = \frac{\bar{5}.7559 - \bar{4}.0569}{\bar{2}.6990 - \bar{1}.0000} = \frac{1.6990}{1.6990} = 1$$

Hence, the rate expression is

$$-\frac{d[Br_2]}{dt} = [CH_3COCH_3]\,[H^+]$$

Making use of the first experiment, we get

$$5.7 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{s}^{-1} = k\ (0.30\ \text{mol dm}^{-3})\ (0.05\ \text{mol dm}^{-3})$$

$$k = \frac{(5.7\times10^{-5}\ \text{mol dm}^{-3}\,\text{s}^{-1})}{(0.3\ \text{mol dm}^{-3})(0.05\ \text{mol dm}^{-3})} = 3.80 \times 10^{-3}\ (\text{mol/dm}^3)^{-1}\ \text{s}^{-1}$$

10. The following data were obtained during the saponification of an ester. Determine the order of the reaction by the half-life method and the value of rate constant.

t/s	0	100	200	300	400	500	600	700	800
[A]/(mol dm^{-3})	0.050	0.035 5	0.027 5	0.022 5	0.018 5	0.016 0	0.014 8	0.014 0	0.013 8

Solution

From the given data, we plot a graph between [A] and t and determine from the graph $t_{\frac{1}{2}}$ for various initial concentrations of A. If these times are independent of $[A]_0$, we may conclude that the reaction is of first-order. If it is not so we plot $t_{\frac{1}{2}}$ versus $1/[A]_0$ to determine whether the reaction is second-order. If we get a straight-line plot, we conclude that the reaction is of second-order. If a straight-line plot is not obtained, we may plot $t_{\frac{1}{2}}$ versus $1/[A]_0^2$ to determine whether the reaction is of third-order

The graph between [A] and t is shown in Fig. 2.7.6a. From the graph, we obtain the following data:

$[A]_0$/mol dm^{-3}	0.05	0.045	0.040	0.035	0.030
$t_{\frac{1}{2}}$/s	245	270	300	325	400

Since $t_{\frac{1}{2}}$ is not independent of $[A]_0$, we plot a graph between $t_{\frac{1}{2}}$ and $1/[A]_0$ (Fig. 2.7.6b). The graph obtained is a straight line and thus the reaction is of second-order. The slope of the rate expression, which is equal to $1/k_2$, is equal 11.57 mol dm^{-3} s. Thus

$$k = \frac{1}{\text{slope}} = \frac{1}{11.57\ \text{mol dm}^{-3}\ \text{s}} = 0.086\,4\ (\text{mol dm}^{-3})^{-1}\ \text{s}^{-1}$$

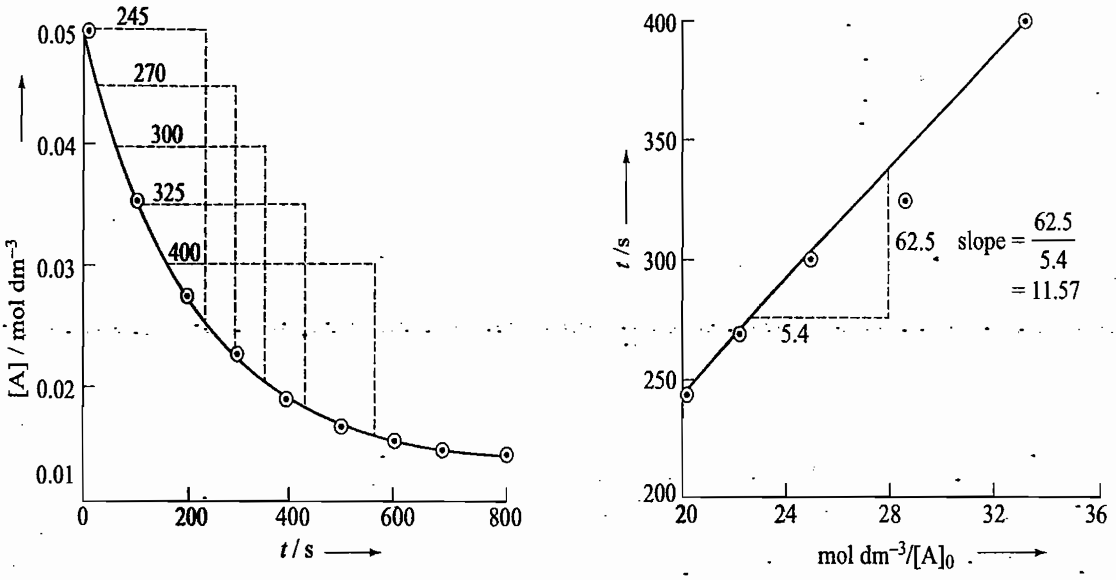


Fig. 2.7.6

(a)

(b)

11. The reaction $2NO + H_2 = N_2O + H_2O$ follows the rate law

$$\frac{dp(N_2O)}{dt} = k(p_{NO})^2\, p_{H_2}$$

The following data have been obtained.

Run	$(p_{NO})_0$	$(p_{H_2})_0$	*Half-life Time*	*Temperature*
	mmHg	mmHg	s	°C
1	600	10	19.2	820
2	600	20	?	820
3	10	600	830	820
4	20	600	?	820
5	600	10	10	840

Answer the following.

(a) What is the value of half-life time not shown above?

(b) What is the value of k at 820 °C?

(c) Calculate the half-life time at 820 °C if $p_{NO} = 20$ mmHg and $p_{H_2} = 10$ mmHg.

(d) Calculate the value of E_a from the equation

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Solution

(a) In runs 1 and 2, $(p_{NO})_0$ is very large in comparison to $(p_{H_2})_0$. Thus, under these conditions, we may consider the rate of reaction to be independent of $p(NO)$ and hence reaction will follow the rate law

$$\left(\frac{dp_{N_2O}}{dt}\right)_0 = k(p_{H_2})_0$$

that is, the reaction is first-order. Its half-life time will be given by

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{2.303\times 0.310}{k} = \frac{0.693}{k}$$

Since $t_{\frac{1}{2}}$ is independent of initial concentration, it follows that $t_{\frac{1}{2}}$ in run 2 will be the same as that of run 1, i.e. 19.2 s.

Now in runs 3 and 4, $(p_{H_2})_0$ is very large and the reaction will follow the rate law

$$\left(\frac{dp_{N_2O}}{dt}\right)_0 = k(p_{NO})_0^2$$

that is, the reaction is second-order. Its half-time will be given by

$$t_{\frac{1}{2}} \propto \frac{1}{(p_{NO})_0}$$

Now since $(p_{NO})_0$ is doubled in run 4 as compared to run 3, it follows that $t_{0.5}$ will be reduced to half, i.e. 830 s/2 = 415 s.

(b) For the data of run 1, we have

$$k_{app} = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{(19.2\ s)} = 0.036\ s^{-1}$$

But $k_{app} = k\,(p_{NO})_0^2$

so $$k = \frac{k_{app}}{(p_{NO})_0^2} = \frac{(0.036\ s^{-1})}{(600\ mmHg)^2} = 1 \times 10^{-7}\ mmHg^{-2}\ s^{-1}$$

(c) For the given data of $(p_{NO})_0 = 20$ mmHg and $(p_{H_2})_0 = 10$ mmHg, the system becomes a special case for which the rate expression is

$$-\frac{d\{p(H_2)\}}{dt} = k\,\{p(NO)\}^2\,p(H_2)$$
$$= k\,\{2p(H_2)\}^2\,p(H_2) = 4k\,\{p(H_2)\}^3$$

On integration, we get

$$\frac{1}{\{p(H_2)\}^2} - \frac{1}{\{p(H_2)\}_0^2} = 8kt$$

and the half-life is given by

$$\frac{1}{\{p(H_2)/2\}_0^2} - \frac{1}{\{p(H_2)\}_0^2} = 8kt_{\frac{1}{2}}$$

or $$t_{\frac{1}{2}} = \frac{3}{8k\{p(H_2)\}_0^2}$$

Hence, $$t_{\frac{1}{2}} = \frac{3}{8(1\times10^{-7}\ mmHg^{-2}s^{-1})(10\ mmHg)^2} = 3.8 \times 10^4\ s$$

(d) At 840 °C, $t_{\frac{1}{2}} = 10$ s. Hence k is given by

$$k_{app} = \frac{0.693}{t_{\frac{1}{2}}} = 0.069\ 3\ s^{-1}$$

$$k = \frac{k_{app}}{(p_{NO})^2} = \frac{(0.069\ 3s^{-1})}{(600\,mmHg)^2} = 1.92 \times 10^{-7}\ mmHg^{-2}\ s^{-1}$$

Hence by using the given expression, we get

$$\ln\left(\frac{1.92}{1}\right) = \frac{E_a}{R}\left(\frac{1}{1\ 093\,K} - \frac{1}{1\ 113\,K}\right)$$

or $$E_a = \frac{(2.303\times 0.2833)(8.314\,\mathrm{J\,K^{-1}mol^{-1}})(1\,093\,\mathrm{K})(1\,113\,\mathrm{K})}{20\,\mathrm{K}}$$

$$= 3.299\,4 \times 10^5\ \mathrm{J\,mol^{-1}} = 329.94\ \mathrm{kJ\,mol^{-1}}$$

2.8 REACTION ORDER AND REACTION MECHANISM

One of the most important applications of studying the order of a reaction is to use it in establishing the molecular path or the mechanism of the reaction. A given reaction may proceed in one elementary step or more than one elementary step. It was stated earlier that the order of an elementary step is always equal to its molecularity, i.e. a unimolecular elementary reaction will observe first-order kinetics, a bimolecular elementary reaction will follow second-order kinetics and a termolecular reaction will follow third-order kinetics. It is reasonable to assume that the reaction of any one elementary step results when the reacting species come close and collide with each other. Only during collision, molecular rearrangement can take place which leads to the formation of products. Since the probability of four molecules coming together and colliding with one another is very remote, the elementary reactions with molecularity more than three (and order greater than three) are not observed.

It can be stated that if the over-all order of a reaction corresponds to the stoichiometric equation, the reaction mechanism may or may not involve only one elementary reaction that is identical with the stoichiometric equation.[†] When the reaction order does not correspond to the stoichiometry of the reaction, the reaction certainly involves more than one elementary reaction. It is then necessary to devise a series of elementary reactions that is consistent with the reaction order found experimentally. In many cases, it is possible to design more than one mechanism consistent with the experimental findings. However, additional experimental evidences can be collected to prove or disprove any proposed mechanism.

In many reaction mechanisms, the following types of elementary reactions are involved.

1. Opposed or reversible elementary reactions.
2. Side or concurrent elementary reactions.
3. Consecutive or sequential reactions.

Before considering the reaction mechanisms of important reactions, it is worthwhile to study the characteristics of the above elementary steps.

2.9 OPPOSED OR REVERSIBLE ELEMENTARY REACTIONS

Opposed or reversible elementary reactions are those reactions in which both forward and backward reactions take place simultaneously. To start with, the rate of forward reaction is very large and it diminishes as the concentrations of reactants decrease with time. On the other hand, initially the rate of backward reaction is slow and it increases as the concentrations of products increase with time. Very

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[†] One of the examples where it is not true is the dehydrogenation of ethane, see Eq. (2.14.10).

soon, a stage is reached where the rate of forward reaction becomes equal to that of backward reaction and thus no further net progress is observed. This situation is known as the equilibrium state. Thus, equilibrium is a dynamic equilibrium where all the participants of a reaction are being formed as fast as they are being destroyed and hence no further change in the various concentrations is observed.

A reversible reaction may be classified on the basis of orders of elementary forward and backward reactions. We describe below a few reversible reactions classified according to the above scheme.

FIRST-ORDER OPPOSED BY FIRST-ORDER

Differential Rate Law

Such type of reactions may be represented as

$$\mathrm{A} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{B} \qquad (2.9.1)$$

where k_f and k_b are the reaction rate constants of forward and back reactions, respectively.

The rate at which the reaction proceeds will be given by

Rate of reaction = Rate of forward reaction − Rate of backward reaction

i.e.
$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_f[\mathrm{A}] - k_b[\mathrm{B}]$$

Let the reaction be started with only reactant A. If x is the extent of reaction divided by volume, we will have

$$[\mathrm{A}] = [\mathrm{A}]_0 - x$$

$$[\mathrm{B}] = x$$

Substituting these in the previous expression, we get

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_f([\mathrm{A}]_0 - x) - k_b x \qquad (2.9.2)$$

At equilibrium state, $\mathrm{d}x/\mathrm{d}t$ will be equal to zero and hence Eq. (2.9.2) may be written as

$$k_f([\mathrm{A}]_0 - x_{eq}) = k_b x_{eq} \qquad (2.9.3)$$

where x_{eq} is the concentration of A that has been transformed into B at the equilibrium state. From Eq. (2.9.3), we get

$$k_b = k_f\left(\frac{[\mathrm{A}]_0 - x_{eq}}{x_{eq}}\right) \qquad (2.9.4)$$

Substituting Eq. (2.9.4) into Eq. (2.9.2), we get

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_f([\mathrm{A}]_0 - x) - k_f\left(\frac{[\mathrm{A}]_0 - x_{eq}}{x_{eq}}\right) x$$

i.e.
$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_f \frac{[\mathrm{A}]_0}{x_{eq}} (x_{eq} - x) \qquad (2.9.5)$$

Equation (2.9.5) is the differential rate expression for the reaction given by Eq. (2.9.1).

Integrated Rate Law

The integrated rate expression can be obtained by integrating Eq. (2.9.5). Thus, we have

$$\int_0^x \frac{\mathrm{d}x}{x_{\mathrm{eq}} - x} = k_{\mathrm{f}} \frac{[\mathrm{A}]_0}{x_{\mathrm{eq}}} \int_0^t \mathrm{d}t$$

which yields

$$-\ln(x_{\mathrm{eq}} - x) + \ln x_{\mathrm{eq}} = k_{\mathrm{f}} \frac{[\mathrm{A}]_0}{x_{\mathrm{eq}}}\, t$$

or

$$\ln\left(\frac{x_{\mathrm{eq}}}{x_{\mathrm{eq}} - x}\right) = k_{\mathrm{f}} \frac{[\mathrm{A}]_0}{x_{\mathrm{eq}}}\, t \qquad (2.9.6)$$

Equation (2.9.6) can be used to determine the value of k_{f} from the measurable quantities $[\mathrm{A}]_0$, x_{eq} and x at time t. Knowing k_{f}, k_{b} can be determined from Eq. (2.9.4).

Equation (2.9.6) can be written in an alternative form. From Eq. (2.9.3), we may write

$$k_{\mathrm{f}}[\mathrm{A}]_0 = (k_{\mathrm{f}} + k_{\mathrm{b}})\, x_{\mathrm{eq}}$$

or

$$\frac{[\mathrm{A}]_0}{x_{\mathrm{eq}}} = \frac{k_{\mathrm{f}} + k_{\mathrm{b}}}{k_{\mathrm{f}}} \qquad (2.9.7)$$

Substituting the above expression in Eq. (2.9.6), we get

$$\ln\left(\frac{x_{\mathrm{eq}}}{x_{\mathrm{eq}} - x}\right) = (k_{\mathrm{f}} + k_{\mathrm{b}})\, t \qquad (2.9.8)$$

Equation (2.9.8) has a form of a simple first-order reaction (Eq. 2.5.6) where $[\mathrm{A}]_0$ has been replaced by x_{eq}, and k by $k_{\mathrm{f}} + k_{\mathrm{b}}$.

Concentration of A and B at Time *t*

Rearranging Eq. (2.9.8), we get

$$x = x_{\mathrm{eq}}[1 - \exp\{-(k_{\mathrm{f}} + k_{\mathrm{b}})\, t\}] \qquad (2.9.9)$$

Eliminating x_{eq} by making use of Eq. (2.9.7), we get

$$x = \frac{[\mathrm{A}]_0 k_{\mathrm{f}}}{(k_{\mathrm{f}} + k_{\mathrm{b}})}[1 - \exp\{-(k_{\mathrm{f}} + k_{\mathrm{b}})\, t\}] \qquad (2.9.10)$$

Now since $[\mathrm{B}] = x$ and $[\mathrm{A}] = [\mathrm{A}]_0 - x$, we get

$$[\mathrm{B}] = \frac{[\mathrm{A}]_0 k_{\mathrm{f}}}{(k_{\mathrm{f}} + k_{\mathrm{b}})}[1 - \exp\{-(k_{\mathrm{f}} + k_{\mathrm{b}})\, t\}] \qquad (2.9.11)$$

$$\begin{aligned}[\mathrm{A}] &= [\mathrm{A}]_0 - \frac{[\mathrm{A}]_0 k_{\mathrm{f}}}{(k_{\mathrm{f}} + k_{\mathrm{b}})}[1 - \exp\{-(k_{\mathrm{f}} + k_{\mathrm{b}})\, t\}] \\ &= [\mathrm{A}]_0 \frac{k_{\mathrm{f}}}{(k_{\mathrm{f}} + k_{\mathrm{b}})}\left[\frac{k_{\mathrm{b}}}{k_{\mathrm{f}}} + \exp\{-(k_{\mathrm{f}} + k_{\mathrm{b}})\, t\}\right] \qquad (2.9.12)\end{aligned}$$

Equilibrium Constant of the Reaction

The equilibrium reaction described by Eq. (2.9.1) can be characterized by the equilibrium constant K_{eq}, given as

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{x_{eq}}{[A]_0 - x_{eq}} \tag{2.9.13}$$

From Eq. (2.9.3), we find that

$$\frac{x_{eq}}{[A]_0 - x_{eq}} = \frac{k_f}{k_b}$$

and hence

$$K_{eq} = \frac{k_f}{k_b} \tag{2.9.14}$$

that is, *the equilibrium constant is simply the ratio of the forward and backward rate constants*. Equation (2.9.14) is, in fact, applicable to all types of one-step reversible reactions.

Rate Expression if $[B]_0$ is not Equal to Zero

Equations (2.9.5) and (2.9.6) are applicable when the equilibrium reaction (Eq. 2.9.1) is started with only A and no B. If to start with both A and B are present with concentrations $[A]_0$ and $[B]_0$, respectively, then Eq. (2.9.2) takes the form

$$\frac{dx}{dt} = k_f([A]_0 - x) - k_b([B]_0 + x) \tag{2.9.15}$$

Thus, at equilibrium, we will have

$$k_f\,([A]_0 - x_{eq}) = k_b\,([B]_0 + x_{eq})$$

or $$k_b = k_f\left(\frac{[A]_0 - x_{eq}}{[B]_0 + x_{eq}}\right) \tag{2.9.16}$$

With Eq. (2.9.16), Eq. (2.9.15) becomes

$$\frac{dx}{dt} = k_f\,([A]_0 - x) - k_f\left(\frac{[A]_0 - x_{eq}}{[B]_0 + x_{eq}}\right)([B]_0 + x)$$

$$= k_f\left(\frac{[A]_0 + [B]_0}{[B]_0 + x_{eq}}\right)(x_{eq} - x) \tag{2.9.17}$$

On integrating Eq. (2.9.17), we have

$$\int_0^x \frac{dx}{x_{eq} - x} = k_f\left(\frac{[A]_0 + [B]_0}{[B]_0 + x_{eq}}\right)\int_0^t dt$$

i.e. $$\ln\frac{x_{eq}}{x_{eq} - x} = k_f\left(\frac{[A]_0 + [B]_0}{[B]_0 + x_{eq}}\right)t \tag{2.9.18}$$

Equation (2.9.18) is reduced to Eq. (2.9.8) if x_{eq} on the right-hand side is eliminated with the help of Eq. (2.9.16) with $[B]_0 = 0$.

Examples

The examples of reaction described by Eq. (2.9.1) include the mutarotation of π-bromonitrocamphor in chloroform solution at 14 °C and isomerization of cyclopropane into propene.

Example 2.9.1 For the reaction

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{P}$$

The percentage of A varies with time as follows

Time/h	0	1	2	3	4	∞
% A	100	72.5	56.8	45.6	39.5	30

Calculate k_1, k_{-1} and K_1.

Solution The given reaction will follow first-order kinetics with

$$\ln\left(\frac{x_{\mathrm{eq}} - x}{x_{\mathrm{eq}}}\right) = -(k_1 + k_{-1})\,t \qquad \text{(Eq. 2.9.8)}$$

where x and x_{eq} are the concentrations of P at times t and t_{eq}, respectively. The value of $-(k_1 + k_{-1})/2.303$ is determined from the straight-line plot of $\log\{(x_{\mathrm{eq}} - x)/x_{\mathrm{eq}}\}$ versus t (Fig. 2.9.1). Thus, we have

t/h	0	1	2	3	4
$(x_{\mathrm{eq}} - x)/x_{\mathrm{eq}} = \dfrac{70-(100-\%\mathrm{A})}{70}$	1	0.607	0.383	0.223	0.136
$\log\{(x_{\mathrm{eq}} - x)/x_{\mathrm{eq}}\}$	0	$\bar{1}.783$	$\bar{1}.583$	$\bar{1}.348$	$\bar{1}.133$

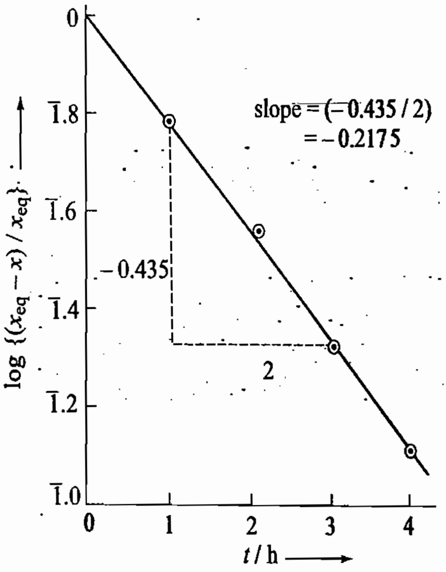


Fig. 2.9.1 Plot of $\log\{x_{\mathrm{eq}} - x)/x_{\mathrm{eq}}\}$ versus t

From Fig. 2.9.1, we get

$$\text{slope} = -0.2175$$

i.e.

$$\frac{\Delta\{\log(x_{\mathrm{eq}} - x)/x_{\mathrm{eq}}\}}{\Delta(t/\mathrm{h})} = -0.2175$$

Hence, the slope of the rate law is

$$\frac{\Delta\{\log(x_{\mathrm{eq}} - x)/x_{\mathrm{eq}}\}}{\Delta t} = -0.2175\ \mathrm{h}^{-1}$$

Thus, we have

$$\frac{k_1 + k_{-1}}{2.303} = 0.217\,5\ \mathrm{h^{-1}}$$

or $$k_1 + k_{-1} = 2.303 \times 0.217\,5\ \mathrm{h^{-1}} \tag{1}$$

Now at equilibrium, we will have

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\mathrm{P}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{70}{30} = 2.333 \tag{2}$$

Solving for k_1 and k_{-1} from Eqs (1) and (2), we get

$$k_1 = 0.350\,7\ \mathrm{h^{-1}} = (0.350\,7/3\,600)\ \mathrm{s^{-1}} = 9.74 \times 10^{-5}\ \mathrm{s^{-1}}$$

$$k_{-1} = 0.150\,4\ \mathrm{h^{-1}} = (0.150\,4/3\,600)\ \mathrm{s^{-1}} = 4.18 \times 10^{-5}\ \mathrm{s^{-1}}$$

FIRST-ORDER OPPOSED BY SECOND-ORDER

Differential Rate Law

The general reaction may be written as

$$\mathrm{A} \underset{k_{\mathrm{b}}}{\overset{k_{\mathrm{f}}}{\rightleftharpoons}} \mathrm{B} + \mathrm{C} \tag{2.9.19}$$

The rate of production of B or C will be given by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{f}}([\mathrm{A}]_0 - x) - k_{\mathrm{b}}\,x^2 \tag{2.9.20}$$

where x is the concentration of A that has transformed into products at time t. Since at equilibrium $\mathrm{d}x/\mathrm{d}t = 0$, we have

$$k_{\mathrm{f}}([\mathrm{A}]_0 - x_{\mathrm{eq}}) = k_{\mathrm{b}}\,x_{\mathrm{eq}}^2$$

or $$k_{\mathrm{b}} = k_{\mathrm{f}}\,\frac{[\mathrm{A}]_0 - x_{\mathrm{eq}}}{x_{\mathrm{eq}}^2} \tag{2.9.21}$$

Substituting the above expression in Eq. (2.9.20), we get

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{f}}\left[([\mathrm{A}]_0 - x) - \frac{[\mathrm{A}]_0 - x_{\mathrm{eq}}}{x_{\mathrm{eq}}^2}\,x^2\right] \tag{2.9.22}$$

Equation (2.9.22) is the differential rate law of the reaction given by Eq. (2.9.19).

Integrated Rate Law

Equation (2.9.22) can be integrated to obtain the integrated rate expression. Without going into the details, we write only the integrated rate expression:

$$\ln\frac{[\mathrm{A}]_0\,x_{\mathrm{eq}} + x([\mathrm{A}]_0 - x_{\mathrm{eq}})}{[\mathrm{A}]_0\,(x_{\mathrm{eq}} - x)} = k_{\mathrm{f}}\,\frac{2[\mathrm{A}]_0 - x_{\mathrm{eq}}}{x_{\mathrm{eq}}}\,t \tag{2.9.23}$$

Examples

The examples of the reaction are the decomposition of certain alkylammonium halides into a tertiary amine and an alkyl halide in aqueous medium.

SECOND-ORDER OPPOSED BY FIRST-ORDER

Differential Rate Law

The general reaction may be written as

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \tag{2.9.24}$$

The rate of production of C will be given by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{f}([\mathrm{A}] - x)([\mathrm{B}]_0 - x) - k_\mathrm{b}\, x \qquad (2.9.25)$$

where x is the concentration of A or B reacted in time t. At equilibrium, we will have

$$k_\mathrm{f}([\mathrm{A}]_0 - x_\mathrm{eq})\,([\mathrm{B}]_0 - x_\mathrm{eq}) = k_\mathrm{b}\, x_\mathrm{eq}$$

or $$k_\mathrm{b} = k_\mathrm{f}\,\frac{([\mathrm{A}]_0 - x_\mathrm{eq})([\mathrm{B}]_0 - x_\mathrm{eq})}{x_\mathrm{eq}} \qquad (2.9.26)$$

Substituting the above expression in Eq. (2.9.25), we get

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{f}\left[([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x) - \frac{([\mathrm{A}]_0 - x_\mathrm{eq})([\mathrm{B}]_0 - x_\mathrm{eq})}{x_\mathrm{eq}}\,x\right] \qquad (2.9.27)$$

Integrated Rate Law

The integrated form of Eq. (2.9.27) when $[\mathrm{A}]_0 = [\mathrm{B}]_0 = a$ is

$$\ln\frac{x_\mathrm{eq}(a^2 - x\,x_\mathrm{eq})}{a^2(x_\mathrm{eq} - x)} = k_\mathrm{f}\,\frac{a^2 - x_\mathrm{eq}^2}{x_\mathrm{eq}}\,t \qquad (2.9.28)$$

Examples

One of the examples is the isomerization of an alkyl ammonium cyanate to the corresponding substituted urea in aqueous solution, i.e.

$$\mathrm{NH_3R^+ + CNO^- \rightleftharpoons H_2NCONHR}$$

SECOND-ORDER OPPOSED BY SECOND-ORDER

Differential Rate Law

The general reaction may be represented as

$$\mathrm{A + B \rightleftharpoons C + D} \qquad (2.9.29)$$

The rate of production of C or D will be given by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{f}([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x) - k_\mathrm{b}\, x^2 \qquad (2.9.30)$$

where x is the concentration of A or B reacted at time t. At equilibrium, we will have

$$k_\mathrm{f}([\mathrm{A}]_0 - x_\mathrm{eq})([\mathrm{B}]_0 - x_\mathrm{eq}) = k_\mathrm{b}\, x_\mathrm{eq}^2$$

or $$k_\mathrm{b} = k_\mathrm{f}\,\frac{([\mathrm{A}]_0 - x_\mathrm{eq})([\mathrm{B}]_0 - x_\mathrm{eq})}{x_\mathrm{eq}^2} \qquad (2.9.31)$$

With the above expression, Eq. (2.9.30) becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{f}\left[([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x) - \frac{([\mathrm{A}]_0 - x_\mathrm{eq})([\mathrm{B}]_0 - x_\mathrm{eq})}{x_\mathrm{eq}^2}\,x^2\right] \qquad (2.9.32)$$

Integrated Rate Law

The integrated form of Eq. (2.9.32) when $[\mathrm{A}]_0 = [\mathrm{B}]_0 = a$ is

$$\ln\frac{x(a - 2x_\mathrm{eq}) + a x_\mathrm{eq}}{a(x_\mathrm{eq} - x)} = k_\mathrm{f}\,\frac{2a(a - x_\mathrm{eq})}{x_\mathrm{eq}^2}\,t \qquad (2.9.33)$$

Examples Examples include the reactions

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

$$O_3(g) + NO(g) \rightleftharpoons O_2(g) + NO_2(g)$$

$$CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$$

PRINCIPLE OF MICROSCOPIC REVERSIBILITY

The equilibrium constant K_{eq} of the reaction A $\rightleftharpoons$ B given by Eq. (2.9.14) is

$$K_{eq} = \frac{k_f}{k_b} \qquad \text{(Eq. 2.9.14)}$$

The above relation was derived from the principle that at equilibrium the rate of forward reaction is equal to the rate of backward reaction. In fact, Eq. (2.9.14) is applicable to all types of one-step elementary reversible reactions. For example, consider a reaction of the type second-order opposed by second-order, i.e.

$$A + B \rightleftharpoons C + D$$

At equilibrium, we will have

Rate of forward reaction = Rate of backward reaction

$$k_f[A]_{eq}[B]_{eq} = k_b[C]_{eq}[D]_{eq}$$

Hence $$K_{eq} = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}} = \frac{k_f}{k_b}$$

The principle that for one-step elementary reaction at equilibrium, the rate of forward reaction is equal to the rate of backward reaction, is known as the *principle of microscopic reversibility*. This principle helps us in establishing the connection between the equilibrium constant of an elementary reaction and the rate constants of its forward and backward processes. If a reaction mechanism involves more than one elementary process, each elementary process follows the principle of microscopic reversibility. For example, the reaction

$$2NO_2 + F_2 \rightleftharpoons 2NO_2F \qquad (2.9.34)$$

involves the following two elementary reactions.

$$NO_2 + F_2 \xrightarrow{k_f} NO_2F + F$$

$$F + NO_2 \xrightarrow{k_f'} NO_2F$$

The condition for equilibrium of the reaction of Eq. (2.9.34) is that each elementary process and its reverse proceed at the same rate. The reverse reactions of the above two elementary reactions are

$$F + NO_2F \xrightarrow{k_b} NO_2 + F_2$$

$$NO_2F \xrightarrow{k_b'} NO_2 + F$$

Thus, from the principle of microscopic reversibility, we have

$$k_f[NO_2]_{eq}[F_2]_{eq} = k_b[F]_{eq}[NO_2F]_{eq}$$

and $$k_f'[F]_{eq}[NO_2]_{eq} = k_b'[NO_2F]_{eq}$$

Eliminating $[F]_{eq}$ in the above relations, we get

$$k_f\,[NO_2]_{eq}\,[F_2]_{eq} = k_b\,\frac{k_b'[NO_2F]_{eq}}{k_f'[NO_2]_{eq}}\,[NO_2F]_{eq}$$

or

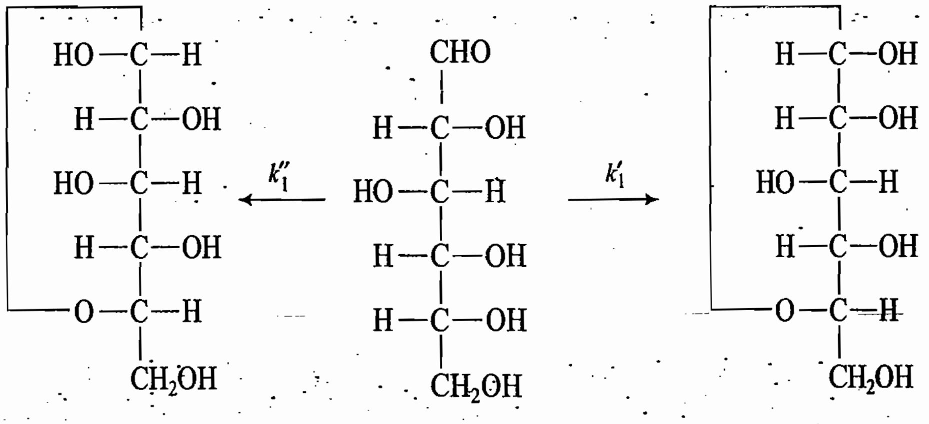
$$\frac{k_f k_f'}{k_b k_b'} = \frac{[NO_2F]^2_{eq}}{[NO_2]^2_{eq}[F_2]_{eq}}$$

The right side of the above equation is the equilibrium constant of the reaction described by Eq. (2.9.34) and hence

$$K_{eq} = \frac{k_f k_f'}{k_b k_b'} \tag{2.9.35}$$

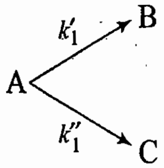
2.10 SIDE OR CONCURRENT ELEMENTARY REACTIONS

A Typical Example Sometimes the products observed are formed by the same reactants undergoing more than one reaction. For example, α-D- glucose and β-D-glucose are formed in solution from the aldehydic form of D-glucose following the different reactions:



β-D-glucose aldehydic form of D-glucose α-D-glucose

The example cited above may be written as



Differential Rate Law The differential rate expressions for the above two reactions are

$$r_1' = -\frac{d[A]}{dt} = k_1'[A]$$

$$r_1'' = -\frac{d[A]}{dt} = k_1''[A]$$

The overall-rate of disappearance of A is given as

$$r_1' + r_1'' = -\frac{d[A]}{dt} = (k_1' + k_1'')[A] = k_1[A] \tag{2.10.1}$$

The first-order rate constant k_1 is the sum of the two rate constants k_1' and k_1'' of the two side reactions.

Integrated Rate Law

Equation (2.10.1) can be integrated to get the integrated rate expression. Thus, we have

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k_1 \int_0^t dt$$

$$\ln \frac{[A]_0}{[A]_t} = k_1 t = (k_1' + k_1'')\, t \qquad (2.10.2)$$

Since the rate of formation of products B and C are given by

$$\frac{d[B]}{dt} = k_1'[A]_t \qquad \text{and} \qquad \frac{d[C]}{dt} = k_1''[A]_t$$

it follows that the ratio of concentrations of B and C at any instant will be given by

$$\frac{[B]}{[C]} = \frac{k_1'}{k_1''}$$

Hence, if the ratio of B and C is determined at any instant (or at the end of the experiment) and $k_1' + k_1''$ is determined from the kinetic study (Eq. 2.10.2), it is possible to determine the individual constants k_1' and k_1''.

A More Involved Example

In many cases, stoichiometric coefficients of reactants in concurrent reactions are not the same. For example, we may have the concurrent reactions of the type

$$A \xrightarrow{k_1} B$$

$$2A \xrightarrow{k_2} C$$

$$3A \xrightarrow{k_3} D$$

If we assume the above reactions to be elementary, we may write their differential rate expressions for the appearance of products as

$$r_1 = \frac{d[B]}{dt} = k_1[A]$$

$$r_2 = \frac{d[C]}{dt} = k_2[A]^2$$

$$r_3 = \frac{d[D]}{dt} = k_3[A]^3$$

The rate expressions for the disappearance of reactant will be given by

$$r_1 = -\frac{d[A]}{dt} = k_1[A]$$

$$r_2 = -\frac{1}{2}\frac{d[A]}{dt} = k_2[A]^2$$

$$r_3 = -\frac{1}{3}\frac{d[A]}{dt} = k_3[A]^3$$

The total rate of disappearance of A will be given by

$$-\frac{d[A]}{dt} = k_1[A] + 2k_2[A]^2 + 3k_3[A]^3$$

2.11 CONSECUTIVE OR SEQUENTIAL REACTIONS

A Typical Example

In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$

$$\mathrm{B} \xrightarrow{k_1'} \mathrm{C}$$

Let the initial concentration of A be $[\mathrm{A}]_0$ and let after time t, the concentrations of A, B and C be [A], [B] and [C], respectively. It is obvious that

$$[\mathrm{A}]_0 = [\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}] \tag{2.11.1}$$

Differential Rate Law

The differential rate expressions are

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_1[\mathrm{A}] \tag{2.11.2}$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_1[\mathrm{A}] - k_1'[\mathrm{B}] \tag{2.11.3}$$

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_1'[\mathrm{B}] \tag{2.11.4}$$

On integrating Eq. (2.11.2), we get

$$[\mathrm{A}] = [\mathrm{A}]_0\ \mathrm{e}^{-k_1 t} \tag{2.11.5a}$$

Substituting [A] from Eq. (2.11.5a) into Eq. (2.11.3), we get

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_1[\mathrm{A}]_0\ \mathrm{e}^{-k_1 t} - k_1'[\mathrm{B}]$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} + k_1'[\mathrm{B}] = k_1[\mathrm{A}]_0\ \mathrm{e}^{-k_1 t}$$

Integrated Rate Law

Multiplying the above expression throughout by $\exp(k_1' t)$, we get

$$\left(\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} + k_1'[\mathrm{B}]\right)\mathrm{e}^{k_1' t} = k_1[\mathrm{A}]_0\ \mathrm{e}^{-(k_1 - k_1')t}$$

The left side of the above expression is equal to $\mathrm{d}([\mathrm{B}]\ \mathrm{e}^{k_1' t})/\mathrm{d}t$. Hence, the above expression can be written as

$$\mathrm{d}\{[\mathrm{B}]\mathrm{e}^{k_1' t}\} = k_1[\mathrm{A}]_0\ \mathrm{e}^{-(k_1 - k_1')t}\ \mathrm{d}t$$

Integrating the above expression with [B] = 0 at $t = 0$, we get

$$[\mathrm{B}]\mathrm{e}^{k_1' t} = k_1[\mathrm{A}]_0 \left[\frac{\mathrm{e}^{-(k_1 - k_1')t}}{-(k_1 - k_1')} + \frac{1}{k_1 - k_1'}\right]$$

$$[\mathrm{B}] = k_1[\mathrm{A}]_0 \left[\frac{\mathrm{e}^{-k_1 t}}{k_1' - k_1} + \frac{\mathrm{e}^{-k_1' t}}{k_1 - k_1'}\right]$$

$$[\mathrm{B}] = [\mathrm{A}]_0 \left(\frac{k_1}{k_1' - k_1}\right)\{\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_1' t}\} \tag{2.11.5b}$$

Substituting Eqs (2.11.5a) and (2.11.5b) in Eq. (2.11.1), we get

$$[A]_0 = [A]_0\ e^{-k_1 t} + [A]_0 \left(\frac{k_1}{k_1' - k_1}\right) (e^{-k_1 t} - e^{-k_1' t}) + [C]$$

or

$$[C] = [A]_0 \left\{1 - \frac{1}{k_1' - k_1}(k_1' e^{-k_1 t} - k_1 e^{-k_1' t}\right\} \qquad (2.11.5c)$$

Figure (2.11.1) illustrates the general appearance of the variations of concentrations of A, B and C during the progress of the reaction.

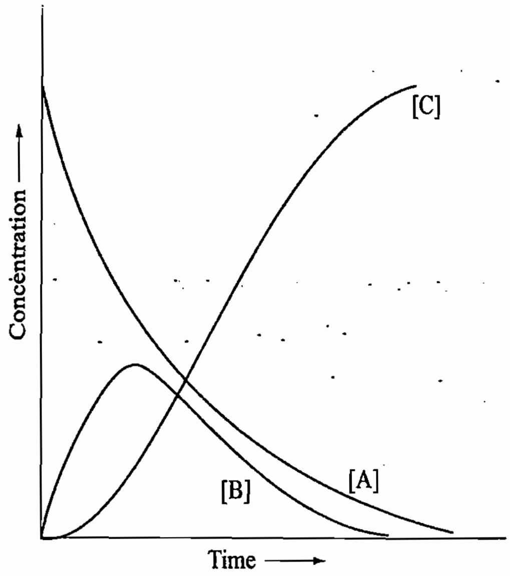


Fig. 2.11.1 Typical variations of concentrations of A, B and C during the progress of the reaction A → B → C. The actual variations depend on the values of k_1 and k_1'

In general, the concentration of A decreases exponentially, the concentration of B initially increases up to a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value $[A]_0$, when all A has changed into C.

Maximum Concentration of B

Equation (2.11.5b) is

$$[B] = [A]_0 \left(\frac{k_1}{k_1' - k_1}\right) \{e^{-k_1 t} - e^{-k_1' t}\} \qquad \text{(Eq. 2.11.5b)}$$

At the maximum concentration of B, we will have

$$\frac{d[B]}{dt} = 0$$

Hence, differentiating Eq. (2.11.5b) with respect to t, we get

$$\frac{d[B]}{dt} = [A]_0 \left(\frac{k_1}{k_1' - k_1}\right) \{- k_1\, e^{-k_1 t} + k_1'\, e^{-k_1' t}\} \qquad (2.11.6)$$

Equating Eq. (2.11.6) to zero, we get

$$- k_1\, e^{-k_1 t_{\max}} + k_1'\, e^{-k_1' t_{\max}} = 0$$

or

$$\frac{k_1}{k_1'} = e^{(k_1 - k_1') t_{\max}}$$

or $$\ln\left(\frac{k_1}{k_1'}\right) = (k_1 - k_1')\, t_{\max}$$

or $$t_{\max} = \frac{1}{k_1 - k_1'} \ln\left(\frac{k_1}{k_1'}\right) \tag{2.11.7}$$

Substituting Eq. (2.11.7) in Eq. (2.11.5b), we get

$$[\mathrm{B}]_{\max} = [\mathrm{A}]_0 \left(\frac{k_1'}{k_1}\right)^{k_1'/(k_1 - k_1')} \tag{2.11.8}$$

Examples of First-Order Consecutive Reactions

One of the most common examples is the radioactive decay. Other examples include the decomposition of dimethyl ether in the gaseous phase and that of the ethylene oxide. The reactions are

$$\mathrm{CH_3OCH_3} \xrightarrow{k_1} \mathrm{CH_4} + \mathrm{HCHO}$$

$$\mathrm{HCHO} \xrightarrow{k_2} \mathrm{H_2} + \mathrm{CO}$$

and $$\mathrm{(CH_2)_2O} \xrightarrow{k_1} \mathrm{(CH_3CHO)^*} \xrightarrow{k_2} \mathrm{CH_4} + \mathrm{CO}$$

Two Important Conclusions from Eqs (2.11.5)

From Eqs (2.11.5a), (2.11.5b) and (2.11.5c), two important conclusions which form the basis for deriving the differential rate laws of complex reactions can be derived. These are: (1) the slowest elementary process (i.e. the process having the smallest rate constant) is the *rate-determining step* of the reaction and (2) the *steady-state approximation* (which states that the reactive intermediates are present at constant concentrations) can be assumed to hold good for all reactive intermediates. We derive these conclusions as follows.

Rate-Determining Step

Suppose that in the consecutive reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_1'} \mathrm{C}$$

the reaction rate constant k_1' is very much larger than k_1. In other words, the reaction A → B is much slower than the reaction B → C. Qualitatively, we can say that the moment B is formed from A, it immediately transforms to C. Thus, the rate of formation of the product C depends wholly on the rate at which the intermediate B is formed from A. The same conclusion can be derived from Eq. (2.11.5c). We have

$$[\mathrm{C}] = [\mathrm{A}]_0 \left\{1 - \frac{1}{k_1' - k_1}\left(k_1' \mathrm{e}^{-k_1 t} - k_1 \mathrm{e}^{-k_1' t}\right)\right\} \tag{Eq. 2.11.5c}$$

Since $k_1' \gg k_1$, the $\mathrm{e}^{-k_1' t}$ will be much smaller than $\mathrm{e}^{-k_1 t}$ and hence $k_1 \mathrm{e}^{-k_1' t}$ may be ignored in comparison to $k_1' \mathrm{e}^{-k_1 t}$. Hence, Eq. (2.11.5c) in the present case simplifies to

$$[\mathrm{C}] \simeq [\mathrm{A}]_0 \left\{1 - \frac{k_1'}{k_1' - k_1} \mathrm{e}^{-k_1 t}\right\}$$

Since k_1 is much smaller than k_1', we may also ignore k_1 in comparison to k_1'. Thus, the above equation becomes

$$[\mathrm{C}] \simeq [\mathrm{A}]_0 (1 - \mathrm{e}^{-k_1 t}) \tag{2.11.9}$$

Equation (2.11.9) can be obtained directly if we consider alone the reaction

$$\mathrm{A} \rightarrow \mathrm{C}$$

Now $$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_1[\mathrm{A}] = k_1([\mathrm{A}]_0 - [\mathrm{C}]) \tag{2.11.10}$$

or $$\frac{\mathrm{d}[\mathrm{C}]}{[\mathrm{A}]_0 - [\mathrm{C}]} = k_1 \mathrm{d}t$$

or $$\int_0^{[\mathrm{C}]} \frac{\mathrm{d}[\mathrm{C}]}{[\mathrm{A}]_0 - [\mathrm{C}]} = k_1 \int_0^t \mathrm{d}t$$

or $$\ln \frac{[\mathrm{A}]_0 - [\mathrm{C}]}{[\mathrm{A}]_0} = -k_1 t$$

or $$\frac{[\mathrm{A}]_0 - [\mathrm{C}]}{[\mathrm{A}]_0} = \mathrm{e}^{-k_1 t}$$

Hence $[\mathrm{C}] = [\mathrm{A}]_0 (1 - \mathrm{e}^{-k_1 t})$

which is identical to Eq. (2.11.9). Thus, we may conclude that the reaction with the smaller rate constant is the rate-determining step. The same conclusion would be obtained if we consider that the first step is much faster than the second step, i.e. $k_1 \gg k_1'$. In this case, we will ignore k_1' in comparison to k_1 and $k_1' \mathrm{e}^{-k_1 t}$ in comparison to $k_1 \mathrm{e}^{-k_1' t}$. Hence, Eq. (2.11.5c) in the present case will simplify to

$$[\mathrm{C}] = [\mathrm{A}]_0 (1 - \mathrm{e}^{-k_1' t}) \tag{2.11.11}$$

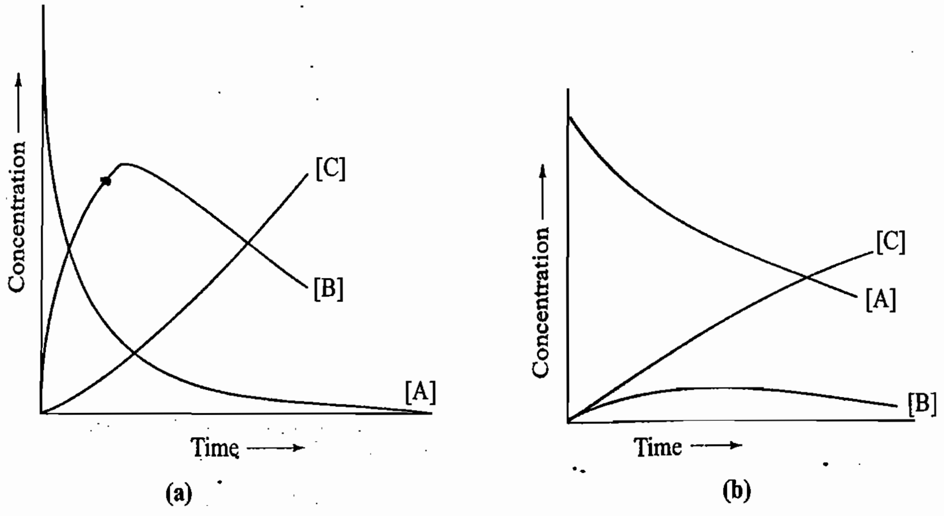
The above equation can be obtained directly if we consider alone the reaction

$$\mathrm{B} \longrightarrow \mathrm{C}$$

with $[\mathrm{B}]_0 = [\mathrm{A}]_0$ as the transformation A to B is very fast.

Steady-State Approximation

Figures 2.11.2a and 2.11.2b illustrate the typical variations in the concentrations of A, B and C for the two consecutive first-order reactions with $k_1 \gg k'_1$ and $k_1 \ll k'_1$, respectively.



(a)

(b)

Fig. 2.11.2 A typical variation in concentrations in a consecutive first-order reaction $\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_1'} \mathrm{C}$ with (a) $k_1 \gg k_1'$ and (b) $k_1 \ll k_1'$

In Fig. 2.11.2a, the concentration of A disappears very rapidly as $k_1 \gg k_1'$ and since the rate at which B disappears is relatively slow, the concentration of B increases rapidly and after attaining the maximum in a small time interval, starts decreasing.

In Fig. 2.11.2b, the concentration of A decreases slowly as the reaction rate constant k_1 has a small value. The concentration of B practically remains constant for a reasonable length of time during the reaction, except at the very beginning and at the end. This constancy results from the fact that the intermediate B is very reactive as its transformation to C occurs at a very fast rate. In fact, the concentration of B at any instant will be much smaller than that of A. This follows from Eq. (2.11.5b) where on ignoring k_1 in comparisons to k'_1 and $\exp(-k_1' t)$ in comparison to $\exp(-k_1 t)$, we get

$$[\mathrm{B}] \simeq [\mathrm{A}]_0 \frac{k_1}{k_1'} \mathrm{e}^{-k_1 t} \tag{2.11.12}$$

Since at any instant the concentration of A is given by Eq. (2.11.5a), we get

$$[\mathrm{B}] \simeq \frac{k_1}{k_1'} [\mathrm{A}] \tag{2.11.13}$$

that is, the concentration of B is smaller than the concentration of A by a factor of about k_1/k_1'.

The fact that the concentration of the reactive intermediate B has a small value and that it practically remains constant throughout the reaction is known as the *steady-state approximation*. Mathematically, the latter can be written as

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = 0 \tag{2.11.14}$$

The use of Eq. (2.11.14) very much simplifies the kinetics of a reaction. For example, in a consecutive first-order reaction with $k_1' \gg k_1$, Eq. (2.11.3) gives

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_1[\mathrm{A}] - k_1'[\mathrm{B}] = 0$$

or

$$[\mathrm{B}] = \frac{k_1}{k_1'} [\mathrm{A}] \tag{2.11.15}$$

Substituting the above equation in Eq. (2.11.4), we get

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_1'[\mathrm{B}] = k_1' \frac{k_1}{k_1'} [\mathrm{A}] = k_1[\mathrm{A}] \tag{2.11.16}$$

Note the identity of Eqs (2.11.13) and (2.11.15) and Eqs (2.11.10) and (2.11.16).

2.12 SIMPLE REACTION MECHANISMS

In this section, we will see how the use of steady-state approximation helps in deriving the differential rate expression from the proposed reaction mechanism of a given reaction.

Many of reactions fall into the following four categories of simple reaction mechanisms.

Type I First step is the rate-determining slow step and is followed by rapid subsequent reactions.

Type II First step is a rapid equilibrium which produces an intermediate which reacts slowly in the rate determining step.

Type III Reactions involving more than two elementary steps with at least one slow step.

Type IV Reactions involving more than one step with comparable rate constants (or whether the steps are slow or fast are not known).

The differential rate law for the first two types of mechanisms can be derived without the use of the steady-state approximation. Nevertheless, the steady-state approximation can be equally applied to derive the differential rate law of a reaction belong to these categories. We now describe a few typical reactions belonging to the types listed above.

TYPE I

Reactions exhibiting this type of mechanism may, in general, be represented as

$$A \xrightarrow{k_1} B \qquad \text{(slow)}$$

$$B \xrightarrow{k_2} \text{products} \qquad \text{(fast)}$$

Since the first step is slow and is the rate-determining step, the rate at which products are formed will depend only on this reaction irrespective of the number and nature of subsequent fast reactions. Thus, we have

$$\frac{dx}{dt} = k_1[A]$$

A few examples are given below.

Decomposition of Ozone

The decomposition reaction

$$2O_3 \rightarrow 3O_2 \qquad (2.12.1)$$

follows the first-order differential rate law

$$-\frac{1}{2}\frac{d[O_3]}{dt} = k_1[O_3] \qquad (2.12.2)$$

Equation (2.12.2) suggests that the rate-determining step involves one molecule of ozone. The proposed mechanism is

$$O_3 \xrightarrow{k_1} O_2 + O$$

$$O + O_3 \xrightarrow{k_2} 2O_2$$

It is expected that $k_1 \ll k_2$ since the second reaction involves atomic oxygen which is very reactive. Thus, the rate law would be

$$-\frac{1}{2}\frac{d[O_3]}{dt} = k_1[O_3] \qquad \text{(Eq. 2.12.2)}$$

(Note the division by 2 on the left-hand side. This is done as two molecules of O_3 are removed in the over-all reaction mechanism.)

The use of steady-state approximation also yields the rate expression of Eq. (2.12.2). Applying the approximation to the reactive intermediate oxygen atom, we get

$$\frac{d[O]}{dt} = 0 = k_1[O_3] - k_2[O][O_3]$$

Hence, $[O] = \frac{k_1}{k_2}$ (2.12.3)

The rates of decomposition of O_3 will be given as

$$r_1 = -\frac{d[O_3]}{dt} = k_1[O_3]$$

$$r_2 = -\frac{d[O_3]}{dt} = k_2[O_3][O]$$

The total rate of disappearance of O_3 will be given by

$$-\frac{d[O_3]}{dt} = k_1[O_3] + k_2[O_3][O] \qquad (2.12.4)$$

Substituting the concentration of O from Eq. (2.12.3), we get

$$-\frac{d[O_3]}{dt} = k_1[O_3] + k_2[O_3]\frac{k_1}{k_2} = 2k_1[O_3]$$

or $$-\frac{1}{2}\frac{d[O_3]}{dt} = k_1[O_3] \qquad \text{(Eq. 2.12.2)}$$

Reaction between NO_2 and F_2

The reaction

$$2NO_2 + F_2 \rightarrow 2NO_2F$$

is found to obey the rate expression

$$-\frac{1}{2}\frac{d[NO_2]}{dt} = k[NO_2][F_2] \qquad (2.12.5)$$

Equation (2.12.5) suggests that one molecule each of NO_2 and F_2 is involved in the rate-determining step. The proposed mechanism is

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + F \qquad \text{(slow)}$$

$$F + NO_2 \xrightarrow{k_2} NO_2F \qquad \text{(fast)}$$

Since the first step is slow, we immediately write

$$-\frac{1}{2}\frac{d[NO_2]}{dt} = k_1[NO_2][F_2] \qquad \text{(Eq. 2.12.5)}$$

The use of steady-state approximation would have given us

$$\frac{d[F]}{dt} = 0 = k_1[NO_2][F_2] - k_2[NO_2][F]$$

or $$[F] = \frac{k_1}{k_2}[F_2] \qquad (2.12.6)$$

The rate of disappearance of NO_2 is given by

$$-\frac{d[NO_2]}{dt} = k_1[NO_2][F_2] + k_2[NO_2][F]$$

Substituting the concentration of F from Eq. (2.12.6), we get

$$-\frac{d[NO_2]}{dt} = k_1[NO_2][F_2] + k_2[NO_2]\left(\frac{k_1}{k_2}[F_2]\right)$$

$$= 2k_1[NO_2][F_2]$$

or
$$-\frac{1}{2}\frac{d[NO_2]}{dt} = k_1[NO_2][F_2] \qquad \text{(Eq. 2.12.5)}$$

Reaction between NO_2 and CO at Low Temperatures

The reaction

$$NO_2 + CO \rightarrow NO + CO_2$$

is found to obey

$$-\frac{d[NO_2]}{dt} = k[NO_2]^2 \qquad (2.12.7)$$

at low temperatures. From Eq. (2.12.7), we conclude that two molecules of NO_2 are involved in the rate-determining step. The proposed mechanism is

$$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO \qquad \text{(slow)}$$

$$NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2 \qquad \text{(fast)}$$

Since the first step is slow, we may write

$$-\frac{d[NO_2]}{dt} = k_1[NO_2]^2 \qquad \text{(Eq. 2.12.7)}$$

(Note that the left-hand side is not divided by two as one molecule of NO_2 reappears in the second fast step.)

The steady-state approximation would have given us

$$\frac{d[NO_3]}{dt} = 0 = k_1[NO_2][NO_2] - k_2[NO_3][CO]$$

or
$$k_2\,[NO_3]\,[CO] = k_1\,[NO_2]^2 \qquad (2.12.8)$$

The rates of reactions in terms of concentratio of NO_2 are

$$r_1 = -\frac{1}{2}\frac{d[NO_2]}{dt} = k_1[NO_2]^2$$

$$r_2 = \frac{d[NO_2]}{dt} = k_2[NO_3][CO]$$

The overall rate of disappearance of NO_2 is given by

$$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 - k_2[NO_3]\,[CO]$$

Making use of Eq. (2.12.18), we get

$$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 - k_1[NO_2]^2$$

$$= k_1[NO_2]^2 \qquad \text{(Eq. 2.12.7)}$$

At temperatures above approximately 500 K, the reaction between NO_2 and CO follows the rate law

$$-\frac{d[NO_2]}{dt} = k\,[NO_2]\,[CO]$$

indicating that the reaction may involve only a single elementary process.

Reaction between Br^- and H_2O_2 in Acidic Medium

The reaction is

$$2Br^- + H_2O_2 + 2H^+ \rightarrow Br_2 + 2H_2O$$

The rate law is found to be

$$\frac{d[Br_2]}{dt} = k[Br^-][H_2O_2][H^+] \qquad (2.12.9)$$

The proposed mechanism is

$$Br^- + H_2O_2 + H^+ \xrightarrow{k_1} HOBr + H_2O \qquad \text{(slow)}$$

$$HOBr + H^+ + Br^- \xrightarrow{k_2} Br_2 + H_2O \qquad \text{(fast)}$$

Since the first step is slow, we may write

$$\frac{d[Br_2]}{dt} = k_1[Br^-][H_2O_2][H^+] \qquad \text{(Eq. 2.12.9)}$$

The steady-state approximation would have given us

$$\frac{d[HOBr]}{dt} = 0 = k_1[Br^-][H_2O_2][H^+] - k_2[HOBr][H^+][Br^-]$$

or $$[HOBr] = \frac{k_1}{k_2}\,[H_2O_2] \qquad (2.12.10)$$

The rate of formation of Br_2 from the second step is

$$\frac{d[Br_2]}{dt} = k_2[HOBr][H^+][Br^-]$$

Substituting the concentration of HOBr from Eq. (2.12.10), we get

$$\frac{d[Br_2]}{dt} = k_2\left(\frac{k_1}{k_2}[H_2O_2]\right)\,[H^+][Br^-]$$

$$= k_1[H_2O_2][H^+][Br^-] \qquad \text{(Eq. 2.12.9)}$$

TYPE II

Reactions exhibiting this type of mechanism are, in general, represented as

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB \qquad \text{(in rapid equilibrium)}$$

$$AB \xrightarrow{k_2} \text{product} \qquad \text{(slow)}$$

Since, the second step is slow and is the rate-determining step, we have

$$\frac{d[\text{product}]}{dt} = k_2[AB] \qquad (2.12.11)$$

For the first step, the equilibrium constant is given by

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[AB]}{[A][B]}$$

Hence, $[AB] = \dfrac{k_1}{k_{-1}}[A][B]$

Substitution of the above expression in Eq. (2.12.11) gives

$$\frac{d[\text{product}]}{dt} = k_2 \frac{k_1}{k_{-1}} [A]\,[B] = k_2\, K_{eq}\, [A]\,[B]$$

$$= k[A][B] \tag{2.12.12}$$

Hence, the reaction

$$A + B \rightarrow \text{products}$$

follows the second-order kinetics. The reaction-rate constant k is equal to $k_2\, k_1/k_{-1}$.

The use of steady-state approximation also produces Eq. (2.12.12) as the differential rate expression. The rate of formation of AB is given by

$$\frac{d[AB]}{dt} = k_1[A][B] - k_{-1}[AB] - k_2[AB]$$

Since the intermediate AB dissociates at a very slow rate in comparison with the rates at which it both forms from and decays back into A and B, the rate constant k_2 may be neglected in the rate equation for the change in concentration of AB. Thus, we have

$$\frac{d[AB]}{dt} = k_1[A][B] - k_{-1}[AB]$$

If we apply the steady-state approximation to AB, then we have

$$\frac{d[AB]}{dt} = 0 = k_1[A][B] - k_{-1}[AB]$$

or $\quad [AB] = \dfrac{k_1}{k_{-1}}[A][B] = K_{eq}[A][B]$

Now, the rate of formation of product is given by

$$\frac{d[\text{product}]}{dt} = k_2[AB]$$

$$= k_2 \frac{k_1}{k_{-1}} [A][B] = k_2\, K_{eq}\, [AB] = k[A][B]$$

which is, in fact, Eq. (2.12.12).

A few examples are given below.

Reaction between NO and O_2

The reaction

$$2NO + O_2 \longrightarrow 2NO_2$$

is experimentally found to obey the third-order kinetics with its differential rate law given as

$$\frac{1}{2}\frac{d[NO_2]}{dt} = k\,[NO]^2\,[O_2] \tag{2.12.13}$$

In order to account for the experimental fact that the rate constant decreases with increase in temperature, the following mechanism has been proposed:

$$\mathrm{NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2} \qquad \text{(in rapid equilibrium)}$$

$$\mathrm{N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2} \qquad \text{(slow)}$$

We have

$$\frac{1}{2}\frac{\mathrm{d[NO_2]}}{\mathrm{d}t} = k_2\,[\mathrm{N_2O_2}]\,[\mathrm{O_2}] \tag{2.12.14}$$

For the fast equilibrium reaction, we have

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} = \frac{[\mathrm{N_2O_2}]}{[\mathrm{NO}]^2}$$

Hence, $[\mathrm{N_2O_2}] = K_{\mathrm{eq}}\,[\mathrm{NO}]^2$

Substituting this in Eq. (2.12.14), we get

$$\frac{1}{2}\frac{\mathrm{d[NO_2]}}{\mathrm{d}t} = k_2K_{\mathrm{eq}}\,[\mathrm{NO}]^2\,[\mathrm{O_2}] \tag{2.12.15}$$

Comparing Eqs (2.12.13) and (2.12.15), we have

$$k = k_2K_{\mathrm{eq}} \tag{2.12.16}$$

The experimental fact that the reaction rate decreases with increasing temperature can be explained from Eq. (2.12.16). The rate constant of the reaction consists of two constants k_2 and K_{eq}. The constant k_2 behaves normally and increases with temperature. The equilibrium constant K_{eq} decreases with increase in temperature as the dimerization reaction is exothermic in nature. The decrease of K_{eq} is sufficiently large to make the term k_2K_{eq} to decrease with increase in temperature.

Reaction between Ammonium and Cynate Ions

The reaction is

$$\mathrm{NH_4^+ + OCN^- \xrightarrow{k} \underset{urea}{OC(NH_2)_2}}$$

The reaction follows the rate law

$$\frac{\mathrm{d[urea]}}{\mathrm{d}t} = k\,[\mathrm{NH_4^+}][\mathrm{OCN^-}] \tag{2.12.17}$$

The proposed mechanism is

$$\mathrm{NH_4^+ + OCN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(complex)}{NH_4OCN}} \qquad \text{(in rapid equilibrium)}$$

$$\mathrm{NH_4OCN \xrightarrow{k_2} OC(NH_2)_2} \qquad \text{(slow)}$$

We have

$$\frac{\mathrm{d[urea]}}{\mathrm{d}t} = k_2[\mathrm{NH_4OCN}] \tag{2.12.18}$$

From the fast equilibrium reaction, we have

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} = \frac{[\mathrm{NH_4OCN}]}{[\mathrm{NH_4^+}][\mathrm{OCN^-}]}$$

Hence, $[\mathrm{NH_4OCN}] = K_{\mathrm{eq}}[\mathrm{NH_4^+}][\mathrm{OCN^-}]$

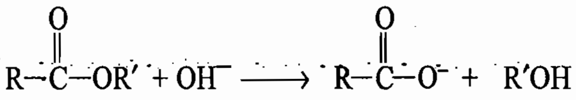
Substituting the above relation in Eq. (2.12.18), we get

$$\frac{\mathrm{d[urea]}}{\mathrm{d}t} = k_2K_{\mathrm{eq}}\,[\mathrm{NH_4^+}]\,[\mathrm{OCN^-}]$$

which is the required rate law (Eq. 2.12.17).

Saponification of an Ester

The reaction may be represented as

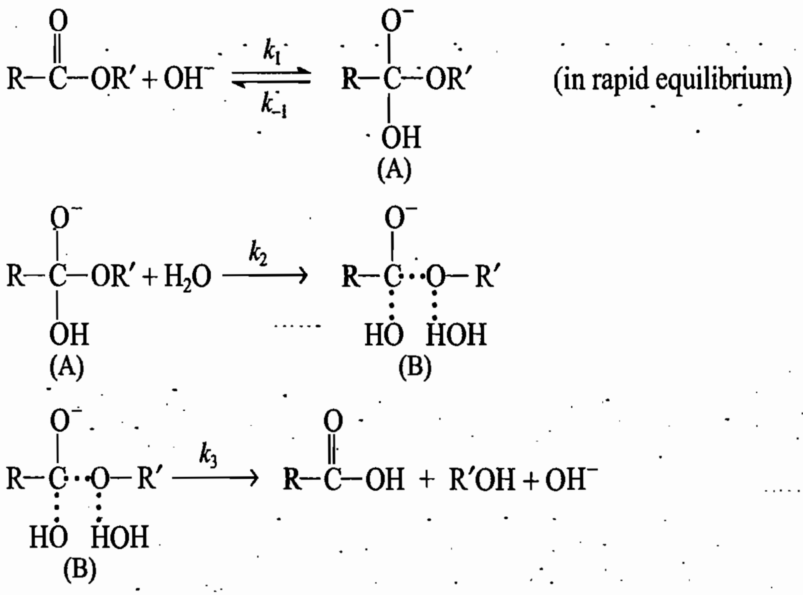


$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR' + OH^- \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^- + R'OH}$$

The reaction follows the rate law

$$-\frac{\mathrm{d\,[ester]}}{\mathrm{d}t} = k\,|\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR'}|\,[\mathrm{OH^-}]$$

The following mechanism has been suggested.



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR' + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\displaystyle (A)}{R{-}\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{-}OR'}}\qquad\text{(in rapid equilibrium)}$$

$$\mathrm{\underset{\displaystyle (A)}{R{-}\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{-}OR'} + H_2O \xrightarrow{k_2} \underset{\displaystyle (B)}{R{-}\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle HO}{\vdots}}{C}}\cdot\cdot\underset{\underset{\displaystyle HOH}{\vdots}}{O}{-}R'}}$$

$$\mathrm{\underset{\displaystyle (B)}{R{-}\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle HO}{\vdots}}{C}}\cdot\cdot\underset{\underset{\displaystyle HOH}{\vdots}}{O}{-}R'} \xrightarrow{k_3} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + R'OH + OH^-}$$

The rate of formation of alcohol is

$$\frac{\mathrm{d[R'OH]}}{\mathrm{d}t} = k_3[\mathrm{B}] \tag{2.12.19}$$

Applying steady-state approximation to B, we get

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = k_2[\mathrm{A}] - k_3[\mathrm{B}] = 0$$

or $$k_3[\mathrm{B}] = k_2[\mathrm{A}] \tag{2.12.20}$$

From the fast equilibrium reaction, we have

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} = \frac{[\mathrm{A}]}{[\mathrm{ester}][\mathrm{OH^-}]}$$

or $$[\mathrm{A}] = \frac{k_1}{k_{-1}}\,[\mathrm{ester}][\mathrm{OH^-}]$$

Making use of the above expression and Eq. (2.12.20) in Eq. (2.12.19), we get

$$\frac{d[R'OH]}{dt} = k_2\left(\frac{k_1}{k_{-1}}\right)[\text{ester}][OH^-]$$
$$= k\,[\text{ester}][OH^-]$$

which is the required rate law.

Hydrogen-Iodine Reaction

The reaction is

$$H_2(g) + I_2(g) = 2HI(g)$$

and the rate law is

$$\frac{1}{2}\frac{d[HI]}{dt} = k\,[H_2][I_2] \qquad (2.12.21)$$

The proposed mechanism is

(i) $I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I$ (in rapid equilibrium)

(ii) $H_2 + 2I \xrightarrow{k_2} 2HI$ (slow)

From step (ii), we have

$$\frac{1}{2}\frac{d[HI]}{dt} = k_2[H_2][I]^2 \qquad (2.12.22)$$

From the rapid step (i), we have

$$K = \frac{k_1}{k_{-1}} = \frac{[I]^2}{[I_2]}$$

or $\quad [I]^2 = \dfrac{k_1}{k_{-1}}[I_2]$

Substituting the above relation in Eq. (2.12.22), we get

$$\frac{1}{2}\frac{d[HI]}{dt} = k_2\frac{k_1}{k_{-1}}[H_2][I_2]$$

which is the required rate law (Eq. 2.12.21).

TYPE III

A few examples of reactions involving more than two elementary steps with only one slow step are described in the following.

Reaction between Hypochlorite and Iodide Ions in Alkaline Medium

The reaction is

$$OCl^- + I^- \xrightarrow{OH^-} OI^- + Cl^-$$

The rate law is found to be

$$-\frac{d[I^-]}{dt} = k\frac{[OCl^-][I^-]}{[OH^-]} \qquad (2.12.23)$$

Though the hydroxyl ion does not appear in the reaction, yet the rate of the reaction depends on the hydroxyl-ion concentration. The presence of $[OH^-]$ in the denominator of Eq. (2.12.23) implies that the rate of the reaction is retarded in the presence of $[\mathrm{OH^-}]$ ions. From Eq. (2.12.23) it also follows that the mechanism of the reaction must also include elementary step (or steps) involving hydroxyl ion as the reactant or product. The proposed mechanism is

$$\text{(i) } \mathrm{OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^-} \qquad \text{(fast)}$$

$$\text{(ii) } \mathrm{I^- + HOCl \xrightarrow{k_2} HOI + Cl^-} \qquad \text{(slow)}$$

$$\text{(iii) } \mathrm{OH^- + HOI \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2O + OI^-} \qquad \text{(fast)}$$

Since step (ii) is slow, we may write

$$-\frac{\mathrm{d[I^-]}}{\mathrm{d}t} = k_2\,\mathrm{[I^-][HOCl]} \tag{2.12.24}$$

From the fast step (i), we have

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} = \frac{\mathrm{[HOCl][OH^-]}}{\mathrm{[OCl^-][H_2O]}}$$

$$\text{Hence,}\quad \mathrm{[HOCl]} = \frac{k_1}{k_{-1}}\,\frac{\mathrm{[OCl^-][H_2O]}}{\mathrm{[OH^-]}} \tag{2.12.25}$$

Substituting Eq. (2.12.25) in Eq. (2.12.24), we get

$$-\frac{\mathrm{d[I^-]}}{\mathrm{d}t} = k_2\,\mathrm{[I^-]}\left\{\frac{k_1}{k_{-1}}\,\frac{\mathrm{[OCl^-][H_2O]}}{\mathrm{[OH^-]}}\right\}$$

$$= \frac{k_2 k_1}{k_{-1}}\,\frac{\mathrm{[I^-][OCl^-][H_2O]}}{\mathrm{[OH^-]}}$$

Since the reaction occurs in aqueous solution, the concentration of water does not change appreciably during the course of the reaction. The concentration of H_2O may thus be grouped with the other constants. Hence, we have

$$-\frac{\mathrm{d[I^-]}}{\mathrm{d}t} = \left(\frac{k_2 k_1}{k_{-1}}\mathrm{[H_2O]}\right)\frac{\mathrm{[I^-][OCl^-]}}{\mathrm{[OH^-]}} = k\,\frac{\mathrm{[I^-][OCl^-]}}{\mathrm{[OH^-]}}$$

which is the required rate law (Eq. 2.12.23).

Alternative Mechanism An alternative mechanism which also gives the rate expression of Eq. (2.12.23) is the following:

$$\text{(i) } \mathrm{OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^-} \qquad \text{(fast)}$$

$$\text{(ii) } \mathrm{I^- + HOCl \xrightarrow{k_2} ICl + OH^-} \qquad \text{(slow)}$$

$$\text{(iii) } \mathrm{ICl + 2OH^- \xrightarrow{k_3} OI^- + Cl^- + H_2O} \qquad \text{(fast)}$$

Rate Expressed as* d[OI⁻]/d*t The derivation of rate expression (Eq. 2.12.23) is the same as given above. However, if we want to express the rate as $\mathrm{d[OI^-]}/\mathrm{d}t$ or $\mathrm{d[Cl^-]}/\mathrm{d}t$, then the derivations of rate expression differ, but both of them lead to the same final expression. We derive below the rate expression as $\mathrm{d[OI^-]}/\mathrm{d}t$.

For the first mechanism, we have

$$\frac{\mathrm{d}[\mathrm{OI}^-]}{\mathrm{d}t} = k_3[\mathrm{OH}^-][\mathrm{HOI}] - k_{-3}[\mathrm{H_2O}][\mathrm{OI}^-] \qquad (2.12.26)$$

We can apply the steady-state approximation to HOI, which gives

$$\frac{\mathrm{d}[\mathrm{HOI}]}{\mathrm{d}t} = 0 = k_2[\mathrm{I}^-][\mathrm{HOCl}] - k_3[\mathrm{OH}^-][\mathrm{HOI}] + k_{-3}[\mathrm{H_2O}][\mathrm{OI}^-]$$

or
$$[\mathrm{HOI}] = \frac{k_2[\mathrm{I}^-][\mathrm{HOCl}] + k_{-3}[\mathrm{H_2O}][\mathrm{OI}^-]}{k_3[\mathrm{OH}^-]}$$

Substituting the above relation in Eq. (2.12.26), we get

$$\frac{\mathrm{d}[\mathrm{OI}^-]}{\mathrm{d}t} = k_3[\mathrm{OH}^-]\left(\frac{k_2[\mathrm{I}^-][\mathrm{HOCl}] + k_{-3}[\mathrm{H_2O}][\mathrm{OI}^-]}{k_3[\mathrm{OH}^-]}\right) - k_{-3}[\mathrm{H_2O}][\mathrm{OI}^-]$$
$$= k_2[\mathrm{I}^-][\mathrm{HOCl}]$$

Substituting [HOCl] from Eq. (2.12.25) in the above expression, we get

$$\frac{\mathrm{d}[\mathrm{OI}^-]}{\mathrm{d}t} = k_2[\mathrm{I}^-]\left(\frac{k_1}{k_{-1}}\frac{[\mathrm{OCl}^-][\mathrm{H_2O}]}{[\mathrm{OH}^-]}\right) = \left(\frac{k_2k_1}{k_{-1}}[\mathrm{H_2O}]\right)\frac{[\mathrm{I}^-][\mathrm{OCl}^-]}{[\mathrm{OH}^-]}$$
$$= k\frac{[\mathrm{I}^-][\mathrm{OCl}^-]}{[\mathrm{OH}^-]} \qquad (2.12.27)$$

Equation (2.12.27) is the required expression of the rate law.

For the second mechanism, we have

$$\frac{\mathrm{d}[\mathrm{OI}^-]}{\mathrm{d}t} = k_3[\mathrm{ICl}][\mathrm{OH}^-]^2 \qquad (2.12.28)$$

Applying the steady-state approximation to ICl, we get

$$\frac{\mathrm{d}[\mathrm{ICl}]}{\mathrm{d}t} = 0 = k_2[\mathrm{I}^-][\mathrm{HOCl}] - k_3[\mathrm{ICl}][\mathrm{OH}^-]^2$$

or
$$[\mathrm{ICl}] = \frac{k_2}{k_3}\frac{[\mathrm{I}^-][\mathrm{HOCl}]}{[\mathrm{OH}^-]^2}$$

Substituting this relation in Eq. (2.12.28), we have

$$\frac{\mathrm{d}[\mathrm{OI}^-]}{\mathrm{d}t} = k_3\left(\frac{k_2}{k_3}\frac{[\mathrm{I}^-][\mathrm{HOCl}]}{[\mathrm{OH}^-]^2}\right)[\mathrm{OH}^-]^2$$
$$= k_2[\mathrm{I}^-][\mathrm{HOCl}]$$

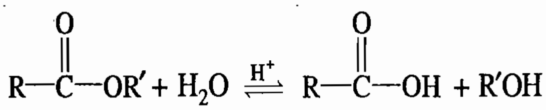
Substituting [HOCl] from Eq. (2.12.25), we get

$$\frac{\mathrm{d}[\mathrm{OI}^-]}{\mathrm{d}t} = k_2[\mathrm{I}^-]\left(\frac{k_1}{k_{-1}}\frac{[\mathrm{OCl}^-][\mathrm{H_2O}]}{[\mathrm{OH}^-]}\right) = \left(\frac{k_2k_1}{k_{-1}}[\mathrm{H_2O}]\right)\frac{[\mathrm{I}^-][\mathrm{OCl}^-]}{[\mathrm{OH}^-]}$$
$$= k\frac{[\mathrm{I}^-][\mathrm{OCl}^-]}{[\mathrm{OH}^-]} \qquad (2.12.29)$$

Equation (2.12.29) is the required rate expression and has the same form as given by Eq. (2.12.27)

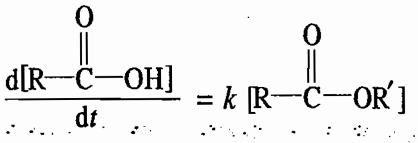
Acid Hydrolysis of an Ester

The reaction is



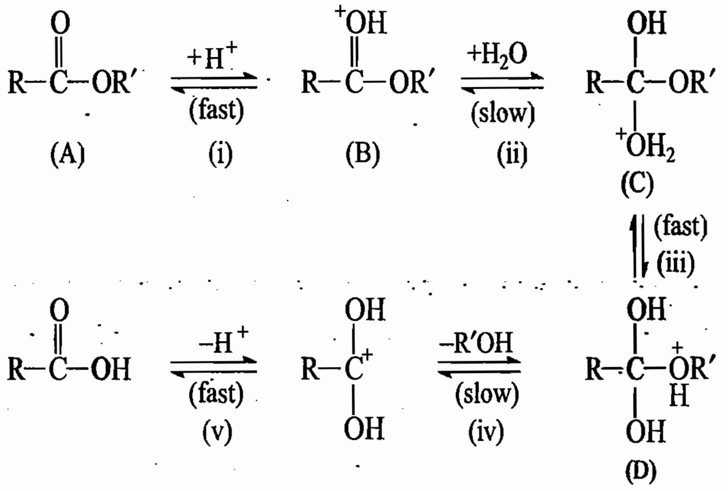
$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}OR' + H_2O \overset{H^+}{\rightleftharpoons} R{-}\overset{\overset{O}{\|}}{C}{-}OH + R'OH}$$

Acid hydrolysis of an ester is an example of pseudo first-order reaction.



$$\frac{d[\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}OH}]}{dt} = k\,[\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}OR'}] \qquad (2.12.30)$$

The proposed mechanism is



Steps (ii) and (iv) are slower steps as these involve making and breaking of bond, respectively. The proton transfer steps are fast. Step (iv) is slower than step (ii),

The rate of reaction may be written as

$$r = k_4[\mathrm{D}] = k_4(K_3[\mathrm{C}]) = k_4K_3(K_2[\mathrm{B}][\mathrm{H_2O}])$$

$$= k_4K_3K_2(K_1[\mathrm{A}][\mathrm{H^+}][\mathrm{H_2O}])$$

that is, $r = k[\text{ester}][\mathrm{H^+}][\mathrm{H_2O}]$ (2.12.31)

In the above expressions K_1, K_2 and K_3 are the equilibrium constants for the steps (i), (ii) and (iii), respectively. Since H_2O is present in excess amount and $[H^+]$ remains constant throughout, we can write

$$r = k'[\text{ester}] \qquad (2.12.32)$$

which is the required rate expression (Eq. 2.12.30).

Formation of Phosgene from CO and Cl_2

The reaction is

$$\mathrm{CO + Cl_2 \rightarrow COCl_2}$$

and the rate expression is

$$\frac{d[\mathrm{COCl_2}]}{dt} = k\,[\mathrm{CO}][\mathrm{Cl_2}]^{3/2} \qquad (2.12.33)$$

The proposed mechanism is

(i) $\mathrm{Cl_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{2Cl}$ (fast equilibrium)

(ii) $\mathrm{Cl + CO} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{COCl}$ (fast equilibrium)

(iii) $COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$ (slow)

The rate of formation of phosgene from step (iii) is

$$\frac{d[COCl_2]}{dt} = k_3\,[COCl]\,[Cl_2] \qquad (2.12.34)$$

For steps (i) and (ii), we may write

$$\frac{k_1}{k_{-1}} = \frac{[Cl]^2}{[Cl_2]} \qquad (2.12.35)$$

$$\frac{k_2}{k_{-2}} = \frac{[COCl]}{[Cl][CO]} \qquad (2.12.36)$$

From Eqs (2.12.35) and (2.12.36), we get

$$[COCl] = \frac{k_2}{k_{-2}}\,[Cl][CO] = \frac{k_2}{k_{-2}}\left(\frac{k_1}{k_{-1}}[Cl_2]\right)^{1/2}[CO] \qquad (2.12.37)$$

Substituting Eq. (2.12.37) in Eq. (2.12.34), we get

$$\frac{d[COCl_2]}{dt} = k_3\left\{\frac{k_2}{k_{-2}}\left(\frac{k_1}{k_{-1}}[Cl_2]\right)^{1/2}[CO]\right\}[Cl_2]$$

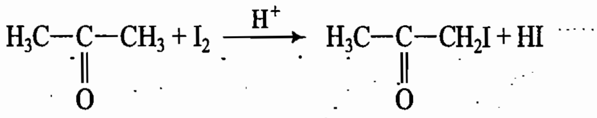
$$= k_3\,\frac{k_2}{k_{-2}}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{3/2}\,[CO]$$

$$= k\,[CO][Cl_2]^{3/2}$$

which is the required rate expression (Eq. 2.12.33).

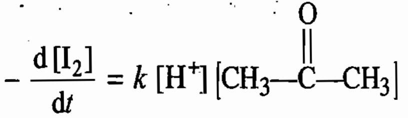
Iodination of Acetone

The reaction in aqueous medium is



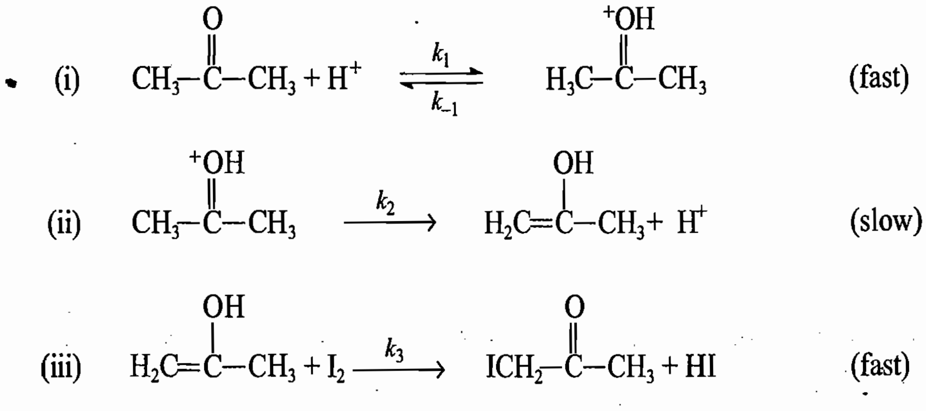
$$H_3C-\underset{\underset{O}{\|}}{C}-CH_3 + I_2 \xrightarrow{H^+} H_3C-\underset{\underset{O}{\|}}{C}-CH_2I + HI$$

and the rate expression is



$$-\frac{d[I_2]}{dt} = k\,[H^+]\left[CH_3-\overset{\overset{O}{\|}}{C}-CH_3\right] \qquad (2.12.38)$$

Thus, the reaction is first-order with respect to each of H^+ and acetone and zero order with respect to iodine. The proposed mechanism is

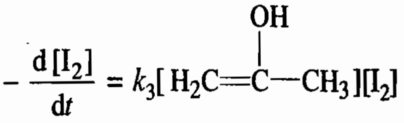


(i) $$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_3C-\overset{\overset{+OH}{\|}}{C}-CH_3 \quad \text{(fast)}$$

(ii) $$CH_3-\overset{\overset{+OH}{\|}}{C}-CH_3 \xrightarrow{k_2} H_2C=\overset{\overset{OH}{|}}{C}-CH_3 + H^+ \quad \text{(slow)}$$

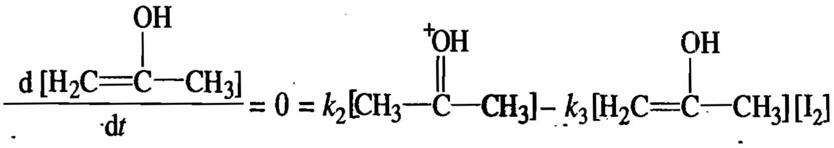
(iii) $$H_2C=\overset{\overset{OH}{|}}{C}-CH_3 + I_2 \xrightarrow{k_3} ICH_2-\overset{\overset{O}{\|}}{C}-CH_3 + HI \quad \text{(fast)}$$

From step (iii), we have



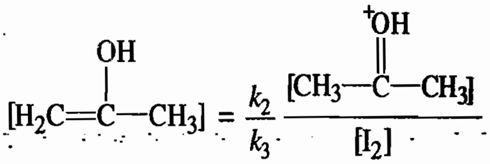
$$-\frac{d[I_2]}{dt} = k_3[H_2C{=}\overset{\text{OH}}{\overset{|}{\text{C}}}{-}CH_3][I_2] \qquad (2.12.39)$$

Applying the steady-state approximation to $H_2C{=}\overset{\text{OH}}{\overset{|}{\text{C}}}{-}CH_3$, we get



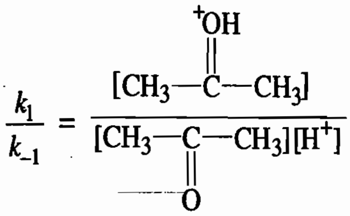
$$\frac{d[H_2C{=}\overset{\text{OH}}{\overset{|}{\text{C}}}{-}CH_3]}{dt} = 0 = k_2[CH_3{-}\overset{\overset{+}{\text{O}}\text{H}}{\overset{\|}{\text{C}}}{-}CH_3] - k_3[H_2C{=}\overset{\text{OH}}{\overset{|}{\text{C}}}{-}CH_3][I_2]$$

i.e.



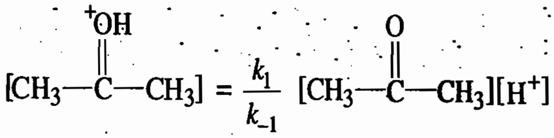
$$[H_2C{=}\overset{\text{OH}}{\overset{|}{\text{C}}}{-}CH_3] = \frac{k_2}{k_3}\,\frac{[CH_3{-}\overset{\overset{+}{\text{O}}\text{H}}{\overset{\|}{\text{C}}}{-}CH_3]}{[I_2]} \qquad (2.12.40)$$

From the fast step (i), we have



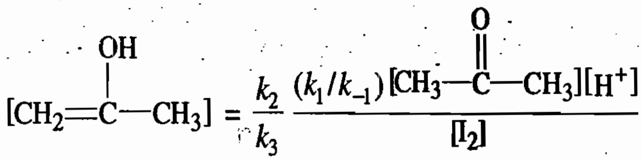
$$\frac{k_1}{k_{-1}} = \frac{[CH_3{-}\overset{\overset{+}{\text{O}}\text{H}}{\overset{\|}{\text{C}}}{-}CH_3]}{[CH_3{-}\underset{\text{O}}{\underset{\|}{\text{C}}}{-}CH_3][H^+]}$$

or



$$[CH_3{-}\overset{\overset{+}{\text{O}}\text{H}}{\overset{\|}{\text{C}}}{-}CH_3] = \frac{k_1}{k_{-1}}[CH_3{-}\overset{\text{O}}{\overset{\|}{\text{C}}}{-}CH_3][H^+]$$

Substituting the above relation in Eq. (2.12.40), we get



$$[CH_2{=}\overset{\text{OH}}{\overset{|}{\text{C}}}{-}CH_3] = \frac{k_2}{k_3}\,\frac{(k_1/k_{-1})[CH_3{-}\overset{\text{O}}{\overset{\|}{\text{C}}}{-}CH_3][H^+]}{[I_2]}$$

which on substituting in Eq. (2.12.39) gives

$$-\frac{d[I_2]}{dt} = k_3\left(\frac{k_2}{k_3}\frac{k_1}{k_{-1}}\frac{[CH_3COCH_3][H^+]}{[I_2]}\right)[I_2]$$

$$= k_2\,\frac{k_1}{k_{-1}}\,[CH_3COCH_3][H^+]$$

or $$-\frac{d[I_2]}{dt} = k\,[CH_3COCH_3][H^+]$$

which is the required rate expression (Eq. 2.12.38). Note that iodine does not appear in the final rate expression as it appears only in the fast reaction.

TYPE IV

A few examples of reactions involving more than one elementary step with comparable rate constants (or whether the steps are slow or fast are not known) are described below.

Decomposition of Gaseous N_2O_5

The reaction is

$$2\,N_2O_5 \rightarrow 4NO_2 + O_2$$

and the rate law is

$$\frac{d[O_2]}{dt} = k[N_2O_5] \tag{2.12.41}$$

The proposed mechanism is

(i) $N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$

(ii) $NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2$

(iii) $NO_3 + NO \xrightarrow{k_3} 2\,NO_2$

From step (ii), the rate of formation of O_2 is

$$\frac{d[O_2]}{dt} = k_2[NO_3][NO_2] \tag{2.12.42}$$

Applying the steady-state approximation to NO and NO_3, we get

$$\frac{d[NO]}{dt} = 0 = k_2[NO_3][NO_2] - k_3[NO_3][NO] \tag{2.12.43}$$

$$\frac{d[NO_3]}{dt} = 0 = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_3][NO_2] - k_3[NO_3][NO] \tag{2.12.44}$$

Equation (2.12.43) gives

$$[NO] = \frac{k_2}{k_3}[NO_2] \tag{2.12.45}$$

From Eq. (2.12.44), we have

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2] + k_3[NO]}$$

Substituting [NO] from Eq. (2.12.45), we get

$$[NO_3] = \frac{k_1[N_2O_5]}{(k_{-1} + 2k_2)[NO_2]} \tag{2.12.46}$$

Substituting Eq. (2.12.46) in Eq. (2.12.42), we get

$$\frac{d[O_2]}{dt} = k_2\left(\frac{k_1[N_2O_5]}{(k_{-1} + 2k_2)[NO_2]}\right)[NO_2]$$

$$= \frac{k_2k_1}{k_{-1} + 2k_2}[N_2O_5] = k[N_2O_5]$$

which is the required rate law (Eq. 2.12.41).

Problem 2.12.1 Nitramide O_2NNH_2 decomposes slowly in aqueous solution according to the reaction

$$O_2NNH_2 \rightarrow N_2O + H_2O$$

The experimental rate law is

$$\frac{d[N_2O]}{dt} = k\frac{[O_2NNH_2]}{[H^+]}$$

Which one of the following mechanisms seems most appropriate?

1. $O_2NNH_2 \xrightarrow{k_1} N_2O + H_2O$ (slow)

2. $O_2NNH_2 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH_3^+$ (fast equilibrium)

   $O_2NNH_3^+ \xrightarrow{k_2} N_2O + H_3O^+$ (slow)

3. $O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^- + H^+$ (fast equilibrium)

   $O_2NNH^- \xrightarrow{k_2} N_2O + OH^-$ (slow)

   $H^+ + OH^- \xrightarrow{k_3} H_2O$ (fast)

Solution 1. For mechanism 1, the rate law would be given as

$$\frac{d[N_2O]}{dt} = k_1[O_2NNH_2]$$

Obviously, this mechanism is not applicable.

2. For mechanism 2, we have

$$\frac{d[N_2O]}{dt} = k_2[O_2NNH_3^+]$$

From the fast equilibrium step, we have

$$K = \frac{k_1}{k_{-1}} = \frac{[O_2NNH_3^+]}{[O_2NNH_2][H^+]}$$

Therefore

$$[O_2NNH_3^+] = \frac{k_1}{k_{-1}}[O_2NNH_2][H^+]$$

With this, the rate law becomes

$$\frac{d[N_2O]}{dt} = k_2\frac{k_1}{k_{-1}}[O_2NNH_2][H^+]$$

The above rate law also does not match with the given one and hence this mechanism is also ruled out.

3. For mechanism 3, we have

$$\frac{d[N_2O]}{dt} = k_2[O_2NNH^-]$$

From the fast equilibrium step, we have

$$K = \frac{k_1}{k_{-1}} = \frac{[O_2NNH^-][H^+]}{[O_2NNH_2]}$$

Therefore

$$[O_2NNH^-] = \frac{k_1}{k_{-1}} \frac{[O_2NNH_2]}{[H^+]}$$

With this, the rate law becomes

$$\frac{d[N_2O]}{dt} = k_2 \frac{k_1}{k_{-1}} \frac{[O_2NNH_2]}{[H^+]}$$

The above rate law agrees with the given one and hence this mechanism seems most appropriate for the given reaction.

2.13 A GENERAL MECHANISM FOR THE THERMAL DECOMPOSITION AND ISOMERIZATION REACTIONS

Mechanism Many thermal decomposition and isomerization reactions follow the mechanism given below:

$$\text{(i)} \quad A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M \qquad (2.13.1)$$

$$\text{(ii)} \quad A^* \xrightarrow{k_2} \text{products} \qquad (2.13.2)$$

where A represents the molecule undergoing the thermal decomposition or isomerization reaction, and M represents any other molecule. Step (i) represents an equilibrium reaction. The forward reaction represents a collision of molecule A with a molecule of M and thereby the molecule A is activated. The backward reaction represents the deactivation of A molecule. Step (ii) represents the decomposition of the activated A molecule. Two simple cases may be distinguished.

Step (i) is Rate-Determining Step If step (i) is slow and rate-determining, then the reaction follows second-order kinetics with the rate law given by

$$\frac{d[\text{product}]}{dt} = k_1[A][M] \qquad (2.13.3)$$

Step (ii) is Rate-Determining Step If step (i) represents a fast equilibrium process and step (ii) is slow, then we have

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[A^*]}{[A]} \qquad (2.13.4)$$

and

$$\frac{d[\text{product}]}{dt} = k_2[A^*] \qquad (2.13.5)$$

From Eq. (2.13.4), we have

$$[A^*] = \frac{k_1}{k_{-1}} [A]$$

Substituting the above relation in Eq. (2.13.5), we get

$$\frac{d[\text{product}]}{dt} = k_2 \frac{k_1}{k_{-1}} [A] \qquad (2.13.6)$$

Thus, the reaction follows first-order kinetics.

General Treatment

If, in advance, it is not known which step is slow or if all the rate constants have comparable values, we can derive the rate law by using the steady-state approximation. Since products are formed in step (ii), we may write

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = k_2\,[\mathrm{A}^*] \tag{2.13.7}$$

Applying the steady-state approximation to A*, we get

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = 0 = k_1[\mathrm{A}][\mathrm{M}] - k_{-1}[\mathrm{A}^*][\mathrm{M}] - k_2[\mathrm{A}^*]$$

$$[\mathrm{A}^*] = \frac{k_1[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}]+k_2}$$

Substitution of the above relation in Eq. (2.13.7) gives the rate law as

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = \frac{k_2k_1[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}]+k_2} \tag{2.13.8}$$

Equations (2.13.3) and (2.13.6) which are applicable to specific cases may be derived from Eq. (2.13.8).

Equation (2.13.3) is obtained if we neglect k_{-1} [M] in comparison to k_2 (i.e. k_{-1} [M] $\ll k_2$) in Eq. (2.13.8). The factor k_{-1} [M] will be negligible in comparison to k_2 under the following three conditions.

(i) The rate constant k_2 has a large value, i.e. step (ii) represents a fast reaction.
(ii) The backward reaction rate constant k_{-1} has a small value, i.e. the step (ii) does not represent a rapid equilibrium reaction.
(iii) The concentration of M may be low. For gaseous reactions, this condition may be realized at low gaseous pressures.

Equation (2.13.6) is obtained if we neglect k_2 in comparison to k_{-1} [M] (i.e. $k_2 \ll k_{-1}$ [M]) in Eq. (2.13.8). The factor k_2 will be negligible in comparison to k_{-1} [M] under the following three conditions.

(i) The backward reaction rate constant k_{-1} has a large value, i.e. step (i) represents a rapid equilibrium reaction.
(ii) The concentration of M may be high. For gaseous reactions, this condition may be realized at high gaseous pressures.
(iii) The rate constant k_2 has a low value, i.e. step (ii) is slow and rate-determining step.

Lindemann Mechanism for the First-Order Reactions

It was stated in Section 2.4 that the products are formed only when reactant molecules come close and collide together at one and the same time. During the collision, molecular rearrangement takes place which leads to the formation of products. For example, a second-order reaction of the types

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products}$$

or

$$\mathrm{A} + \mathrm{A} \rightarrow \text{products}$$

may be traced to a bimolecular collision process involving A and B, and A and A, respectively. However, the first-order reactions in the gas phase cannot be accounted for by the above collision theory. The first successful explanation of first-order reactions was provided by Lindemann. The mechanism is

(i) $A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$ (in rapid equilibrium)

(ii) $A^* \xrightarrow{k_2}$ products (slow)

Step (i) involves a rapid equilibrium reaction where in the forward reaction, a molecule A is activated by colliding with another A molecule and in the backward reaction, the excited molecule A is deactivated by colliding with another A molecule. Step (ii) represents another possibility of deactivation where the excited molecule is decomposed to give the products. Since the step (ii) is slow and rate determining, the rate at which products are formed will be determined by the unimolecular decay and hence first-order kinetics will be observed.

Differential Rate Law

The Lindemann scheme is similar to the general scheme as given by Eqs (2.13.1) and (2.13.2) where a molecule of M is replaced by a molecule of A. The general rate law (Eq. 2.13.8), in the present case, will become

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = \frac{k_2 k_1 [\mathrm{A}]^2}{k_{-1}[\mathrm{A}] + k_2} \qquad (2.13.9)$$

From Eq. (2.13.9), it is obvious that the Lindemann mechanism will follow a complicated rate law if the rate constants k_2, k_1 and k_{-1} have comparable values. However, the first-order kinetics will emerge only under the condition that $k_2 < k_{-1}[\mathrm{A}]$. As stated earlier, this condition will be observed only when the reaction is carried out at high gaseous pressures.

At low pressures where $k_{-1}[\mathrm{A}] < k_2$, the Lindemann mechanism will follow the rate law

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = k_1[\mathrm{A}]^2$$

that is, a second-order kinetics. The reason for the above rate law is that at low pressures the rate-determining step is the bimolecular formation of the excited molecules.

Therefore, a real test for the Lindemann mechanism is to study the reaction over a wide range of pressure starting from a very low pressure to a high pressure.[†] If the rate $\boldsymbol{r}$ of formation of products is determined by the *initial slope* of the curve of concentration of a product versus time and if log (r/r°) is plotted against log $\{[\mathrm{A}]/\mathrm{M}\}$ {or log (p/p°)}, the plot will show a slope of two at low concentrations (or pressures) and a slope one at high concentrations (or pressures).

At the end, a very important point may be mentioned. The steady-state approximation used above seems to be self-contradictory. From Eq. (2.13.7), the

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[†] One of the ways to increase the gaseous pressure is to introduce an inactive gas into the system.

rate of reaction is proportional to [A*], which is assumed to be constant, yet from Eq. (2.13.8) the rate of the reaction is a function of [A], which is steadily decreasing as the reaction proceeds. This contradiction is removed if the rate of formation of product is determined with the help of initial-slope method. The initial slope refers to the rate at fixed values of [A] and [A*]. It is assumed that at the very first measurement on the concentration of product with time, the steady-state has been reached.

2.14 CHAIN REACTIONS

Characteristics of Chain Reactions

Chain reactions proceed through a complex sequence of elementary steps. The various steps can be classified as follows.

Chain Initiation Step The first step in which highly reactive intermediate species such as atoms, free radicals are produced is known as the chain initiation step.

Chain Propagation Steps In these steps, the highly reactive intermediate from the chain initiation step reacts with one of the reactant molecules and thereby produce a product molecule and another reactive intermediate. The produced reactive intermediate, in turn, reacts with another reactant molecule and produce a product molecule and another reactive intermediate. The above process of generating a new reactive intermediate when an old reactive intermediate combines with a reactant molecule is continued till the reactive intermediate is somehow destroyed. Thus, one reactive intermediate produced in the initiation step may result in thousands of product molecules via the propagation steps.

Chain Inhibition Step In this step, the reactive intermediate combines with a product molecule producing a reactant molecule and another reactive intermediate. Though a reactive intermediate is generated, the net effect of chain inhibition step is to decrease the rate of overall reaction.

Chain Termination Step In this step, the reactive intermediate is destroyed by combining with another reactive intermediate. This combination may result at the wall of the vessel or by direct collision between the two reactive intermediates within the vessel. Certain substances when added also help in terminating the reactive intermediates. For example, nitric oxide molecule can react very rapidly with free radicals and thus may be introduced to remove radicals in a chain reaction.

Chain Length

The number of chain propagation steps in between the chain initiation step and termination step is usually expressed as the *chain length*. The latter may be defined as the number of product molecules formed per chain carrier produced in the initiation reaction. The chain length depends on the relative rates of chain propagation and chain-terminating step. Mathematically, the chain length may be defined as the ratio of the overall rate of formation of product and the rate of initiation reaction, i.e.

$$\text{Chain length} = \frac{\mathrm{d}[\text{product}]/\mathrm{d}t}{\mathrm{d}(\text{initiation step})/\mathrm{d}t} \tag{2.14.1}$$

Kinetics of Chain Reactions

A chain reaction may be classified into two categories namely, *stationary* (or nonbranched) and *nonstationary* (or branched) chain reactions depending on one or more than one radical produced in each chain propagation step, respectively. In general, a chain reaction may be represented as follows.

Initiation $\mathrm{A} \xrightarrow{k_1} \mathrm{R}^\bullet$

Propagation $\mathrm{R}^\bullet + \mathrm{A} \xrightarrow{k_2} \mathrm{P} + \alpha\mathrm{R}^\bullet$

Termination $\mathrm{R}^\bullet \xrightarrow{k_3}$ destruction

where A, R and P represent the reactant, radical and product molecules, respectively. If $\alpha = 1$, we have stationary chain reaction and if $\alpha > 1$, the chain reaction is a nonstationary one. The destruction of radical may result at the walls of the vessel or by direct collision with other radical within the gaseous phase. The concentration of radical can be determined by applying steady-state approximation to the radical. Thus, we have

$$\frac{\mathrm{d}[\mathrm{R}^\bullet]}{\mathrm{d}t} = 0 = k_1[\mathrm{A}] + k_2(\alpha - 1)[\mathrm{R}^\bullet][\mathrm{A}] - k_3[\mathrm{R}^\bullet]$$

or
$$[\mathrm{R}^\bullet] = \frac{k_1[\mathrm{A}]}{k_2(1-\alpha)[\mathrm{A}] + k_3}$$

Since the destruction of radical can occur in two ways, namely, at the wall, and within the gaseous phase, the constant k_3 may be replaced by $k_w + k_g$. Thus, we have

$$[\mathrm{R}^\bullet] = \frac{k_1[\mathrm{A}]}{k_2(1-\alpha)[\mathrm{A}] + k_w + k_g} \tag{2.14.2}$$

We now discuss a few examples of stationary and nonstationary chain reactions.

STATIONARY CHAIN REACTIONS

In stationary chain reactions $\alpha = 1$ and Eq. (2.14.2) is given by

$$[\mathrm{R}^\bullet] = \frac{k_1[\mathrm{A}]}{k_w + k_g}$$

that is, the concentration of radical is simply equal to the ratio of rate of formation of radical in the chain initiation step and rate of destruction of radical in the chain termination step. A few examples of reactions in this category are discussed below.

Reaction between H_2 and Br_2

One of the well-known examples of chain reactions is the reaction between H_2 and Br_2, i.e.

$$\mathrm{H_2} + \mathrm{Br_2} \longrightarrow 2\,\mathrm{HBr}$$

The elementary steps proposed for this reaction are

Initiation $\mathrm{Br_2} \xrightarrow{k_1} 2\mathrm{Br}$

Propagation $\mathrm{Br} + \mathrm{H_2} \xrightarrow{k_2} \mathrm{HBr} + \mathrm{H}$

$\mathrm{H} + \mathrm{Br_2} \xrightarrow{k_3} \mathrm{HBr} + \mathrm{Br}$

Inhibition $\mathrm{H} + \mathrm{HBr} \xrightarrow{k_4} \mathrm{H_2} + \mathrm{Br}$

Termination $\mathrm{Br} + \mathrm{Br} \xrightarrow{k_5} \mathrm{Br_2}$

The rate law for the above reaction can be conveniently derived by using the steady-state approximation. The rate of formation of HBr is given by

$$\frac{d[HBr]}{dt} = k_2\,[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \tag{2.14.3}$$

Applying the steady-state approximation to H and Br, we get

$$\frac{d[H]}{dt} = 0 = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] \tag{2.14.4}$$

$$\begin{aligned}\frac{d[Br]}{dt} = 0 = 2k_1[Br_2] - k_2[Br][H_2] + k_3\,[H][Br_2]\\ + k_4[H][HBr] - 2k_5[Br]^2\end{aligned} \tag{2.14.5}$$

Making use of Eq. (2.14.4) in Eq. (2.14.5), we get

$$2k_1[Br_2] - 2k_5[Br]^2 = 0$$

or
$$[Br] = \left(\frac{k_1}{k_5}[Br_2]\right)^{1/2} \tag{2.14.6}$$

From Eq. (2.14.4), we get

$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]}$$

Substituting [Br] from Eq. (2.14.6) in the above relation, we get

$$[H] = \frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \tag{2.14.7}$$

Invoking Eq. (2.14.4) in Eq. (2.14.3), we get

$$\frac{d[HBr]}{dt} = 2k_3[H][Br_2]$$

Substituting [H] from Eq. (2.14.7) in the above expression, we get

$$\begin{aligned}\frac{d[HBr]}{dt} &= 2k_3\left(\frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2]+k_4[HBr]}\right)[Br_2]\\ &= \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1+(k_4/k_3)[HBr]/[Br_2]}\\ &= \frac{k'[Br_2]^{1/2}[H_2]}{1+k''[HBr]/[Br_2]}\end{aligned} \tag{2.14.8}$$

where $k' = 2k_2(k_1/k_5)^{1/2}$

and $k'' = k_4/k_3$

Initial Rate of the Reaction

In the initial stage of the reaction, [HBr] is negligibly small and hence

$$1 + k'' \,[\mathrm{HBr}]/[\mathrm{Br_2}]_0 = 1$$

and the initial rate becomes

$$\left(\frac{\mathrm{d[HBr]}}{\mathrm{d}t}\right)_0 = k'[\mathrm{Br_2}]_0^{1/2}[\mathrm{H_2}]_0 \qquad (2.14.9)$$

that is, in the initial stage, the order of the reaction is 1.5.

Dehydrogenation of Ethane

The reaction is

$$\mathrm{CH_3CH_3 \rightarrow CH_2{=}CH_2 + H_2}$$

The observed rate law is

$$\frac{\mathrm{d[CH_2{=}CH_2]}}{\mathrm{d}t} = k[\mathrm{CH_3CH_3}] \qquad (2.14.10)$$

Though the observed rate law follows a simple first-order kinetics and could be interpreted by a Lindemann-type process, yet it proceeds through a complex chain mechanism as the formation of free radicals are observed during the course of the reaction. The following mechanism has been proposed.

Initiation (i) $\mathrm{CH_3CH_3 \xrightarrow{k_1} 2\,{}^{\bullet}CH_3}$

Propagation (ii) $\mathrm{{}^{\bullet}CH_3 + CH_3CH_3 \xrightarrow{k_2} CH_4 + {}^{\bullet}CH_2CH_3}$

(iii) $\mathrm{{}^{\bullet}CH_2CH_3 \xrightarrow{k_3} CH_2{=}CH_2 + H^{\bullet}}$

(iv) $\mathrm{{}^{\bullet}H + CH_3CH_3 \xrightarrow{k_4} H_2 + {}^{\bullet}CH_2CH_3}$

Termination (v) $\mathrm{{}^{\bullet}H + {}^{\bullet}CH_2CH_3 \xrightarrow{k_5} CH_3CH_3}$

The rate of formation of ethylene from step (iii) is

$$\frac{\mathrm{d[CH_2{=}CH_2]}}{\mathrm{d}t} = k_3[\mathrm{{}^{\bullet}CH_2CH_3}] \qquad (2.14.11)$$

Applying the steady-state approximation to $\mathrm{{}^{\bullet}CH_3}$, $\mathrm{{}^{\bullet}CH_2CH_3}$ and $\mathrm{{}^{\bullet}H}$, we get

$$\frac{\mathrm{d[{}^{\bullet}CH_3]}}{\mathrm{d}t} = 0 = 2k_1[\mathrm{CH_3CH_3}] - k_2[\mathrm{{}^{\bullet}CH_3}][\mathrm{CH_3CH_3}] \qquad (2.14.12)$$

$$\frac{\mathrm{d[{}^{\bullet}CH_2CH_3]}}{\mathrm{d}t} = 0 = k_2[\mathrm{{}^{\bullet}CH_3}][\mathrm{CH_3CH_3}] - k_3[\mathrm{{}^{\bullet}CH_2CH_3}] + k_4[\mathrm{H^{\bullet}}][\mathrm{CH_3CH_3}] - k_5[\mathrm{H^{\bullet}}][\mathrm{{}^{\bullet}CH_2CH_3}] \qquad (2.14.13)$$

$$\frac{\mathrm{d[H^{\bullet}]}}{\mathrm{d}t} = 0 = k_3[\mathrm{{}^{\bullet}CH_2CH_3}] - k_4[\mathrm{H^{\bullet}}][\mathrm{CH_3CH_3}] - k_5[\mathrm{H^{\bullet}}][\mathrm{{}^{\bullet}CH_2CH_3}] \qquad (2.14.14)$$

Equations (2.14.12) and (2.14.14) respectively give

$$[\mathrm{{}^{\bullet}CH_3}] = \frac{2k_1}{k_2}$$

$$[\mathrm{H^{\bullet}}] = \frac{k_3[\mathrm{{}^{\bullet}CH_2CH_3}]}{k_4[\mathrm{CH_3CH_3}] + k_5[\mathrm{{}^{\bullet}CH_2CH_3}]}$$

Substituting the above two relations in Eq. (2.14.13), we get

$$k_2\left(\frac{2k_1}{k_2}\right)[\mathrm{CH_3CH_3}] - k_3[^{\bullet}\mathrm{CH_2CH_3}] + (k_4[\mathrm{CH_3CH_3}] - k_5[^{\bullet}\mathrm{CH_2CH_3}]) \times \left(\frac{k_3[^{\bullet}\mathrm{CH_2CH_3}]}{k_4[\mathrm{CH_3CH_3}] + k_5[^{\bullet}\mathrm{CH_2CH_3}]}\right) = 0$$

or $\quad k_3k_5\,[^{\bullet}\mathrm{CH_2CH_3}]^2 - k_1k_5\,[\mathrm{CH_3CH_3}]\,[^{\bullet}\mathrm{CH_2CH_3}] - k_1k_4\,[\mathrm{CH_3CH_3}]^2 = 0$

Solving the above quadratic equation, we get

$$[^{\bullet}\mathrm{CH_2CH_3}] = \frac{k_1k_5 + \sqrt{k_1^2k_5^2 + 4k_3k_5k_1k_4}}{2\,k_3k_5}\,[\mathrm{CH_3CH_3}]$$

Substituting the above relation in Eq. (2.14.11), we get

$$\frac{\mathrm{d}\,[\mathrm{CH_2{=}CH_2}]}{\mathrm{d}t} = \frac{k_1k_5 + \sqrt{k_1^2k_5^2 + 4\,k_1k_3k_4k_5}}{2\,k_5}\,[\mathrm{CH_3CH_3}]$$

$$= k\,[\mathrm{CH_3CH_3}] \qquad (2.14.15)$$

Equation (2.14.15) is the required rate law (Eq. 2.14.10). The rate constant k is given as

$$k = \frac{k_1k_5 + (k_1^2k_5^2 + 4\,k_1k_3k_4k_5)^{1/2}}{2k_5} \qquad (2.14.16)$$

Since the chain initiation step is a slow step, the rate constant k_1 has a very small value. Hence, the above expression may be simplified by ignoring (i) $k_1^2k_5^2$ in comparison to $4k_1\,k_3k_4k_5$ and (ii) k_1k_5 in comparison to $(4k_1k_3k_4k_5)^{1/2}$.

Thus, we get

$$k \simeq \left(\frac{k_1k_3k_4}{k_5}\right)^{1/2} \qquad (2.14.17)$$

The chain length of the reaction as defined by Eq. (2.14.1) is

$$\text{Chain length} = \frac{\mathrm{d[product]}/\mathrm{d}t}{\mathrm{d(initiation\ step)}/\mathrm{d}t} = \frac{(k_1k_3k_4/k_5)^{1/2}[\mathrm{CH_3CH_3}]}{k_1[\mathrm{CH_3CH_3}]}$$

$$= \left(\frac{k_3k_4}{k_1k_5}\right)^{1/2} \qquad (2.14.18)$$

Since k_1 is small, the chain length is expected to have a large value.

Thermal Decomposition of Acetaldehyde

The reaction is

$$\mathrm{CH_3CHO \rightarrow CH_4 + CO}$$

The observed rate law is

$$\frac{\mathrm{d[CH_4]}}{\mathrm{d}t} = k\,[\mathrm{CH_3CHO}]^{3/2} \qquad (2.14.19)$$

The proposed mechanism is

Initiation (i) $CH_3CHO \xrightarrow{k_1} {}^{\bullet}CH_3 + {}^{\bullet}CHO$

Propagation (ii) ${}^{\bullet}CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + {}^{\bullet}CH_2CHO$

(iii) ${}^{\bullet}CH_2CHO \xrightarrow{k_3} {}^{\bullet}CH_3 + CO$

Termination (iv) ${}^{\bullet}CH_3 + {}^{\bullet}CH_3 \xrightarrow{k_4} CH_3CH_3$

The rate of formation of CH_4 from step (ii) is

$$\frac{d[CH_4]}{dt} = k_2\,[{}^{\bullet}CH_3][CH_3CHO] \qquad (2.14.20)$$

Applying the steady-state approximation to ${}^{\bullet}CH_3$ and ${}^{\bullet}CH_2CHO$, we get

$$\frac{d[{}^{\bullet}CH_3]}{dt} = 0 = k_1[CH_3CHO] - k_2[{}^{\bullet}CH_3][CH_3CHO] + k_3[{}^{\bullet}CH_2CHO] - 2k_4[{}^{\bullet}CH_3]^2 \qquad (2.14.21)$$

$$\frac{d[{}^{\bullet}CH_2CHO]}{dt} = 0 = k_2[{}^{\bullet}CH_3][CH_3CHO] - k_3[{}^{\bullet}CH_2CHO] \qquad (2.14.22)$$

Making use of Eq. (2.14.22) in Eq. (2.14.21), we get

$$k_1[CH_3CHO] - 2k_4[{}^{\bullet}CH_3]^2 = 0$$

or $$[{}^{\bullet}CH_3] = \left(\frac{k_1}{2k_4}[CH_3CHO]\right)^{1/2}$$

Substituting the above relation in Eq. (2.14.20), we get

$$\frac{d[CH_4]}{dt} = k_2\left(\frac{k_1}{2k_4}[CH_3CHO]\right)^{1/2}[CH_3CHO] = k_2\left(\frac{k_1}{2k_4}\right)^{1/2}[CH_3CHO]^{3/2}$$

$$= k[CH_3CHO]^{3/2}$$

which is the required rate law (Eq. 2.14.19).

The chain length of the reaction is

$$\frac{d[\text{product}]/dt}{d(\text{initiation step})/dt} = \frac{k_2(k_1/2k_4)^{1/2}[CH_3CHO]^{3/2}}{k_1[CH_3CHO]}$$

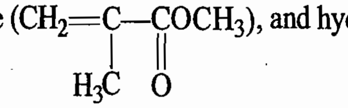
$$= \frac{k_2}{(2k_1k_4)^{1/2}}[CH_3CHO]^{1/2}$$

Polymerization of Vinyl Derivatives

The formation of many of the synthetic vinyl polymers involves chain mechanism. The various involved steps are as follows.

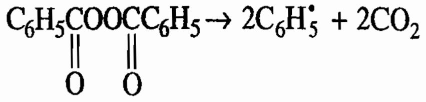
Chain Initiation Step

The polymerization reaction is initiated with the help of free radical which may be produced by using a suitable catalyst. For example, lead tetramethyl which produces methyl radicals has been found to induce polymerization in methyl α-methylacrylate ($CH_2{=}C(CH_3){-}C({=}O)OCH_3$), and hydrogen atoms induce polymerization



$$CH_2{=}\underset{\displaystyle H_3C}{\underset{|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{C}}OCH_3$$

in ethylene. Benzoyl or substituted benzoyl peroxides are found to be very good catalyst as they readily decompose according to the reaction



$$C_6H_5\underset{\underset{O}{\|}}{C}OO\underset{\underset{O}{\|}}{C}C_6H_5 \rightarrow 2C_6H_5^{\bullet} + 2CO_2$$

Let the reaction producing radical $R^{\bullet}$ from a catalyst C be represented as

$$C \xrightarrow{k_1} R^{\bullet}$$

The rate of formation of radical is given by

$$\frac{d[R^{\bullet}]}{dt} = k_1\,[C] \tag{2.14.23}$$

Chain Propagation Steps

The radical produced in the chain initiation step adds to the double bond of vinyl derivative $CH_2{=}CHX$ (X may be H, Cl, C_6H_5, COOH, etc.) and thus produces a new radical. The latter, on adding to another vinyl derivative, produces the next higher radical. This addition process is continued to produce polymerized radical. Thus, we have

$$CH_2{=}CHX + R^{\bullet} \xrightarrow{k_2} RCH_2CHX^{\bullet}$$

$$RCH_2CHX^{\bullet} + CH_2{=}CHX \longrightarrow R(CH_2CHX)_2^{\bullet}$$

and so on. The addition of monomer into the polymer chain is quite rapid.

The rate at which the monomer disappears is given by

$$-\frac{d[CH_2{=}CHX]}{dt} = k_2[CH_2{=}CHX][R^{\bullet}] \tag{2.14.24}$$

Chain Termination Step

The growth of the chain is terminated when the free radical is destroyed. One of the ways involves the combination of two polymerized radicals, i.e.

$$R(CH_2CHX)_n^{\bullet} + {}^{\bullet}(XCHCH_2)_nR \xrightarrow{k_3} R(CH_2CHX)_n - (XCHCH_2)_nR$$

The rate of disappearance of polymerized radical will be given by

$$-\frac{d[R(CH_2CHX)_n^{\bullet}]}{dt} = 2k_3\,[R(CH_2CHX)_n^{\bullet}]^2$$

or written simply as

$$-\frac{d[R^{\bullet}]}{dt} = 2k_3[R^{\bullet}]^2 \tag{2.14.25}$$

Since the concentration of radical is usually very small, the steady-state approximation in the following form may be assumed.

$$\begin{array}{l}\text{Rate of producing radicals}\\ \text{in the initiation step}\end{array} = \begin{array}{l}\text{Rate of consumption of radicals}\\ \text{in the termination step}\end{array}$$

Thus, from Eqs (2.14.23) and (2.14.25), we get

$$k_1[C] = 2k_3[R^{\bullet}]^2$$

or $$[\mathrm{R}^\bullet] = \left(\frac{k_1}{2k_3}[\mathrm{C}]\right)^{1/2}$$

Substituting the above relation in Eq. (2.14.24), we get

$$-\frac{\mathrm{d}[\mathrm{CH_2{=}CHX}]}{\mathrm{d}t} = k_2\left(\frac{k_1}{2k_3}\right)^{1/2}[\mathrm{C}]^{1/2}[\mathrm{CH_2{=}CHX}] \tag{2.14.26}$$

The chain length or the number-average degree of polymerization $\bar{P}_N$ as given by Eq. (2.14.1) is

$$\bar{P}_N = \frac{\mathrm{d[product]}/\mathrm{d}t}{\mathrm{d(initiation\ step)}/\mathrm{d}t} = \frac{-\mathrm{d[reactant]}/\mathrm{d}t}{\mathrm{d(initiation\ step)}/\mathrm{d}t}$$

$$= \frac{k_2(k_1/2k_3)^{1/2}[\mathrm{C}]^{1/2}[\mathrm{CH_2{=}CHX}]}{k_1[\mathrm{C}]}$$

$$= \frac{k_2}{(2k_1k_3)^{1/2}}\,\frac{[\mathrm{CH_2{=}CHX}]}{[\mathrm{C}]^{1/2}} \tag{2.14.27}$$

NONSTATIONARY CHAIN REACTIONS

Explanation of Explosions

In nonstationary reactions, $\alpha > 1$, i.e. chain propagative steps include reactions which consume one radical and produce more than one radical. The explosion characteristic of nonstationary chain reactions can be best understood from Eq. (2.14.2). We have

$$[\mathrm{R}^\bullet] = \frac{k_1[\mathrm{A}]}{k_2[\mathrm{A}](1-\alpha) + k_\mathrm{w} + k_\mathrm{g}}$$

$$= \frac{k_1[\mathrm{A}]}{-k_2[\mathrm{A}](\alpha-1) + (k_\mathrm{w} + k_\mathrm{g})} \tag{2.14.28}$$

Since $\alpha > 1$, more and more radicals are produced during the course of the reaction. Eventually, a stage may be reached when

$$k_2[\mathrm{A}](\alpha - 1) = k_\mathrm{w} + k_\mathrm{g}$$

At this stage, the denominator of Eq. (2.14.28) becomes zero and radical concentration becomes infinite. Since the reaction rate is expected to be proportional to the concentration of radicals, the reaction proceeds with such a large rate that an explosion occurs.

The occurrence of an explosion depends on the temperature and pressure of the reacting system. In general, three explosion limits are observed as the pressure of the system increases during the course of the reaction. These explosions may be understood from the change in the value of denominator of Eq. (2.14.28) with pressure. We have

$$\text{denominator} = -k_2[\mathrm{A}](\alpha - 1) + (k_\mathrm{w} + k_\mathrm{g}) \tag{2.14.29}$$

Fist-Explosion Limit At low pressures, the diffusion of radicals to the walls of the vessel is rapid and thus the rate at which these radicals are destroyed is quite high, i.e. k_w has a large value. On the other hand, the rate constant k_g has a small value. Thus at low pressures, Eq. (2.14.29) has a positive value and the reaction proceeds smoothly without any explosion. As the pressure is increased, k_w decreases more rapidly than the increase in the value of k_g. At a certain pressure, the condition of explosion, i.e.

$$k_2[A](\alpha - 1) = k_w + k_g$$

is reached and thus an explosion is observed. This gives the *first explosion limit.*

Second-Explosion Limit The explosion continues over a range of pressure. Now as the pressure is further raised, the value of k_w becomes less and less while that of k_g becomes more and more, and thus the rate at which radicals are destroyed at the walls decreases while that within the gaseous phase increases. Ultimately, a pressure is reached when k_g has become so high that Eq. (2.14.29) again becomes positive and the reaction starts proceeding with a finite rate. This gives the *second explosion limit.*

Third-Explosion Limit If the pressure is raised still further, the reaction continues to proceed with finite rate. The temperature of the system continues to rise as the heat liberated in various elementary steps cannot escape at the rate at which it is produced. Consequently, the rate of reaction continues to increase which leads ultimately to an explosion. This gives the *third explosion limit* and is entirely due to the thermal effects.

Figures (2.14.1) and (2.14.2) illustrate the three explosion limits of a branched chain reactions.

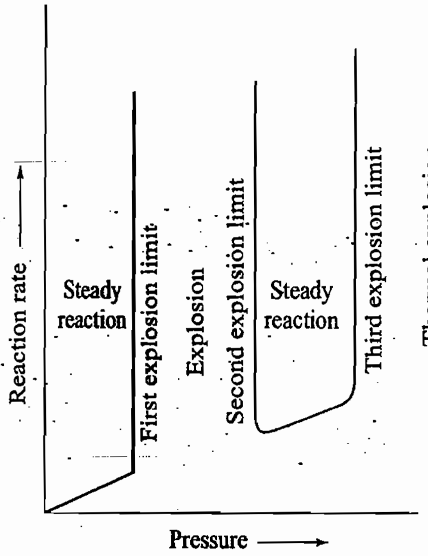


Fig. 2.14.1 Variation of rate reaction with pressure and the three explosion limits

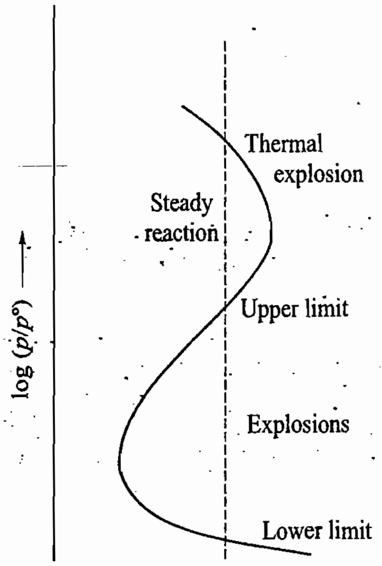


Fig. 2.14.2 Explosion regions

Example Exhibiting Three Explosion Limits

One of the reactions which exhibit the three explosion limits is the reaction between H_2 and O_2. Although the net reaction is very simple:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

the mechanism is very complex. The proposed mechanism includes the following steps.

Initiation $\quad H_2 + O_2 \longrightarrow HO_2^\bullet + H^\bullet$

Propagation $\quad H_2 + HO_2^\bullet \longrightarrow HO^\bullet + H_2O$

$H_2 + HO^\bullet \longrightarrow H^\bullet + H_2O$

$H^\bullet + O_2 \longrightarrow HO^\bullet + O^\bullet$ (branching)

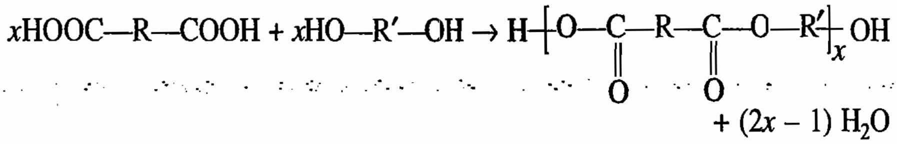
$O^\bullet + H_2 \longrightarrow HO^\bullet + H^\bullet$ (branching)

Nuclear explosion is an another example of nonstationary chain reaction.

2.15 KINETICS OF STEP-GROWTH POLYMERIZATION

Polymerization Reaction

The step-growth polymerization involves the reactions between two functional groups present in two different difunctional species with the elimination of small molecule such as water. For example, a polyester can be formed by the reaction of diacids with dialcohols:



$$x\text{HOOC—R—COOH} + x\text{HO—R}'\text{—OH} \rightarrow \text{H}\left[\text{O—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—R—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—O—R}'\right]_x\text{OH} + (2x-1)\,\text{H}_2\text{O}$$

In polymerization reaction, two monomers react to form a dimer. The dimer then reacts with another monomer to form a trimer, and so on. The individual reactions occurring in polymerization may be represented as

$$\begin{gathered} A + B \rightarrow AB \\ AB + A \rightarrow A_2B \\ AB + B \rightarrow AB_2 \\ \vdots \\ A_mB_n + A_{m'}B_{n'} \rightarrow A_{m+m'}B_{n+n'} \end{gathered}$$

where m, n, m' and n' can have any integral values including zero. Each of the above reactions occurs independently of the other reactions and proceeds with more or less identical rate constant.

Kinetics of Polymerization

The polymerization reaction is also catalysed by acids. The rate of polymerization is proportional to the concentration of ~~—CO_2H gr~~oups and —OH groups.

Two cases may be distinguished as described in the following.

Polymerization without adding Acid Catalyst

In this case, the polymerization is catalysed by the carboxylic groups of the reactant. Its rate expression may be written as

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{OH}]\underset{\text{(catalyst)}}{[\text{COOH}]}$$

$$= k[\text{COOH}]^2[\text{OH}] \tag{2.15.1}$$

If the species containing COOH and OH groups are present in equal amounts (the ratio of these two species remains same throughout), then we can write

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}]^3 \tag{2.15.2}$$

which on integration yields

$$\frac{1}{[\text{COOH}]^2} - \frac{1}{[\text{COOH}]_0^2} = 2kt \tag{2.15.3}$$

It is convenient to express the extent of reaction in terms of the fraction p of —COOH group reacted. In terms of p, we will have

$$[\text{COOH}] = [\text{COOH}]_0\,(1-p)$$

With this, Eq. (2.15.3) becomes

$$\frac{1}{(1-p)^2} = 1 + 2\,[\mathrm{COOH}]_0^2\, kt \qquad (2.15.4)$$

The above expression is found to be obeyed very well after 80% conversion.

Polymerization with the addition of Acid Catalyst

In this case, the rate expression may be written as

$$-\frac{\mathrm{d[COOH]}}{\mathrm{d}t} = [\mathrm{COOH}][\mathrm{OH}]\{k'\,[\mathrm{COOH}] + \underset{\text{(catalyst)}}{k''[\mathrm{H^+}]}\} \qquad (2.15.5)$$

If k' [COOH] << k'' [H$^+$], we can write

$$-\frac{\mathrm{d[COOH]}}{\mathrm{d}t} = k''\,[\mathrm{COOH}][\mathrm{OH}][\mathrm{H^+}] = k[\mathrm{COOH}][\mathrm{OH}] \qquad (2.15.6)$$

If we have equal concentrations of species containing COOH and OH groups, the rate expression becomes

$$-\frac{\mathrm{d[COOH]}}{\mathrm{d}t} = k\,[\mathrm{COOH}]^2 \qquad (2.15.7)$$

Its integrated rate expression is

$$\frac{1}{[\mathrm{COOH}]} - \frac{1}{[\mathrm{COOH}]_0} = kt \qquad (2.15.8)$$

In terms of the fraction p (= – [COOH]/[COOH]$_0$), we have

$$\frac{1}{(1-p)} = 1 + k\,[\mathrm{COOH}]_0\, t \qquad (2.15.9)$$

2.16 EFFECT OF TEMPERATURE ON REACTION RATE

Arrhenius Equation

The dependence of rate constant on temperature may be derived from the van't Hoff equation as applicable to a reaction at equilibrium. Consider a general equilibrium reaction

$$\mathrm{A + B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C + D}$$

The equilibrium constant of the reaction is given by

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} \qquad (2.16.1)$$

The van't Hoff equation is

$$\frac{\mathrm{d}\ln K_{\mathrm{eq}}}{\mathrm{d}t} = \frac{\Delta E}{RT^2} \qquad (2.16.2)$$

where ΔE is the energy change of the reaction. Substituting Eq. (2.16.1) in Eq. (2.16.2), we get

$$\frac{\mathrm{d}\ln(k_1/k_{-1})}{\mathrm{d}T} = \frac{\Delta E}{RT^2}$$

or $$\frac{\mathrm{d}\ln(k_1/k^\circ)}{\mathrm{d}T} - \frac{\mathrm{d}\ln(k_{-1}/k^\circ)}{\mathrm{d}T} = \frac{\Delta E}{RT^2} \tag{2.16.3†}$$

The term ΔE in Eq. (2.16.3) may be written as

$$\Delta E = E_1 - E_{-1} \tag{2.16.4}$$

Substituting Eq. (2.16.4) in Eq. (2.16.3), we get

$$\frac{\mathrm{d}\ln(k_1/k^\circ)}{\mathrm{d}T} - \frac{\mathrm{d}\ln(k_{-1}/k^\circ)}{\mathrm{d}T} = \frac{E_1}{RT^2} - \frac{E_{-1}}{RT^2} \tag{2.16.5}$$

From Eq. (2.16.5), it may be concluded that

$$\frac{\mathrm{d}\ln(k_1/k^\circ)}{\mathrm{d}T} = \frac{E_1}{RT^2} + I \quad \text{and} \quad \frac{\mathrm{d}\ln(k_{-1}/k^\circ)}{\mathrm{d}T} = \frac{E_{-1}}{RT^2} + I$$

where I represents a constant which may have any value including a value of zero. If we take it to be zero, then the above two relations may be written as

$$\frac{\mathrm{d}\ln(k/k^\circ)}{\mathrm{d}T} = \frac{E_a}{RT^2} \tag{2.16.6}$$

Integrating Eq. (2.16.6), we get

$$\ln(k/k^\circ) = -\frac{E_a}{RT} + \text{constant} \tag{2.16.7a}$$

or $$k = A\exp(-E_a/RT) \tag{2.16.7b}$$

Equations (2.16.7a) and (2.16.7b) are the alternative forms of *Arrhenius equation.* According to Eq. (2.16.7b), the rate constant increases exponentially with temperature. The constant A is frequently referred to as the *pre-exponential factor.* According to Eq. (2.16.7a), if a plot is made between ln (k/k°) and $1/T$, one would get a straight line of slope $-E_a/R$ (Fig. 2.16.1).

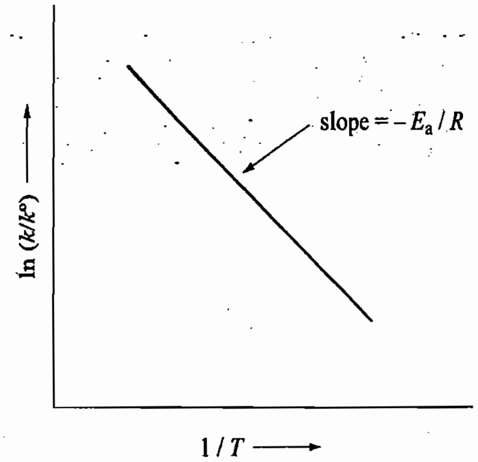


Fig. 2.16.1 A typical variation of ln *k* with temperature

Physical Significance of the Constant E_a

The constant E_a in Eq. (2.16.7) is known as the *energy of activation.* Its significance may be explained as follows.

It was stated in Section 2.4 that the products are formed only when the reactant molecules come close and collide each other at one and the same time. During

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[†] The symbol k° represents the unit of rate constant k.

the collision the molecular rearrangement takes place which leads to the formation of products. The molecular rearrangement usually involves breaking of some bonds and making others. The breaking of bonds or in general molecular rearrangement can take place only when the colliding molecules have energy equal to or greater than the minimum energy required for the said rearrangement. If the energy of colliding molecules is less than this minimum energy, it is obvious that molecular rearrangement will not take place and thus the molecules will remain unchanged after the collision, i.e. no product will be formed. Thus, all collisions will not lead to the formation of products but only those collisions which involve sufficient energy are expected to form products. The difference between the minimum energy required to bring about molecular rearrangement and the average energy of reactant molecules is identified with the constant E_a and is known as energy of activation.

Energies of Activation in a Reversible Reaction

Figure 2.16.2 illustrates the activation energies of forward and backward reactions of a reversible reaction. State X represents the average energy of the reactants, state Y represents that of products and state Z represents the minimum energy which the reactants or products must possess in order to react. Molecules in state Z are said to be *activated* or to be in an *activated state*. From Fig. 2.16.2, it is obvious that

$$E_{a(f)} = E_Z - E_X$$

$$E_{a(b)} = E_Z - E_Y$$

Thus $\quad E_{a(f)} - E_{a(b)} = (E_Z - E_X) - (E_Z - E_Y) = E_Y - E_X = \Delta E$

which is, in fact, Eq. (2.16.4).

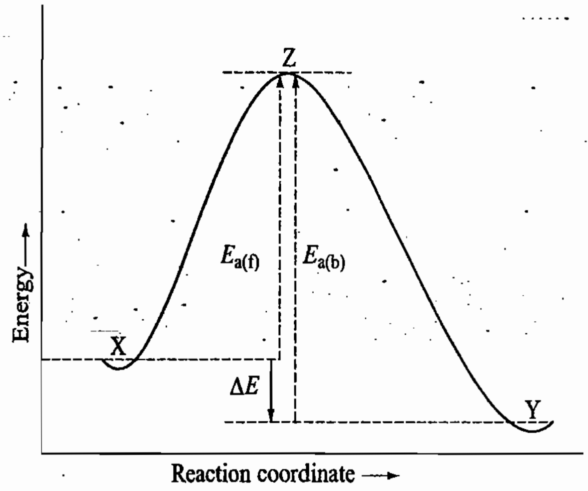


Fig. 2.16.2 The concept of energy of activation

Temperature Coefficient of Reaction Rates

The temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differing by 10 K. Thus, from Eq. (2.16.7a), we have

$$\ln (k_T/k^\circ) = -\frac{E_a}{RT} + \text{constant}$$

$$\ln (k_{T+10\text{K}}/k^\circ) = -\frac{E_a}{R(T+10\,\text{K})} + \text{constant}$$

Hence $\quad \ln (k_{T+10\text{K}}/k^\circ) - \ln (k_T/k^\circ) = -\frac{E_a}{R(T+10\,\text{K})} + \frac{E_a}{RT}$

or $$\ln \frac{k_{T+10\,\mathrm{K}}}{k_T} = \frac{E_\mathrm{a}}{R}\,\frac{(10\,\mathrm{K})}{T(T+10\,\mathrm{K})}$$

or $$\frac{k_{T+10\,\mathrm{K}}}{k_T} = \exp\left(\frac{(10\,\mathrm{K})\,E_\mathrm{a}}{RT(T+10\,\mathrm{K})}\right) \tag{2.16.8}$$

For many reactions at ordinary temperatures, the energy of activation is of the order of 80 kJ mol^{-1}. Thus at 300 K, temperature coefficient of many reactions has a value of

$$\frac{k_{T+10\,\mathrm{K}}}{k_T} = \exp\left\{\frac{(10\,\mathrm{K})\,(80\,000\ \mathrm{J\ mol^{-1}})}{(8{\cdot}314\ \mathrm{J\ K^{-1}\ mol^{-1}})\,(300\,\mathrm{K})\,(310\,\mathrm{K})}\right\} \simeq \mathrm{e}^{1.03} \simeq 2.8$$

that is, the rate constant for the given value of E_a increases about 2.8 for every ten degree rise in temperature. For most reactions, the observed value usually lies between 2 and 3.

Main Characteristics of Arrhenius Equation

The main characteristics of Arrhenius equation are described below.

1. Larger the activation energy, smaller the value of rate constant. This follows immediately from Eq. (2.16.7b).
2. Larger the activation energy, greater the effect of a given temperature rise on k. This follows from Eq. (2.16.8) as $k_{T+10\mathrm{K}}/k_T$ will be larger for a large value of E_a.
3. At lower temperatures, increase in temperature causes more change in the value of k than that at higher temperatures. This also follows from Eq. (2.16.8) where T appears in the denominator.

The above characteristics are in agreement with the experimental results.

Temperature Dependence of Rate Constant of Complex Reaction

In many complex reactions, the observed rate constant is found to decrease with increase in temperature. One of the examples cited in Section 2.12 is the reaction between NO and O_2. The explanation given there was that the reaction involves more than one step. The mechanism is

$$\mathrm{NO + NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2} \qquad \text{(in rapid equilibrium)}$$

$$\mathrm{N_2O_2 + O_2} \xrightarrow{k_2} \mathrm{2\,NO_2} \qquad \text{(slow)}$$

The observed rate constant k is given by

$$k = k_2\left(\frac{k_1}{k_{-1}}\right) = k_2 K_\mathrm{eq}$$

Since the reaction is exothermic, the decrease in K_eq with increase in temperature outweighs the increase in k_2 and thus k decreases with increasing temperature.

The dependence of the observed rate constant of a reaction following simple differential rate law but proceeding through a complex mechanism may be rationalized if we equate the observed rate constant with that found in the rate expression derived from the steady-state approximation. For example, the decomposition of ethane follows the simple kinetics

$$-\frac{d[CH_3CH_3]}{dt} = k\,[CH_3CH_3] \tag{2.16.9}$$

but proceeds through a complex mechanism. According to Eq. (2.14.17), we have

$$k = \left(\frac{k_1 k_3 k_4}{k_5}\right)^{1/2}$$

where k_1, k_3, k_4 and k_5 are the rate constants of various elementary steps. If the temperature dependence of rate constant of each elementary step is replaced by the Arrhenius equation, we get

$$k = \left(\frac{A_1 A_3 A_4}{A_5}\right)^{1/2} \exp\{-(E_{a1} + E_{a3} + E_{a4} - E_{a5})/2RT\} \tag{2.16.10}$$

This is equivalent to the Arrhenius equation for the complex reaction

$$k = A\exp(-E_a/RT) \tag{2.16.11}$$

From Eqs (2.16.10) and (2.16.11), we get

$$A = \left(\frac{A_1 A_3 A_4}{A_5}\right)^{1/2}$$

$$E_a = \tfrac{1}{2}\,[E_{a1} + E_{a3} + E_{a4} - E_{a5}]$$

The values of E_as of elementary reactions were found to be

$E_{a1} = 351.47$ kJ mol^{-1}

$E_{a3} = 167.37$ kJ mol^{-1}

$E_{a4} = 29.29$ kJ mol^{-1}

$E_{a5} = 0$

The activation energy of the overall reaction is

$$E_a = \frac{1}{2}\,(351.47 + 167.37 + 29.29)\ \text{kJ mol}^{-1} = 274.06\ \text{kJ mol}^{-1}$$

Example 2.16.1 For the reaction

$$C_2H_5I + OH^- \rightarrow C_2H_5OH + I^-$$

the rate constant was found to have a value of 5.03×10^{-2} mol^{-1} dm^3 s^{-1} at 289 K and 6.71 mol^{-1} dm^3 s^{-1} at 333 K. What is the activation energy of the reaction? What is the rate constant at 305 K?

Solution We have

$k_1 = 5.03 \times 10^{-2}$ mol^{-1} dm^3 s^{-1} at $T_1 = 289$ K

$k_2 = 6.71$ mol^{-1} dm^3 s^{-1} at $T_2 = 333$ K

Substituting the above data in the expression

$$\ln\{k/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}\} = -\frac{E_a}{RT} + \text{constant}$$

we get

$$\ln(5.03 \times 10^{-2}) = -\frac{E_a}{R(289\ \text{K})} + \text{constant}$$

$$\ln(6.71) = -\frac{E_a}{R(333\ \mathrm{K})} + \text{constant}$$

Subtracting the former from the latter, we get

$$\ln\left(\frac{6.71}{5.03\times10^{-2}}\right) = \frac{E_a}{R}\left(\frac{1}{289\mathrm{K}} - \frac{1}{333\mathrm{K}}\right)$$

$$= \frac{E_a}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})}\left(\frac{44\mathrm{K}}{(289\ \mathrm{K})(333\ \mathrm{K})}\right)$$

Hence $$E_a = \left\{\frac{(8.314\ \mathrm{J\ mol^{-1}})(289)(333)}{44}\right\}\left\{2.303\log\left(\frac{6.71}{5.03\times10^{-2}}\right)\right\}$$

$$= 88\,999\ \mathrm{J\ mol^{-1}} = 88.999\ \mathrm{kJ\ mol^{-1}}$$

The rate constant at 305 K may be determined from the relation

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Thus, $$\log\left(\frac{k_2/\mathrm{mol^{-1}\ dm^3\ s^{-1}}}{5.03\times10^{-2}}\right) = \frac{88\,999\ \mathrm{J\ mol^{-1}}}{2.303(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})}\left(\frac{1}{289\ \mathrm{K}} - \frac{1}{305\ \mathrm{K}}\right)$$

$$\log(k_2/\mathrm{mol^{-1}\ dm^3\ s^{-1}}) - \log(5.03\times10^{-2}) = 0.843\,7$$

or $$\log(k_2/\mathrm{mol^{-1}\ dm^3\ s^{-1}}) = \log(5.03\times10^{-2}) + 0.843\,7$$

$$= \bar{2}.7016 + 0.843\,4 = \bar{1}.5450$$

Hence $k_2 = 0.35\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$

Example 2.16.2 For the reaction

$$2\ \mathrm{NOCl(g)} \rightarrow 2\ \mathrm{NO(g)} + \mathrm{Cl_2(g)}$$

the rate constant is $2.8\times10^{-5}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ at 300 K and $7.0\times10^{-1}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ at 400 K. What is the energy of activation for the reaction?

Solution We have $k_1 = 2.8\times10^{-5}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ at $T_1 = 300$ K

$k_2 = 7.0\times10^{-1}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ at $T_2 = 400$ K

Substituting the above data in the expression

$$\ln(k/\mathrm{mol^{-1}\ dm^3\ s^{-1}}) = -\frac{E_a}{RT} + \text{constant}$$

we get

$$\ln(2.8\times10^{-5}) = -\frac{E_a}{R(300\ \mathrm{K})} + \text{constant}$$

$$\ln(7.0\times10^{-1}) = -\frac{E_a}{R(400\ \mathrm{K})} + \text{constant}$$

Subtracting the former from the latter, we get

$$\ln\left(\frac{7.0\times10^{-1}}{2.8\times10^{-5}}\right) = \frac{E_a}{R}\left(\frac{1}{300\ \mathrm{K}} - \frac{1}{400\ \mathrm{K}}\right) = \frac{E_a}{(8.314\ \mathrm{J\ mol^{-1}})}\left(\frac{100}{300\times400}\right)$$

$$\text{Hence,}\quad E_a = (8.314\ \text{J mol}^{-1})\left(\frac{300\times 400}{100}\right)\left\{2.303\log\left(\frac{7.0\times 10^{-1}}{2.8\times 10^{-5}}\right)\right\}$$

$$= 101\ 048\ \text{J mol}^{-1} = 101.048\ \text{kJ mol}^{-1}$$

Example 2.16.3

For the first-order reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

A is $4.3 \times 10^{13}\ \text{s}^{-1}$ and E_a is 103.35 kJ mol^{-1}. What is k at 300 K?

Solution

We have

$$k = A\exp(-E_a/RT)$$

or
$$\ln(k/\text{s}^{-1}) = \ln(A/\text{s}^{-1}) - \frac{E_a}{RT}$$

or
$$\log(k/\text{s}^{-1}) = \log(A/\text{s}^{-1}) - \frac{E_a}{2.303\,RT}$$

Substituting the given data, we get

$$\log(k/\text{s}^{-1}) = \log(4.3\times 10^{13}) - \frac{103\,350\ \text{J mol}^{-1}}{2.303(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}$$

$$= 13.634 - 17.992 = -4.358 = \bar{5}.642$$

Hence, $k = 4.329 \times 10^{-5}\ \text{s}^{-1}$

2.17 COLLISION THEORY OF BIMOLECULAR GASEOUS REACTIONS

Principle Underlying Collision Theory

Collision theory of bimolecular gaseous reactions aims at the quantitative calculation of the rate of a reaction based on the following two postulates.

1. The products are formed only when the reactant molecules come close and collide with each other.
2. Only those collisions are effective in producing the products which satisfy the criteria of energy of activation and the specific orientation of molecules.

If every collision leads to the formation of product, then the rate of the reaction will entirely be determined by the collision rate, i.e. the frequency with which reactants collide. The calculated rate on this basis sets the upper limit of the reaction rate, i.e. the maximum reaction rate that can be observed experimentally. If the molecules are considered to be rigid, hard spheres with no forces of attraction and repulsion, then for the bimolecular elementary reaction

$$A + A \rightarrow \text{products} \tag{2.17.1}$$

the number of collisions per unit volume per unit time is given by

$$Z_{AA} = \frac{1}{\sqrt{2}}\,\pi\sigma^2\,\bar{u}\,N_A^{*2} \tag{2.17.2}$$

where σ is the diameter of the molecule A and represents the closeness of approach for the molecular collisions, $\bar{u}$ is the average speed of molecules and N_A^* is the number of molecules per unit volume of the vessel. The average speed is given by

$$\bar{u} = \sqrt{\frac{8k_BT}{\pi m_A}}$$

where k_B is Boltzmann constant and m_A is the mass of a single molecule.

Derivation of Expression of Rate Constant

For a general elementary reaction

$$A + B \rightarrow \text{products} \tag{2.17.3}$$

the number of collisions per unit volume per unit time between A and B is given by

$$Z_{AB} = \pi\sigma_{AB}^2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A^* N_B^* \tag{2.17.4}$$

where σ_{AB} is the closeness of approach for the collisions and is equal to the sum of the radii of the molecules A and B or $\sigma_{AB} = (1/2)(\sigma_A + \sigma_B)$, μ is the reduced mass and is given by $\mu = m_Am_B/(m_A + m_B)$, N_A^* and N_B^* are the respective number of molecules of A and B per unit volume of the vessel.

As stated above, Eq. (2.17.4) provides the maximum possible rate of the reaction as given by Eq. (2.17.3). Thus, we may write

$$-\left(\frac{dN_A^*}{dt}\right)_{\max} = Z_{AB} = \pi\sigma_{AB}^2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A^* N_B^* \tag{2.17.5}$$

The amounts of A and B per unit volume will be related to N_A^* and N_B^* by the relations

$$[A] = \frac{N_A^*}{N_A} \quad \text{and} \quad [B] = \frac{N_B^*}{N_A}$$

where N_A is the Avogadro constant. Substituting the above concentration terms in the conventional rate expression

$$\left(-\frac{d[A]}{dt}\right)_{\max} = k_2[A][B]$$

we get

$$\left(-\frac{1}{N_A}\frac{dN_A^*}{dt}\right)_{\max} = k_2\left(\frac{N_A^*}{N_A}\right)\left(\frac{N_B^*}{N_A}\right)$$

or

$$-\left(\frac{dN_A^*}{dt}\right)_{\max} = k_2\frac{1}{N_A}N_A^*N_B^* \tag{2.17.6}$$

Comparing Eqs (2.17.5) and (2.17.6), we get

$$k_2 = N_A\pi\sigma_{AB}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \tag{2.17.7}$$

Illustration

As an illustration, let us calculate the expected maximum rate from Eq. (2.17.5) for most of bimolecular gaseous reactions at 1 atm and 0 °C. We may assume common values of 3×10^{-9} dm and 5×10^3 dm s^{-1} for σ and $\bar{u}$, respectively. At the given conditions of temperature and pressure, we have

$$N_{\mathrm{A}}^{*} = N_{\mathrm{B}}^{*} = \frac{(6.022\times 10^{23}\,\mathrm{mol^{-1}})}{(22.414\,\mathrm{dm^{3}\,mol^{-1}})} \simeq 2.8\times 10^{22}\,\mathrm{dm^{-3}}$$

Hence

$$-\left(\frac{\mathrm{d}N_{\mathrm{A}}^{*}}{\mathrm{d}t}\right)_{\max} = \pi\,\sigma_{\mathrm{AB}}^{2}\,\bar{u}\,N_{\mathrm{A}}^{*}N_{\mathrm{B}}^{*}$$

$$= (3.14)(3\times 10^{-9}\,\mathrm{dm})^{2}\,(5\times 10^{3}\,\mathrm{dm\,s^{-1}})(2.8\times 10^{22}\,\mathrm{dm^{-3}})^{2}$$

$$= 1.11\times 10^{32}\,\mathrm{dm^{-3}\,s^{-1}}$$

$$-\left(\frac{\mathrm{d[A]}}{\mathrm{d}t}\right)_{\max} = -\frac{1}{N_{\mathrm{A}}}\left(\frac{\mathrm{d}N_{\mathrm{A}}^{*}}{\mathrm{d}t}\right)_{\max}$$

$$= \frac{(1.11\times 10^{32}\,\mathrm{dm^{-3}\,s^{-1}})}{(6.022\times 10^{23}\,\mathrm{mol^{-1}})} \simeq 2\times 10^{8}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$$

Comment on the Computed Value of Rate of Reaction

Since the number of collisions are $1.11\times 10^{32}\,\mathrm{dm^{-3}\,s^{-1}}$, it is obvious that the same number of molecules of A and B will react per second. But the number of available molecules of A or B per $\mathrm{dm^3}$ are 2.8×10^{22} and hence the reaction is expected to be over in a very small interval of time of the order of 10^{-10} s. Few reactions are known which proceed with such a large speed. They invariably contain reactive atomic species; amongst them are

$$\mathrm{N + NO \rightarrow N_2 + O}$$

$$\mathrm{O + NO_2 \rightarrow NO + O_2}$$

It is worthwhile to consider the effect of temperature on the maximum rate (Eq. 2.17.5) of a bimolecular reaction. From Eq. (2.17.5), we find that

$$r_{\max} \propto \sqrt{T} \qquad (2.17.8)$$

and hence if we raise the temperature from 300 K to 310 K (i.e. a difference of 10 K), the ratio of the two rates is given by

$$\frac{(r_{\max})_{310\mathrm{K}}}{(r_{\max})_{300\mathrm{K}}} = \left(\frac{310}{300}\right)^{1/2} = 1.015 \qquad (2.17.9)$$

that is, the maximum rate is not very sensitive to temperature.

Most chemical reactions neither have rates as fast as given by Eq. (2.17.7) nor are they insensitive to temperature as predicted by Eq. (2.17.9). The observed rates are about 10^{-2} and $10^{-3}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$ (i.e. the maximum rate of Eq. (2.17.7) is 10^{10} or 10^{11} times as fast as the observed ones) and they become double or triple with every 10 K rise in temperature. These facts are accounted for by the second postulate given in the beginning of this section which states that only those collisions which meet the criteria of energy of activation and the specific orientations of molecules are effective in producing the products. These two criteria are now discussed.

Energy of Activation

The term energy of activation implies that the colliding molecules must be sufficiently energetic to cause the molecular rearrangement which ultimately gives rise to the products. The energy which is effective in promoting reaction is not the total kinetic energy of the two colliding molecules, but rather the kinetic energy corresponding to the component of the relative velocity of the two molecules along the line of their centres at the moment of collision. This is the energy with which the two molecules are pressed together and for a reaction to occur, this energy must be equal to or greater than some minimum energy ε_0. The difference between this minimum energy and the average energy of reacting molecules is known as the *energy of activation*, and is represented by the symbol E_a.

It can be shown that the fraction of all collisions with a line-of-centres component of the kinetic energy greater than the minimum energy ε_0 is given by the Boltzmann factor $\exp(-\varepsilon_0/kT)$.

Thus, the rate of a bimolecular gaseous reaction will be given by

$$\text{Rate} = \begin{pmatrix}\text{total number of}\\ \text{collisions}\end{pmatrix}\begin{pmatrix}\text{fraction of molecules having}\\ \text{component energy equal to } \varepsilon_0\end{pmatrix}$$

or

$$-\frac{\mathrm{d}N_A^*}{\mathrm{d}t} = r_{\max}\exp(-\varepsilon_0/kT) \doteq Z_{AB}\exp(-\varepsilon_0/kT)$$

$$= \left\{\pi\sigma_{AB}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A^* N_B^*\right\}\exp(-\varepsilon_0/kT) \qquad (2.17.10)$$

The constant k_2 as given by Eq. (2.17.7) will now become

$$k_2 = N_A\pi\sigma_{AB}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\exp(-\varepsilon_0/kT) \qquad (2.17.11)$$

The variation of k with temperature is largely due to the Boltzmann factor $\exp(-\varepsilon_0/kT)$. For example, if we change the temperature from 300 K to 310 K of a reaction, the ratio of the two Boltzmann factor is

$$\text{Ratio} = \frac{\exp\left(\dfrac{-\varepsilon_0}{k_B(310\ \text{K})}\right)}{\exp\left(\dfrac{-\varepsilon_0}{k_B(300\ \text{K})}\right)} = \exp\left\{\frac{\varepsilon_0}{k_B}\left(\frac{1}{300\ \text{K}} - \frac{1}{310\ \text{K}}\right)\right\}$$

$$= \exp\left\{\frac{E_0}{R}\left(\frac{1}{300\text{K}} - \frac{1}{310\text{K}}\right)\right\}$$

where E_0 is the minimum energy per mole. Taking a typical case of E_0 = 80.0 kJ mol^{-1}, we have

$$\text{Ratio} = \exp\left\{\frac{(80\,000\ \text{J mol}^{-1})}{(8.314\ \text{J K}^{-1}\text{mol}^{-1})}\left(\frac{1}{300\ \text{K}} - \frac{1}{310\ \text{K}}\right)\right\}$$

$$= \exp(1.035) \simeq 2.8$$

Specific Orientation of Molecules

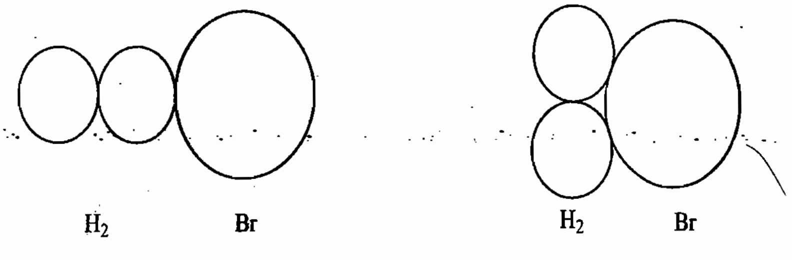
According to this criterion, the formation of products when the two molecules collide also depends upon the relative orientations of the two molecules at the time of collision. This may be understood from the following example.

Reaction between Br and H_2

The reaction is

$$Br + H_2 \rightarrow HBr + H$$

The collision between Br and H_2 may involve a structure where all the three atoms either lie or do not lie on a straight line such as shown in Fig. 2.17.1.



(i) (ii)

Fig. 2.17.1 (i) Three atoms lie on a straight line, and (ii) three atoms do not lie on a straight line

If we draw a potential energy diagram as a function of the reaction coordinate that represents the progress of three atoms from the form of reactants to that of products, we get plots as shown in Fig. 2.17.2.

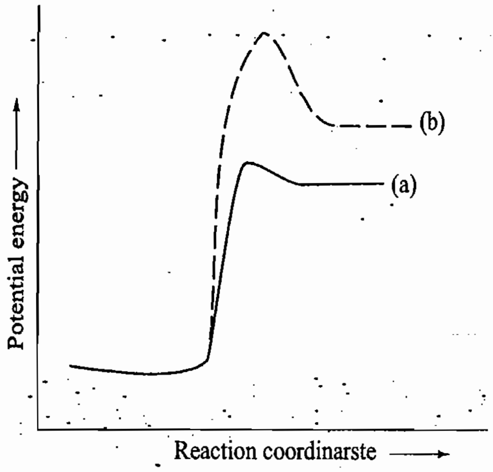


Fig. 2.17.2 Potential energy of H_2 and Br molecules versus reaction coordinates involving (a) a linear structure, and (b) a bent structure

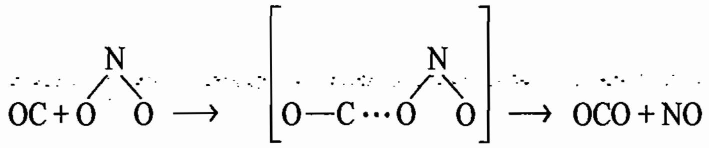
Initial decrease in potential energy is due to the van der Waals attractions. But when Br atom comes closer to H_2, the potential energy of the system increases. It attains a maximum value when the three atoms are partially bonded to each other. This configuration is known as the *activated complex*. The activated complex decays to give products, and as H atom is moved away from HBr, the potential energy decreases. The potential energy diagram of Fig. 2.17.2 explains the following two facts regarding the rate of the said reaction.

(i) It explains very nicely the concept of minimum energy which the colliding molecules must possess so that on collisions they form the products. This minimum energy may be identified with the maximum of the potential energy curve.

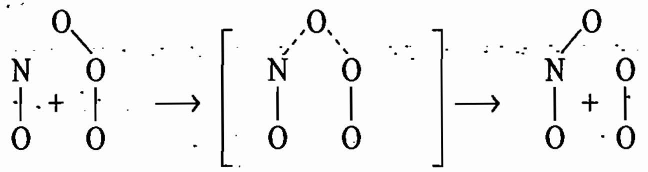
(ii) The maximum of potential energy curve depends on the structure of the activated complex. In Fig. 2.17.2, the maximum for the linear structure lies at a lower value than that of the bent structure. It implies that the energy ε_0 which appeared in Eq. (2.17.11) has a lesser value for the linear structure and consequently the rate constant k_2 has a comparatively larger value. Thus, the formation of products is a much quicker when the reaction coordinate involves a straight line. Thus, we may conclude that:

The rate of formation of products not only depends on E_0 but also on the orientation of molecules at the time of collision.

For more complicated reactions, the criterion of specific orientation of molecules plays a very important role. For example, the reaction between CO and NO_2, the geometry of the activated complex having lowest energy is zigzag.



Thus, if a molecule of CO collides the way it is shown above, the chance of forming the products is most favourable. If the collision involves some other geometry, the chance of forming the product is fairly low owing to the higher energy barrier between reactants and products. Similarly, the reaction between NO and O_3 must involve the geometry given below.



The criterion of specific orientation of molecules at the time of collision is taken into account by multiplying Eq. (2.17.10) by a term p known as the *steric factor*. The steric factor p is usually less than 1 and consequently predicts a reduced rate:

$$r = p\, r_{\max} \exp(-E_0/RT) = p\, Z_{AB} \exp(-E_0/RT)$$

$$= p \left\{ \pi \sigma_{AB}^2 \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} N_A^* N_B^* \right\} \exp(-E_0/RT) \qquad (2.17.12)$$

Equation (2.17.11) will be given as

$$k_2 = p N_A \pi\, \sigma_{AB}^2 \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \exp(-E_0/RT) \qquad (2.17.13)$$

Problem 2.17.1

The bimolecular decomposition of hydrogen iodide is given by the equation $2HI \rightarrow H_2 + I_2$. Assuming a collision diameter of 3.5 nm and an activation energy of 183.9 kJ mol^{-1} for the reaction, calculate (a) the collision rate, (b) the rate of reaction, and (c) the rate constant for the above reaction at 700 K and one atmospheric pressure.

Solution

(a) The number of collisions per unit volume per unit time between two identical molecules is given by

$$Z = \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{u} N^{*2}$$

where $\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \left[\frac{8(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(700\text{K})}{(3.14)(128 \times 10^{-3}\ \text{kg mol}^{-1})} \right]^{1/2} = 340.4\ \text{m s}^{-1}$

$$N^* = \frac{N_A}{V_m} = \frac{(6.022 \times 10^{23}\ \text{mol}^{-1})}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(700\ \text{K})/(101.325 \times 10^3\ \text{Pa})}$$

$$= 1.05 \times 10^{25}\ \text{m}^{-3}$$

Hence, $$Z = \frac{1}{\sqrt{2}}\ \pi \sigma^2 \bar{u} N^{*2}$$

$$= \left(\frac{1}{1.414}\right)(3.14)\,(3.5 \times 10^{-9}\ \text{m})^2\ (340.4\ \text{m s}^{-1})\,(1.05 \times 10^{25}\ \text{m}^{-3})^2$$

$$= 1.02 \times 10^{36}\ \text{m}^{-3}\ \text{s}^{-1}$$

The exponential factor is

$$e^{-Ea/RT} = \exp[-\ 183.9 \times 10^3\ \text{J mol}^{-1}/\{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (700\ \text{K})\}]$$

$$= \exp(-\ 31.6) = 1.89 \times 10^{-14}$$

Hence, $$-\frac{1}{2}\,\frac{dN^*_{HI}}{dt} = Z\,e^{-Ea/RT} = (1.02 \times 10^{36}\ \text{m}^{-3}\ \text{s}^{-1})\ (1.89 \times 10^{-14})$$

$$= 1.93 \times 10^{22}\ \text{m}^{-3}\ \text{s}^{-1}$$

$$-\frac{1}{2}\,\frac{d[\text{HI}]}{dt} = \frac{1.93 \times 10^{22}\ \text{m}^{-3}\ \text{s}^{-1}}{6.022 \times 10^{23}\ \text{mol}^{-1}} = 0.032\ \text{mol m}^{-3}\ \text{s}^{-1}$$

Now $$[\text{HI}] = \frac{N^*_{HI}}{N_A} = \frac{1.05 \times 10^{25}\ \text{m}^{-3}}{6.022 \times 10^{23}\ \text{mol}^{-1}} = 17.43\ \text{mol m}^{-3}$$

Hence, $$k = \frac{-(1/2)\,d[\text{HI}]/dt}{[\text{HI}]^2} = \frac{0.032\ \text{mol m}^{-3}\ \text{s}^{-1}}{(17.43\ \text{mol m}^{-3})^2} = 1.053 \times 10^{-4}\ \text{mol}^{-1}\ \text{m}^3\ \text{s}^{-1}$$

Arrhenius Equation and Collision Theory

The Arrhenius equation is

$$k_2 = A\ \exp(-\ E_a/RT) \qquad \text{(Eq. 2.16.7b)}$$

and according to the collision theory, the rate constant is given by

$$k_2 = pN_A \pi \sigma^2_{AB} \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\ \exp(-\ E_0/RT) \qquad \text{(Eq. 2.17.13)}$$

Equation (2.17.13) may be written as

$$k_2 = K\sqrt{T}\ \exp(-\ E_0/RT) \qquad (2.17.14)$$

where K represents a term which is independent of temperature and is given by

$$K = pN_A \pi \sigma^2_{AB} \left(\frac{8k_B}{\pi\mu}\right)^{1/2} \qquad (2.17.15)$$

The relation between the activation energy E_a (appeared in Eq. 2.16.7b) and the minimum energy E_0 (appeared in Eq. 2.17.14) may be obtained through the derivation of the expression d ln (k/k°)/dT. Equation (2.16.7b) gives

$$\ln(k_2/k^\circ) = \ln(A/k^\circ) - \frac{E_a}{RT}$$

i.e. $$\frac{\mathrm{d}\ln(k_2/k^\circ)}{\mathrm{d}T} = \frac{E_a}{RT^2} \qquad (2.17.16)$$

and Eq. (2.17.14) gives

$$\ln(k_2/k^\circ) = \ln(K/K^\circ) + \frac{1}{2}\ln(T/\mathrm{K}) - \frac{E_0}{RT} \qquad (2.17.17)^\dagger$$

i.e. $$\frac{\mathrm{d}\ln(k_2/k^\circ)}{\mathrm{d}T} = \frac{1}{2T} + \frac{E_0}{RT^2} \qquad (2.17.18)$$

Equating (2.17.16) with (2.17.18), we have

$$\frac{E_a}{RT^2} = \frac{1}{2T} + \frac{E_0}{RT^2}$$

or $$E_a = \frac{RT}{2} + E_0 \qquad (2.17.19)$$

Thus, the activation energy E_a shows temperature dependence. Since E_0 is usually much larger than $RT/2$, the difference between the Arrhenius activation energy E_A and the minimum energy E_0 of the simple kinetic theory is not sufficient.

Substitution of Eq. (2.17.19) in Eq. (2.17.14), we get

$$k_2 = K\sqrt{T}\,\exp\{-(E_a - RT/2)/RT\}$$

or $$k_2 = K\sqrt{T}\,e^{1/2}\exp(-E_a/RT)$$

Comparing the above relation with the Arrhenius equation, we have

$$A = K\sqrt{T}\,e^{1/2}$$

i.e. $$A = pN_A\pi\sigma_{AB}^2\left(\frac{8k_B}{\pi\mu}\right)^{1/2}\sqrt{T}\,e^{1/2} \qquad (2.17.20a)$$

or $$A = p\,N_A\,\frac{Z_{AB}}{N_A^* N_B^*}\,e^{1/2} \qquad (2.17.20b)$$

2.18 THE ACTIVATED COMPLEX THEORY

Figure 2.16.2 displays the variation of potential energy with the reaction coordinate for the reaction between Br and H_2. The maximum of the curve corresponds to the energy of the activated complex (or transition state complex) where all the three atoms are bonded to each other as shown below:

$$\mathrm{Br} + \mathrm{H_2} \rightarrow \underset{\text{activated complex}}{[\mathrm{Br}\cdots\mathrm{H}\cdots\mathrm{H}]} \rightarrow \mathrm{Br{-}H} + \mathrm{H}$$

The conversion of reactants to products (or vice versa) is through the formation of the activated complex shown above. It is thus obvious that the reacting species can combine only if their energy is equal to or greater than that of the activated complex.

[†] The symbol K° represents the unit of K (= $\mathrm{mol^{-1}\,m^3\,s^{-1}\,K^{-1/2}}$).

The activated complex is not an intermediate compound. It is a molecule in the process of breaking or forming bonds. The reacting molecules can undergo a variety of vibrational motions and can be thought of as existing in a potential energy minimum. However, the activated complex is not stable because it exists at a potential energy maximum.

Eyring and others have developed the quantitative treatment of the activated complex theory (or transition state theory or absolute rate theory) based on the assumptions that there exists an equilibrium between the reactants and the activated complex and that the products are obtained by decomposing the activated complex. Thus, the reaction between the two reactants A and B may be written as

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X}^{\ddagger} \rightarrow \text{product} \tag{2.18.1}$$

where $\mathrm{X}^{\ddagger}$ is the activated complex. The rate of the reaction depends on two factors, namely, the concentration of activated complex and the frequency of decomposition of activated complex. Thus, we have

$$r = \begin{pmatrix}\text{concentration of}\\ \text{activated complex}\end{pmatrix}\begin{pmatrix}\text{frequency of decomposition}\\ \text{of activated complex}\end{pmatrix} \tag{2.18.2}$$

The two terms appearing in the above rate equation have been determined as follows.

Concentration of Activated Complex

Since the reactants are in equilibrium with the activated complex, we may characterize the equilibrium with the equilibrium constant written as

$$K^{\ddagger} = \frac{[\mathrm{X}^{\ddagger}]}{[\mathrm{A}][\mathrm{B}]} \tag{2.18.3}$$

The equilibrium constant $K^{\ddagger}$ may be determined by using the ideas of thermodynamics and statistical mechanics. Thus, the concentration of $\mathrm{X}^{\ddagger}$ is given by

$$[\mathrm{X}^{\ddagger}] = K^{\ddagger}[\mathrm{A}]\,[\mathrm{B}] \tag{2.18.4}$$

Frequency of Decomposition of the Activated Complex

Since the activated complex is in a process of decomposing, one of its vibrational degrees of freedom is in the process of becoming a translational degree of freedom. Let E_{vib} be the average vibrational energy which results in the rupture of the bond. According to the Planck's equation for the quantum of energy, we have

$$E_{\mathrm{vib}} = h\nu \tag{2.18.5}$$

where ν is the vibrational frequency. In the activated complex theory, ν is taken as the frequency of decomposition of the activated complex.

The rupture of bond in the activated complex is due to the large vibrational energy which it acquires during the formation of the complex. The vibrational quantum number corresponding to such a large vibrational energy will be quite high and thus we may equate E_{vib} with the classical vibrational energy expression which is equal to $k_{\mathrm{B}}T$, where k_{B} is the Boltzmann constant. Thus, we have

$$E_{\mathrm{vib}} = k_{\mathrm{B}}T \tag{2.18.6}$$

Equating (2.18.5) and (2.18.6), we get

$$h\nu = k_{\mathrm{B}}T = \left(\frac{R}{N_{\mathrm{A}}}\right)T$$

or $$v = \frac{RT}{N_A h} \tag{2.18.7}$$

where N_A is the Avogadro constant.

Substituting Eqs (2.18.4) and (2.18.7) in Eq. (2.18.2), we have

$$r = (K^{\ddagger}[\mathrm{A}][\mathrm{B}])\left(\frac{RT}{N_A h}\right) \quad \text{or} \quad r = \left(K^{\ddagger}\frac{RT}{N_A h}\right)[\mathrm{A}][\mathrm{B}] \tag{2.18.8}$$

Comparing Eq. (2.18.8) with the experimentally obtained rate law

$$r = k_2\,[\mathrm{A}][\mathrm{B}]$$

we get $$k_2 = \frac{RT}{N_A h}K^{\ddagger} \tag{2.18.9}$$

Now from thermodynamics, we have

$$\Delta^{\ddagger}G^{\circ} = -RT\ln K^{\circ\ddagger}$$

where $\Delta^{\ddagger}G^{\circ}$ is change in the standard free energy in going from reactants to the activated complex, i.e. for a reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{X}^{\ddagger}$$

and is given by

$$\Delta^{\ddagger}G^{\circ} = G^{\circ}(\mathrm{X}^{\ddagger}) - G^{\circ}(\mathrm{A}) - G^{\circ}(\mathrm{B})$$

Hence, $K^{\circ\ddagger}$ is given by

$$K^{\circ\ddagger} = \exp(-\Delta^{\ddagger}G^{\circ}/RT)$$

Since $\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}H^{\circ} - T\Delta^{\ddagger}S^{\circ}$, we may write the above expression as

$$K^{\circ\ddagger} = \exp\{-(\Delta^{\ddagger}H^{\circ} - T\Delta^{\ddagger}S^{\circ})/RT\}$$

$$= \exp(-\Delta^{\ddagger}H^{\circ}/RT)\exp(\Delta^{\ddagger}S^{\circ}/R) \tag{2.18.10}$$

The constants $K^{\circ\ddagger}$ and $K^{\ddagger}$ are related to each other through the expression

$$K^{\circ\ddagger} = K^{\ddagger}c^{\circ} \tag{2.18.11}$$

where c° is the unit concentration, i.e. 1 mol dm^{-3}.

Substituting Eqs (2.18.10) and (2.18.11) in Eq. (2.18.9), we get

$$k_2 = \frac{RT}{c^{\circ}N_A h}\exp(-\Delta^{\ddagger}H^{\circ}/RT)\exp(\Delta^{\ddagger}S^{\circ}/R) \tag{2.18.12}$$

Arrhenius Equation and the Activated Complex Theory

The Arrhenius equation is

$$k_2 = A\exp(-E_a/RT) \qquad \text{(Eq. 2.16.7b)}$$

and according to the activated complex theory, the rate constant is given by

$$k_2 = \frac{RT}{c^{\circ}N_A h}\exp(\Delta^{\ddagger}S^{\circ}/R)\exp(-\Delta^{\ddagger}H^{\circ}/RT) \qquad \text{(Eq. 2.18.12)}$$

Also $\Delta^{\ddagger}H^{\circ} = \Delta^{\ddagger}U^{\circ} + (\Delta^{\ddagger}\nu_g)RT$

Therefore, we have

$$k_2 = \frac{RT}{c^\circ N_A h}\exp(\Delta^\ddagger S^\circ/R)\exp\{-(\Delta^\ddagger U^\circ + \Delta^\ddagger \nu_g\, RT)/RT\}$$

or

$$= \frac{RT}{c^\circ N_A h}\exp(\Delta^\ddagger S^\circ/R)\exp(-\Delta^\ddagger \nu_g)\exp(-\Delta^\ddagger U^\circ/RT) \qquad (2.18.13)$$

The relation between the activation energy E_a of Eq. (2.16.7b) and the energy change $\Delta^\ddagger U^\circ$ in the formation of activated complex from reactants may be obtained through the derivation of the expression d ln $(k/k^\circ)/\mathrm{d}T$. Equation (2.16.7b) gives

$$\ln(k_2/k^\circ) = \ln(A/k^\circ) - \frac{E_a}{RT}$$

$$\frac{\mathrm{d}\ln(k_2/k^\circ)}{\mathrm{d}T} = \frac{E_a}{RT^2} \qquad (2.18.14)$$

and Eq. (2.18.13) gives

$$\ln(k_2/k^\circ) = \ln\left(\frac{R}{N_A h}\Big/\mathrm{s^{-1}\,K^{-1}}\right) + \ln(T/\mathrm{K}) + \frac{\Delta^\ddagger S^\circ}{R} - \Delta^\ddagger \nu_g - \frac{\Delta^\ddagger U^\circ}{RT}$$

where k° represent the unit of k, i.e. $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$.

Hence,

$$\frac{\mathrm{d}\ln(k_2/k^\circ)}{\mathrm{d}T} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2} \qquad (2.18.15)$$

Equating (2.18.14) and (2.18.15), we get

$$\frac{E_a}{RT^2} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2}$$

or

$$E_a = RT + \Delta^\ddagger U^\circ \qquad (2.18.16)$$

Substituting Eq. (2.18.16) in Eq. (2.18.13), we get

$$k_2 = \frac{RT}{c^\circ N_A h}\exp(\Delta^\ddagger S^\circ/R)\exp(-\Delta^\ddagger \nu_g)\exp\{-(E_a - RT)/RT\}$$

$$= \frac{RT}{c^\circ N_A h}\exp(\Delta^\ddagger S^\circ/R)\exp(1 - \Delta^\ddagger \nu_g)\exp(-E_a/RT) \qquad (2.18.17)$$

which on comparing with the Arrhenius equation gives

$$A = \frac{RT}{c^\circ N_A h}\exp(\Delta^\ddagger S^\circ/R)\exp(1 - \Delta^\ddagger \nu_g) \qquad (2.18.18a)$$

$$= (\nu_{\mathrm{vib}}/c^\circ)\exp(\Delta^\ddagger S^\circ/R)\exp(1 - \Delta^\ddagger \nu_g) \qquad (2.18.18b)$$

where ν_{vib} is the frequency of decomposition of the activated complex.

Note that $\Delta^\ddagger \nu_g$ represents the change in the stoichiometric number of gaseous molecules in going from reactants to the activate complex and is given by

$$\Delta^\ddagger \nu_g = 1 - \sum_{\text{reactant}} \nu_g$$

The relation connecting E_a and $\Delta^\ddagger H^\circ$ is

$$\begin{aligned}\Delta^\ddagger H^\circ &= \Delta^\ddagger U^\circ + (\Delta^\ddagger \nu_g)\, RT = (E_a - RT) + (\Delta^\ddagger \nu_g)\, RT \qquad (2.18.19)\\ &= E_a + (\Delta^\ddagger \nu_g - 1)\, RT\end{aligned}$$

Collision Theory and the Activated Complex Theory

The expressions for the rate constant are as follows.

Collision theory

$$k_2 = pN_A\, \pi\, \sigma_{AB}^2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \exp(-E_0/RT) \qquad \text{(Eq. 2.17.14)}$$

The activated complex theory

$$k_2 = \frac{RT}{c^\circ N_A h}\exp(\Delta^\ddagger S^\circ/R)\exp(-\Delta^\ddagger U^\circ/RT)\exp(-\Delta^\ddagger \nu_g) \qquad (2.18.20)$$

The expressions for d ln $(k/k^\circ)/\mathrm{d}T$ are as follows.

Collision theory

$$\frac{\mathrm{d}\ln(k_2/k^\circ)}{\mathrm{d}T} = \frac{1}{2T} + \frac{E_0}{RT^2} \qquad \text{(Eq. 2.17.18)}$$

The activated complex theory

$$\frac{\mathrm{d}\ln(k_2/k^\circ)}{\mathrm{d}T} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2} \qquad \text{(Eq. 2.18.15)}$$

Equating the above two relations, we get

$$\frac{1}{2T} + \frac{E_0}{RT^2} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2}$$

$$E_0 = \Delta^\ddagger U^\circ + \frac{1}{2}RT \qquad (2.18.21)$$

Substituting Eq. (2.18.21) in Eq. (2.18.20), we get

$$\begin{aligned}k_2 &= \frac{RT}{c^\circ N_A h}\exp(\Delta^\ddagger S^\circ/R)\exp\{-(E_0 - RT/2)/RT\}\exp(-\Delta^\ddagger \nu_g)\\ &= \frac{RT}{c^\circ N_A h}\exp(\Delta^\ddagger S^\circ/R)\exp(1/2)\exp(-\Delta^\ddagger \nu_g)\exp(-E_0/RT)\end{aligned}$$

which on comparing with Eq. (2.17.13) gives

$$pN_A\, \pi\sigma_{AB}^2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = \frac{RT}{c^\circ N_A h}\exp(\Delta^\ddagger S^\circ/R)\exp\{-(\Delta^\ddagger \nu_g - 1/2)\} \qquad (2.18.22a)$$

or

$$pN_A \frac{Z_{AB}}{N_A^* N_B^*} = \frac{\nu_{vib}}{c^\circ}\exp(\Delta^\ddagger S^\circ/R)\exp\{-(\Delta^\ddagger \nu_g - 1/2)\} \qquad (2.18.22b)$$

The unit of the term RT/N_Ah is s^{-1} and thus approximately corresponds to the frequency of collision Z_{AB}. Thus, the steric factor p may be interpreted in terms of entropy of activation. The latter is expected to have a negative value as the activated complex represents a more ordered state than the reactants. If reactants are only atoms or simple molecules, then there is a relatively small amount of rearrangement of energy among the various degrees of freedom in the activated complex. Consequently, $\Delta^{\ddagger}S^{\circ}$ is expected to have a small negative value so that $\exp(\Delta^{\ddagger}S^{\circ}/R)$ or p is close to unity. On the other hand, if the activated complex is formed from the larger number of reactants or the activated complex formed is relatively rigid (i.e. the bonds formed in the activated complex are relatively strong), then the entropy of activation has a large negative value, and thus $\exp(\Delta^{\ddagger}S^{\circ}/R)$ or p has a small value.

For a process of the type

$$AB \rightarrow AB^{\ddagger} \rightarrow A + B$$

the entropy of activation will generally be positive, since the activated complex will most likely have acquired some of the disorder which eventually results in its total breakdown into A and B.

Activated Complex Theory applied to a Reaction at Equilibrium

In the activated complex theory, an equilibrium reaction such as

$$A + B \rightleftharpoons C + D$$

will be represented as

$$A + B \rightleftharpoons X^{\ddagger} \rightleftharpoons C + D$$

where $X^{\ddagger}$ is the activated complex. Figure 2.18.1 displays $\Delta^{\ddagger}G^{\circ}$ for the forward and backward reactions. Obviously, free energy change of the reaction will be given by

$$\Delta G^{\circ} = \Delta^{\ddagger}G^{\circ}_{f} - \Delta^{\ddagger}G^{\circ}_{b} \qquad (2.18.23)$$

The rate constants for the forward and backward reactions will be given by

$$k_f = \frac{RT}{c^{\circ}N_A h}\exp(-\Delta^{\ddagger}G^{\circ}_{f}/RT) \qquad (2.18.24)$$

$$k_b = \frac{RT}{c^{\circ}N_A h}\exp(-\Delta^{\ddagger}G^{\circ}_{b}/RT) \qquad (2.18.25)$$

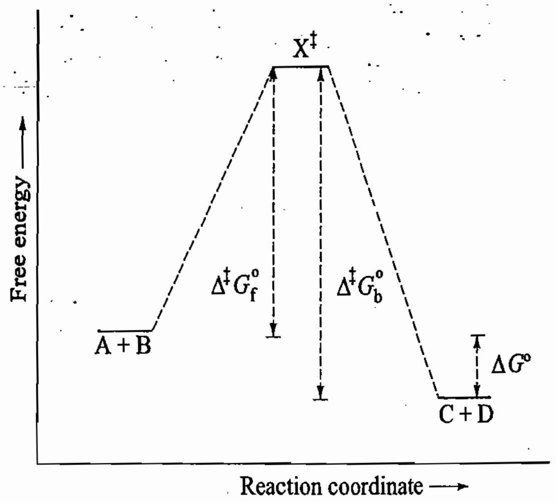


Fig. 2.18.1 Free energy change versus reaction coordinate

The rate laws are given by

$$r_f = k_f\,[A][B]$$

$$r_b = k_b\,[C][D]$$

At equilibrium, we will have

$$r_f = r_b$$

or $$k_f\,[A][B] = k_b[C][D]$$

Substituting k_f and k_b from Eqs (2.18.24) and (2.18.25), we get

$$\left(\frac{RT}{c^\circ N_A h}\exp(-\Delta^\ddagger G^\circ_f/RT)\right)[A][B] = \left(\frac{RT}{c^\circ N_A h}\exp(-\Delta^\ddagger G^\circ_b/RT)\right)[C]\,[D]$$

On rearranging, we get

$$\frac{[C][D]}{[A][B]} = K^\circ_{eq} = \exp\{-(\Delta^\ddagger G^\circ_f - \Delta^\ddagger G^\circ_b)/RT\} = \exp(-\Delta G^\circ/RT)$$

or $$\Delta G^\circ = -RT\ln K^\circ_{eq}$$

an expression which can be derived thermodynamically.

Equation (2.18.23) predicts correctly the fact that some reactions proceed with a very slow rate (or do not occur at all) even though ΔG° of the reaction is highly negative. This happens when $\Delta^\ddagger G^\circ_f$ has a very large positive value and the rate as predicted by Eq. (2.18.24) is quite small.

Example 2.18.1

A dimerization reaction at about 300 K in the gaseous phase follows the Arrhenius equation

$$k_2 = A\exp(-E_a/RT)$$

where $A = 10^{5.61}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$ and $E_a = 65.40\ \text{kJ mol}^{-1}$. Calculate $\Delta^\ddagger H^\circ$, $\Delta^\ddagger S^\circ$, $\Delta^\ddagger U^\circ$ and $\Delta^\ddagger G^\circ$ for the reaction.

Solution

For the Arrhenius equation

$$k_2 = A\exp(-E_a/RT)$$

we have $$A = \frac{RT}{c^\circ N_A h}\exp\left(\frac{\Delta^\ddagger S^\circ}{R} + 1 - \Delta^\ddagger \nu_g\right) \qquad \text{(Eq. 2.18.18)}$$

and $$E_a = \Delta^\ddagger E^\circ + RT \qquad \text{(Eq. 2.18.16)}$$

For the dimerization reaction $\Delta^\ddagger \nu_g = -1$. Hence, we have

$$\frac{RT}{c^\circ N_A h}\exp\left(\frac{\Delta^\ddagger S^\circ}{R} + 2\right) = A = 10^{5.61}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

Taking the natural logarithm on the both sides, we get

$$\left(\ln\frac{RT}{N_A h}\Big/\text{s}^{-1}\right) + \left(\frac{\Delta^\ddagger S^\circ}{R} + 2\right) = \ln(10^{5.61})$$

or $$2.303\log\left(\frac{RT}{N_A h}\Big/\text{s}^{-1}\right) + \left(\frac{\Delta^\ddagger S^\circ}{R} + 2\right) = 2.303 \times 5.61$$

or $$\log\left(\frac{RT}{N_\mathrm{A}h}\Big/\mathrm{s}^{-1}\right)\frac{1}{2.303}\left(\frac{\Delta^{\ddagger}S^\circ}{R}+2\right)=5.61$$

$$\log\left(\frac{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\ \mathrm{K})}{(6.023\times10^{23}\ \mathrm{mol^{-1}})(6.6\times10^{-34}\ \mathrm{J\ s})}\Big/\mathrm{s}^{-1}\right)+\frac{1}{2.303}\left(\frac{\Delta^{\ddagger}S^\circ}{R}+2\right)=5.61$$

or $$12.797\,6+\frac{1}{2.303}\left(\frac{\Delta^{\ddagger}S^\circ}{R}+2\right)=5.61$$

or $$\frac{1}{2.303}\left(\frac{\Delta^{\ddagger}S^\circ}{R}+2\right)=5.61-12.797\,6=-7.187\,6$$

or $$\frac{\Delta^{\ddagger}S^\circ}{R}+2=-7.187\,6\times2.303=-16.553$$

or $$\begin{aligned}\Delta^{\ddagger}S^\circ&=R(-16.553-2)=(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(-18.553)\\&=-154.25\ \mathrm{J\ K^{-1}\ mol^{-1}}\end{aligned}$$

Now $$\begin{aligned}\Delta^{\ddagger}U^\circ&=E_\mathrm{a}-RT\\&=65\,400\ \mathrm{J\ mol^{-1}}-(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\ \mathrm{K})\\&=62\,906\ \mathrm{J\ mol^{-1}}=62.906\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta^{\ddagger}H^\circ&=\Delta^{\ddagger}U^\circ+(\Delta^{\ddagger}\nu_\mathrm{g})RT=\Delta^{\ddagger}U^\circ-RT\\&=(62\,906\ \mathrm{J\ mol^{-1}})-(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\ \mathrm{K})=60\,412\ \mathrm{J\ mol^{-1}}\\&=60.412\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta^{\ddagger}G^\circ&=\Delta^{\ddagger}H^\circ-T\Delta^{\ddagger}S^\circ\\&=(60\,412\ \mathrm{J\ mol^{-1}})-(300\ \mathrm{K})(-154.25\ \mathrm{J\ K^{-1}\ mol^{-1}})\\&=106\,687\ \mathrm{J\ mol^{-1}}=106.687\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Alternatively, $\Delta^{\ddagger}G^\circ$, $\Delta^{\ddagger}H^\circ$ and $\Delta^{\ddagger}U^\circ$ may be calculated as follows. We have

$$k_2=\frac{RT}{c^\circ N_\mathrm{A}h}\exp(-\Delta^{\ddagger}G^\circ/RT)$$

where k_2 is obtained from the Arrhenius equation. Thus, we have

$$A\exp(-E_\mathrm{a}/RT)=\frac{RT}{c^\circ N_\mathrm{A}h}\exp(-\Delta^{\ddagger}G^\circ/RT)$$

Taking the natural logarithm on both sides, we get

$$\ln(c^\circ A/\mathrm{s}^{-1})-\frac{E_\mathrm{a}}{RT}=\ln\left(\frac{RT}{N_\mathrm{A}h}\Big/\mathrm{s}^{-1}\right)-\frac{\Delta^{\ddagger}G^\circ}{RT}$$

Converting into the common logarithm and substituting the given values, we have

$$\log(10^{5.61}) - \frac{(65400\ \mathrm{J\ mol^{-1}})}{2.303(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\ \mathrm{K})}$$

$$= \log\left(\frac{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\ \mathrm{K})}{(6.022\times10^{23}\ \mathrm{mol^{-1}})(6.6\times10^{-34}\ \mathrm{J\ s})}\Big/\mathrm{s^{-1}}\right)$$

$$- \frac{\Delta^{\ddagger}G^{\circ}}{2.303(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\ \mathrm{K})}$$

$$5.61 - 11.386 = 12.798 - \frac{\Delta^{\ddagger}G^{\circ}}{2.303(8.314\ \mathrm{J\ mol^{-1}})(300)}$$

or $\Delta^{\ddagger}G^{\circ} = (18.574)\ (2.303)\ (8.314\ \mathrm{J\ mol^{-1}})\ (300)$

$= 106\ 692\ \mathrm{J\ mol^{-1}} = 106.692\ \mathrm{kJ\ mol^{-1}}$

Now $\Delta^{\ddagger}H^{\circ} = \Delta^{\ddagger}G^{\circ} + T\Delta^{\ddagger}S^{\circ} = (106\ 692\ \mathrm{J\ mol^{-1}}) + (300\ \mathrm{K})(-154.25\ \mathrm{J\ K^{-1}\ mol^{-1}})$

$= 60\ 417\ \mathrm{mol^{-1}} = 60.417\ \mathrm{kJ\ mol^{-1}}$

$\Delta^{\ddagger}U^{\circ} = \Delta^{\ddagger}H^{\circ} - (\Delta^{\ddagger}\nu_g)\ RT$

$= (60\ 417\ \mathrm{J\ mol^{-1}}) - (-\ 1)\ (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ (300\ \mathrm{K})$

$= 62\ 911\ \mathrm{J\ mol^{-1}} = 62.911\ \mathrm{kJ\ mol^{-1}}$

Example 2.18.2 The electron-exchange reaction between naphthalene ($C_{10}H_8$) and its anion radical can be represented by

$$C_{10}H_8^- + C_{10}H_8 = C_{10}H_8 + C_{10}H_8^-$$

The reaction is second-order as well as bimolecular. The rate constants are

T/K	307	299	289	273
$k \times 10^{-9}/\mathrm{mol^{-1}\ dm^3\ s^{-1}}$	2.71	2.40	1.96	1.43

Calculate $\Delta^{\ddagger}H^{\circ}$, E_a, $\Delta^{\ddagger}S^{\circ}$ and $\Delta^{\ddagger}H^{\circ}$ at 307 K for the reaction.

Solution We may employ Eq. (2.18.12) to compute $\Delta^{\ddagger}S^{\circ}$ and $\Delta^{\ddagger}H^{\circ}$ Equation (2.18.12) is

$$k = \frac{RT}{c^{\circ}N_{\mathrm{A}}h}\ \exp(\Delta^{\ddagger}S^{\circ}/R)\ \exp(-\ \Delta^{\ddagger}H^{\circ}/RT) \qquad (1)$$

Dividing by T and taking logarithm, we get

$$\log\left(\frac{k}{T}\Big/\mathrm{mol^{-1}\ dm^3\ s^{-1}\ K^{-1}}\right) = \log\left(\frac{R}{N_{\mathrm{A}}h}\Big/\mathrm{s^{-1}\ K^{-1}}\right) + \frac{\Delta^{\ddagger}S^{\circ}}{2.303R} - \frac{\Delta^{\ddagger}H^{\circ}}{2.303RT} \qquad (2)$$

Thus, if a plot is made between $\log\left(\frac{k}{T}\Big/\mathrm{mol^{-1}\ dm^3\ s^{-1}\ K^{-1}}\right)$ and $1/T$, one would get a straight line with

$$\text{slope} = -\frac{\Delta^{\ddagger}H^{\circ}}{2.303R} \tag{3}$$

$$\text{intercept} = \log\left(\frac{R}{N_{A}h}\Big/\text{s}^{-1}\,\text{K}^{-1}\right) + \frac{\Delta^{\ddagger}S^{\circ}}{2.303R} \tag{4}$$

We have

T/K	307	299	289	273
K/T	0.003 26	0.003 34	0.003 46	0.003 66
k/mol^{-1} dm^{3} s^{-1}	2.71×10^{9}	2.40×10^{9}	1.96×10^{9}	1.43×10^{9}
$\frac{k}{T}\Big/\text{mol}^{-1}\,\text{dm}^{3}\,\text{s}^{-1}\,\text{K}^{-1}$	8.827×10^{6}	8.027×10^{6}	6.782×10^{6}	5.238×10^{6}
$\log\left(\frac{k}{T}\Big/\text{mol}^{-1}\,\text{dm}^{3}\,\text{s}^{-1}\,\text{K}^{-1}\right)$	6.946	6.905	6.831	6.719

The plot of $\log\left\{(k/T)/\text{mol}^{-1}\,\text{dm}^{-3}\,\text{s}^{-1}\,\text{K}^{-1}\right\}$ versus (K/T) is shown in Fig. 2.18.2. Its slope is − 560.98, i.e.

$$\frac{\Delta\log\left\{\frac{k}{T}\Big/\text{mol}^{-1}\,\text{dm}^{3}\,\text{s}^{-1}\,\text{K}^{-1}\right\}}{\Delta(\text{K}/T)} = -\,560.98$$

Hence,
$$\frac{\Delta\log\left\{\frac{k}{T}\Big/\text{mol}^{-1}\,\text{dm}^{3}\,\text{s}^{-1}\,\text{K}^{-1}\right\}}{\Delta(1/T)} = -\,560.98\ \text{K}$$

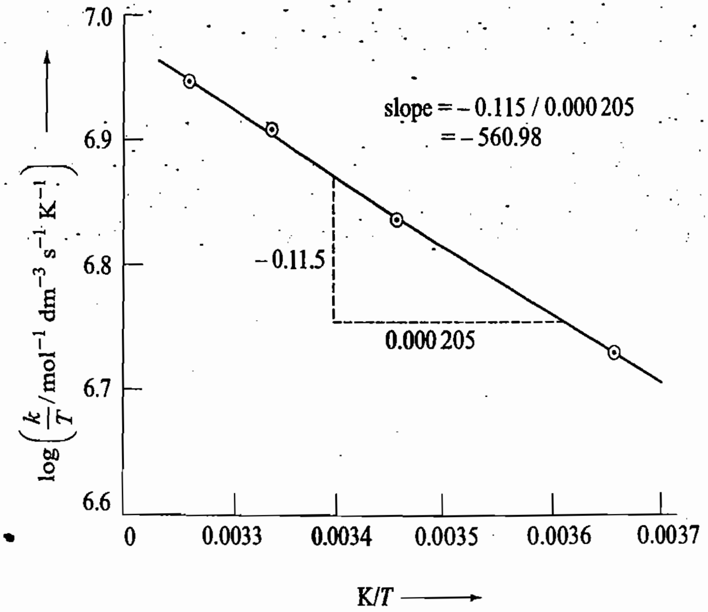


Fig. 2.18.2

Hence from Eq. (3), we get

$$\Delta^{\ddagger}H^{\circ} = -(-\,560.98\ \text{K})(2.303)(8.314\ \text{J K}^{-1}\,\text{mol}^{-1})$$

$$= 10\,741\ \text{J mol}^{-1} = 10.741\ \text{kJ mol}^{-1}$$

Now substituting the data at 307 K in Eq. (2), we get

$$\log(8.827\times10^{6})=\log\left\{\frac{(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})}{(6.022\times10^{23}\mathrm{mol^{-1}})(6.6\times10^{-34}\ \mathrm{J\,s})}\bigg/\mathrm{K^{-1}\,s^{-1}}\right\}$$

$$+\frac{\Delta^{\ddagger}S^{\circ}}{(2.303)(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})}-\frac{10\,741\ \mathrm{J\,mol^{-1}}}{2.303(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(307\ \mathrm{K})}$$

$$6.946=10.320+\frac{\Delta^{\ddagger}S^{\circ}}{19.147\ \mathrm{J\,K^{-1}\,mol^{-1}}}-1.827$$

$$\Delta^{\ddagger}S^{\circ}=(6.946-10.320+1.827)(19.147\ \mathrm{J\,K^{-1}\,mol^{-1}})$$
$$=-29.62\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

Now $\Delta^{\ddagger}G^{\circ}=\Delta^{\ddagger}H^{\circ}-T\Delta^{\ddagger}S^{\circ}$

Substituting the values, we get

$$\Delta^{\ddagger}G^{\circ}=(10\,741\ \mathrm{J\,mol^{-1}})-(307\ \mathrm{K})(-29.62\ \mathrm{J\,K^{-1}\,mol^{-1}})$$
$$=19\,834\ \mathrm{J\,mol^{-1}}=19.834\ \mathrm{kJ\,mol^{-1}}$$

Now $\Delta^{\ddagger}H^{\circ}=\Delta^{\ddagger}U^{\circ}+(\Delta^{\ddagger}\nu_{\mathrm{g}})\,RT=\Delta^{\ddagger}U^{\circ}-RT$

and $\Delta^{\ddagger}U^{\circ}=E_{\mathrm{a}}-RT$

Therefore

$$\Delta^{\ddagger}H^{\circ}=E_{\mathrm{a}}-2RT$$

or $E_{\mathrm{a}}=\Delta^{\ddagger}H^{\circ}+2RT$

Substituting the values, we get

$$E_{\mathrm{a}}=(10\,741\ \mathrm{J\,mol^{-1}})+2\times(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(307\ \mathrm{K})=15\,846\ \mathrm{J\,mol^{-1}}$$
$$=15.846\ \mathrm{kJ\,mol^{-1}}$$

Alternatively, we may plot a graph between log (k/k°) and $1/T$ which will give us slope equal to $E_{\mathrm{a}}/2.303R$. Hence, E_{a} can be determined. Knowing E_{a}, we will calculate A, the pre-exponential factor. From A, we will calculate $\Delta^{\ddagger}S^{\circ}$ as indicated in the last problem. From E_{a}, we can calculate $\Delta^{\ddagger}U^{\circ}$, $\Delta^{\ddagger}H^{\circ}$ and then finally $\Delta^{\ddagger}G^{\circ}$.

Example 2.18.3 A certain reaction can proceed in the absence as well as in the presence of a catalyst. The rate constants for two mechanisms are k_{a} and k_{c}, respectively. If $\Delta^{\ddagger}S_{\mathrm{a}}$ is 41.84 J K^{-1} mol^{-1} greater than $\Delta^{\ddagger}S_{\mathrm{c}}$ and $\Delta^{\ddagger}H_{\mathrm{a}}$ is 20.92 kJ mol^{-1} greater than $\Delta^{\ddagger}H_{\mathrm{c}}$, show which rate constant is larger at 298 K and in what proportion.

Solution The rate constant in terms of $\Delta^{\ddagger}S^{\circ}$ and $\Delta^{\ddagger}H^{\circ}$ is given by

$$k_2=\frac{RT}{c^{\circ}N_{\mathrm{A}}h}\exp(-\Delta^{\ddagger}H^{\circ}/RT)\exp(\Delta^{\ddagger}S^{\circ}/R)$$

Thus, we have

$$\frac{k_{\mathrm{a}}}{k_{\mathrm{c}}}=\frac{\exp(-\Delta^{\ddagger}H_{\mathrm{a}}^{\circ}/RT)}{\exp(-\Delta^{\ddagger}H_{\mathrm{c}}^{\circ}/RT)}\ \frac{\exp(\Delta^{\ddagger}S_{\mathrm{a}}^{\circ}/R)}{\exp(\Delta^{\ddagger}S_{\mathrm{c}}^{\circ}/R)}$$

$$=\exp\{-(\Delta^{\ddagger}H_{\mathrm{a}}^{\circ}-\Delta^{\ddagger}H_{\mathrm{c}}^{\circ})/RT\}\exp\{(\Delta^{\ddagger}S_{\mathrm{a}}^{\circ}-\Delta^{\ddagger}S_{\mathrm{c}}^{\circ})/R\}$$

Substituting the given values, we get

$$\frac{k_a}{k_c} = \exp\{-(20\,920 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})\} \times \exp\{(41.84 \text{ J K}^{-1} \text{ mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})\}$$

$$= \exp(-8.444)\exp(5.033) = 0.033$$

Example 2.18.4 The frequency factors for a unimolecular gas reaction occurring at 473 K is 2.5×10^{13} s^{-1}. Calculate the entropy of activation.

Solution We have

$$A = \frac{RT}{N_A h}\exp(\Delta^{\ddagger}S/R)\exp(1-\Delta^{\ddagger}\nu_g)$$

In this case, $\Delta^{\ddagger}\nu_g = 0$. Thus

$$A = \frac{RT}{N_A h}\exp(\Delta^{\ddagger}S/R)\,e^1$$

or $$\exp(\Delta^{\ddagger}S/R) = A\left(\frac{N_A h}{RT}\right)e^{-1}$$

or $$\Delta^{\ddagger}S = 2.303 \times R \times \log\left(\frac{AN_A h}{RT}\right) - R$$

Substituting the values, we get

$$\Delta^{\ddagger}S = 2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \log\left\{\frac{(2.5\times10^{13}\text{ s}^{-1})(6.022\times10^{23}\text{ mol}^{-1})(6.626\times10^{-34}\text{ J s})}{(8.314\text{ J K}^{-1}\text{ mol}^{-1})(473\text{ K})}\right\} - (8.314\text{ J K}^{-1}\text{ mol}^{-1})$$

$$= 2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})\log(2.537) - (8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= (7.742 \text{ J K}^{-1} \text{ mol}^{-1}) - (8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= -0.572 \text{ J K}^{-1} \text{ mol}^{-1}$$

2.19 EFFECT OF PRESSURE ON REACTION RATE

The effect of pressure on the rate of the reaction

$$A + B \xrightarrow{k_2} \text{products}$$

may conveniently be derived with the help of the activated complex theory. According to Eq. (2.18.9), we have

$$k_2 = \frac{RT}{N_A h}K^{\ddagger} \tag{2.19.1}$$

where $K^{\ddagger}$ is the equilibrium constant of the reaction between the reactants and the activated complex, i.e.

$$A + B \rightleftharpoons AB^{\ddagger}$$

Taking the logarithm of Eq. (2.19.1), we get

$$\ln (k_2/k_2^{\circ}) = \ln \left(\frac{RT}{N_{A}h} \Big/ \text{s}^{-1} \right) + \ln K^{\circ\ddagger}$$

Differentiating it with respect to pressure at constant temperature, we get

$$\left(\frac{\partial \ln (k_2/k^{\circ})}{\partial p} \right)_T = \left(\frac{\partial \ln K^{\circ\ddagger}}{\partial p} \right)_T \tag{2.19.2}$$

From thermodynamics, we have

$$\ln K^{\circ\ddagger} = -\frac{\Delta^{\ddagger}G^{\circ}}{RT} = -\frac{\Delta^{\ddagger}H^{\circ}}{RT} + \frac{\Delta^{\ddagger}S^{\circ}}{R} \tag{2.19.3}$$

Now $\quad \Delta^{\ddagger}H^{\circ} = \Delta^{\ddagger}U^{\circ} + p\Delta^{\ddagger}V$

Therefore

$$\ln K^{\circ\ddagger} = -\frac{\Delta^{\ddagger}U^{\circ}}{RT} - \frac{p\,\Delta^{\ddagger}V}{RT} + \frac{\Delta^{\ddagger}S^{\circ}}{R} \tag{2.19.4}$$

Hence,

$$\left(\frac{\partial \ln K^{\circ\ddagger}}{\partial p} \right)_T = -\frac{\Delta^{\ddagger}V}{RT} \tag{2.19.5}$$

Substituting Eq. (2.19.5) in Eq. (2.19.2), we get

$$\left(\frac{\partial \ln (k_2/k_2^{\circ})}{\partial p} \right)_T = -\frac{\Delta^{\ddagger}V}{RT} \tag{2.19.6}$$

Equation (2.19.6) implies that the rate constant of a chemical reaction increases with increasing pressure, when the volume of the activated complex is less than the total volume of the reactants.

Equation (2.19.6) may be written as

$$\text{d} \ln (k_2/k^{\circ}) = \frac{\Delta^{\ddagger}V}{RT}\,\text{d}p \tag{2.19.7}$$

Integrated form of the above equation is

$$\ln \left(\frac{(k_2)_{p_2}}{(k_1)_{p_1}} \right) = -\frac{\Delta^{\ddagger}V}{RT}\,(p_2 - p_1) \tag{2.19.8}$$

The open integration of Eq. (2.19.7) gives

$$\ln (k_2/k^{\circ}) = -\frac{\Delta^{\ddagger}V}{RT}\,p + \text{constant} \tag{2.19.9}$$

The value of $\Delta^{\ddagger}V$ (i.e. the volume change due to the formation of an activated complex) can be determined from the slope of the plot of log (k_2/k°) versus p.

2.20 EFFECT OF IONIC STRENGTH AND DIELECTRIC CONSTANT ON IONIC REACTIONS

Effect of Ionic Strength (Primary and Secondary Salt Effects)

For an ionic reaction

$$A^{z_A} + B^{z_B} \rightarrow C \tag{2.20.1}$$

we may write it as

$$A^{z_A} + B^{z_B} \rightleftharpoons [AB^{(z_A + z_B)\ddagger}] \rightarrow C \tag{2.20.2}$$

where $AB^{(z_A + z_B)\ddagger}$ is the transition-state complex. For the equilibrium between the reactants and the activated complex, we may write

$$K^{o\ddagger} = \frac{a(AB^{(z_A+z_B)\ddagger})}{a(A^{z_A})\,a(B^{z_B})} \qquad \text{(where } a \text{ stands for activity)}$$

$$K^{\ddagger} = \frac{[AB^{(z_A+z_B)\ddagger}]}{[A^{z_A}][B^{z_B}]}\,\frac{\gamma(AB^{(z_A+z_B)\ddagger})}{\gamma(A^{z_A})\,\gamma(B^{z_B})} \tag{2.20.3}$$

or

$$[AB^{(z_A + z_B)\ddagger}] = K^{\ddagger}[A^{z_A}]\,[B^{z_B}]\,\frac{\gamma(A^{z_A})\,\gamma(B^{z_B})}{\gamma(AB^{(z_A+z_B)\ddagger})} \tag{2.20.4}$$

Now according to the activated complex theory, we have

$$r = [AB^{(z_A + z_B)\ddagger}]\left(\frac{RT}{N_A h}\right) \qquad \text{(Eq. 2.18.2)}$$

$$= \left(K^{\ddagger}\frac{RT}{N_A h}\right)\left(\frac{\gamma(A^{z_A})\,\gamma(B^{z_B})}{\gamma(AB^{(z_A+z_B)\ddagger})}\right)[A^{z_A}]\,[B^{z_B}] \tag{2.20.5}$$

Equating Eq. (2.20.5) with

$$r = k[A^{z_A}]\,[B^{z_B}]$$

we get

$$(k/k^{\circ}) = \left(K^{\ddagger}\frac{RT}{N_A h}\Big/k^{\circ}\right)\left(\frac{\gamma(A^{z_A})\,\gamma(B^{z_B})}{\gamma(AB^{(z_A+z_B)\ddagger})}\right)$$

or

$$\log\,(k/k^{\circ}) = \log\left(K^{\ddagger}\frac{RT}{N_A h}\Big/k^{\circ}\right) + \log\,\{\gamma(A^{z_A})\} + \log\,\{\gamma(B^{z_B})\} - \log\,\{\gamma(AB^{(z_A + z_B)\ddagger})\} \tag{2.20.6}$$

The activity coefficient of the ion depends upon the ionic strength μ of the solution. The latter is defined as

$$\mu = \frac{1}{2}\,\sum\nolimits_i c_i z_i^2 \tag{2.20.7}$$

where c_i is the molarity and z_i is the charge number of the ith ionic species. The summation is to be carried over all the ionic species present in the solution. The relation connecting γ with μ as given by Debye-Hückel law is

$$\log \gamma_i = -A\,z_i^2\,\sqrt{\mu} \tag{2.20.8}$$

where A is a constant.

Making use of Eq. (2.20.8) in Eq. (2.20.6), we get

$$\log (k/k^\circ) = \log \left(K^\ddagger \frac{RT}{N_A h} \Big/ k^\circ \right) - A\, z_A^2 \sqrt{\mu} - A\, z_B^2 \sqrt{\mu} + A(z_A + z_B)^2 \sqrt{\mu}$$

or $$\log (k/k^\circ) = \log \left(K^\ddagger \frac{RT}{N_A h} \Big/ k^\circ \right) + 2A z_A z_B \sqrt{\mu}$$

For aqueous solution at 25 °C, $A = 0.5\ \text{mol}^{-1/2}\ \text{dm}^{3/2}$, thus we have

$$\log (k/k^\circ) = \log (k_0/k^\circ) + z_A z_B \sqrt{\mu / c^\circ} \qquad (2.20.9)$$

where $$k_0 = K^\ddagger \left(\frac{RT}{N_A h} \right)$$

Equation (2.20.9) is the required relation which depicts the effect of ionic strength on the rate constant of ionic reactions. According to this relation, if a plot is made between $\log (k/k^\circ)$ and $\sqrt{\mu / c^\circ}$, in dilute solution one would get a straight line with a slope equal to $z_A z_B$ (Fig. 2.20.1).

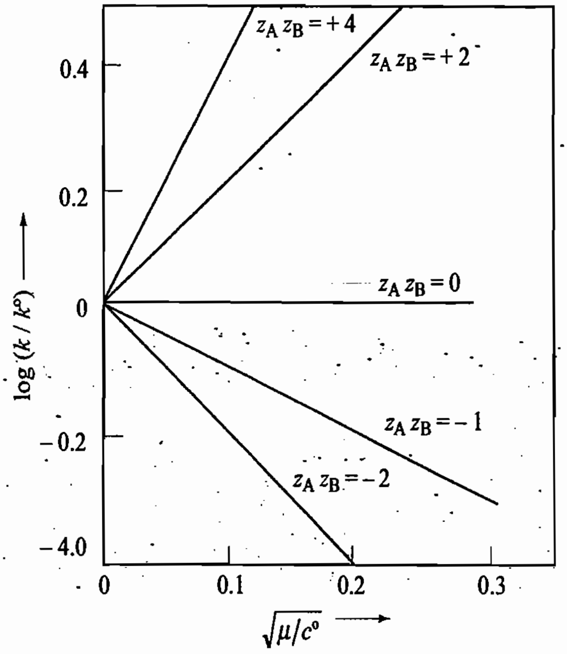


Fig. 2.20.1 Primary salt effect

Examples of the plots given in Fig. 2.20.1 are described below.

System	*Reactants*	*Slope* $z_A z_B$
I	$Co(NH_3)_5Br^{2+} + Hg^{2+}$	4
II	$S_2O_8^{2-} + I^-$	2
III	$NO_2NCO_2C_2H_5^- + I^-$	1
IV	$C_{12}H_{22}O_{11} + OH^-$	0
V	$H_2O_2 + H^+ + Br^-$	−1
VI	$Co(NH_3)_5Br^{2+} + OH^-$	−2

Primary Salt Effect

The change in k with ionic strength is known as the *primary salt effect*. Thus, in principle, we can have

Product of $z_A z_B$	k
+	Increases with ionic strength
–	Decreases with ionic strength
0	Independent of ionic strength

The primary salt effect is due to the change in the value of activity coefficients of reactants and intermediate complex due to the ionic strength of the solution.

Secondary Salt Effect

There is another type of salt action, known as the *secondary salt effect* which influences the rate of reaction by altering the effective concentration of the catalyzing species. Take, for example, the hydrolysis of cane sugar catalyzed by a weak acid. The experimental rate constant is given by

$$k_{\text{exp}} = k[\text{H}_3\text{O}^+] \tag{2.20.10}$$

The catalyst comes from the dissociation of weak acid HA by the equilibrium reaction

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$$

characterized by the equilibrium constant

$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \frac{\gamma(\text{H}_3\text{O}^+)\gamma(\text{A}^-)}{\gamma(\text{HA})}$$

Therefore

$$[\text{H}_3\text{O}^+] = K \frac{[\text{HA}]}{[\text{A}^-]} \frac{\gamma(\text{HA})}{\gamma(\text{H}_3\text{O}^+)\gamma(\text{A}^-)}$$

If the reaction is carried out at fixed ratio of [HA]/[A$^-$], by making use of a buffer solution, then

$$[\text{H}_3\text{O}^+] = (\text{constant}) \frac{\gamma(\text{HA})}{\gamma(\text{H}_3\text{O}^+)\gamma(\text{A}^-)} \tag{2.20.11}$$

Substituting Eq. (2.20.11) in Eq. (2.20.10), we get

$$k_{\text{exp}} = k' \frac{\gamma(\text{HA})}{\gamma(\text{H}_3\text{O}^+)\gamma(\text{A}^-)}$$

so that $\log (k_{\text{exp}}/k^\circ) = \log (k'/k^\circ) + \log \gamma_{\text{HA}} - \log \gamma_{\text{H}_3\text{O}^+} - \log \gamma_{\text{A}^-}$

Using Debye–Hückel limiting law (Eq. 2.20.8), we get

$$\log (k_{\text{exp}}/k^\circ) = \text{constant} + \sqrt{\mu/c^\circ} \tag{2.20.12}$$

that is, we have positive salt effect and thus k_{exp} increases with the increase in ionic strength of the solution.

If the catalyzing acid is NH_4^+, giving H_3O^+ by the reaction

$$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3$$

then, we will have

$$\log(k_{\mathrm{exp}}/k^{\circ}) = \text{constant} + \log\gamma_{\mathrm{NH_4^+}} - \log\gamma_{\mathrm{H_3O^+}} - \log\gamma_{\mathrm{NH_3}}$$

On using Debye–Hückel limiting law, we will have

$$\log(k_{\mathrm{exp}}/k^{\circ}) = \text{constant}$$

that is, we will have zero salt effect.

If H_3O^+ is produced from $Fe(H_2O)_6^{3+}$ according to the reaction

$$H_2O + [Fe(H_2O)_6]^{3+} \rightleftharpoons H_3O^+ + [Fe(H_2O)_5(OH)]^{2+}$$

Then, we will have

$$\log(k_{\mathrm{exp}}/k^{\circ}) = \text{constant} - 2\sqrt{\mu/c^{\circ}} \tag{2.20.13}$$

that is, we will have negative salt effect.

Effect of Dielectric Constant

According to the theory of absolute reaction rate, the rate constant is given by

$$k = \frac{RT}{c^{\circ}N_{\mathrm{A}}h}\exp(-\Delta^{\ddagger}G^{\circ}/RT) \tag{2.20.14}$$

where $\Delta^{\ddagger}G^{\circ}$ is the change in standard free energy in going from reactants to the activated complex state. In case of ionic reactions, $\Delta^{\ddagger}G^{\circ}$ includes two contributions due to non-electrostatic and electrostatic interactions, i.e.

$$\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}G^{\circ}_{\mathrm{ne}} + \Delta^{\ddagger}G^{\circ}_{\mathrm{e}} \tag{2.20.15}$$

If we assume that the two ions of charges $z_{\mathrm{A}}e$ and $z_{\mathrm{B}}e$, respectively, are brought together from the distance of infinity to the distance d to form the activated complex in a medium of dielectric constant D, then the work involved in this process is

$$w_{\mathrm{e}} = \int_{\infty}^{d} F\,\mathrm{d}x = \int_{\infty}^{d} \frac{(z_{\mathrm{A}}e)(z_{\mathrm{B}}e)}{(4\pi\varepsilon_0)D}\frac{1}{x^2}\,\mathrm{d}x$$

$$= -\frac{(z_{\mathrm{A}}e)(z_{\mathrm{B}}e)}{(4\pi\varepsilon_0)D}\frac{1}{d}$$

For one mole of each ion, we get

$$w_{\mathrm{e}} = -\frac{(z_{\mathrm{A}}e)(z_{\mathrm{B}}e)}{(4\pi\varepsilon_0)D}\frac{N_{\mathrm{A}}}{d} \tag{2.20.16}$$

Since $\Delta G = w$, Eq. (2.20.15) on making use of Eq. (2.20.16) becomes

$$\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}G^{\circ}_{\mathrm{ne}} - \left(\frac{z_{\mathrm{A}}z_{\mathrm{B}}e^2N_{\mathrm{A}}}{(4\pi\varepsilon_0)Dd}\right)$$

Substitution of Eq. (2.20.16) in Eq. (2.20.14) gives

$$k = \frac{RT}{c^{\circ}N_{\mathrm{A}}h}\exp\left(-\frac{\Delta^{\ddagger}G^{\circ}_{\mathrm{ne}}}{RT}\right)\exp\left(-\frac{z_{\mathrm{A}}z_{\mathrm{B}}e^2N_{\mathrm{A}}}{(4\pi\varepsilon_0)D}\frac{1}{dRT}\right)$$

or
$$\ln (k/k^\circ) = \ln (k_0/k^\circ) - \frac{z_A z_B e^2 N_A}{dRT} \frac{1}{(4\pi \varepsilon_0) D} \tag{2.20.17}$$

where
$$k_0 = \frac{RT}{c^\circ N_A h} \exp\left(-\frac{\Delta^{\ddagger} G^\circ_{\text{ne}}}{RT}\right) \tag{2.20.18}$$

According to Eq. (2.20.17), ln (k/k°) varies linearly with $1/D$ with a slope of $-z_A z_B e^2 N_A/(4\pi\,\varepsilon_0)\,dRT$.

If the activated complex is considered to be a single entity with a charge of $(z_A + z_B)e$, then Eq. (2.20.17) takes the form of

$$\ln (k/k^\circ) = \ln (k_0/k^\circ) - \frac{e^2 N_A}{2(4\pi \varepsilon_0) DRT} \left[\frac{(z_A + z_B)^2}{r_{\pm}} - \frac{z_A^2}{r_A} - \frac{z_B^2}{r_B}\right] \tag{2.20.19}$$

where $r_{\pm}$ is the radius of the activated complex.

2.21 KINETICS OF CATALYTIC REACTIONS

Characteristic Effects of a Catalyst

Sometimes, the rate of a chemical reaction is very much enhanced in the presence of a substance, called the catalyst. Though catalyst is involved in the reaction, it does not appear in the overall reaction. Thus, its concentration remains constant throughout the chemical reaction. In fact, a catalyst goes through a cycle in which it is used up and regenerated so that it is used over and over again. The mechanism of catalytic reactions depends on a reaction to reaction. Broadly, two types of catalyst are known, namely, *homogeneous catalyst* and *heterogeneous catalyst.* A homogeneous catalyst exists in the same phase as the reaction whose rate it increases. Examples include acid hydrolysis of an ester, saponification of an ester and enzyme reactions. A heterogeneous catalyst exists in a different phase from the reaction it catalyzes. Generally, solid surfaces act as heterogeneous catalyst. Examples include decomposition of NH_3 on tungsten, decomposition of N_2O on gold and decomposition of ethyl alcohol vapour on the surface of Cu. The rate of a catalytic reaction is usually proportional to the concentration of the catalyst or to the area of the surface.

The function of a catalyst can be best understood in terms of transition-state theory. In general, it operates by providing another path for the reaction that has a lower free energy of activation (Fig. 2.21.1). The lowering of free energy may be due to the decrease in the energy of activation or higher frequency factor or both. Thus from the transition state theory, the rate of a reaction changes from

$$k_f = \frac{RT}{c^\circ N_A h} \exp(-\Delta^{\ddagger} G^\circ_f / RT) \tag{2.21.1}$$

to
$$k'_f = \frac{RT}{c^\circ N_A h} \exp(-\Delta^{\ddagger} G^\circ_f{}' / RT) \tag{2.21.2}$$

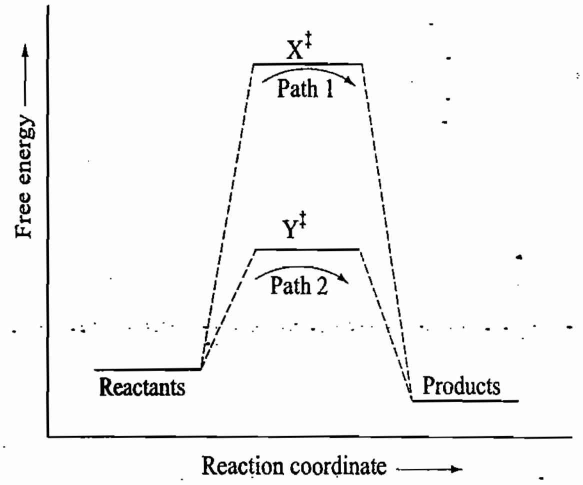


Fig. 2.21.1 Lowering of free energy of activation in the presence of a catalyst. Path 1 is without catalyst; Path 2 with catalyst

Since $\Delta^{\ddagger}G_f^{\circ\prime}$ is less than $\Delta^{\ddagger}G_f^{\circ}$, it is obvious that k_f' is greater than k_f, i.e. the rate of forward reaction is increased. From Fig. 2.21.1, it is obvious that the free-energy of activation is lowered for both the forward and backward reactions without changing the overall free energy change of the reaction. Thus, a catalyst not only changes the rate of forward reaction but also that of the backward reaction. Since ΔG° is not changed, the equilibrium constant remains unchanged in the presence of a catalyst. Thus, the use of a catalyst can help in attaining the equilibrium position rapidly but cannot help in changing the relative proportion of products and reactants at equilibrium, i.e. the relative amounts of products that can be obtained at equilibrium cannot be altered. Mathematically, we may derive the above conclusion as follows.

The rates of forward and backward reactions in the presence of a catalyst are

$$k_f = \frac{RT}{c^{\circ}N_A h}\exp(-\Delta^{\ddagger}G_f^{\circ\prime}/RT) \tag{2.21.3}$$

$$k_b = \frac{RT}{c^{\circ}N_A h}\exp(-\Delta^{\ddagger}G_b^{\circ\prime}/RT) \tag{2.21.4}$$

$$\text{Hence,}\quad K_{eq} = \frac{k_f}{k_b} = \frac{(RT/c^{\circ}N_A h)\exp(-\Delta^{\ddagger}G_f^{\circ\prime}/RT)}{(RT/c^{\circ}N_A h)\exp(-\Delta^{\ddagger}G_b^{\circ\prime}/RT)}$$

$$= \exp(-(\Delta^{\ddagger}G_f^{\circ\prime} - \Delta^{\ddagger}G_b^{\circ\prime})/RT) = \exp(-\Delta G^{\circ}/RT) \tag{2.21.5}$$

Since ΔG°, which is $\Delta^{\ddagger}G_f^{\circ\prime} - \Delta^{\ddagger}G_b^{\circ\prime}$ has the same value with or without a catalyst, K_{eq} remains the same in the presence or absence of a catalyst.

The mechanism of a catalytic reaction depends on the type of the catalyst, i.e. whether the catalyst is homogeneous or heterogeneous. In the present section, we discuss the mechanism of a few important examples of homogeneous and heterogeneous catalysis.

HOMOGENEOUS CATALYSIS

The first step of reaction mechanism of homogeneous catalysis generally involves an equilibrium reaction between one of the reactants (known as the substrate of

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the catalytic reaction) and the catalyst. We discuss below the mechanisms of the two important examples of homogeneous catalysis, namely, acid and base catalysis, and the enzyme catalysis.

Acid Catalyzed Reactions

The mechanism of acid catalyzed reactions involves an equilibrium reaction in which there occurs a transfer of proton from an acid to a substrate S. The protonated substrate then reacts with water to form the product P.

$$\mathrm{S + HA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{SH^+ + A^-}$$

$$\mathrm{SH^+ + H_2O} \xrightarrow{k_2} \mathrm{P + H_3O^+}$$

The rate of appearance of product is given by

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_2\,[\mathrm{SH^+}] \tag{2.21.6}$$

(**Note** that the concentration of H_2O is not included in the above rate expression as its concentration does not change appreciably.)

The concentration of SH^+ can be obtained by applying the steady-state approximation to SH^+. Thus, we have

$$\frac{\mathrm{d[SH^+]}}{\mathrm{d}t} = 0 = k_1[\mathrm{S}][\mathrm{HA}] - k_{-1}[\mathrm{SH^+}][\mathrm{A^-}] - k_2[\mathrm{SH^+}]$$

Hence, $$[\mathrm{SH^+}] = \frac{k_1[\mathrm{S}][\mathrm{HA}]}{k_{-1}[\mathrm{A^-}] + k_2} \tag{2.21.7}$$

Substituting Eq. (2.21.7) in Eq. (2.21.6), we get

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = \frac{k_2 k_1[\mathrm{S}][\mathrm{HA}]}{k_{-1}[\mathrm{A^-}] + k_2} \tag{2.21.8}$$

Two Specific Cases

Two cases may be distinguished.

(i) $k_2 \gg k_{-1}\,[\mathrm{A^-}]$. In this case, Eq. (2.21.8) may be written as

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_1[\mathrm{S}][\mathrm{HA}] \tag{2.21.9}$$

that is, the reaction rate is first-order with respect to each of the substrate and acid molecules. The reaction for which the rate depends on the concentration of HA is said to be subject to *general acid catalysis*.

(ii) $k_2 \ll k_{-1}\,[\mathrm{A^-}]$. In this case, Eq. (2.21.8) may be written as

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_2\,\frac{k_1}{k_{-1}}\,[\mathrm{S}]\,\frac{[\mathrm{HA}]}{[\mathrm{A^-}]} \tag{2.21.10}$$

Invoking the equilibrium constant expression

$$K_\mathrm{a} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

for [HA] in Eq. (2.21.10), we get

$$\frac{d[P]}{dt} = k_2 \frac{k_1}{k_{-1}} \frac{1}{K_a} [S][H^+] \tag{2.21.11}$$

Thus, the reaction rate depends on the hydrogen-ion concentration although the proton is initially transferred from HA. In this case, the reaction is said to be subject to *specific hydrogen-ion catalysis.*

Since H^+ acts as a catalyst, its concentration remains constant and thus Eq. (2.21.11) may be written as

$$\frac{d[P]}{dt} = k'[S] \tag{2.21.12}$$

where. $k' = k_2 \frac{k_1}{k_{-1}} \frac{1}{K_a} [H^+] = k_{H^+} [H^+]$ (2.21.13)

The constant k_{H^+} is known as the *catalytic coefficient of hydrogen ion.* Writing Eq. (2.21.13) in the logarithm form, we have

$$\log(k'/s^{-1}) = \log (k_{H^+}/mol^{-1}\,dm^3\,s^{-1}) - pH$$

Thus, if a plot is made between log (k'/s^{-1}) and pH, it would yield a straight line of slope – 1.

Base Catalyzed Reactions

The base catalyzed reactions involve the transfer of a proton from the substrate molecule to the base. If the rate of the reaction depends on the concentration of the base, the reaction is said to be subject to *general base catalysis.* For a reaction catalyzed by OH^-, the rate constant is given by

$$k = k_{OH^-} [OH^-]$$

that is, it varies linearly with the hydroxyl-ion concentration.

Generalization of Rate Constant

In general, if a reaction which follows the rate law

$$\frac{d[S]}{dt} = k[S]$$

and is catalyzed by all of the catalytic species H^+, OH^-, HA and A^-, then the first-order rate constant k in a buffer solution containing HA and A^- may be written as

$$k = k_0 + k_{H^+} [H^+] + k_{OH^-} [OH^-] + k_{HA} [HA] + k_{A^-}[A^-] \tag{2.21.14}$$

where the constants k_{H^+}, k_{OH^-}, k_{HA} and k_{A^-} are the various catalytic coefficients and k_0 is the rate constant at low concentrations of all of the catalytic species.

It may happen that the constant k_{H^+} is much larger than other constants and thus Eq. (2.21.14) reduces to

$$k = k_0 + k_{H^+} [H^+]$$

and the reaction to which this belongs to is an example of specific hydrogen-ion catalyst reaction.

Enzyme Catalysis

One of the most important examples of homogeneous catalysis is the catalysis of reactions in biological systems by enzymes. Enzymes are complex protein molecules and are usually very specific, catalyzing only one type of reaction.

Michaelis-Menten Mechanism

The mechanism of enzyme-catalyzed reactions was initially proposed by L. Michaelis and M.L. Menten and is known as *Michaelis-Menten mechanism*. The mechanism involves the following steps:

$$\mathrm{E + S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES}$$

$$\mathrm{ES} \xrightarrow{k_2} \mathrm{P + E}$$

where E is the enzyme, S the substrate, ES an enzyme complex, and P the product.

Derivation of Rate Expression

The rate of appearance of product is given by

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_2[\mathrm{ES}] \tag{2.21.15}$$

Applying the steady-state approximation to ES, we get

$$\frac{\mathrm{d[ES]}}{\mathrm{d}t} = 0 = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}]$$

$$[\mathrm{ES}] = \frac{k_1[\mathrm{E}][\mathrm{S}]}{k_{-1} + k_2} \tag{2.21.16}$$

The proposed mechanism is usually tested with the experimentally determined initial rate of reaction under the condition that $[\mathrm{S}]_0 \gg [\mathrm{E}]_0$. Thus, in Eq. (2.21.16), we may replace [E] and [S] be~~the re~~lations

$$[\mathrm{S}] \simeq [\mathrm{S}]_0$$

$$[\mathrm{E}] = [\mathrm{E}]_0 - [\mathrm{ES}] \tag{2.21.17}$$

Substituting the above relations in Eq. (2.21.16), we get

$$[\mathrm{ES}] = \frac{k_1([\mathrm{E}]_0 - [\mathrm{ES}])[\mathrm{S}]_0}{k_{-1} + k_2}$$

which on rearranging gives

$$[\mathrm{ES}] = \frac{k_1[\mathrm{E}]_0[\mathrm{S}]_0}{k_1[\mathrm{S}]_0 + k_{-1} + k_2} = \frac{[\mathrm{E}]_0[\mathrm{S}]_0}{[\mathrm{S}]_0 + \{(k_{-1} + k_2)/k_1\}}$$

$$= \frac{[\mathrm{E}]_0[\mathrm{S}]_0}{[\mathrm{S}]_0 + K_\mathrm{M}} \tag{2.21.18}$$

where $$K_\mathrm{M} = \frac{k_{-1} + k_2}{k_1} \tag{2.21.19}$$

and is known as the *Michaelis-Menten constant*. The constants K_M and k_2 are characteristic constants for a particular enzyme-catalyzed reaction. When $k_{-1} \gg k_2$, K_M is equal to k_{-1}/k_1 which represents the dissociation constant of the enzyme-substrate complex.

Substituting Eq. (2.21.18) in the rate expression (Eq. 2.21.15), we have

$$\left(\frac{\mathrm{d[P]}}{\mathrm{d}t}\right)_0 = r_0 = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]_0}{[\mathrm{S}]_0 + K_\mathrm{M}} \tag{2.21.20}$$

It is of interest to see how the initial rate as given by Eq. (2.21.20) behaves under the two extreme conditions of high and low concentrations of S.

Initial Rate at High Concentration of S

When the concentration of S is very high, the constant K_M may be ignored in comparison to $[\mathrm{S}]_0$. With this, Eq. (2.21.20) modifies to

$$\left(\frac{\mathrm{d[P]}}{\mathrm{d}t}\right)_0 = k_2\,[\mathrm{E}]_0 \tag{2.21.21}$$

that is, the initial rate is independent of the concentration of S. In order words, the reaction is zero-order with respect to S. Equation (2.21.21) gives the maximum possible rate for the enzyme reaction at a given initial concentration of the enzyme. Hence, we may write Eq. (2.21.21) as

$$r_\mathrm{max} = k_2[\mathrm{E}]_0 \tag{2.21.22}$$

Initial Rate at Low Concentration of S

At low substrate concentration, Eq. (2.21.20) reduces to

$$\left(\frac{\mathrm{d[P]}}{\mathrm{d}t}\right)_0 = \frac{k_2}{K_\mathrm{M}}\,[\mathrm{E}]_0\,[\mathrm{S}]_0 \tag{2.21.23}$$

that is, the reaction is first-order with respect to the enzyme and also first-order with respect to the substrate. Using Eq. (2.21.22), Eq. (2.21.23) may be written as

$$r_0 = \frac{r_\mathrm{max}}{K_\mathrm{M}}\,[\mathrm{S}]_0 \tag{2.21.24}$$

Figure 2.21.2 represents the typical variation of initial rate with the initial substrate concentration. In the beginning, the reaction is first-order with respect to S and its slope as given by Eq. (2.21.24) is $r_\mathrm{max}/K_\mathrm{M}$. At very high concentration of S, initial rate is zero-order with respect to S and its slope as given by Eq. (2.21.22) is zero. Thus from data at low and high substrate concentrations, both r_max and $r_\mathrm{max}/K_\mathrm{M}$ can be determined. Knowing r_max, k_2 can also be determined from Eq. (2.21.22).

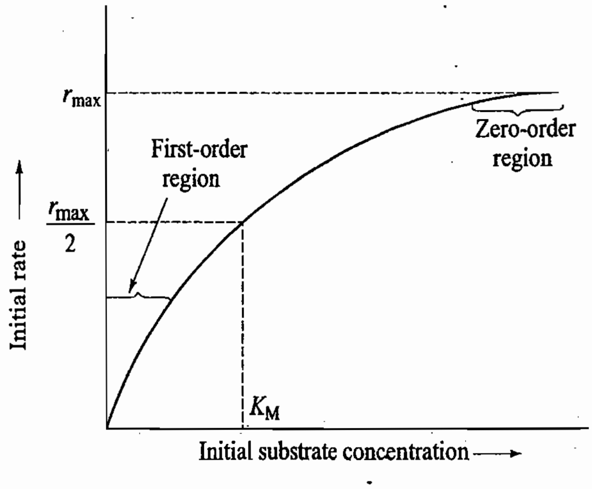

Fig. 2.21.2 A typical variation of initial rate versus initial substrate concentration

Determination of r_{max} by Lineweaver and Burk Method

For many reactions, it is not possible to obtain data close enough to the plateau region to determine r_{max}. However, the characteristic constants r_{max} and K_M can be obtained following the procedure given by Lineweaver and Burk where Eq. (2.21.20) is rearranged by taking the inverse of both sides which gives

$$\frac{1}{r_0} = \frac{1}{k_2[E]_0} + \frac{K_M}{k_2[E]_0[S]_0}$$

$$\text{or} \quad \frac{1}{r_0} = \frac{1}{r_{max}} + \frac{K_M}{r_{max}[S]_0} \tag{2.21.25}$$

Thus, a plot of $1/r_0$ versus $1/[S]_0$ will be a straight line with slope K_M/r_{max} and with an intercept on the $1/r_0$ axis of $1/r_{max}$ (Fig. 2.21.3). The extrapolated intercept on the $1/[S]_0$ axis is equal to $-1/K_M$. Thus, from the two intercepts or from the slope and the intercept on either of two axes, the constants r_{max} and K_M can be determined.

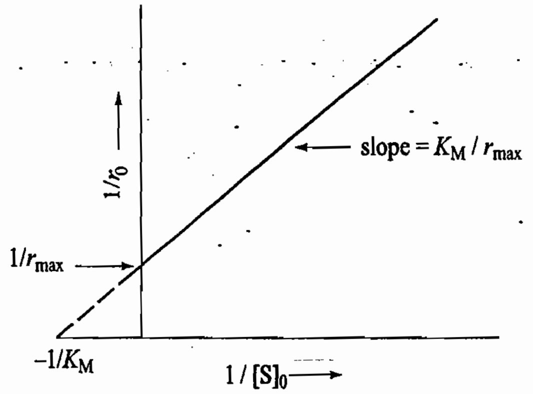

Fig. 2.21.3 A typical Lineweaver-Burk plot

Determination of r_{max} by Eadie Method

The above method involves a considerable extrapolation to the intercept. Since a small absolute uncertainty in $1/r_{max}$ may produce a large relative uncertainty in the value of r_{max}, an alternate graphical method as suggested by G.S. Eadie may be followed. In this method, Eq. (2.21.25) is written as

$$\frac{r_0}{[S]_0} = \frac{r_{max}}{K_M} - \frac{1}{K_M} r_0 \tag{2.21.26}$$

Thus, a plot of $r_0/[S]_0$ against r_0 gives a straight line with an intercept on $r_0/[S]_0$ axis equal to r_{max}/K_M and that on r_0 axis equal to r_{max} (Fig. 2.21.4).

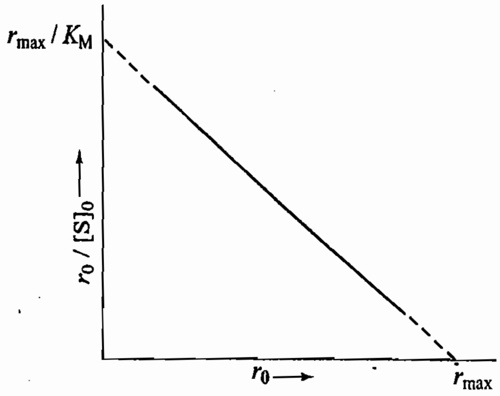

Fig. 2.21.4 A typical Eadie plot

Equation (2.21.25) may be rewritten as

$$K_M = \left(\frac{r_{max} - r_0}{r_0}\right)[S]_0 \qquad (2.21.27)$$

From Eq. (2.21.27), it follows that

$$K_M = [S]_0$$

when $r_0 = r_{max}/2$.

Potential Energy Diagram

The potential energy diagram of enzyme catalyzed reaction will contain two potential energy barriers, one for the equilibrium reaction and the second for the dissociation of the enzyme-substrate complex. Since the first step is usually fast, the corresponding energy of activation has a small value (Fig. 2.21.5). The energy of activation for the dissociation step has a large value.

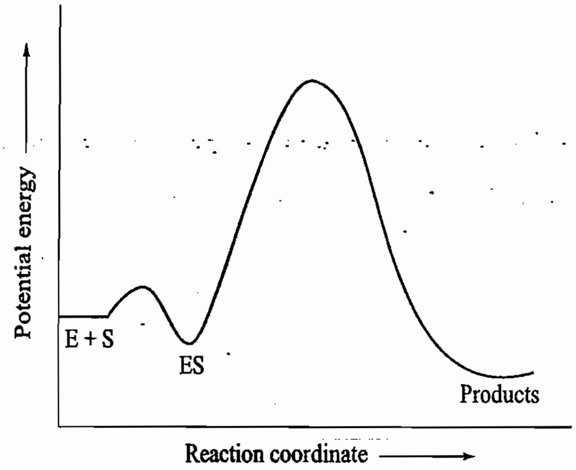

Fig. 2.21.5 The potential energy diagram of the Michaelis-Menten mechanism

Problem 2.21.1 Michaelis and Menten originally derived the rate equation (2.21.20) without the use of steady-state approximation and making the assumption, that $k_2 \ll k_{-1}$. For the latter assumption, the equilibrium

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

may be described by the constant

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[ES]}{[E][S]}$$

Using the above equation, derive Eq. (2.21.20) and show that $K_M = 1/K_{eq}$.

Solution We have the relation

$$[E]_0 = [E] + [ES]$$

Replacing [E] in terms of [ES], we get

$$[E]_0 = \frac{[ES]}{K_{eq}[S]} + [ES]$$

Rearranging this, we get

$$[ES] = \frac{[E]_0}{1 + 1/K_{eq}[S]} = \frac{[S][E]_0}{[S] + 1/K_{eq}}$$

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Substituting the above relation in the rate expression

$$r = k_2\,[\mathrm{ES}]$$

we get $$r = \frac{k_2[\mathrm{S}][\mathrm{E}]_0}{[\mathrm{S}] + 1/K_{\mathrm{eq}}}$$

For the initial rate, we may write

$$[\mathrm{S}] = [\mathrm{S}]_0$$

Thus, we have

$$r_0 = \frac{k_2[\mathrm{S}]_0[\mathrm{E}]_0}{[\mathrm{S}]_0 + 1/K_{\mathrm{eq}}}$$

Comparing the above relation with Eq. (2.21.20), we get

$$K_{\mathrm{M}} = \frac{1}{K_{\mathrm{eq}}}$$

The above relation also follows directly since

$$K_{\mathrm{M}} = (k_{-1} + k_2)/k_1 \text{ and } k_{-1} \gg k_2,$$

therefore $$K_{\mathrm{M}} = \frac{k_{-1} + k_2}{k_1} \simeq \frac{k_{-1}}{k_1} = \frac{1}{K_{\mathrm{eq}}}$$

Problem 2.21.2

The hydrolysis of *p*-nitrophenylacetate to *p*-nitrophenol is catalyzed by α-chymotrypsin enzyme. The proposed mechanism is

$$\mathrm{E} + \mathrm{S} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{ES}' \xrightarrow{k_1} \mathrm{ES} + \mathrm{P}_1 \xrightarrow{k_2} \mathrm{E} + \mathrm{P}_2$$

where ES′, P_1 and P_2 are acetyl enzyme, nitrophenol and acetate ion, respectively. If k_1 is much smaller than k_2, draw a qualitative plot of potential energy versus reaction coordinate for the above reaction.

Solution

Since the equilibrium reaction is fast, the energy of activation for this step will have a small value in comparison to other steps. The energy of activation for the second step will be much larger than the third step since $k_1 \ll k_2$. Hence, the required potential energy diagram will have an appearance as shown in Fig. 2.21.6.

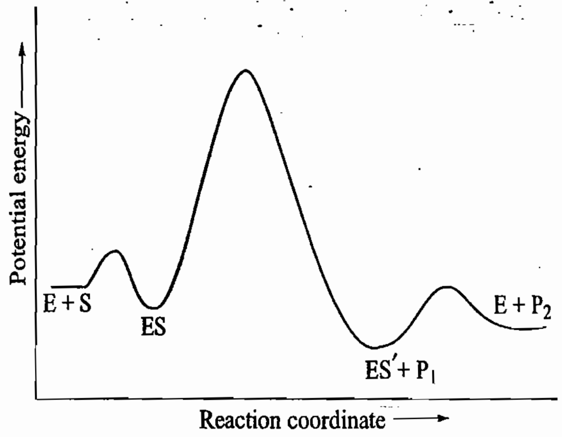

Fig. 2.21.6 The required potential energy diagram

Example 2.21.1

The following data are obtained in an enzyme catalyzed reaction

$[\mathrm{S}] \times 10^4/\mathrm{mol\ dm^{-3}}$	2.5	5.0	10.0	15.0
$r_0 \times 10^6/\mathrm{mol\ dm^{-3}\ min^{-1}}$	2.2	3.8	5.9	7.1

Assuming Michaelis-Menten kinetics, calculate r_{max}, K_M and k_1 using the Lineweaver-Burk plot and Eadie plot. Given: $[E]_0 = 4.0 \times 10^{-6}$ mol dm^{-3}.

Solution For the given data, we have

$[S]_0 \times 10^4$/mol dm^{-3}	2.5	5.0	10.0	15.0
$\frac{1}{[S]_0} \times 10^{-4}$/mol^{-1} dm^3	0.4000	0.2000	0.1000	0.066 7
$r_0 \times 10^6$/mol dm^{-3} min^{-1}	2.2	3.8	5.9	7.1
$\frac{1}{r_0} \times 10^{-6}$/mol^{-1} dm^3 min	0.454 5	0.263 2	0.169 5	0.140 8
$\frac{r_0}{[S]_0} \times 10^2$/min^{-1}	0.88	0.76	0.59	0.473

Lineweaver-Burk Plot A graph between $1/r_0$ and $1/[S]_0$ is drawn (Fig. 2.21.7) and its slope and intercept are determined.

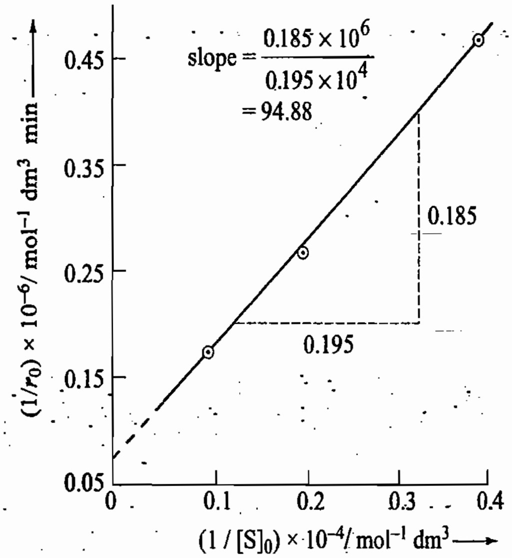

Fig. 2.21.7

Thus, for Eq. (2.21.25) we have

$$\text{Intercept} = \frac{1}{r_{max}} = 0.08 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ min}$$

$$\text{Slope} = \frac{K_M}{r_{max}} = 94.88 \text{ min}$$

Hence, $r_{max} = \frac{1}{\text{Intercept}} = \frac{1}{0.08 \times 10^6 (\text{mol dm}^{-3})^{-1} \text{min}}$

$$= 1.25 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$K_M = \text{Slope} \times r_{max} = (94.88 \text{ min})(1.25 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1})$$

$$= 1.19 \times 10^{-3} \text{ mol dm}^{-3}$$

Now $r_{max} = k_1 [E]_0$

Hence, $k_1 = \frac{r_{max}}{[E]_0} \quad \frac{1.25 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}}{4.0 \times 10^{-6} \text{ mol dm}^{-3}} = 3.125 \text{ min}^{-1}$

Eadie plot A graph between $r_0/[S]_0$ and r_0 is plotted (Fig. 2.21.8) and its intercepts on the two axes are determined.

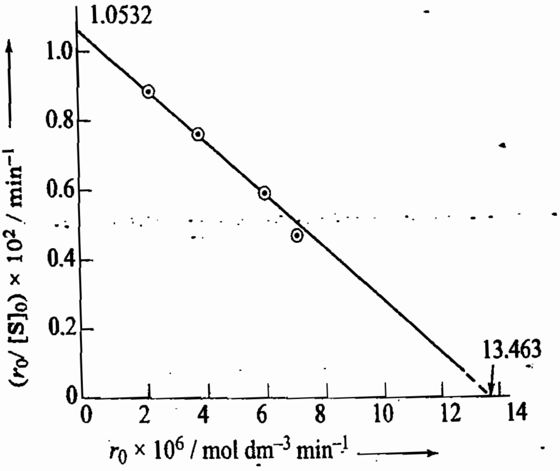

Fig. 2.21.8

Thus, for Eq. (2.21.26) we have

$$\text{Intercept on } r_0/[S]_0 \text{ axis} = \frac{r_{\text{max}}}{K_M} = 1.053\,2 \times 10^{-2}\ \text{min}^{-1}$$

$$\text{Intercept on } r_0 \text{ axis} = r_{\text{max}} = 13.463 \times 10^{-6}\ \text{mol dm}^{-3}\ \text{min}^{-1}$$

$$= 1.346 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{min}^{-1}$$

$$K_M = \frac{r_{\text{max}}}{1.0532 \times 10^{-2}\ \text{min}^{-1}} = \frac{1.346 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{min}^{-1}}{1.0532 \times 10^{-2}\ \text{min}^{-1}}$$

$$= 1.278 \times 10^{-3}\ \text{mol dm}^{-3}$$

$$k_1 = \frac{r_{\text{max}}}{[E]_0} = \frac{1.346 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{min}^{-1}}{4.0 \times 10^{-6}\ \text{mol dm}^{-3}} = 3.365\ \text{min}^{-1}$$

ENZYME INHIBITIONS

Inhibitors are compounds that decrease the rate of a catalyzed reaction. The equations that describe the most common kinds of reversible enzyme inhibition will be derived in this section.

Fully Competitive Inhibition

The conditions of fully competitive inhibiton are: (a) E will bind with both S and I, separately and (b) only ES will break down to the products. Mathematically, we may write it as

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

$$E + I \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} EI$$

Applying the steady-state approximation to ES, we get

$$\frac{d[ES]}{dt} = 0 = k_1\,[E][S] - k_{-1}[ES] - k_2[ES]$$

or $$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \qquad (2.21.28)$$

If $[\mathrm{S}]_0 \gg [\mathrm{E}]_0$, we will have

$$[\mathrm{S}] \simeq [\mathrm{S}]_0 \tag{2.21.29}$$

$$[\mathrm{E}] = [\mathrm{E}]_0 - [\mathrm{ES}] - [\mathrm{EI}] \tag{2.21.30}$$

Now $\dfrac{1}{K_3} = K_\mathrm{I} = \dfrac{[\mathrm{E}][\mathrm{I}]}{[\mathrm{EI}]}$

Therefore

$$[\mathrm{EI}] = \frac{[\mathrm{E}][\mathrm{I}]}{K_\mathrm{I}}$$

Substituting this in Eq. (2.21.30), we get

$$[\mathrm{E}] = [\mathrm{E}]_0 - [\mathrm{ES}] - [\mathrm{E}][\mathrm{I}]/K_\mathrm{I}$$

or

$$[\mathrm{E}] = \frac{[\mathrm{E}]_0 - [\mathrm{ES}]}{1 + [\mathrm{I}]/K_\mathrm{I}} \tag{2.21.31}$$

Substituting Eqs (2.21.29) and (2.21.31) in Eq. (2.21.28), we get

$$[\mathrm{ES}] = \frac{k_1[\mathrm{S}]_0([\mathrm{E}]_0 - [\mathrm{ES}])/(1 + [\mathrm{I}]/K_1)}{k_{-1} + k_2}$$

or

$$[\mathrm{ES}] = \frac{k_1[\mathrm{S}]_0[\mathrm{E}]_0/(1 + [\mathrm{I}]/K_\mathrm{I})}{\{k_1[\mathrm{S}]_0/(1 + [\mathrm{I}]/K_\mathrm{I})\} + k_{-1} + k_2}$$

$$= \frac{[\mathrm{E}]_0[\mathrm{S}]_0/(1 + [\mathrm{I}]/K_\mathrm{I})}{\{[\mathrm{S}]_0/(1 + [\mathrm{I}]/K_\mathrm{I})\} + K_\mathrm{M}} \tag{2.21.32}$$

The rate of formation of product is given by

$$r_0 = k_2\,[\mathrm{ES}]$$

Substituting the concentration of ES from Eq. (2.21.32), we get

$$r_0 = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]_0/(1 + [\mathrm{I}]/K_\mathrm{I})}{\{[\mathrm{S}]_0/(1 + [\mathrm{I}]/K_\mathrm{I})\} + K_\mathrm{M}} \tag{2.21.33}$$

If the factor $[\mathrm{S}]_0/(1 + [\mathrm{I}]/\mathrm{K}_\mathrm{I}) \gg K_\mathrm{M}$, we get the maximum rate as

$$r_\mathrm{max} = k_2\,[\mathrm{E}]_0 \tag{2.21.34}$$

Taking the inverse of Eq. (2.21.33) and making use of Eq. (2.21.34), we get the required Lineweaver-Burk equation

$$\frac{1}{r_0} = \frac{1}{r_\mathrm{max}} + \frac{K_\mathrm{M}}{r_\mathrm{max}}\left(1 + \frac{[\mathrm{I}]}{K_\mathrm{I}}\right)\frac{1}{[\mathrm{S}]_0} \tag{2.21.35}$$

On comparing Eq. (2.21.35) with Eq. (2.21.25) we find that the intercept is the same whereas the slope has increased from $K_\mathrm{M}/r_\mathrm{max}$ to $K_\mathrm{M}\,(1 + [\mathrm{I}]/K_\mathrm{I})/r_\mathrm{max}$. In other words, r_max is same but K_M has modified to $K_\mathrm{M}\,(1 + [\mathrm{I}]/K_\mathrm{I})$. Figure 2.21.9 displays the two plots.

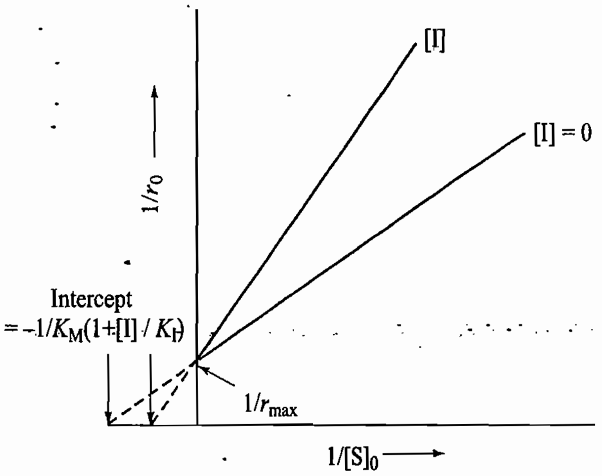

Fig. 2.21.9 Display of the two plots

Partially Competitive Inhibition

In this type of inhibition, E combines with both I and S. The complexes EI and ES also combine respectively with S and I to give the same EIS complex. Both ES and EIS break down to products at the same rate. Thus the mechanism involves the following equations:

$$E + S \xrightleftharpoons{K_1'} ES \xrightarrow{k_2} E + P$$

$$E + I \xrightleftharpoons{K_2'} EI$$

$$EI + S \xrightleftharpoons{K_3'} EIS$$

$$ES + I \xrightleftharpoons{K_4'} EIS$$

$$EIS \xrightarrow{k_2} EI + P$$

We may follow the classical Michaelis-Menten treatment (where we assume $k_2 \ll k'_{-1}$ and thus $K_M \simeq 1/K_1'$) to derive the rate expression. For the given equilibrium reactions, we may write

$$\frac{1}{K_1'} \simeq K_M = \frac{[E][S]}{[ES]} \tag{2.21.36a}$$

$$\frac{1}{K_2'} = K_2 = \frac{[E][I]}{[EI]} \tag{2.21.36b}$$

$$\frac{1}{K_3'} = K_3 = \frac{[EI][S]}{[EIS]} \tag{2.21.36c}$$

$$\frac{1}{K_4'} = K_4 = \frac{[ES][I]}{[EIS]} \tag{2.21.36d}$$

The enzyme conservation reaction is

$$[E]_0 = [E] + [ES] + [EI] + [EIS]$$

Making use of Eqs (2.21.36), we get

$$[E]_0 = [E] + \frac{[E][S]}{K_M} + \frac{[E][I]}{K_2} + \frac{[E][I][S]}{K_2 K_3}$$

or
$$[E] = \frac{[E]_0}{1 + \dfrac{[S]}{K_M} + \dfrac{[I]}{K_2} + \dfrac{[I][S]}{K_2K_3}}$$

$$= \frac{K_M[E]_0}{K_M(1+[I]/K_2)+[S](1+[I]K_M/K_2K_3)} \qquad (2.21.37)$$

The rate of the reaction is given by

$$r = k_2\,([ES] + [EIS])$$

$$= k_2\left(\frac{[E][S]}{K_M} + \frac{[E][I][S]}{K_2K_3}\right)$$

$$= k_2[S]\left(\frac{1}{K_M} + \frac{[I]}{K_2K_3}\right)[E]$$

Substituting [E] from Eq. (2.21.37), we get

$$r = \frac{k_2[S]\{(1/K_M)+[I]/K_2K_3\}[E]_0K_M}{K_M(1+[I]/K_2)+[S](1+[I]K_M/K_2K_3)}$$

$$= \frac{k_2[E]_0[S](1+[I]K_M/K_2K_3)}{K_M(1+[I]/K_2)+[S](1+[I]K_M/K_2K_3)}$$

$$= \frac{k_2[E]_0[S]}{\{K_M(1+[I]/K_2)/(1+[I]K_M/K_2K_3)\}+[S]}$$

The Lineweaver-Burk equation is

$$\frac{1}{r} = \frac{K_M\{(1+[I]/K_2)/(1+[I]K_M/K_2K_3)\}}{k_2[E]_0}\,\frac{1}{[S]} + \frac{1}{k_2[E]_0}$$

A plot between $1/r_0$ and $1/[S]_0$ will be linear with intercept $1/r_{max}$ (same for all [I]) and slope $\dfrac{K_M}{r_{max}}\left(\dfrac{1+[I]/K_2}{1+[I]K_M/K_2K_3}\right)$.

The general nature of the graph is thus same as that of Fig. 2.21.9.

Fully Noncompetitive Inhibition

In this type of inhibition, an inhibitor binds reversibly with E, the complexes ES and EI bind respectively with I and S, to give the same EIS complex and the product is obtained only through the decomposition of ES. Thus, the mechanism includes the following reactions:

$$E + S \overset{K_1'}{\rightleftharpoons} ES \xrightarrow{k_2} E + P$$

$$E + I \overset{K_2'}{\rightleftharpoons} EI$$

$$\mathrm{EI + S \overset{K_I'}{\rightleftharpoons} EIS}$$

$$\mathrm{ES + I \overset{K_2'}{\rightleftharpoons} EIS}$$

Following the classical Michaelis-Menten treatment, we may proceed as follows.

From the given equilibrium expressions, we have

$$\frac{1}{K_I'} = K_M = \frac{[E][S]}{[ES]} = \frac{[EI][S]}{[EIS]}; \qquad (\text{since } k_2 \ll k'_{-1}) \qquad (2.21.38a)$$

$$\frac{1}{K_2'} = K_I = \frac{[E][I]}{[EI]} = \frac{[ES][I]}{[EIS]} \qquad (2.21.38b)$$

The enzyme conservation equation is

$$[E]_0 = [E] + [ES] + [EI] + [EIS]$$

Making use of Eqs (2.21.38), we get

$$[E]_0 = [E] + \frac{[E][S]}{K_M} + \frac{[E][I]}{K_I} + \frac{[E][S][I]}{K_M K_I}$$

or
$$[E] = \frac{[E]_0}{1 + ([S]/K_M) + ([I]/K_I) + ([S][I]/K_M K_I)}$$

$$= \frac{[E]_0}{(1 + [S]/K_M)(1 + [I]/K_I)} \qquad (2.21.39)$$

The rate of formation of product is given by

$$r = k_2\,[ES] = k_2\,\frac{[E][S]}{K_M}$$

Substituting [E] from Eq. (2.21.39), we get

$$r = \frac{k_2}{K_M}\,[S]\left\{\frac{[E]_0}{(1 + [S]/K_M)(1 + [I]/K_I)}\right\}$$

$$= \frac{k_2[E]_0[S]}{(K_M + [S])(1 + [I]/K_I)}$$

Since $r_{\max} = k_2\,[E]_0$, we may write the above expression as

$$r = \frac{r_{\max}[S]}{(K_M + [S])(1 + [I]/K_I)}$$

$$= \frac{r_{\max}[S]}{K_M(1 + [I]/K_I) + [S](1 + [I]/K_I)} \qquad (2.21.40a)$$

Inverting the above expression, we get

$$\frac{1}{r} = \frac{K_M}{r_{max}}\left(1+\frac{[I]}{K_I}\right)\frac{1}{[S]} + \frac{1}{r_{max}}\left(1+\frac{[I]}{K_I}\right) \tag{2.21.40b}$$

Equation (2.21.40b) is the required rate expression.

On comparing Eq. (2.21.40) with Eq. (2.21.25), we find that K_M is unaffected whereas r_{max} has modified to $r_{max}/(1 + [I]/K_I)$. This is just opposite from what occurs in a fully competitive inhibition.

Figure 2.21.10 displays the plots of normal enzyme and fully noncompetitive enzyme reactions.

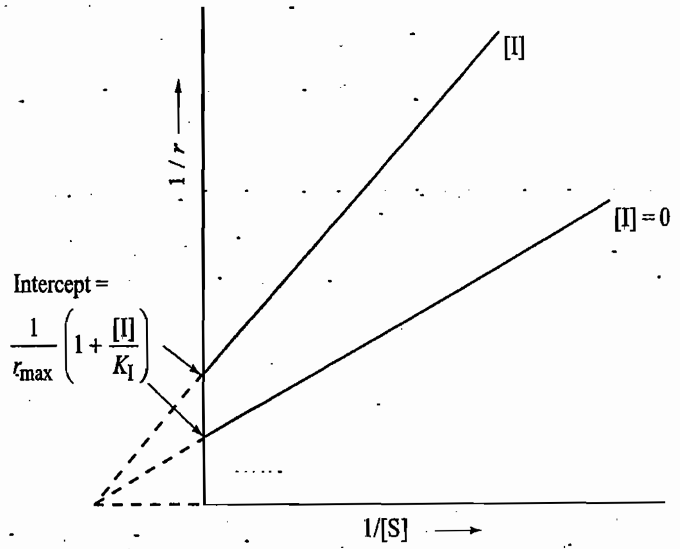

Fig. 2.21.10

Partially Noncompetitive Inhibition

In this case, the mechanism is the same as that of fully noncompetitive inhibition with one more step.

$$\text{EIS} \xrightarrow{k'} \text{EI} + \text{P}$$

Thus, the overall speed of enzyme reaction is given by

$$r = k_2\,[\text{ES}] + k'\,[\text{EIS}]$$

$$= k_2\,\frac{[\text{E}][\text{S}]}{K_M} + k'\,\frac{[\text{E}][\text{S}][\text{I}]}{K_M K_I}$$

$$= \left(\frac{k_2[\text{S}]}{K_M} + \frac{k'[\text{S}][\text{I}]}{K_M K_I}\right)\left(\frac{[\text{E}]_0}{(1+[\text{S}]/K_M)(1+[\text{I}]/K_I)}\right)$$

$$= \frac{k_2[\text{E}]_0[\text{S}]/(1+[\text{I}]/K_I)}{K_M+[\text{S}]} + \frac{k'[\text{E}]_0[\text{S}]([\text{I}]/K_I)/(1+[\text{I}]/K_I)}{K_M+[\text{S}]}$$

$$= \frac{(k_2[\text{E}]_0[\text{S}]+k'[\text{E}]_0[\text{S}][\text{I}]/K_I)/(1+[\text{I}]/K_I)}{K_M+[\text{S}]}$$

The Lineweaver-Burk equation is

$$\frac{1}{r} = \frac{K_M(1+[I]/K_I)}{(k_2[E]_0 + k'[E]_0[I]/K_I)}\frac{1}{[S]} + \frac{1+[I]/K_I}{k_2[E]_0 + k'[E]_0[I]/K_I} \qquad (2.21.41)$$

Uncompetitive Inhibition

In this case, inhibitor can react only with the complex ES. Thus, the mechanism is

$$E + S \xrightleftharpoons{K_1'} ES \xrightarrow{k_2} E + P$$

$$ES + I \xrightleftharpoons{K_2'} EIS$$

We may write

$$\frac{1}{K_1'} = K_M = \frac{[E][S]}{[ES]} \qquad (2.21.42a)$$

$$\frac{1}{K_2'} = K_I = \frac{[ES][I]}{[EIS]} \qquad (2.21.42b)$$

The conservation equation is

$$[E]_0 = [E] + [ES] + [EIS]$$

Making use of Eqs (2.21.42), we get

$$[E]_0 = [E] + \frac{[E][S]}{K_M} + \frac{[E][S][I]}{K_M K_I}$$

or $$[E] = \frac{[E]_0}{1+([S]/K_M)+([S][I]/K_M K_I)}$$

The rate expression is

$$r = k_2\,[ES] = \frac{k_2[E][S]}{K_M} = \frac{k_2[E]_0[S]}{K_M + [S](1+[I]/K_I)}$$

$$= \frac{r_{max}[S]}{K_M + [S](1+[I]/K_I)} \qquad (2.21.43)$$

The Lineweaver-Burk form of the equation will be

$$\frac{1}{r} = \frac{K_M}{r_{max}}\frac{1}{[S]} + \frac{1+[I]/K_I}{r_{max}} \qquad (2.21.44)$$

Thus, slope of the plot between $1/r$ and $1/[S]$ is the same as that of a simple enzyme reaction but the intercept increases with the increase in concentration of I (Fig. 2.21.11).

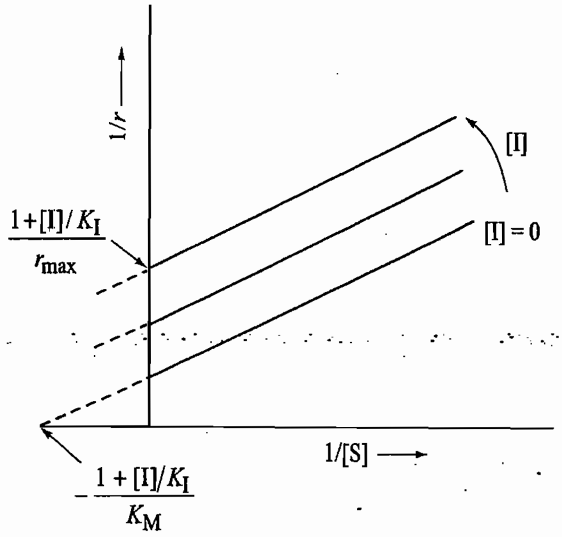

Fig. 2.21.11

Example 2.21.2 An enzyme-catalyzed reaction ($K_M = 2.7 \times 10^{-3}$ mol dm^{-3}) is inhibited by a competitive inhibitor I ($K_I = 3.1 \times 10^{-5}$ mol dm^{-3}). Suppose the substrate concentration is 3.6×10^{-4} mol dm^{-3}. How much of the inhibitor is needed for a 65% inhibition? How much does the substrate concentration have to be increased in order to reduce the inhibition to 25%?

Solution For a noninhibition reaction, we have

$$(r_0)_{non} = \frac{k_2[E]_0[S]_0}{[S]_0 + K_M} \qquad \text{(Eq. 2.21.20)}$$

For a competitive inhibition reaction, we have

$$(r_0)_{inh} = \frac{k_2[E]_0[S]_0/(1+[I]/K_I)}{\{[S]_0/(1+[I]/K_I)\} + K_M} \qquad \text{(Eq. 2.21.33)}$$

Dividing Eq. (2.21.33) by Eq. (2.21.20), we get

$$\frac{(r_0)_{inh}}{(r_0)_{non}} = \frac{([S]_0 + K_M)/(1+[I]/K_I)}{\{[S]_0/(1+[I]/K_I)\} + K_M}$$

Rearranging for [I] and $[S]_0$, we get

$$[I] = \left(\frac{(r_0)_{non} - (r_0)_{inh}}{(r_0)_{inh}}\right)\left(\frac{([S]_0 + K_M)K_I}{K_M}\right)$$

$$[S]_0 = \frac{(r_0)_{inh}}{(r_0)_{non} - (r_0)_{inh}}\left(\frac{K_M[I]}{K_I}\right) - K_M$$

Substituting the given data, we get

$$[I] = \left(\frac{1-0.35}{0.35}\right)$$

$$\times\left(\frac{(3.6\times10^{-4}\,\text{mol dm}^{-3} + 2.7\times10^{-3}\,\text{mol dm}^{-3})(3.1\times10^{-5}\,\text{mol dm}^{-3})}{2.7\times10^{-3}\,\text{mol dm}^{-3}}\right)$$

$$= 6.524 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\mathrm{S}]_0 = \left(\frac{0.75}{1-0.75}\right)\left(\frac{(2.7\times10^{-3}\ \mathrm{mol\ dm^{-3}})(6.524\times10^{-5}\ \mathrm{mol\ dm^{-3}})}{3.1\times10^{-5}\ \mathrm{mol\ dm^{-3}}}\right) - 2.7\times10^{-3}\ \mathrm{mol\ dm^{-3}}$$

$$= 14.346\times10^{-3}\ \mathrm{mol\ dm^{-3}} = 0.014\,3\ \mathrm{mol\ dm^{-3}}$$

Example 2.21.3

Calculate the concentration of a noncompetitive inhibitor ($K_\mathrm{I} = 2.9\times10^{-4}$ mol dm^{-3}) needed to yield a 90% inhibition of an enzyme-catalyzed reaction.

Solution

For a normal enzyme-catalyzed reaction, we have

$$r_0 = \frac{r_\mathrm{max}[\mathrm{S}]_0}{K_\mathrm{M}+[\mathrm{S}]_0}$$

and for a fully noncompetitive inhibition, we have

$$(r_0)_\mathrm{inh} = \frac{r_\mathrm{max}[\mathrm{S}]_0}{(K_\mathrm{M}+[\mathrm{S}]_0)(1+[\mathrm{I}]/K_\mathrm{I})} \qquad \text{(Eq. 2.21.40a)}$$

Dividing the two, we get

$$\frac{r_0}{(r_0)_\mathrm{inh}} = 1 + \frac{[\mathrm{I}]}{K_\mathrm{I}}$$

Therefore $[\mathrm{I}] = K_\mathrm{I}\left(\dfrac{r_0-(r_0)_\mathrm{inh}}{(r_0)_\mathrm{inh}}\right)$

Substituting the given values, we get

$$[\mathrm{I}] = (2.9\times10^{-4}\ \mathrm{mol\ dm^{-3}})\left(\frac{0.9}{0.1}\right) = 2.61\times10^{-3}\ \mathrm{mol\ dm^{-3}}$$

HETEROGENEOUS CATALYSIS

Characteristics of Heterogeneous Catalysts

Most heterogeneous catalytic reactions involve the solid surface as the catalyst. The catalytic effect has been explained on the basis of adsorption of reactants on the active sites available at the surface of the catalyst. Invariably, the adsorption is of chemisorption in nature where the adsorbed molecules are held to the surface by valence forces. This, in turn, weakens some of the bonds within the molecule and thereby the molecule gets activated and its reactivity is enhanced. For example, platinum catalyst which is used in many reactions involving hydrogen involves the adsorption of the hydrogen molecule on the surface of the metal which weakens the bond holding the two hydrogen atoms together. This facilitates the cleavage of that bond and thus accelerates the rate of reaction.

The adsorbed molecules are more near to the transition state and thus heterogeneous catalyst primarily function by lowering of activation energy. If a reaction involves more than one substance, the catalytic effect has been explained on the basis that the reacting molecules are adsorbed in the neighbouring active centres which facilitate the intermolecular arrangement more rapidly. In general, a gaseous reaction on the surface of a catalyst involves the following major steps.

1. Diffusion of reactant molecules to the surface.
2. Adsorption of reactant molecules onto the surface.

3. Chemical reaction on the surface.
4. Desorption of product molecules from the surface.
5. Diffusion of product molecules away from the surface.

The rate of overall reaction may depend on any or all the the steps listed above.

In general, the catalytic effect depends upon the surface area available for adsorption. A solid catalyst present in the powder form is more effective as it has larger surface area. The catalyst may be activated by heating to a high temperature in vacuum.

The kinetics of gaseous reactions on solid surfaces may be accounted for by postulating the reactions of the following types.

(i) An equilibrium reaction involving monolayer adsorption and desorption at the surface of the catalyst. There will be as many equilibrium reactions as the number of reacting molecules.
(ii) Chemical reaction between the adsorbed molecules to give product molecules.

The first reaction will lead to the Langmuir adsorption isotherm. According to the second reaction, the rate of reaction depends on the concentration of adsorbed molecules, which in turns, depends on the fraction of surface covered. Thus, according to Langmuir and Hinshelwood, the rate of reaction may be written as

$$r \propto \theta$$

i.e. $$r = k_1 \theta \qquad (2.21.45)$$

where k_1 is the constant of proportionality. For bimolecular reaction, we have

$$r = k\theta_A \theta_B$$

where θ_A and θ_B are the fractions of surface covered by A and B molecules, respectively.

We give below an account of unimolecular and bimolecular surface reactions.

Unimolecular Surface Reaction

A unimolecular surface reaction involves the following elementary processes.

$$\mathrm{A} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}$$

$$\mathrm{AS} \xrightarrow{k_2} \text{products}$$

where A is the reacting molecule, S is the vacant site on the surface and AS is the adsorbed molecule (or the occupied sites at the surface of the catalyst).

According to Langmuir and Hinshelwood, the rate of reaction is given by

$$r = k_2 \theta \qquad \text{(Eq. 2.21.45)}$$

where θ is the fraction of the surface covered. If c_s is the total concentration of surface sites of the catalyst, then we will have

Concentration of vacant sites, i.e. $[\mathrm{S}] = c_s(1 - \theta)$ (2.21.46)

Concentration of occupied sites, i.e. $[\mathrm{AS}] = c_s\theta$ (2.21.47)

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The steady-state approximation is assumed to hold good for AS. Thus, we have

$$\frac{d[AS]}{dt} = 0 = k_1[A][S] - k_{-1}[AS] - k_2[AS]$$

Substituting the [S] and [AS] in terms of θ, we get

$$k_1\,[A]\,c_s\,(1-\theta) - k_{-1}\,c_s\theta - k_2\,c_s\theta = 0$$

or
$$\theta = \frac{k_1[A]}{k_1[A]+k_{-1}+k_2} \tag{2.21.48}$$

Substituting Eq. (2.21.48) in Eq. (2.21.45), we get

$$r = \frac{k_2k_1[A]}{k_1[A]+k_{-1}+k_2} \tag{2.21.49}$$

Inverting the above relation, we get

$$\frac{1}{r} = \frac{1}{k_2} + \frac{k_{-1}+k_2}{k_2k_1}\,\frac{1}{[A]} \tag{2.21.50}$$

Thus, a plot of $1/r$ versus $1/[A]$ would yield a straight line of slope and intercept equal to $(k_{-1} + k_2)/k_2k_1$ and $1/k_2$, respectively.

For the gaseous reactions, partial pressures may be used instead of the concentration terms. Thus, Eq. (2.21.49) modifies to

$$r = \frac{k_2k_1p_A}{k_1p_A+k_{-1}+k_2} \tag{2.21.51}$$

or
$$\frac{1}{r} = \frac{1}{k_2} + \frac{k_{-1}+k_2}{k_1k_2}\,\frac{1}{p_A} \tag{2.21.52}$$

Hence, a plot of $1/r$ versus $1/p_A$ would yield a straight line.

Limiting Cases of Eq. (2.21.51)

Two limiting cases of (2.21.51) are discussed below.

- $k_2 \gg (k_1p_A + k_{-1})$: Since k_2 is very large in comparison to $k_1p_A + k_{-1}$, it means that the rate of formation of products is very fast as compared to the rate of adsorption and desorption. Equation (2.20.51) in the presence case may be written as

$$r_1 = k_1p_A \tag{2.21.53}$$

Thus, the surface reaction is first-order with respect to the pressure of adsorbent. The rate constant is k_1 indicating that the adsorption is the rate determining step. Examples of reactions which follow Eq. (2.21.53) include the decomposition reactions: N_2O on gold, HI on platinium, phosphine on glass, and formic acid vapours on platinum.

- $k_2 \ll k_1p_A + k_{-1}$: Since k_2 is very small in comparison to $k_1p_A + k_{-1}$, it means that the rate at which products is formed is a slow step and the adsorption and desorption processes are fast. Equation (2.21.51), in the present case becomes

$$r = \frac{k_1k_2p_A}{k_1p_A+k_{-1}} = \frac{(k_1/k_{-1})k_2p_A}{(k_1/k_{-1})p_A+1} = \frac{K_{eq}k_2p_A}{K_{eq}p_A+1} \tag{2.21.54}$$

where K_{eq} is the adsorption equilibrium constant. Equation (2.21.54) is identical with the Langmuir adsorption isotherm (Eq. 2.1.9).

Subcases of Eq. (2.21.54)

Two subcases may be distinguished. These are

(a) **Low pressure region** At low pressures $K_{eq}\,p_A \ll 1$, and thus (Eq. 2.21.54) reduces to

$$r = K_{eq}\,k_2\,p_A \qquad (2.21.55)$$

that is, the reaction is first order with to A.

(b) **High pressure region** At high pressure $K_{eq}\,p_A \gg 1$, and thus Eq. (2.21.54) reduces to

$$r = k_2 \qquad (2.21.56)$$

that is, the reaction is zero order with respect to A.

Equation (2.21.55) and (2.21.56) may be explained by the fact that the rate determining step is the decomposition reaction at the surface. At low pressures, the fraction of area covered by the molecules (or the concentration of adsorbed molecules) increases linearly with pressure and so also the rate of the surface reaction. In the high pressure region, all the sites on the surface are occupied (i.e. $\theta = 1$) and thus the concentration of adsorbed molecules remains constant and hence the reaction becomes zero-order with respect to the adsorbed substance. The variation of rate of reaction with pressure is shown in Fig. 2.21.12. Example of reactions exhibiting above characteristics include decomposition of HI on gold and that of NH_3 on molybdenum.

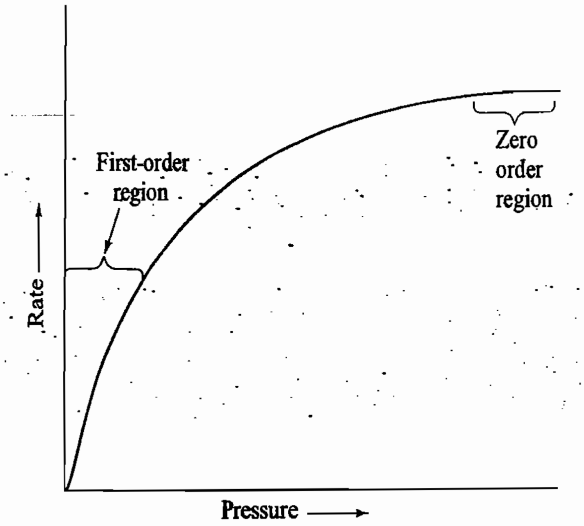


Fig. 2.21.12 Variation of rate of unimolecular surface reaction with pressure

Classification of Gaseous Reactions

Gaseous reactions on the surface may be classified depending on the extent of adsorption of reactant. Thus, we have

Reactant slightly adsorbed In this case, K_{eq} is small and hence $K_{eq}\,p_A$ may be ignored in comparison to 1 in Eq. (2.21.54) which gives

$$r = K_{eq}\,k_2\,p_A = k'\,p_A \qquad (2.21.57)$$

that is, the reaction is first order with respect to A. Equation (2.21.57) may be written as

$$-\frac{\mathrm{d}p_A}{\mathrm{d}t} = k'\,p_A$$

Hence, the variation of pressure with time will be given as

$$\ln \frac{(p_A)_0}{(p_A)_t} = kt \tag{2.21.58}$$

Reactant strongly absorbed In this case, we have

$$K_{eq}\, p_A \gg 1$$

and hence Eq. (2.21.54) modifies to

$$r = k_2 \tag{2.21.59}$$

that is, the reaction is zero order with respect to A. The variation of pressure with time will be given as

$$(p_A)_0 - (p_A)_t = kt \tag{2.21.60}$$

Reactant moderately adsorbed In this case, rate will be given by Eq. (2.21.54) and the rate may be approximated by the expression

$$r = k\, p^{1/n}$$

which makes the rate proportional to the amount adsorbed as given by the Freundlich isotherm.

Bimolecular Surface Reaction

A bimolecular surface reaction involves the following elementary processes.

$$A + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AS$$

$$B + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} BS$$

$$AS + BS \xrightarrow{k_3} \text{products} + 2S$$

The rate of formation of products is given by

$$r = k_3 \theta_A \theta_B \tag{2.21.61}$$

where θ_A and θ_B are the fractions of surface covered by A and B molecules, respectively. If c_s is the total concentration of surface sites, it is obvious that

Concentration of sites occupied by A, i.e. $[AS] = c_s\theta_A$
Concentration of sites occupied by B, i.e. $[BS] = c_s\theta_B$
Concentration of vacant sites, i.e. $[S] = c_s(1 - \theta_A - \theta_B)$

We can apply steady-state approximation to AS and BS to determine θ_A and θ_B. Thus, we have

$$\frac{d[AS]}{dt} = 0 = k_1[A][S] - k_{-1}[AS] - k_3[AS][BS]$$

$$\frac{d[BS]}{dt} = 0 = k_2[B][S] - k_{-2}[BS] - k_3[AS][BS]$$

Substituting the concentrations of S, AS and BS in terms of θ, we get

$$k_1[A]c_s(1 - \theta_A - \theta_B) - k_{-1}c_s\theta_A - k_3c_s^2\theta_A\theta_B = 0 \tag{2.21.62}$$

$$k_2[B]c_s(1 - \theta_A - \theta_B) - k_{-2}c_s\theta_B - k_3c_s^2\theta_A\theta_B = 0 \tag{2.21.63}$$

There are two equations and two unknown variables θ_A and θ_B, and hence can be solved for θ_A and θ_B. These can be substituted in the rate Eq. (2.21.61) to determine rate of the reaction.

We may, however, discuss a simple case where k_3 has a very small value, i.e. the rate determining step is the chemical reaction between the adsorbed molecules. Equations (2.21.62) and (2.21.63) in the present case become

$$k_1[A](1-\theta_A-\theta_B)-k_{-1}\,\theta_A=0$$

$$k_2[B](1-\theta_A-\theta_B)-k_{-2}\,\theta_B=0$$

or

$$K_{eq1}[A](1-\theta_A-\theta_B)-\theta_A=0$$

$$K_{eq2}[B](1-\theta_A-\theta_B)-\theta_B=0$$

where $K_{eq1}=k_1/k_{-1}$ and $K_{eq2}=k_2/k_{-2}$ and are the two adsorption equilibrium constants. Solving for θ_A and θ_B, we get

$$\theta_A=\frac{K_{eq1}[A]}{1+K_{eq1}[A]+K_{eq2}[B]}$$

$$\theta_B=\frac{K_{eq2}[B]}{1+K_{eq1}[A]+K_{eq2}[B]}$$

Substituting the above relations in Eq. (2.21.61), we get

$$r=k_3\left(\frac{K_{eq1}[A]}{1+K_{eq1}[A]+K_{eq2}[B]}\right)\left(\frac{K_{eq2}[B]}{1+K_{eq1}[A]+K_{eq2}[B]}\right)$$

$$=\frac{k_3K_{eq1}K_{eq2}[A][B]}{(1+K_{eq1}[A]+K_{eq2}[B])^2} \tag{2.21.64}$$

For gaseous reactions, Eq. (2.21.64) may be written as

$$r=\frac{k_3K_{eq1}K_{eq2}\,p_Ap_B}{(1+K_{eq1}\,p_A+K_{eq2}\,p_B)^2} \tag{2.21.65}$$

Subcases of Eq. (2.21.65)

Three subcases may be distinguished. These are:

Both* A *and* B *are weakly adsorbed In the present case, $K_{eq1}p_A$ and $K_{eq2}p_B$ will be very small and may be ignored in comparison to 1. Thus, Eq. (2.21.65) becomes

$$r=k_3\,K_{eq1}\,K_{eq2}\,p_A\,p_B \tag{2.21.66}$$

that is, the reaction is first order with respect to each of A and B.

Example includes the reaction between NO and O_2 on glass.

One of the components (say,* A*) is more strongly adsorbed than other In the present case, we have

$$K_{eq1}\,p_A \gg K_{eq2}\,p_B$$

and hence Eq. (2.21.65) may be written as

$$r = \frac{k_3 K_{\mathrm{eq1}} K_{\mathrm{eq2}}\, p_{\mathrm{A}}\, p_{\mathrm{B}}}{(1+K_{\mathrm{eq1}}\, p_{\mathrm{A}})^2} \tag{2.21.67}$$

Examples include the reactions between NH_3 and O_2 on iron surface and between CO_2 and H_2 on platinum.

One of the components (Say, A) is very strongly adsorbed In the present case, we have

$$K_{\mathrm{eq1}}\, p_{\mathrm{A}} \gg K_{\mathrm{eq2}}\, p_{\mathrm{B}}$$

and $\quad K_{\mathrm{eq1}}\, p_{\mathrm{A}} \gg 1$

Hence, Eq. (2.21.65) reduces to

$$r = \left(\frac{k_3 K_{\mathrm{eq2}}}{K_{\mathrm{eq1}}}\right)\frac{p_{\mathrm{B}}}{p_{\mathrm{A}}} \tag{2.21.68}$$

that is, rate depends inversely on the concentration of strongly adsorbed component.

Examples include the reaction between ethylene and hydrogen on copper, between hydrogen and oxygen on platinum, and between carbon monoxide and nitrogen on quartz at about 300 °C.

EFFECT OF TEMPERATURE ON HETEROGENEOUS REACTIONS

Arrhenius equation holds good for the effect of temperature on the heterogeneous reactions. Thus, we have

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E'_{\mathrm{a}}}{RT^2} \tag{2.21.69}$$[†]

where k is rate constant and E'_{a} is known as the *apparent energy of activation.* We may describe below the effect of temperature on the rate constant for a few typical cases.

Unimolecular Surface Reaction

Reactant slightly adsorbed From Eq. (2.21.57), we have

$$r = (K_{\mathrm{eq}} k_2)\, p_{\mathrm{A}}$$

Thus $\quad \dfrac{\mathrm{d}\ln(K_{\mathrm{eq}} k_2)}{\mathrm{d}T} = \dfrac{E'_{\mathrm{a}}}{RT^2}$

or

$$\frac{\mathrm{d}\ln K_{\mathrm{eq}}}{\mathrm{d}T} + \frac{\mathrm{d}\ln k_2}{\mathrm{d}T} = \frac{E'_{\mathrm{a}}}{RT^2} \tag{2.21.70}$$

Now

$$\frac{\mathrm{d}\ln K_{\mathrm{eq}}}{\mathrm{d}T} = \frac{\Delta_{\mathrm{ads}}H}{RT^2} \tag{2.21.71}$$

and

$$\frac{\mathrm{d}\ln k_2}{\mathrm{d}T} = \frac{E_{\mathrm{a}}}{RT^2} \tag{2.21.72}$$

[†] From Eq. (2.21.69) onwards, it is assumed that the logarithm is taken only of the numerical values of the rate constants and equilibrium constants.

where E_a is the true activation energy. Comparing Eqs (2.21.70), (2.21.71) and (2.21.72), we find that

$$E'_a = E_a + \Delta_{ads}H$$

Since $\Delta_{ads}H$ is negative, it is obvious that

$$E'_a < E_a$$

that is, the activation energy of the reaction is lowered. Hence, it may be concluded that the decrease of energy of activation in the heterogeneous catalytic reactions is largely due to the lowering of activation energy.

Reactant strongly adsorbed From Eq. (2.21.59), we find that

$$r = k_2$$

and hence in this case, apparent energy of activation equals the true energy of activation.

Bimolecular Surface Reaction

Both reactants are weakly adsorbed From Eq. (2.21.66), we have

$$r = k_3 K_{eq1} K_{eq2}\, p_A\, p_B = k\, p_A\, p_B$$

Thus
$$\frac{d \ln k}{dT} = \frac{d \ln k_3}{dT} + \frac{d \ln K_{eq1}}{dT} + \frac{d \ln K_{eq2}}{dT}$$

$$\frac{E'_a}{RT^2} = \frac{E_a}{RT^2} + \frac{\Delta_{ads}H_1}{RT^2} + \frac{\Delta_{ads}H_2}{RT^2}$$

Hence, $E'_a = E_a + \Delta_{ads}H_1 + \Delta_{ads}H_2$

Since $\Delta_{ads}H_1$ and $\Delta_{ads}H_2$ are negative, it follows that

$$E'_a < E_a$$

One of the components is very strongly adsorbed From Eq. (2.21.68), we have

$$r = \left(k_3 \frac{K_{eq2}}{K_{eq1}} \right) \frac{p_B}{p_A} = k \frac{p_B}{p_A}$$

where A is very strongly adsorbed. Thus

$$\frac{d \ln k}{dT} = \frac{d \ln k_3}{dT} + \frac{d \ln K_{eq2}}{dT} - \frac{d \ln K_{eq1}}{dT}$$

$$\frac{E'_a}{RT^2} = \frac{E_a}{RT^2} + \frac{\Delta_{ads}H_2}{RT^2} - \frac{\Delta_{ads}H_1}{RT^2}$$

Hence, $E'_a = E_a + \Delta_{ads}H_2 - \Delta_{ads}H_1$

If the reactant A is very strongly adsorbed, the term $-\Delta_{ads}H_1$ will have a large positive value and hence the energy of activation instead of lowering may become more positive.

Problem 2.21.1

(a) The following mechanism has been proposed for the catalyzed dissociation of molecule AB at a metal surface.

$$\mathrm{AB(g) + S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ABS} \qquad \text{(fast)}$$

$$\mathrm{ABS} \xrightarrow{k_2} \mathrm{AS + BS} \qquad \text{(slow)}$$

$$\mathrm{AS} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A(g) + S} \qquad \text{(fast)}$$

$$\mathrm{BS} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{B(g) + S} \qquad \text{(fast)}$$

Show that the rate law is given by

$$-\frac{\mathrm{d}p_{\mathrm{AB}}}{\mathrm{d}t} = \frac{k\,p_{\mathrm{AB}}}{p_{\mathrm{A}}}$$

provided if it be assumed that (i) the adsorption of B is negligible and (ii) A is strongly adsorbed and AB weakly.

(b) If the activation energy of the overall catalyzed reaction is 70 kJ $\mathrm{mol^{-1}}$ and the enthalpies of adsorption of A and AB are -80 kJ $\mathrm{mol^{-1}}$ and -105 kJ $\mathrm{mol^{-1}}$, respectively, what is the activation energy for the postulated rate-determining step?

Solution

(a) The rate of reaction will be given by

$$-\frac{\mathrm{d}p_{\mathrm{AB}}}{\mathrm{d}t} = k_2\theta_{\mathrm{AB}}$$

For the fast adsorption equilibrium for A and AB, we have

$$K_{\mathrm{A}} = \frac{[\mathrm{AS}]}{[\mathrm{A}][\mathrm{S}]} = \frac{\theta_{\mathrm{A}}}{p_{\mathrm{A}}(1-\theta_{\mathrm{AB}}-\theta_{\mathrm{A}}-\theta_{\mathrm{B}})}$$

$$K_{\mathrm{AB}} = \frac{[\mathrm{ABS}]}{[\mathrm{AB}][\mathrm{S}]} = \frac{\theta_{\mathrm{AB}}}{p_{\mathrm{AB}}(1-\theta_{\mathrm{AB}}-\theta_{\mathrm{A}}-\theta_{\mathrm{B}})}$$

Since B is negligibly adsorbed, we have

$$K_{\mathrm{A}} = \frac{\theta_{\mathrm{A}}}{p_{\mathrm{A}}(1-\theta_{\mathrm{AB}}-\theta_{\mathrm{A}})}$$

$$K_{\mathrm{AB}} = \frac{\theta_{\mathrm{AB}}}{p_{\mathrm{AB}}(1-\theta_{\mathrm{AB}}-\theta_{\mathrm{A}})}$$

Thus $$\frac{K_{\mathrm{AB}}}{K_{\mathrm{A}}} = \frac{\theta_{\mathrm{AB}}}{\theta_{\mathrm{A}}}\,\frac{p_{\mathrm{A}}}{p_{\mathrm{AB}}}$$

or $$\theta_{\mathrm{A}} = (\theta_{\mathrm{AB}})\left(\frac{p_{\mathrm{A}}}{p_{\mathrm{AB}}}\right)\left(\frac{K_{\mathrm{A}}}{K_{\mathrm{AB}}}\right)$$

Substituting θ_{A} in the expression of K_{AB} and rearranging, we get

$$\theta_{\mathrm{AB}} = \frac{K_{\mathrm{AB}}p_{\mathrm{AB}}}{1+K_{\mathrm{AB}}p_{\mathrm{AB}}+K_{\mathrm{A}}p_{\mathrm{A}}}$$

Substituting θ_{AB} in the rate expression, we get

$$-\frac{dp_{AB}}{dt} = \frac{k_2 K_{AB} p_{AB}}{1 + K_{AB} p_{AB} + K_A p_A}$$

Since A is strongly adsorbed whereas AB is weakly adsorbed, we may assume

$$K_A p_A \gg 1 + K_{AB} p_{AB}$$

Hence, the rate law reduces to

$$-\frac{dp_{AB}}{dt} = \frac{k_2 K_{AB}}{K_A} \frac{p_{AB}}{p_A} = k \frac{p_{AB}}{p_A}$$

(b) Since

$$k = \frac{k_2 K_{AB}}{K_A}$$

we have $\dfrac{d \ln k}{dt} = \dfrac{d \ln k_2}{dT} + \dfrac{d \ln K_{AB}}{dT} - \dfrac{d \ln K_A}{dT}$

i.e. $\dfrac{E_a'}{RT^2} = \dfrac{E_a}{RT^2} + \dfrac{\Delta H_{AB}}{RT^2} - \dfrac{\Delta H_A}{RT^2}$

or $E_a' = E_a + \Delta H_{AB} - \Delta H_A$

Hence, $E_a = E_a' - \Delta H_{AB} + \Delta H_A$

Substituting the given values, we get

$$E_a = (70 + 105 - 80)\ \text{kJ mol}^{-1} = 95\ \text{kJ mol}^{-1}$$

2.22 AUTOCATALYSIS AND OSCILLATORY CHEMICAL REACTIONS

AUTOCATLYSIS

If one of the products of a reaction acts as a catalyst, it is said to be an autocatalyst and the phenomenon is known as autocatalysis. One of the well-known examples is the oxidation of Fe^{2+} ions by MnO_4^- ions in acidic medium:

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

In this reaction, Mn^{2+} ions act as an autocatalyst.

Kinetics of Catalytic Reaction A + C → 2C

Let the mechanism of the reaction

$$A + C \longrightarrow 2C$$

with an autocatalyst C involves the following steps.

$$A + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D \qquad \text{(fast)}$$

$$D \xrightarrow{k_2} 2C \qquad \text{(Slow)}$$

Differential Rate Low

The rate of the reaction is given by

$$\frac{d[C]}{dt} = 2\,k_2\,[D] \tag{2.22.1}$$

From the fast equilibrium reaction, we have

$$K = \frac{k_1}{k_{-1}} = \frac{[\mathrm{D}]}{[\mathrm{A}][\mathrm{C}]}$$

With this, Eq. (2.22.1) becomes

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = 2\,k_2K\,[\mathrm{A}]\,[\mathrm{C}] = k_{\mathrm{app}}\,[\mathrm{A}]\,[\mathrm{C}] \qquad (2.22.2)$$

The initial concentration of autocatalyst C must be nonzero for the reaction to proceed in the forward direction.

Integrated Rate Expression

Let $[\mathrm{A}]_0$ and $[\mathrm{C}]_0$ be the initial concentrations of A and C, respectively. We will have

$$\begin{array}{cccccc} & \mathrm{A} & + & \mathrm{C} & \longrightarrow & 2\mathrm{C} \\ t=t & [\mathrm{A}]_0 - x & & [\mathrm{C}]_0 - x & & 2x \end{array}$$

The concentration of C at time t will be

$$[\mathrm{C}] = [\mathrm{C}]_0 - x + 2x = [\mathrm{C}]_0 + x$$

The rate law (Eq. 2.22.2) becomes

$$\frac{\mathrm{d}([\mathrm{C}]_0 + x)}{\mathrm{d}t} = K_{\mathrm{app}}\,([\mathrm{A}]_0 - x)\,([\mathrm{C}]_0 + x) \qquad (2.22.3)$$

i.e.
$$\frac{\mathrm{d}x}{([\mathrm{A}]_0 - x)\,([\mathrm{C}]_0 + x)} = k_{\mathrm{app}}\,\mathrm{d}t$$

Resolving the left side into partial fractions, we get

$$\frac{1}{([\mathrm{A}]_0 + [\mathrm{C}]_0)}\left[\frac{\mathrm{d}x}{[\mathrm{A}]_0 - x} + \frac{\mathrm{d}x}{[\mathrm{C}]_0 + x}\right] = K_{\mathrm{app}}\,\mathrm{d}t$$

which on carrying out the integration gives

$$\frac{1}{([\mathrm{A}]_0 + [\mathrm{C}]_0)}\int_0^x\left[\frac{\mathrm{d}x}{[\mathrm{A}]_0 - x} + \frac{\mathrm{d}x}{[\mathrm{C}]_0 + x}\right] = k_{\mathrm{app}}\int_0^t \mathrm{d}t$$

i.e.
$$\frac{1}{([\mathrm{A}]_0 + [\mathrm{C}]_0)}\left[\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x} + \ln\frac{[\mathrm{C}]_0 + x}{[\mathrm{C}]_0}\right] = k_{\mathrm{app}}\,t$$

The above expression may be rearranged as

$$x = \frac{[\mathrm{C}]_0\,(\mathrm{e}^{\beta t} - 1)}{1 + ([\mathrm{C}]_0/[\mathrm{A}]_0)\mathrm{e}^{\beta t}} \qquad (2.22.4)$$

where $\beta = ([\mathrm{A}]_0 + [\mathrm{C}]_0)\,k_{\mathrm{app}}$. Equation (2.22.4) may be written as

$$\frac{x}{[\mathrm{C}]_0} = \frac{\mathrm{e}^{\beta t} - 1}{1 + B\,\mathrm{e}^{\beta t}} \quad ;\text{ where } B = [\mathrm{C}]_0/[\mathrm{A}]_0 \qquad (2.22.5)$$

Figure 2.22.1 displays the plot of $x/[\mathrm{C}]_0$ versus t for some values of β in which

$B = 0.1$. Figure 2.22.2 displays the corresponding rate of reaction. From this figure, it follows that the rate of reaction starts with a smaller value and it increases rapidly due to the formation of more and more of the catalyst. After some time, the rate starts decreasing after attaining a maximum value. This results from the decreasing concentration of the reactant A. Eventually, the rate becomes zero where all the reactant has been consumed.

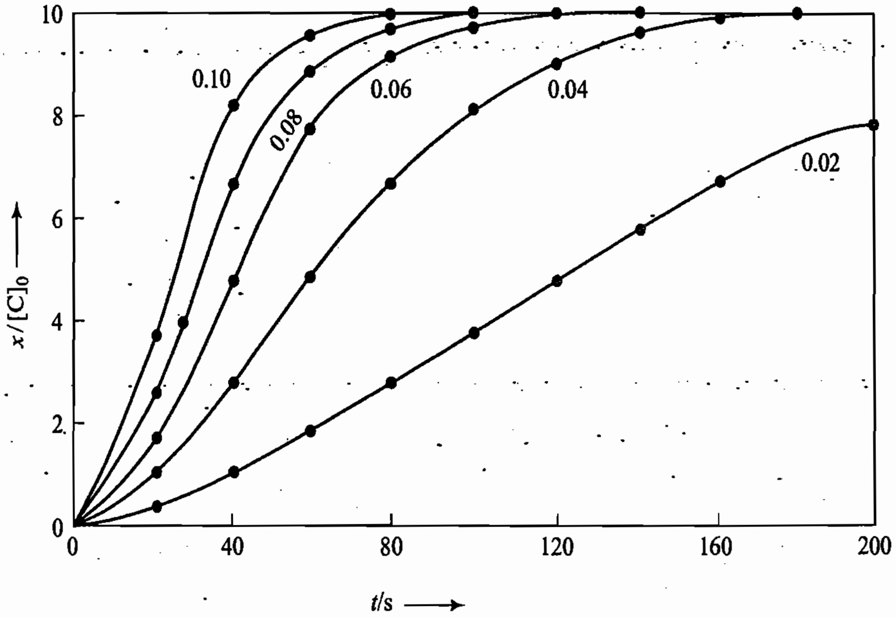


Fig. 2.22.1 Plots of $x/[C]_0$ versus t for $B = 0.1$ and $\beta = 0.02$, 0.04, 0.06, 0.08 and 0.10

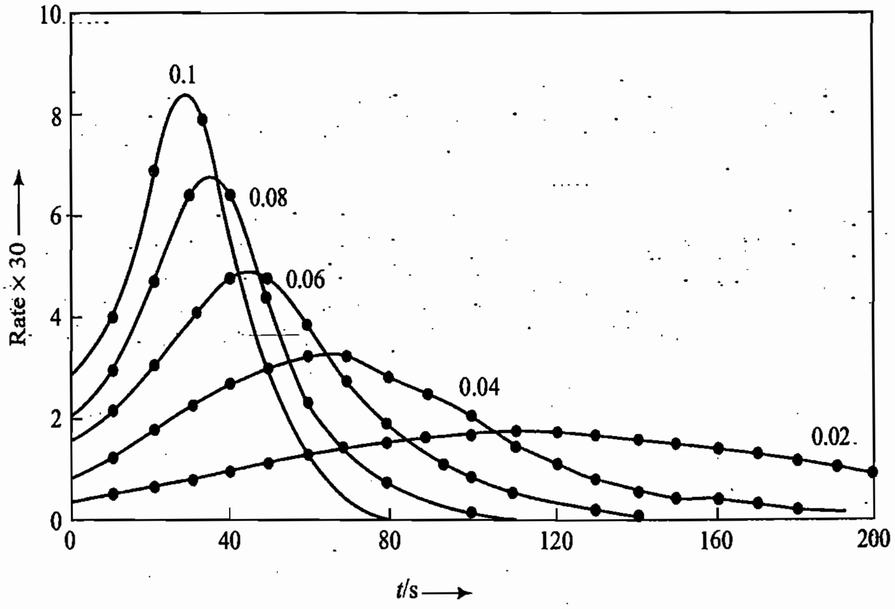


Fig. 2.22.2 Plots of rate of reaction verses t for $B = 0.1$ and $\beta = 0.02, 0.04, 0.06, 0.08$ and 0.10.

Time Corresponding to Maximum Rate of Reaction

The rate expression (Eq. 2.22.3) is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{app}}\,([A]_0 - x)\,([C]_0 + x)$$

To determine $t_{\max}$, we set $\mathrm{d}^2x/\mathrm{d}t^2 = 0$. From Eq. (2.22.3), We get

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = k_{\mathrm{app}}\left[([\mathrm{A}]_0 - x)\frac{\mathrm{d}x}{\mathrm{d}t} - ([\mathrm{C}]_0 + x)\frac{\mathrm{d}x}{\mathrm{d}t}\right]$$

$$= k_{\mathrm{app}}([\mathrm{A}]_0 - [\mathrm{C}]_0 - 2x)\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)$$

Setting this equal to zero, we have

$$[\mathrm{A}]_0 - [\mathrm{C}]_0 - 2x = 0$$

or $$x = \frac{[\mathrm{A}]_0 - [\mathrm{C}]_0}{2}$$

Substituting x from Eq. (2.22.4), we get

$$\frac{[\mathrm{C}]_0\left(\mathrm{e}^{\beta t} - 1\right)}{1 + ([\mathrm{C}]_0/[\mathrm{A}]_0)\mathrm{e}^{\beta t}} = \frac{[\mathrm{A}]_0 - [\mathrm{C}]_0}{2}$$

which on simplification gives

$$t_{\mathrm{max}} = \frac{1}{\beta}\ln\frac{[\mathrm{A}]_0}{[\mathrm{C}]_0} = \frac{1}{k_{\mathrm{app}}([\mathrm{A}]_0 + [\mathrm{C}]_0)}\ln\frac{[\mathrm{A}]_0}{[\mathrm{C}]_0} \qquad (2.22.6)$$

OSCILLATORY CHEMICAL REACTIONS

Some of the reactions involving autocatalyst exhibit the periodic variation in concentration of intermediate with the progress of chemical reaction. In some reaction the periodic variation in concentration may be displayed by the change in colour of the reacting system. This oscillation in concentration is not about the equilibrium concentration as such a movement will be contrary to the second law of thermodynamics.

All chemical oscillatory reactions have three common features in their reaction mechanism. These are as follows.

- The reacting system is far from thermodynamic equilibrium. The system still moves towards equilibrium position with the periodic variation in concentrations of some of the intermediates.
- The mechanism of reaction involves at least two different paths. The system periodically switches from one pathway to another.

  One of the pathway involves the production of a certain intermediate causing its concentration to increase with time and the other pathway involves the consumption of this intermediate causing its concentration to decrease. When the concentration of the intermediate is low, the reaction follows the producing pathway and its concentration rises. When this concentration is reached to some high value, the reaction switches to the consuming pathway and its concentration decreases. When this concentration is reduced to some low value, the entire cycle of switching the pathways is repeated.

The mechanisms of some the well-known oscillatory reactions are described in the following.

The Lotka-Volterra Mechanism

The simplest mechanism of an oscillatory chemical reaction is the Lotka-Volterra mechanism which involves the following steps.

(i) $A + X \xrightarrow{k_1} 2X$

(ii) $X + Y \xrightarrow{k_2} 2Y$

(iii) $Y \xrightarrow{k_3} B$

In the above mechanism A is the reactant (whose concentration is kept constant), B is the product (whose concentration does not appear in the rate law, but it is normally removed from the reaction) and X and Y are intermediates whose concentrations show periodic variations.

The rate expressions for X and Y are

$$\frac{d[X]}{dt} = k_1[A][X] - k_2[X][Y] \qquad (2.22.7)$$

$$\frac{d[Y]}{dt} = k_2[X][Y] - k_3[Y] \qquad (2.22.8)$$

Equations (2.22.7) and (2.22.8) may be solved by the fourth-order Runge Kutta method.

The results obtained from the data

$k_1 = 10\ \text{mol}^{-1}\ \text{L min}^{-1}$; $k_2 = 5\ \text{mol}^{-1}\ \text{L min}^{-1}$; $k_3 = 2\ \text{min}^{-1}$

$[A]_0 = 0.1\ \text{mol L}^{-1}$; $[X]_0 = 0.1\ \text{mol L}^{-1}$; $[Y]_0 = 0.1\ \text{mol L}^{-1}$

are shown in Fig. 2.22.3.

Figure 2.22.3a displays the periodic variations in the concentratinos of X and Y with time.

Figure 2.22.3b displays the corresponding rates of change in concentrations of X and Y which also display the periodic variations. For example,

from x to y; d[Y]/dt > d[X]/dt
and from y to z; d[X]/dt > d[Y]/dt.

To start with d[X]/dt is positive while d[Y]/dt is negative. This trend follows from Eqs (2.22.7) and (2.22.8) where the term k_2[X][Y] has a smaller value in comparison to the second term. Initially, both d[X]/dt and d[Y]/dt increase, the former increases rapidly than the latter. The rapid increase in d[X]/dt may be attributed to the autocatalytic effect of X. As more and more of X is produced in reaction (i), the rate of reaction (ii) also increases along with. Beyond x, d[Y]/dt becomes larger than d[X]/dt with the result that X is consumed rapidly and thus its concentration after attaining a maximum value starts decreasing. At y, d[X]/dt again becomes larger than d[Y]/dt and this may be attributed to sufficient decrease in the concentration of X due to the reaction (ii), consequently, the rate of reaction (i) becomes larger causing the increase in production of X. Thus, there is competition between the reactions (i) and (ii). If the concentration of X is low, the reaction (i) takes over the reaction (ii) causing the increase in the concentration of X. When the concentratin of X becomes larger, the reaction (ii) takes over the reaction (i) causing its consumption faster than its formation.

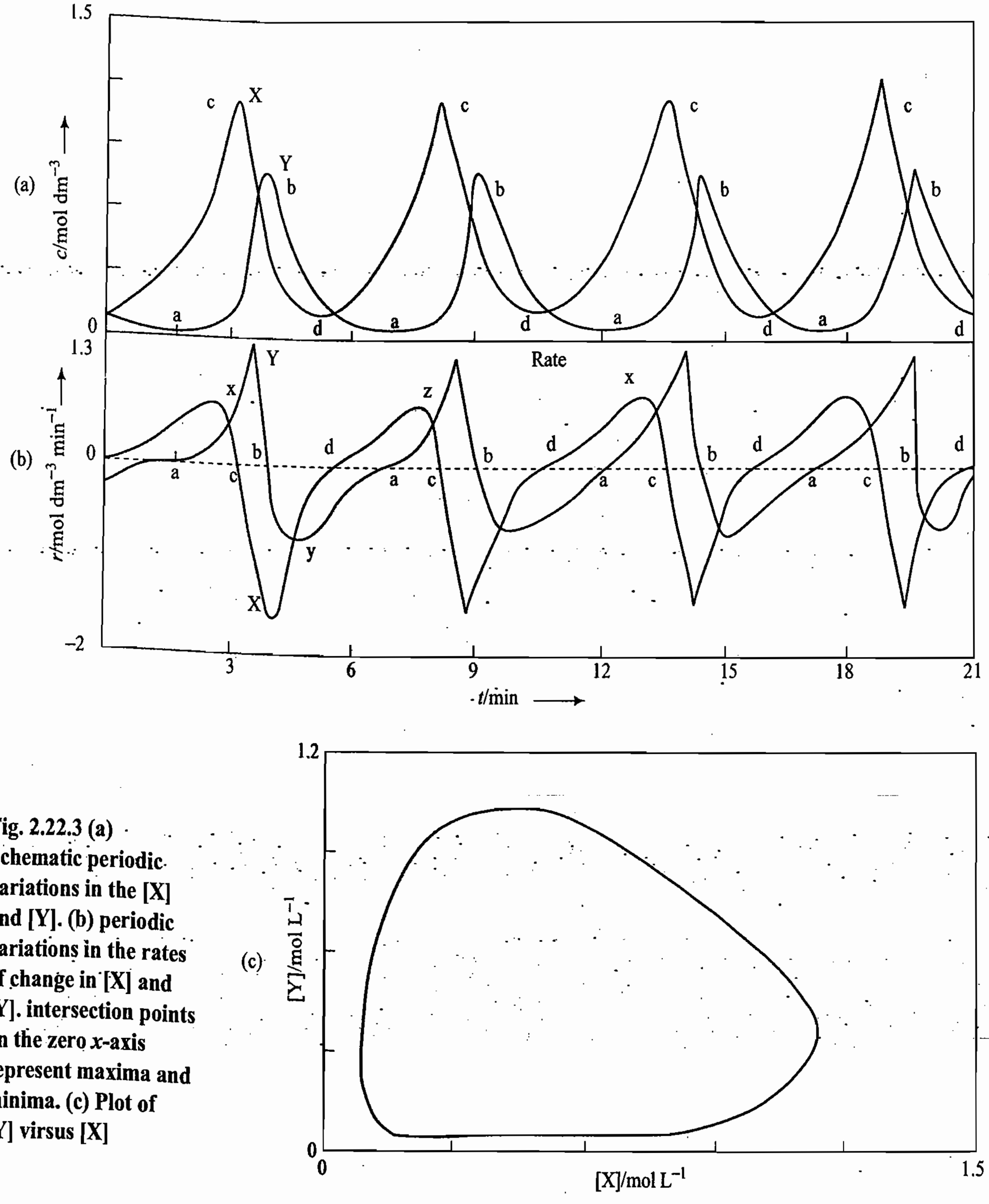


Fig. 2.22.3 (a) Schematic periodic variations in the [X] and [Y]. (b) periodic variations in the rates of change in [X] and [Y]. intersection points on the zero *x*-axis represent maxima and minima. (c) Plot of [Y] virsus [X]

Beyond z, the above pattern is repeated and continues to repeat displaying the periodic variations in the concentrations of X and Y.

The timings at which [X] and [Y] exhibit maximum/minimum are as follows:

(a) $t([X]_{min})$/min →	1.7	7.0	12.3	17.6
(b) $t([X]_{max})$/min →	3.7	9.0	14.3	19.6
(c) $t([X]_{max})$/min →	3.1	8.4	13.7	18.9
(d) $t([X]_{min})$/min →	4.9	10.1	15.4	20.7

The periodic variations in [X] and [Y] are also depicted by the plot between [Y] and [X]. This plot form a closed loop on which the concentraation of X and Y always lie with the progress of the reaction (Fig. 2.22.3c):

The change in concentrations of X and Y depicted in Fig. 2.22.3a may be correlated with those shown in Fig. 2.22.3b.

The Brusselator

The oscillator reaction, named as Brusselator, involves the following steps.

(i) $A \xrightarrow{k_1} X$

(ii) $B + X \xrightarrow{k_2} Y + C$

(iii) $2X + Y \xrightarrow{k_3} 3X$

(iv) $X \xrightarrow{k_4} D$

where A and B are reactants (whose concentrations are kept constant) and C and D are products (which are removed as they are formed). The intermediates are X and Y and the step (iii) is an autocatalytic reaction.

The rate expressions for X and Y are

$$\frac{d[X]}{dt} = k_1 [A] - k_2 [B][X] + k_3 [X]^2 [Y] - k_4 [X]$$

$$\frac{d[Y]}{dt} = k_2 [B][X] - k_3 [X]^2 [Y]$$

The above differential equations may be solved by the fourth-order Runge-Kutta method. The results of the reaction with

$k_1 = 1\ \text{min}^{-1}$; $k_2 = 1.0\ \text{mol}^{-1}\ \text{L}\ \text{min}^{-1}$; $k_3 = 1.0\ \text{mol}^{-2}\ \text{L}^2\ \text{min}^{-1}$

$k_4 = 1.0\ \text{min}^{-1}$; $[A]_0 = 1.0\ \text{mol L}^{-1}$; $[B]_0 = 3.0\ \text{mol L}^{-1}$

$[X]_0 = 1.0\ \text{mol L}^{-1}$; $[Y]_0 = 1.0\ \text{mol L}^{-1}$

are shown in Fig. 2.22.4.

From Fig. 2.22.4b, it is obvious that whenever d[X]/d*t* is maximum, the value of d[Y]/d*t* is minimum and vice versa. Also, when the concentration of X is maximum, the concentration of Y is minimum, and vice versa. The periodic difference between two màximum and two minimum concentrations of X (or Y) is about 7.2 min.

The timings at which [X] and [Y] exhibit maximum/minimum are as follows.

(a) $t([X]_{min})$/min →	1.6	10.2	17.4	24.6
(b) $t([X]_{max})$/min →	6.8	14.0	21.2	28.3
(c) $t([Y]_{max})$/min →	5.7	12.9	20.0	27.2
(d) $t([Y]_{min})$/min →	7.0	14.1	21.3	28.5

The Belousov-Zhabotinsky Reaction

The Belousove-Zhabotinsky oscillatory reaction involves a mixture of potassium bromate, cerium(IV) sulphate and propanedioic acid (HOOCCH$_2$COOH) in dilute sulphuric acid. In this reaction, the ratio [Ce^{4+}]/[Ce^{3+}] oscillates causing the colour

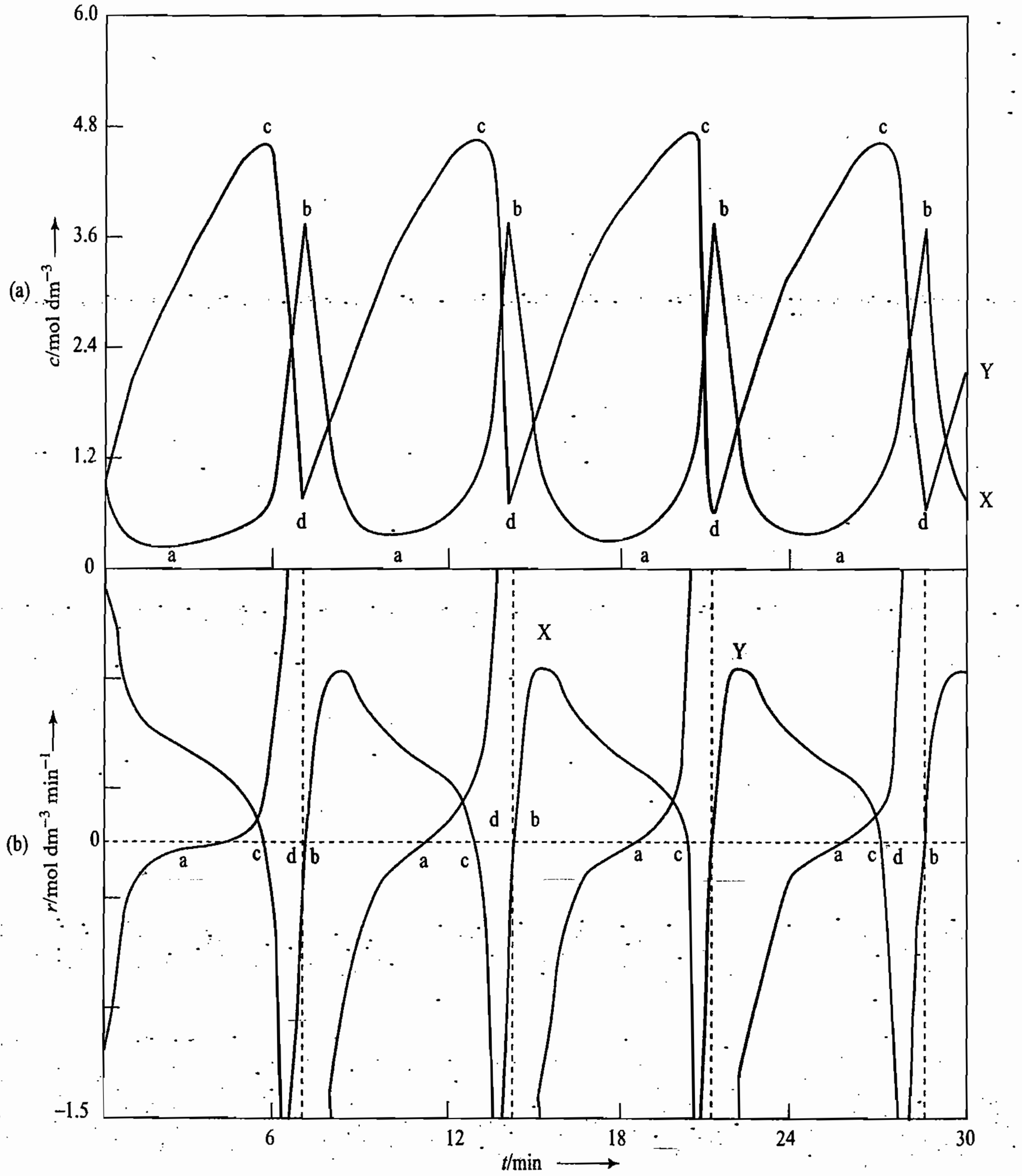


Fig. 2.22.4 (a) Schematic periodic oscillation of [X] and [Y] with time. (b) Rates of change in [X] and and [Y]. Intersection on the zero point on x-axis represent maxima and minima.

of the solution to oscillate between a yellow solution and a colourless solution. This is due to the fact that Ce^{4+} is reduced by propanedioic acid to Ce^{3+} whereas the latter is oxidized back to Ce^{4+} by BrO_3^- ion. The Belousov-Zhabotinsky reaction is a complex reaction involving a large number of reactions steps.

This complex reaction was, studied by Field, Körös and Noyes (FKN) and developed model, known as the FKN-model (also known as Oregonator)[†] based on which the main features of the reaction can be explained. Identifying

$A = BrO_3^-$; $X = HBrO_2$; $Y = Br^-$,

$Z = Ce^{4+}$; $P = HBrO$; $B =$ organic molecule

[†] Oregonator comes from the place Oregon where Noyes and his group worked out the model.

the main steps of FKN model are as follows.

(i) ***Generation of intermediate*** X The reaction is formulated as

$$A + Y \xrightarrow{k_1} X + P$$

that is, $BrO_3^- + Br^- \xrightarrow[H^+]{k_1} HBrO_2 + HBrO$

(*Note:* the concentration of H^+ is included in the rate constants.)

(ii) ***Autocatalytic generation of*** X The reaction is formulated as

$$A + X \xrightarrow{k_2} 2X + 2Z$$

that is $BrO_3^- + HBrO_2 \xrightarrow[k_2]{Ce^{3+}, H^+} 2HBrO_2 + 2Ce^{4+}$

This reaction involves two steps:

$$BrO_3^- + HBrO_2 \xrightarrow{H^+} 2BrO_2^{\bullet} + H_2O$$

$$BrO_2^{\bullet} \xrightarrow{Ce^{3+}, H^+} HBrO_2 + Ce^{4+}$$

This complete balanced reaction is

$$HBrO_2 + 2Ce^{3+} + BrO_3^- + 3H^+ \longrightarrow 2Ce^{4+} + 2HBrO_2 + H_2O$$

(iii) ***Consumption of*** X This occurs in two reactions.

$$X + Y \xrightarrow{k_3} 2P$$

$$2X \xrightarrow{k_4} A + P$$

that is $HBrO_2 + Br^- \xrightarrow{H^+} 2HBrO$

$$2HBrO_2 \longrightarrow BrO_3^- + HBrO$$

(iv) ***Oxidation of organic molecule*** The reactions are

$$CH_2(COOH)_2 + Br_2 \longrightarrow BrCH(COOH)_2 + H^+ + Br^-$$

$$\underset{(Z)}{Ce^{4+}} + \frac{f}{2}\,[CH_2(COOH)_2 + \underset{(B)}{BrCH(COOH)_2}] \xrightarrow{k_5} \frac{1}{2}\underset{(Y)}{Br^-} + Ce^{3+} + \text{Products}$$

The actual oxidation of the malonic acid is a complex reaction. The concentrations of A and B are kept constant during the reaction. The value of f lies in the range 0.5 – 2.4 so as to observe oscillations in the concentrations of intermediates X, Y and Z.

The Belousov–Zhabotinsky reaction consists of two main parts:

(i) The autocatalytic oxidation of Ce^{3+} by $HBrO_3$
(ii) The reduction of Ce^{4+} by malonic acid and its bromoderivative.

The production of Br^- in the oxidation of organic molecule is a strong inhibitor of the autocatalytic oxidation of Ce^{3+} because of its rapid reaction with the autocatalyst, $HBrO_2$.

$$HBrO_2 + H^+ + Br^- \longrightarrow 2HBrO \qquad \text{(Step iii)}$$

Thus, Br^- prevents accumulation of autocatalyst $HBrO_2$.

The rates of change in concentrations of X, Y and Z as given by the FKN model are as follows.

$$\frac{d[X]}{dt} = k_1[A][Y] + k_2[A][X] - k_3[X][Y] - 2k_4\,[X]^2$$

$$\frac{d[Y]}{dt} = -k_1[A][Y] - k_3[X][Y] + \frac{f}{2}\,k_5[B][Z]$$

$$\frac{d[Z]}{dt} = 2k_2\,[A][X] - k_5\,[B][Z]$$

The above differential equations may be solved by the fourth-order Runge-Kutta method. The results of the reaction with the data

$k_1 = 1.28$ mol^{-1} L s^{-1} ; $k_2 = 8.0$ mol^{-1} L s^{-1} ; $k_3 = 8.0 \times 10^4$ mol^{-1} L s^{-1}
$k_4 = 2.0 \times 10^3$ mol^{-1} L s^{-1}; $k_5 = 1.0$ mol^{-1} L s^{-1} .
[A] = 0.6 M ; [B] = 0.02M ; Z = 0.0002M and $f = 1.5$

are shown in Fig. 2.25.5. The starting concentrations of X and Y are zero.

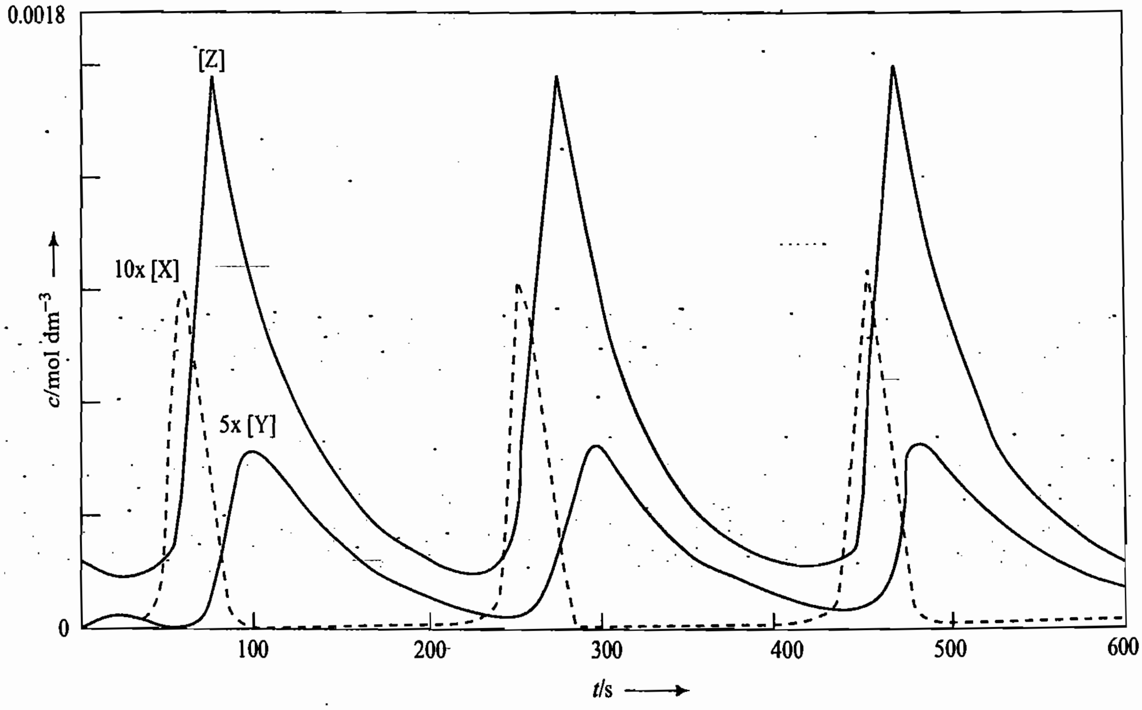


Fig. 2.22.5. Schematic periodic variations in the concentratinos of X, Y and Z

The Belousove-Zhabotinsky reaction may be qualitatively explained as follows.

When [Ce^{4+}] is high, Br$^-$ is produced rapidly and its concentration will also be high (Step iv). This will cause the complete inhibition of oxidation of Ce^{3+} (Step ii) due to inhibiting reaction of Br$^-$ with HBrO$_2$ (Step iii). Soon, the concentration of Ce^{4+} is decreased due ot its reduction by malonic acid and bromomalonic acid. This concentration of Br$^-$ also decreases along with that of Ce^{4+} ions. When the conentration of the latter drops to a minimum, the concentration of Br$^-$ also decreases abruptly due to the inhibitor reaction (Step iii). Here, the rapid autocatalytic oxidation of Ce^{3+} starts and thus raising the concentration of Ce^{4+}

ions. When the concentration of Ce^{4+} ions has reached to its maximum value, there is rapid production of Br^- ions and again it inhibits the oxidation of Ce^{3+} ions. This cycle is repeated periodically. The timing between the two maximum or two minimum concentrations of X or Y as shown in Fig. 2.22.5 in about 194 s.

The timings at which Y and Z exhibit maximum/minimum are as follows.

$t([\mathrm{Y}]_{\max})/\mathrm{s} \rightarrow$	94	288	482
$t([\mathrm{Y}]_{\min})/\mathrm{s} \rightarrow$	56	249	442
$t([\mathrm{Z}])_{\max})/\mathrm{s} \rightarrow$	77	270	464
$t([\mathrm{Z}]_{\min}/\mathrm{s}) \rightarrow$	34	228	422

The Iodate-Iodide Reaction

The steps involved in this reactions are

$$\text{(i)}\quad \underset{(\mathrm{A})}{NaIO_3} \xrightarrow{k_1} Na^+ + \underset{(\mathrm{X})}{IO_3^-}$$

$$\text{(ii)}\quad \underset{(\mathrm{X})}{IO_3^-} \xrightarrow[k_2]{AsO_3^-} \underset{(\mathrm{Y})}{I^-} + \text{products}$$

$$\text{(iii)}\quad \underset{(\mathrm{X})}{IO_3^-} + \underset{(\mathrm{Y})}{2I^-} \xrightarrow[k_3]{AsO_3^-} \underset{(\mathrm{Y})}{3\,I^-}$$

$$\text{(iv)}\quad \underset{(\mathrm{Y})}{I^-} \xrightarrow{k_4} \underset{(\mathrm{B})}{\frac{1}{2}I_2}$$

In the above scheme, X and Y are intermediates and their rates of change of concentrations are given by the expressions

$$\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = k_1\,[\mathrm{A}] - k_2\,[\mathrm{X}] - k_3\,[\mathrm{X}]\,[\mathrm{Y}]^2$$

$$\frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{d}t} = k_2\,[\mathrm{X}] + k_3\,[\mathrm{X}]\,[\mathrm{Y}]^2 - k_4\,[\mathrm{Y}]$$

The concentration of [A] is kept constant.

These equations may be solved by the fourth-order Runge-Kutta method. From the data

$k_1 = 0.001\ \mathrm{min}^{-1}$; $k_2 = 0.01\ \mathrm{min}^{-1}$; $k_3 = 2.5 \times 10^9\ \mathrm{L}^2\ \mathrm{mol}^{-2}\ \mathrm{min}^{-1}$; $k_4 = 1.0\ \mathrm{min}^{-1}$

$[\mathrm{A}]_0 = 0.01\ \mathrm{mol\ L}^{-1}$, $[\mathrm{B}]_0 = 0$, $[\mathrm{X}]_0 = 0$, $[\mathrm{Y}]_0 = 0$

the results obtained are shown in Fig. 2.22.6.

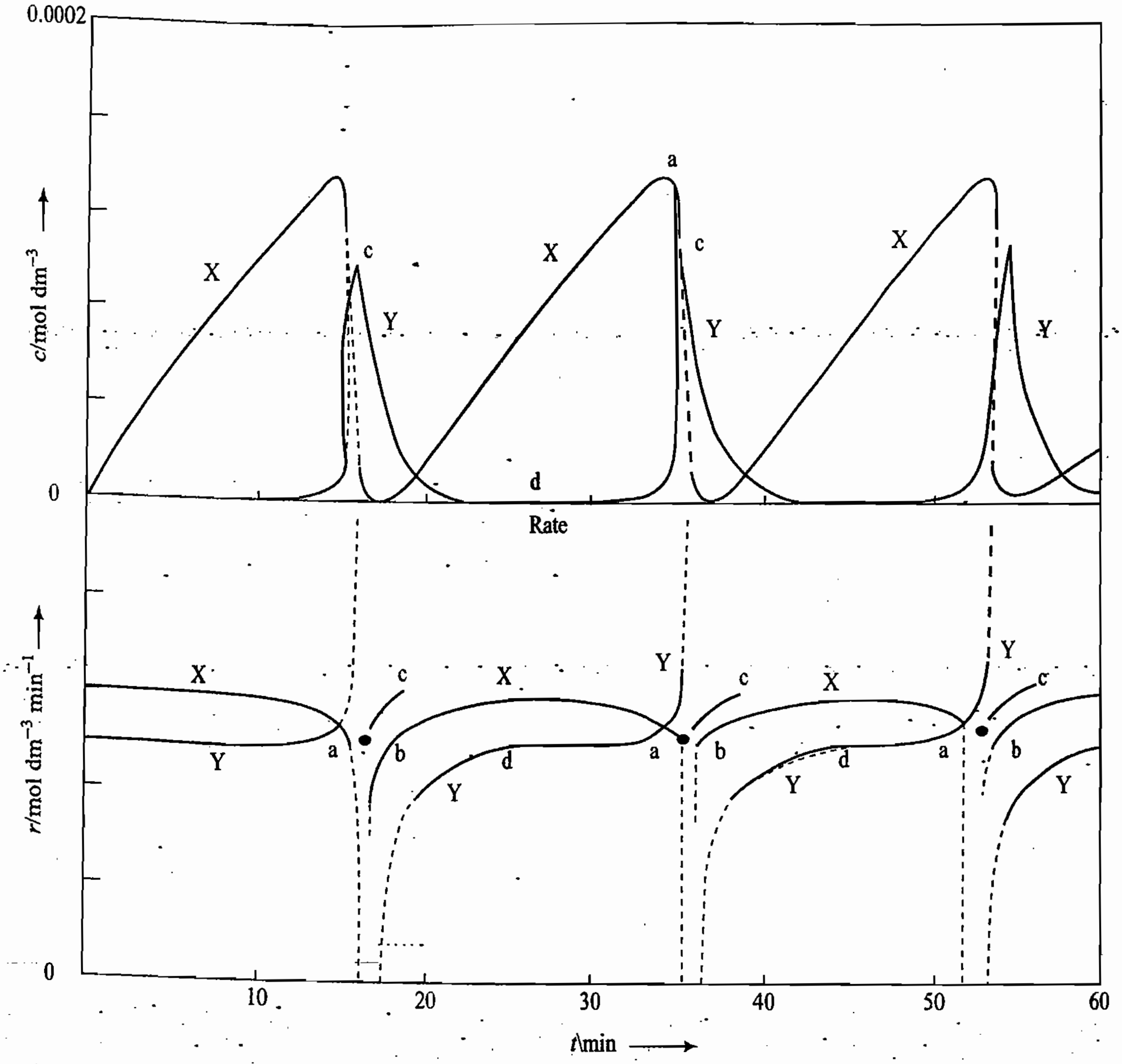


Fig. 2.22.6 (a) Schematic variations in [X] and [Y] with time. (b) The variations in rates d[X]/dt and d[Y]/ dt. Intersection points on the zero x-axis represent maxima and minima

The timings at which [X] and [Y] exhibit maximum/minimum are as follows.

(a) $t([\mathrm{X}]_{\mathrm{max}})$/min →	15.7	34.6	53.6
(b) $t([\mathrm{X}]_{\mathrm{min}})$/min →	16.8	35.7	54.7
(c) $t([\mathrm{Y}]_{\mathrm{max}})$/min →	16.6	35.5	54.5
(d) $t([\mathrm{Y}]_{\mathrm{min}})$/min →	25.4		

2.23 KINETICS OF THE RELAXATION METHOD

In the relaxation method, a system at equilibrium is perturbed by a sudden change in the experimental condition such as temperature, pressure or concentration and then observing the appropriate property of the system as it approaches to the new equilibrium state corresponding to the new condition. This approach is, in particular, useful for studying the fast reactions. For an aqueous system containing ionic species, the temperature can be raised by applying an electric discharge that last not more than 1 μs.

A Typical Example Consider an exothermic reaction

$$\mathrm{A+B} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{C}$$

At equilibrium, we have

$$\text{Rate of forward reaction, } r_f = k_f\,[\mathrm{A}]\,[\mathrm{B}]$$

$$\text{Rate of backward reaction, } r_b = k_b\,[\mathrm{C}]$$

and also
$$r_f = r_b \tag{2.23.1}$$

Differential Rate Law Let the temperature of the system be raised suddenly. At any time, after the temperature jump, the concentrations of reactants and products are the same as in Eq. (2.23.1) but the rate constants is changed to k_f' and k_b'. Thus, we have

$$-\frac{d[\mathrm{A}]}{dt} = k_f'[\mathrm{A}][\mathrm{B}] - k_b'[\mathrm{C}] \tag{2.23.2}$$

At the new temperature, let $[\mathrm{A}]_{eq}$, $[\mathrm{B}]_{eq}$ and $[\mathrm{C}]_{eq}$ be the equilibrium concentrations of A, B and C, respectively. Let we represent

$$[\mathrm{A}] = [\mathrm{A}]_{eq} + |\nu_\mathrm{A}|x = [\mathrm{A}]_{eq} + x \tag{2.23.3a}$$

$$[\mathrm{B}] = [\mathrm{B}]_{eq} + |\nu_\mathrm{B}|x = [\mathrm{B}]_{eq} + x \tag{2.23.3b}$$

$$[\mathrm{C}] = [\mathrm{C}]_{eq} - \nu_c x = [\mathrm{C}]_{eq} - x \tag{2.23.3c†}$$

These changes for an exothermic reaction are in accordance with the Le-Chatelier principle. With these, Eq. (2.23.2) becomes

$$-\frac{d([\mathrm{A}]_{eq}+x)}{dt} = k_f'([\mathrm{A}]_{eq}+x)\,([\mathrm{B}]_{eq}+x) - k_b'([\mathrm{C}]_{eq}-x)$$

i.e.
$$-\frac{dx}{dt} = (k_f'[\mathrm{A}]_{eq}[\mathrm{B}]_{eq} - k_b'[\mathrm{C}]_{eq}) + k_f'x\,([\mathrm{A}]_{eq}+[\mathrm{B}]_{eq}+x) + k_b'x$$

Since at equilibrium, Eq. (2.23.1) holds good, we will have

$$\frac{dx}{dt} = -k_f'x([\mathrm{A}]_{eq}+[\mathrm{B}]_{eq}+x) - k_b'x \tag{2.23.4}$$

Since the perturbation is small, $x \ll ([\mathrm{A}]_{eq} + [\mathrm{B}]_{eq})$, thus Eq. (2.23.4) may be written as

$$\frac{dx}{dt} = -k_f'x([\mathrm{A}]_{eq}+[\mathrm{B}]_{eq}) - k_b'x$$

$$= -\frac{1}{\tau}x \tag{2.23.5††}$$

where
$$\frac{1}{\tau} = k_f'([\mathrm{A}]_{eq}+[\mathrm{B}]_{eq}) + k_b' \tag{2.23.6}$$

---

† For an endothermic reaction, $[\mathrm{A}] = [\mathrm{A}]_{eq} - x$; $[\mathrm{B}] = [\mathrm{B}]_{eq} - x$ and $[\mathrm{C}] = [\mathrm{C}]_{eq} + x$.

†† Ignoring x in comparison to $[\mathrm{A}]_{eq} + [\mathrm{B}]_{eq}$ makes dx/dt a linear function of x. This procedure is known as the linearization of the rate constant.

Equation (2.23.5) indicates that the movement of the system towards new equilibrium position is first order with respect to x (= $[A] - [A]_{eq}$).

Integrated Rate Expression

If x_0 is the value of x at $t = 0$ (the instant time at which temperature jump takes place), then we will have

$$\int_{x_0}^{x} \frac{dx}{x} = -\frac{1}{\tau}\int_{0}^{t} dt$$

which gives

$$\ln\frac{x}{x_0} = -\frac{t}{\tau} \qquad \text{i.e.} \qquad x = x_0\,e^{-t/\tau} \qquad (2.23.7)$$

The term τ in Eq. (2.23.7) is known as the *relaxation time*. It is the time taken to reduce the value of x to x_0/e value. From Eq. (2.23.6), it follows that $1/\tau$ is a linear function of $[A]_{eq} + [B]_{eq}$. The graph between $1/\tau$ and $[A]_{eq} + [B]_{eq}$ is a straight line with slope equal to k'_f and intercept equal to k'_b (Fig.2.23.1). Equation (2.23.6) is valid whether the reaction is exothermic or endothermic.

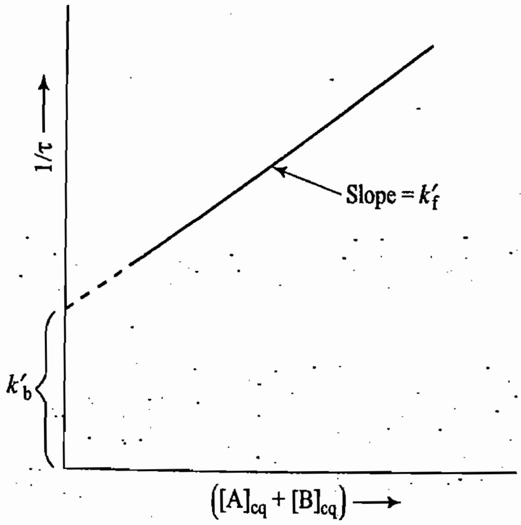


Fig. 2.23.1 Plot of $1/\tau$ versus $([A]_{eq} + [B]_{eq})$

In some cases, there may be practical difficulties in determining $[A]_{eq}$ and $[B]_{eq}$. This difficulty may be overcome by taking one of the reactants (say, A) in a large excess over the other reactant (i.e. B). In this case, the reaction $A + B \rightleftharpoons C$ becomes a pseudo-first order and one can write Eq. (2.23.6) as

$$\frac{1}{\tau} = k'_f[A]_0 + k'_b$$

Thus the plot of $1/\tau$ versus $[A]_0$ is a straight line with slope = k'_f and intercept = k'_b.

Comment

For any type of reaction involving a single step, the chemical relaxation is always a first order process because the rate equation can always be linearized by ignoring the higher term in x in the rate equation provided the perturbation is small.

It may be noted that the process of linearization is not needed where the reaction is of first order or pseudo-first order in both directions and also the restriction of small perturbation in this case is not the prerequisite requirement as the rate equation does not involve higher terms in x.

Table 2.23.1 records some of the most common single-step equilibria.

Table 2.23.1 Expressions of Relaxation time for some single-step equilibria

Equilibrium reaction	*Relaxation time*†
$A \rightleftharpoons B$	$1/\tau = k_f + k_b$
$A + B \rightleftharpoons C$	$1/\tau = k_f + ([A]_{eq} + [B]_{eq}) + k_b$
$nA \rightleftharpoons B$	$1/\tau = n^2 k_f [A]_{eq}^{n-1} + k_b$
$A + B \rightleftharpoons C + D$	$1/\tau = k_f([A]_{eq} + [B]_{eq}) + k_b([C]_{eq} + [D]_{eq})$
$A + B \rightleftharpoons 2C$	$1/\tau = k_f([A]_{eq} + [B]_{eq}) + 4\,k_b[C]_{eq}$

† k_f is the rate constant for the forward reaction and k_b is that of backward reaction.

Example 2.23.1 The relaxation time for the reaction $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$ is found to be 36 μs at 25 °C. Determine the values of k_f and k_b?

Solution From the expression of relaxation time (Eq. 2.23.6), we get

$$k_f([H^+]_{aq} + [OH^-]_{aq}) + k_b = 1/36 \times 10^{-6}\text{s} \tag{1}$$

Also, we have

$$k_f[H^+]_{aq}[OH^-]_{aq} = k_b[H_2O] \tag{2}$$

where $[H^+]_{aq} = [OH^-]_{aq} = 1 \times 10^{-7}\ \text{mol dm}^{-3}$

$$[H_2O] = 1\,000\ \text{g dm}^{-3}/18\ \text{g mol}^{-1} = 55.56\ \text{mol dm}^{-3}$$

With these, Eqs (1) and (2), respectively, become

$$k_f(2 \times 10^{-7}\ \text{mol dm}^{-3}) + k_b = 1/(36 \times 10^{-6}\text{s}) \tag{3}$$

and $k_f(1 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}) = k_b(55.56\ \text{mol dm}^{-3})$

i.e. $$k_f(1 \times 10^{-14}\ \text{mol dm}^{-3}) - 55.56 \times k_b = 0 \tag{4}$$

Multiplying Eq. (3) by 55.56 and them adding it to Eq. (4), we get

$$k_f(55.56 \times 2 \times 10^{-7} + 1 \times 10^{-14})\ \text{mol dm}^{-3} = 55.56/(36 \times 10^{-6}\ \text{s})$$

or $$k_f = \frac{55.56/(36\times10^{-6})}{55.56\times2\times10^{-7}+1\times10^{-14}}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

$$= 1.39 \times 10^{11}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

Finally, from Eq. (4) we get

$$k_b = \frac{k_f(1\times10^{-14}\text{mol dm}^{-3})}{55.56} = \frac{(1.39\times10^{11}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})(1\times10^{-14}\text{mol dm}^{-3})}{55.56}$$

$$= 2.51 \times 10^{-5}\ \text{s}^{-1}$$

REVISIONARY PROBLEMS

2.1 Distinguish between:
  (i) Reaction rate and reaction rate constant.
  (ii) Average rate and instantaneous rate.
  (iii) Order and molecularity.
  (iv) Differential rate law and integrated rate law.
  (v) Overall reaction and elementary reaction.

2.2 For the reaction

$$\nu_1 A_1 + \nu_2 A_2 \longrightarrow \nu_3 A_3 + \nu_4 A_4$$

show that the rate of the reaction is given by any one of the terms given below.

$$r_1 = \frac{dx}{dt} = -\frac{1}{\nu_1}\frac{d[A_1]}{dt} = -\frac{1}{\nu_2}\frac{d[A_2]}{dt} = \frac{1}{\nu_3}\frac{d[A_3]}{dt} = \frac{1}{\nu_4}\frac{d[A_4]}{dt}$$

2.3 Comment upon the following:

(i) Thermodynamic principles can help predicting the feasibility of a reaction not about the time the reaction will require for completion.

(ii) Elementary processes with molecularity greater than three are not known.

(iii) Order of a reaction cannot be predicted from its equation.

(iv) Order of an elementary step is always equal to its molecularity.

(v) Wall effects can also predict a useful criterion for chain reactions. If the reaction is unaffected by changing the wall or by raising the surface to volume ratio, the reaction is probably simple in nature.

(vi) On raising the pressure, the wall effects gradually becomes less important.

2.4 The reaction

$$\nu A \rightarrow \text{products}$$

is zero-order with respect to A. Write down its differential rate law and deduce from it the integrated rate law. What is the unit of rate constant of the above reaction?

2.5 (a) The reaction

$$\nu_1 A + \nu_2 B \rightarrow \text{products}$$

is first-order with respect to A and zero-order with respect to B. Write down its differential rate law and deduce from it the integrated rate law. What is the unit of rate constant of the above reaction?

(b) Define the term half-life. Show that for a first-order reaction, half-life has a constant value.

(c) An acid hydrolysis of an ester is a first-order reaction. What is the role of the acid? What is the order of the reaction with respect to H^+ ions of the solution? Does the rate constant of such a reaction is independent of hydrogen-ion concentration?

(d) The acid hydrolysis of the same quantity of ester is done separately with equal normal solutions of HCl and H_2SO_4. Show that

$$\frac{[H^+]_{HCl}}{[H^+]_{H_2SO_4}} = \frac{k_{HCl}}{k_{H_2SO_4}}$$

where k stands for the rate constant. State with adequate explanation, whether the value of $k_{HCl}/k_{H_2SO_4}$ is less than, equal or greater than one.

2.6 (a) The reaction

$$\nu_1\mathrm{A} + \nu_2\mathrm{B} \rightarrow \text{products}$$

is first-order with respect to each of A and B. Write down its differential rate law and deduce from it the integrated rate law. What is the unit of rate constant of the above reaction?

(b) The reaction

$$\nu\mathrm{A} \rightarrow \text{products}$$

is second-order with respect to A. Write down its differential rate law and deduce from it the integrated rate law.

Show that the half-life of the above reaction is inversely proportional to the initial concentration A.

2.7 (a) The reaction

$$2\mathrm{A} + \mathrm{B} \rightarrow \text{products}$$

is second-order with respect to A and first-order with respect to B. Write down its differential and integrated rate laws.

(b) The reaction

$$\nu\mathrm{A} \rightarrow \text{products}$$

is third-order with respect to A. Write down its differential rate law and deduce from it the integrated rate law. What is the unit of rate constant of such a reaction? Show that the half-life of such a reaction is inversely proportional to the square of the initial concentration of A.

2.8 Derive the integrated rate law for a reaction which follows the differential rate law:

(i) $$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k\,[\mathrm{A}]^{p+1/2}$$

(ii) $$\frac{\mathrm{d}x}{\mathrm{d}t} = k_n\,([\mathrm{A}]_0 - x)^n$$; show also that

$$t_{\frac{1}{2}} = \frac{1}{k_n(n-1)} \cdot \frac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}}$$

What is the unit of k_n?

2.9 Outline the methods which are employed to determine the order of a reaction.

2.10 (a) For the following reversible (first-order opposed by first-order) reaction

$$\mathrm{A} \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftharpoons}} \mathrm{B}$$

derive the integrated rate expressions

$$\ln \frac{x_\mathrm{eq}}{x_\mathrm{eq} - x} = k_\mathrm{f}\,\frac{[\mathrm{A}]_0}{x_\mathrm{eq}}\,t$$

$$\ln \frac{x_\mathrm{eq}}{x_\mathrm{eq} - x} = (k_\mathrm{f} + k_\mathrm{b})\,t$$

(b) Show that the variations in concentrations of A and B in the reversible reaction of part (a) is given by

$$[\mathrm{A}]_t = [\mathrm{A}]_0\,\frac{k_\mathrm{f}}{k_\mathrm{f} + k_\mathrm{b}}\left(\frac{k_\mathrm{b}}{k_\mathrm{f}} + \exp\{(-k_\mathrm{f} + k_\mathrm{b})t\}\right)$$

$$[B]_t = [A]_0 - [A]_t$$

(c) Show that the equilibrium constant of the reversible reaction of part (a) is given by

$$K_{eq} = \frac{k_f}{k_b}$$

2.11 Set up the differential rate law for each of the following types of reversible reactions.

(i) First-order opposed by second-order.
(ii) Second-order opposed by first-order.
(iii) Second-order opposed by second-order.

2.12 State the principle of microscopic reversibility and apply it to find out the equilibrium constant of the reaction

$$2NO_2 + F_2 \rightleftharpoons 2NO_2F$$

Given that the above reaction proceeds through the following two elementary reactions.

$$NO_2 + F_2 \overset{K_1}{\rightleftharpoons} NO_2F + F$$

$$F + NO_2 \overset{K_2}{\rightleftharpoons} NO_2F$$

2.13 (a) What do you understand by concurrent elementary reactions?

(b) Show that the integrated rate expression for the concurrent elementary reactions

$$A \xrightarrow{k_1'} B$$

$$A \xrightarrow{k_1''} C$$

is given by

$$\ln\frac{[A]_0}{[A]_t} = (k_1' + k_1'')t$$

(c) Show that for the reaction given in part (b)

$$\frac{[B]}{[C]} = \frac{k_1'}{k_1''}$$

(d) How will you determine experimentally the values of rate constants k_1' and k_1'' of the reactions given in part (b).

(e) For the reaction

$$A \xrightarrow{k_1} B$$

$$2A \xrightarrow{k_2} C$$

$$3A \xrightarrow{k_3} D$$

set up the differential rate law in terms of the disappearance of A with time.

2.14 (a) What do you understand by consecutive or sequential reactions?

(b) For the reactions

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_1'} C$$

derive the expressions

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t)$$

$$[\mathrm{B}] = [\mathrm{A}]_0 \left(\frac{k_1}{k_1' - k_1}\right) \{\exp(-k_1 t) - \exp(-k_1' t)\}$$

$$[\mathrm{C}] = [\mathrm{A}]_0 \left[1 - \frac{1}{k_1' - k_1}\{k_1' \exp(-k_1 t) - k_1 \exp(-k_1' t)\}\right]$$

Draw a graph illustrating the typical variations of concentrations of A, B and C with time.

(c) Show that the time at which B attains a maximum concentration is given by

$$t_{\max} = \frac{1}{k_1 - k_1'} \ln\left(\frac{k_1}{k_1'}\right)$$

and the maximum concentration B is given by

$$[\mathrm{B}]_{\max} = [\mathrm{A}]_0 \left(\frac{k_1'}{k_1}\right)^{k_1'/(k_1 - k_1')}$$

(d) Suppose that the rate constant k_1' is very much larger than k_1. Show that the concentration of C with time is given by

$$[\mathrm{C}] = [\mathrm{A}]_0 \{1 - \exp(-k_1 t)\}$$

and hence justify the statement that the reaction with the smaller rate constant is the rate-determining step.

(e) Now suppose $k_1 \gg k_1'$. Show that it leads to the same statement given in part (d).

(f) Define the steady-state approximation as applicable to the reactive intermediates. Justify the approximation by taking the consecutive reactions given in part (b) with a very small value of k_1.

2.15 Given the following mechanisms. Set up the corresponding differential rate law:

(i) $\mathrm{A} \xrightarrow{k_1} \mathrm{B}$ (slow)

$\mathrm{B} \xrightarrow{k_2}$ products (fast)

(ii) $\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AB}$ (in rapid equilibrium)

$\mathrm{AB} \xrightarrow{k_2}$ products (slow)

2.16 Reaction between NO and O_2 follows the following mechanism:

$\mathrm{NO} + \mathrm{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2}$ (in rapid equilibrium)

$\mathrm{N_2O_2} + \mathrm{O_2} \xrightarrow{k_2} 2\,\mathrm{NO_2}$ (slow)

Show that the rate of the reaction is given by

$$\frac{1}{2}\frac{\mathrm{d}[\mathrm{NO_2}]}{\mathrm{d}t} = k[\mathrm{NO}]^2\,[\mathrm{O_2}]$$

How will you account for the decrease in rate constant with increase in temperature?

2.17 Derive the differential rate law for each of the following reaction mechanism.

(i) Decomposition of ozone

$$O_3 \xrightarrow{k_1} O_2 + O$$

$$O + O_3 \xrightarrow{k_2} 2O_2$$

(ii) Reaction between NO_2 and F_2

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + F \qquad \text{(slow)}$$

$$F + NO_2 \xrightarrow{k_2} NO_2F \qquad \text{(fast)}$$

(iii) Reaction between NO_2 and CO

$$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO \qquad \text{(slow)}$$

$$NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2 \qquad \text{(fast)}$$

(iv) Reaction between Br^- and H_2O_2 in acidic medium

$$Br^- + H_2O_2 + H^+ \xrightarrow{k_1} HOBr + H_2O \qquad \text{(slow)}$$

$$HOBr + H^+ + Br^- \xrightarrow{k_2} Br_2 + H_2O \qquad \text{(fast)}$$

(v) Reaction between NO and O_2

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad \text{(in rapid equilibrium)}$$

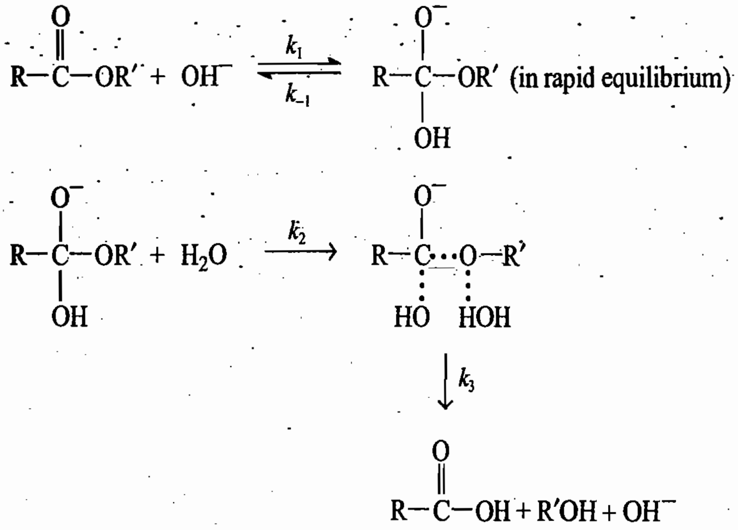
$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2 \qquad \text{(slow)}$$

(vi) Reaction between ammonium and cyanate ions

$$NH_4^+ + OCN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NH_4OCN \qquad \text{(in rapid equilibrium)}$$

$$NH_4OCN \xrightarrow{k_2} OC(NH_2)_2 \qquad \text{(slow)}$$

(vii) Saponification of an ester



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R-\underset{OH}{\overset{O^-}{C}}-OR' \quad \text{(in rapid equilibrium)}$$

$$R-\underset{OH}{\overset{O^-}{C}}-OR' + H_2O \xrightarrow{k_2} R-\underset{HO}{\overset{O^-}{C}}\cdots\underset{HOH}{O}-R'$$

$$\downarrow k_3$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'OH + OH^-$$

(viii) Reaction between hydrogen and iodine

$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I \qquad \text{(in rapid equilibrium)}$$

$$H_2 + 2I \xrightarrow{k_2} 2HI \qquad \text{(slow)}$$

(ix) Reaction between hypochlorite and iodide ions in alkaline medium

$$OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^- \qquad \text{(fast)}$$

$I^- + HOCl \xrightarrow{k_2} HOI + Cl^-$ (slow)

$OH^- + HOI \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2O + OI^-$ (fast)

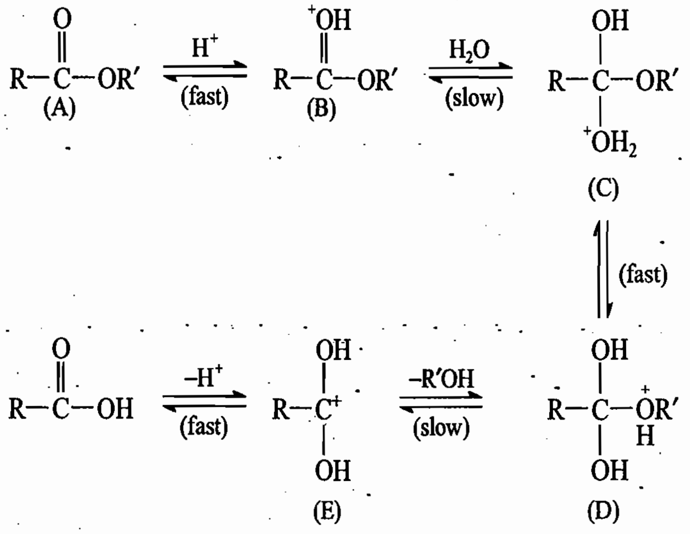
An alternative mechanism is

$OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^-$ (fast)

$I^- + HOCl \xrightarrow{k_2} ICl + OH^-$ (slow)

$ICl + 2OH^- \xrightarrow{k_3} OI^- + Cl^- + H_2O$ (fast)

(x) Acid hydrolysis of an ester



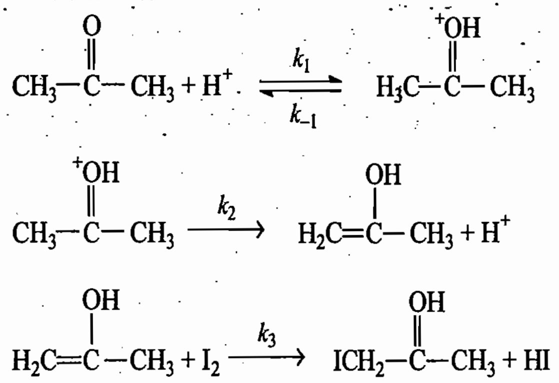
(xi) Reaction between CO and Cl_2

$Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl$ (fast equilibrium)

$Cl + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} COCl$ (fast equilibrium)

$COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$ (slow)

(xii) Iodination of acetone



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_3C-\overset{\overset{^+OH}{\|}}{C}-CH_3 \qquad \text{(fast)}$$

$$CH_3-\overset{\overset{^+OH}{\|}}{C}-CH_3 \xrightarrow{k_2} H_2C{=}\overset{\overset{OH}{|}}{C}-CH_3 + H^+ \qquad \text{(slow)}$$

$$H_2C{=}\overset{\overset{OH}{|}}{C}-CH_3 + I_2 \xrightarrow{k_3} ICH_2-\overset{\overset{OH}{\|}}{C}-CH_3 + HI \qquad \text{(fast)}$$

(xiii) Decomposition of gaseous N_2O_5

$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$

$NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2$

$NO_3 + NO \xrightarrow{k_3} 2NO_2$

2.18 Many thermal decomposition and isomerization reactions follow the mechanism given below.

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_2} \text{products}$$

where A represents the molecule undergoing the thermal decomposition or isomerization reaction and M represents any other molecule. Show that the above mechanism leads to the following differential rate law:-

$$\frac{d(\text{product})}{dt} = \frac{k_2 k_1[A][M]}{k_{-1}[M] + k_2}$$

Determine the order of the reaction when (i) $k_{-1} \gg k_2$ and (ii) $k_2 \gg k_{-1}$. Does the order of the reaction change with the change in the pressure of the system?

2.19 (a) Lindemann mechanism for the first-order reaction is as follows:

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A \qquad \text{(in rapid equilibrium)}$$

$$A^* \xrightarrow{k_2} \text{product} \qquad \text{(slow)}$$

show that it leads to

$$\frac{d(\text{product})}{dt} = \frac{k_2 k_1[A]^2}{k_{-1}[A] + k_2}$$

Under what conditions will the order of the reaction be equal to one?

(b) Given a first-order gaseous reaction. Is it possible to change it to a second order by changing the experimental conditions?

2.20 (a) What are chain reactions? The various elementary steps of chain reactions can be classified as follows?

Chain initiation step.
Chain propagation step.
Chain inhibition step.
Chain termination step.

Explain the above steps with appropriate examples.

(b) What do you understand by the following terms:

(i) Chain length

(ii) Stationary (or nonbranched) and nonstationary (or branched) chain reactions.

(c) In general, a chain reaction may be represented as follows:

$$A \xrightarrow{k_1} R^\bullet$$

$$R^\bullet + A \xrightarrow{k_2} P + \alpha R^\bullet$$

$$R^\bullet \xrightarrow{k_3} \text{destruction}$$

where $k_3 = k_w + k_g$. Show that the concentration of the radical is given by

$$[R^\bullet] = \frac{k_1[A]}{k_2(1-\alpha) + k_w + k_g}$$

(i) What is the value of α for stationary reactions?

(ii) For nonstationary reactions, α is greater than one. Under what conditions, does the concentration of radical $R^{\bullet}$ become infinite? What would happen when $R^{\bullet}$ becomes infinite? What are the first-, second- and third-explosion limits and under what conditions are these explosions observed?

2.21 Derive the differential rate law shown along with each of the following chain reactions.

(i) Reaction between H_2 and Br_2

$$Br_2 \xrightarrow{k_1} 2Br$$

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br$$

$$H + HBr \xrightarrow{k_4} H_2 + Br$$

$$Br + Br \xrightarrow{k_5} Br_2$$

$$\frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1+(k_4/k_3)[HBr]/[Br_2]}$$

(ii) Dehydrogenation of ethane

$$CH_3CH_3 \xrightarrow{k_1} 2{}^{\bullet}CH_3$$

$${}^{\bullet}CH_3 + CH_3CH_3 \xrightarrow{k_2} CH_4 + {}^{\bullet}CH_2CH_3$$

$${}^{\bullet}CH_2CH_3 \xrightarrow{k_3} CH_2=CH_2 + H^{\bullet}$$

$$H^{\bullet} + CH_3CH_3 \xrightarrow{k_4} H_2 + {}^{\bullet}CH_2CH_3$$

$$H^{\bullet} + {}^{\bullet}CH_2CH_3 \xrightarrow{k_5} CH_3CH_3$$

$$\frac{d[CH_2{=}CH_2]}{dt} = k\,[CH_3CH_3]$$

where k is given by

$$k = \frac{k_1k_5 + (k_1^2k_5^2 + 4k_1k_3k_4k_5)^{1/2}}{2k_5}$$

where k_1 is usually very small, show that the above expression may be simplified to

$$k = \left(\frac{k_1k_3k_4}{k_5}\right)^{1/2}$$

and further show that the chain length is given by

$$\text{Chain length} = \left(\frac{k_3k_4}{k_1k_5}\right)^{1/2}$$

(iii) Thermal decomposition of acetaldehyde

$$CH_3CHO \xrightarrow{k_1} {}^{\bullet}CH_3 + {}^{\bullet}CHO$$

$${}^{\bullet}CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + {}^{\bullet}CH_2CHO$$

$$^{\bullet}CH_2CHO \xrightarrow{k_3} {}^{\bullet}CH_3 + CO$$

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \xrightarrow{k_4} CH_3CH_3$$

$$\frac{d[CH_4]}{dt} = k\,[CH_3CHO]^{3/2}$$

where $k = k_2\,(k_1/2k_4)^{1/2}$.
Show that the chain length is given by

$$\frac{d[\text{product}]}{d[\text{initiation step}]/dt} = \left(\frac{k_2}{2k_1k_4}\right)^{1/2} [CH_3CHO]^{1/2}$$

(iv) Polymerization of vinyl derivatives

$$C \xrightarrow{k_1} R^{\bullet}$$

$$CH_2{=}CHX + R^{\bullet} \xrightarrow{k_2} RCH_2CHX^{\bullet}$$

$$RCH_2CHX^{\bullet} + CH_2{=}CHX \longrightarrow R(CH_2CHX)_2^{\bullet}$$

$$R(CH_2CHX)_n^{\bullet} + {}^{\bullet}(XHCCH_2)_n\,R \xrightarrow{k_3} R(CH_2CHX)_n\text{–}(XHCCH_2)_nR$$

where C acts as a catalyst. Show that

$$-\frac{d[CH_2{=}CHX]}{dt} = k_2\left(\frac{k_1}{k_3}\right)^{1/2} [C]^{1/2}\,[CH_2{=}CHX]$$

Number-average degree of polymerization $\bar{P}_N$ is given as

$$\bar{P}_N = \frac{k_2}{(k_1k_3)^{1/2}}\,\frac{[CH_2{=}CHX]}{[C]^{1/2}}$$

2.22 (a) What effect does temperature has on the rate of chemical reactions?

(b) Arrhenius equation is

$$k = A\,\exp(-E_a/RT)$$

Explain the term A and E_a involved in the above expression.

(c) What type of graph do you expect between log (k/k°) and $1/T$? What is its slope?

(d) Show that for a reversible reaction

$$\Delta E = E_{a(f)} - E_{a(b)}$$

where the symbols have their usual meanings.

(e) ΔE of a reaction varies with temperature. What about $E_{a(f)}$ and $E_{a(b)}$?

(f) For the reaction

$$2\,NO + O_2 \longrightarrow 2NO_2$$

the rate constant k is observed to decrease with temperature. Is it violation of the Arrhenius equation? Support your answer.

(g) The rate constant of thermal decomposition of ethane given in Problem 2.21 is given as

$$k = \left(\frac{k_1k_3k_4}{k_5}\right)^{1/2}$$

Following Arrhenius equation, show that the activation energy of the reaction is

$$E_a = \frac{1}{2}\,[E_{a1} + E_{a3} + E_{a4} - E_{a5}]$$

2.23 (a) Describe the collision theory of bimolecular gaseous reactions. Show that it leads to the rate expression

$$r = p\left\{\pi\sigma_{AB}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A^* N_B^*\right\}\exp(-E_0/RT)$$

Explain the significance of the term p in the above expression. The factor p is usually less than 1. Explain, why it is so.

(b) Compare the rate constants as given by Arrhenius equation and the collision theory and show that

$$E_a = E_0 + \frac{RT}{2}$$

$$A = pN_A\pi\,\sigma_{AB}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} e^{1/2}$$

$$= pN_A\,\frac{Z_{AB}}{N_A^* N_B^*}\,e^{1/2}$$

where the various symbols have their usual meanings.

2.24 (a) Describe the activated complex theory. Show that it leads to the rate expression

$$r = \left(K^{\ddagger}\frac{RT}{N_Ah}\right)[A][B]$$

where the various symbols have their usual meaning.

(b) Show that

$$k_2 = \frac{RT}{N_Ah}K^{\ddagger} = \frac{RT}{c^{\circ}N_Ah}\exp(-\Delta^{\ddagger}H^{\circ}/RT)\exp(\Delta^{\ddagger}S^{\circ}/R)$$

(c) Compare the rate constants as given by Arrhenius equation and the activated complex theory and show that

$$E_a = \Delta^{\ddagger}E^{\circ} + RT$$

$$E_a = \Delta^{\ddagger}H^{\circ} + (1 - \Delta^{\ddagger}\nu_g)\,RT$$

$$A = \frac{RT}{c^{\circ}N_Ah}\exp(\Delta^{\ddagger}S^{\circ}/R)\exp(1 - \Delta^{\ddagger}\nu_g)$$

$$= \nu_{vib}\exp(\Delta^{\ddagger}S^{\circ}/R)\exp(1 - \Delta^{\ddagger}\nu_g)$$

where ν_{vib} is the frequency of decomposition of the activated complex. What is the value of $\Delta^{\ddagger}\nu_g$ for a reaction involving only condensed phases?

(d) Compare the rate constants as given by collision theory and the activated complex theory and show that

$$E_0 = E^{\circ\ddagger} + \frac{1}{2}\,RT$$

$$pN_A\,\frac{Z_{AB}}{N_A^* N_B^*} = \nu_{vib}\exp(\Delta^{\ddagger}S^{\circ}/R)\exp[-(\Delta^{\ddagger}\nu_g - 1/2)]$$

(e) Comment on the following:

(i) The steric factor p of collision theory may be interpreted in terms of entropy of activation.

(ii) For most of reactions, entropy of activation is negative except of the type

$$AB \rightarrow AB^{\ddagger} \rightarrow A + B$$

where entropy of activation may be positive.

(f) Apply the activated complex theory for a reaction

$$A + B \rightleftharpoons C + D$$

at equilibrium and show that it leads to the thermodynamic expression

$$\Delta G^\circ = -RT \ln K^\circ_{eq}$$

How will you explain the fact that some reactions proceed with a very slow speed (or do not occur at all) even though ΔG° of the reaction is highly negative.

2.25 What is the effect of pressure on the rate constant?

2.26 What do you understand by the primary salt effect? Derive the relation

$$\ln (k/k^\circ) = \ln (k_0/k^\circ) + z_A z_B \sqrt{\mu / c^\circ}$$

2.27 (a) What is the effect of a catalyst on ΔH° and ΔG° of a reaction?

(b) What do you understand by homogeneous and heterogeneous catalysts?

(c) Show by drawing a potential energy diagram that the catalyst lowers the free energy of activation of forward and backward reactions without changing the overall free energy of the reaction.

(d) How do homogeneous and heterogeneous catalysts act?

2.28 Given below are the mechanisms of a few homogeneous catalyzed reactions. Derive the corresponding rate law shown along with.

(i) *Acid-base catalysis*

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+$$

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [S][HA]}{k_{-1}[A^-] + k_2}$$

Show under what conditions a given catalytic reaction may be classified into a general acid catalysis and a specific hydrogen-ion catalysis.

(ii) *Enzyme catalysis*

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} P + E$$

$$\left(\frac{d[P]}{dt}\right)_0 = r_0 = \frac{k_2[E]_0 [S]_0}{[S]_0 + K_M}$$

where $K_M = (k_2 + k_{-1})/k_1$ and is known as Michaelis-Menten constant. Also, answer the following:

(a) Show that the enzyme reaction is first-order and zero-order with respect to S at low and high concentrations of S, respectively.

(b) What type of a graph is expected between the initial rate and the initial substrate concentration?

(c) If $k_2 \ll k_{-1}$, then K_M represents the dissociation constant for the enzyme-substrate complex.

(d) The rate expression given above can be written as

$$\frac{1}{r_0} = \frac{1}{r_{\max}} + \frac{K_M}{r_{\max}[S]_0}$$

$$\frac{r_0}{[S]_0} = \frac{r_{\max}}{K_M} - \frac{r_0}{K_M}$$

What types of graphs are expected between $1/r_0$ and $1/[S]_0$, and $r_0/[S]$ and r_0?

Show how these plots help in deriving the values of $r_{\max}$ and K_M.

(e) What type of the potential energy diagram is expected for the mechanism of enzyme-catayzed reaction given above?

2.29 What are enzyme inhibitors? Derive the rate expressions for the following types of inhibitors:

(i) Fully competitive inhibition.
(ii) Partially competitive inhibition.
(iii) Fully noncompetitive inhibition.
(iv) Partially noncompetitive inhibition.
(v) Uncompetitive inhibition.

Write the expressions in the Linearweaver-Burk form and draw the plots between $1/r_0$ and $1/[S]_0$. What are their slopes and intercepts? Compare these with those of normal enzyme reaction.

2.30 Explain how Langmuir and Hinshelwood theory can account for the rate of the following types of surface catalyzed reactions. Derive the corresponding rate expression shown along with and discuss the limiting cases of the rate expression.

(i) *Unimolecular surface reaction*

$$A + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AS$$

$$AS \xrightarrow{k_2} \text{products}$$

$$\frac{1}{r} = \frac{1}{k_2} + \frac{k_{-1}+k_2}{k_2 k_1}\frac{1}{p_A}$$

(ii) *Bimolecular surface reaction*

$$A + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AS$$

$$B + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} BS$$

$$AS + BS \xrightarrow{k_3} \text{products}$$

$$r = \frac{k_3 K_1 K_2 p_A p_B}{(1 + K_1 p_A + K_2 p_B)^2}$$

2.31 (a) Show that for the unimolecular surface reaction: (i) order with respect to the reactant is first-order if the reactant is slightly adsorbed, (ii) zero-order if it is strongly adsorbed, and (iii) fractional order if it is moderately adsorbed.

(b) Support the following statements:

(i) The lowering of free energy of activation in the unimolecular surface reactions is largely due to the lowering of activation energy if the reactant is slightly adsorbed.

(ii) The apparent energy of activation equals to the true energy of activation if the reactant is strongly adsorbed.

(iii) For a bimolecular surface reaction, there may be an increase instead of lowering of energy of activation if one of the components is very strongly adsorbed.

TRY YOURSELF PROBLEMS

2.1 (a) For the hypothetical reaction

$$5A + 8B \rightarrow 6C + 12D$$

set up the differential rate expression in terms of disappearance of A and B and appearance of C and D. Given that the reaction is first-order with respect to each of A and B.

(b) For the reaction given in part (a), the following equalities have been established. What are the relations between the various *k*s?

$$-\frac{1}{k}\frac{d[A]}{dt} = -\frac{1}{k'}\frac{d[B]}{dt} = \frac{1}{k''}\frac{d[C]}{dt} = \frac{1}{k'''}\frac{d[D]}{dt}$$

(c) For each of the following rate laws, write the stoichiometric equation for the reaction

(i) $\frac{dx}{dt} = k\,(a - x)^2\,(b - x)$

(ii) $\frac{dx}{dt} = k\,(a - 2x)^2\,(b - x)$

(iii) $\frac{dx}{dt} = k\,(a - x)\,(b - x/2)$

(iv) $\frac{dx}{dt} = kb\,(a - x)$

(v) $\frac{dx}{dt} = k\,(a - x)\,(b + x)$

(d) For each of the following reactions express the rate of change of concentration of the reactants and products given in terms of the rate of change of concentration of the other reactants or products in that reaction.

(i) $N_2 + 3H_2 = 2NH_3$; $\quad -\frac{d[H_2]}{dt} = ?$

(ii) $H_2 + \frac{1}{2}O_2 = H_2O$; $\quad \frac{d[H_2O]}{dt} = ?$

(iii) $H_2O_2 + 2H^+ + 3I^- = I_3^- + 2H_2O$; $\quad -\frac{d[I^-]}{dt} = ?$

2.2 (a) Show that for a first-order reaction, the concentration of the reactant A after n half-life times is given by

$$[\mathrm{A}]_n = [\mathrm{A}]_0 \left(\frac{1}{2}\right)^n$$

(b) Show that Eq. (2.6.1), i.e.

$$n = \frac{\log\left[\left(t_{\frac{1}{2}}\right)_1 / \left(t_{\frac{1}{2}}\right)_2\right]}{\log\left([\mathrm{A}]_{02}/[\mathrm{A}]_{01}\right)} + 1$$

is, in fact, applicable for the time required to complete any fraction of reaction (say 1/4, 10%, etc.); the only change to be made is to put corresponding t instead of $t_{0.5}$.

2.3 (a) The mean life-time of a reaction is defined as

$$\langle t \rangle = \int_{[\mathrm{A}]_0}^{[\mathrm{A}]_\infty} t\,\mathrm{d}[\mathrm{A}] \Bigg/ \int_{[\mathrm{A}]_0}^{[\mathrm{A}]_\infty} \mathrm{d}[\mathrm{A}]$$

Show that for the first-order reaction (stoichiometric $\nu = 1$) if $[\mathrm{A}]_\infty$ is taken to be zero, the mean life-time is given by

$$\langle t \rangle = \frac{1}{k}$$

(b) Show also that the mean life-time $\langle t \rangle$ is equal to the time taken for the concentration of A to drop from $[\mathrm{A}]_0$ to $[\mathrm{A}]_0/\mathrm{e}$, where e is the natural number 2.718. Given the standard integral

$$\int_0^\infty t \exp(-kt)\,\mathrm{d}t = 1/k^2.$$

2.4 (a) In a first-order gaseous reaction

$$4\mathrm{A(g)} \rightarrow \mathrm{B(g)} + 6\mathrm{C(g)}$$

Derive the expression

$$\ln\left(\frac{3p_0}{4p_0 - p}\right) = kt$$

where p_0 and p are total pressure of the system at $t = 0$ and $t = t$.

(b) Show that for a first-order reaction, the time required for 99.9 per cent completion is three times than that required for the completion of 50 per cent of the reaction. By what factor would the time change if the reaction were of the (i) second-order, (ii) zero-order, and (iii) –1-order.

2.5 Using Eq. (2.5.9), show that for the first-order reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$

the concentration of B is given by

$$[\mathrm{B}] = [\mathrm{A}]_0 \{1 - \exp(-k_1 t)\}$$

2.6 Using Eq. (2.5.30), show that for second-order reaction

$$\begin{array}{lcc} & 2\mathrm{A} \xrightarrow{k_2} & \mathrm{B} \\ t = 0 & [\mathrm{A}]_0 & [\mathrm{B}]_0 \\ t = t & [\mathrm{A}] & [\mathrm{B}] \end{array}$$

the concentration of B is given by

$$[\mathrm{B}] = [\mathrm{B}]_0 + [\mathrm{A}]_0 \left\{1 - \frac{1}{1+2k_2t[\mathrm{A}]_0}\right\}$$

2.7 Show that for the second-order reaction

$$\begin{array}{lccc} & \mathrm{A} + \mathrm{B} & \xrightarrow{k_2} & \mathrm{C} \\ t=0 & [\mathrm{A}]_0 \quad [\mathrm{B}]_0 & & 0 \end{array}$$

the concentration of C is given by

$$[\mathrm{C}] = \left(\frac{[\mathrm{A}]_0[\mathrm{B}]_0\{1-\exp(-k_2([\mathrm{B}]_0-[\mathrm{A}]_0)t)\}}{[\mathrm{B}]_0-[\mathrm{A}]_0\{\exp(-k_2([\mathrm{B}]_0-[\mathrm{A}]_0)t)\}}\right)$$

2.8 Using Eq. (2.5.43), show that for a third-order reaction

$$2\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$$

the concentration of C is given by

$$[\mathrm{C}] = \frac{[\mathrm{A}][\mathrm{B}]_0}{2(2[\mathrm{B}]_0-[\mathrm{A}]_0)}\left[(2[\mathrm{B}]_0-[\mathrm{A}]_0)^2kt + \ln\left(\frac{[\mathrm{A}]_0[\mathrm{B}]}{[\mathrm{B}]_0[\mathrm{A}]}\right)\right]$$

2.9 Using Eq. (2.5.45) show that for a third-order reaction

$$\mathrm{A} \rightarrow \text{product}$$

the concentration of A is given by

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{(1+2k[\mathrm{A}]_0^2t)^{1/2}}$$

2.10 Consider the reversible reaction of first-order opposed by first-order:

$$\begin{array}{lcc} & \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & \mathrm{B} \\ t=0 & [\mathrm{A}]_0 & [\mathrm{B}]_0 \\ t=t & [\mathrm{A}] & [\mathrm{B}] \end{array}$$

If the relationship $[\mathrm{B}]-[\mathrm{B}]_0=[\mathrm{A}]_0-[\mathrm{A}]$ holds good, show that

$$[\mathrm{A}] = \left(\frac{[\mathrm{B}]_0+[\mathrm{A}]_0}{(1+k/k_{-1})}\right) - \left(\frac{[\mathrm{B}]_0-(k_1/k_{-1})[\mathrm{A}]_0}{(1+k/k_{-1})}\right)\exp\{-(k_1+k_{-1})t\}$$

$$[\mathrm{B}] = \left(\frac{[\mathrm{B}]_0+[\mathrm{A}]_0}{(1+k_{-1}/k_1)}\right) - \left(\frac{[\mathrm{A}]_0-(k_{-1}/k_1)[\mathrm{B}]_0}{(1+k_{-1}/k_1)}\right)\exp\{-(k_1+k_{-1})t\}$$

2.11 Using Eqs (2.11.5a) and (2.11.5c) show that

$$k_1 = \frac{1}{t}\ln\left(1+\frac{[\mathrm{B}]}{[\mathrm{A}]}+\frac{[\mathrm{C}]}{[\mathrm{A}]}\right)$$

2.12 For the following parallel reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{C}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

show that

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t)$$

$$[\mathrm{B}] = [\mathrm{B}]_0 \exp(-k_2 t)$$

$$[\mathrm{C}] = [\mathrm{A}]_0 \{1 - \exp(-k_1 t)\} + [\mathrm{B}]_0 \{1 - \exp(-k_2 t)\}$$

2.13 For the following parallel first-order reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{C}$$

$$\mathrm{A} \xrightarrow{k_3} \mathrm{D}$$

show that

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp\{-(k_1 + k_2 + k_3)t\} = [\mathrm{A}]_0 \exp(-kt)$$

$$[\mathrm{B}] = [\mathrm{B}]_0 + \frac{k_1 [\mathrm{A}]_0}{k} \{1 - \exp(-kt)\}$$

$$[\mathrm{C}] = [\mathrm{C}]_0 + \frac{k_2 [\mathrm{A}]_0}{k} \{1 - \exp(-kt)\}$$

$$[\mathrm{D}] = [\mathrm{D}]_0 + \frac{k_3 [\mathrm{A}]_0}{k} \{1 - \exp(-kt)\}$$

2.14 For the following parallel reactions of first- and second-order

$$\mathrm{A} \xrightarrow{k_1} \text{product}$$

$$\mathrm{A} + \mathrm{A} \xrightarrow{k_2} \text{product}$$

write down the differential rate expression and then derive from it the integrated rate expression.

$$\left[\textbf{Ans.}\ \frac{\mathrm{d}x}{\mathrm{d}t} = k_1([\mathrm{A}_0] - x) + 2k_2([\mathrm{A}]_0 - x)^2; \right.$$

$$\left. \ln \frac{[\mathrm{A}]_0 [k_1 + 2k_2([\mathrm{A}]_0 - x)]}{([\mathrm{A}]_0 - x)(k_1 + 2k_2[\mathrm{A}]_0)} = k_1 t \right]$$

(***Hint:*** Write the differential rate law as

$$\frac{\mathrm{d}x}{([\mathrm{A}]_0 - x)[k_1 + k_2([\mathrm{A}]_0 - x)]} = \mathrm{d}t$$

resolve into partial fractions and integrate the resultant expression.)

2.15 For the following parallel first- and second-order reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{D} + \mathrm{E}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} \mathrm{C} + \mathrm{D}$$

Write down the differential rate expression and then derive from it the integrated rate expression.

$$\left[\textbf{Ans.}\ \frac{\mathrm{d}x}{\mathrm{d}t} = k_1([\mathrm{A}_0] - x) + k_2([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x) \right.$$

$$\left. \frac{1}{([\mathrm{B}]_0 - [\mathrm{A}]_0) + k_1/k_2} \left\{ \ln \left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x} \right) \left(\frac{([\mathrm{B}]_0 - x) + k_1/k_2}{[\mathrm{B}]_0 + k_1/k_2} \right) = k_2 t \right\} \right]$$

2.16 The value of $\Delta^{\ddagger}S$ for the unimolecular decomposition of isopropyl nitrite in the gas phase is small and positive. Can you explain this?

2.17 Show that the proposed mechanism of

$$2Br^- + H_2O_2 + 2H^+ \longrightarrow Br_2 + 2H_2O$$

leads to the same rate law when written as

$$-\frac{1}{2}\,d[Br^-]/dt \quad \text{or} \quad -\,d[H_2O_2]/dt \quad \text{or} \quad -\frac{1}{2}\,d[H^+]/dt.$$

The mechanism is

$$Br^- + H_2O_2 + H^+ \xrightarrow{k_1} HOBr + H_2O$$

$$HOBr + H^+ + Br^- \xrightarrow{k_2} Br_2 + H_2O$$

2.18 For the reaction

$$2NO + O_2 \longrightarrow 2NO_2$$

Two mechanisms have been proposed:

(i) $NO + NO \underset{}{\overset{K_1}{\rightleftharpoons}} N_2O_2$ (fast, at equilibrium)

$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ (slow)

(ii) $NO + O_2 \overset{K_1}{\rightleftharpoons} NO_3$ (fast, at equilibrium)

$NO + NO_3 \xrightarrow{k_2} 2NO_2$ (slow)

Show that both the mechanisms lead to the same rate law

$$-\frac{d[O_2]}{dt} = k\,[NO]^2\,[O_2]$$

2.19 An endothermic reaction has a positive internal energy change ΔU. In such a case, what is the minimum value that the activation energy can have?

2.20 Given an exothermic reaction, what effect will an increase in temperature have on (i) the amount of product formed, and (ii) the time required for the same amount of product as that at lower temperature.

2.21 (a) For the reaction

$$Hg_2^{2+} + Tl^{3+} = 2Hg^{2+} + Tl^+$$

the rate law is

$$\left(-\frac{d[Tl^{3+}]}{dt} = k\frac{[Hg_2^{2+}][Tl^{3+}]}{[Hg^{2+}]}\right)$$

Devise a mechanism that gives such a law. A rate law with inverse dependence on a particular concentration occurs when the substance is the product of a reversible step prior to the rate determining reaction.

(b) A proposed mechanism for the reaction

$$2Cr^{6+} + 3As^{3+} = 2Cr^{3+} + 3As^{5+}$$

is the following:

$$Cr^{6+} + As^{3+} \overset{K_{eq1}}{\rightleftharpoons} Cr^{4+} + As^{5+}$$

$$Cr^{4+} + Cr^{6+} \overset{K_{eq2}}{\rightleftharpoons} 2Cr^{5+}$$

$$Cr^{5+} + As^{3+} \overset{K_{eq3}}{\rightleftharpoons} Cr^{3+} + As^{5+}$$

The observed rate law is

$$r = k_{app}\,[Cr^{6+}]\,[As^{3+}]$$

What are possible rate laws for the reverse reaction?

2.22 Predict the effect of increase in ionic strength on the rate constant for each of the following reactions:

(a) $[Pr(NH_3)_3Cl]^+ + NO_2^-$

(b) $[PtCl]_4^{2-} + OH^-$

(c) $Pt(NH_3)_2Cl_2 + OH^-$

[**Ans.** (a) decrease, (b) increase, (c) no effect]

2.23 What conclusion can be reached about adsorption on the surface from each of the following facts:

(a) The rate of decomposition of HI on platinum is proportional to the concentration of HI.

(b) On gold, the rate of decomposition of HI is independent of the pressure of HI.

(c) On platinum, the rate of the reaction $SO_2 + (1/2)O_2 \rightarrow SO_3$ is inversely proportional to the pressure of SO_3.

(d) On platinum the rate of the reaction $CO_2 + H_2 \rightarrow H_2O + CO$ is proportional to the pressure of CO_2 at low CO_2 pressure and is inversely proportional to the pressure of CO_2 at high CO_2 pressures.

(e) The decomposition of NH_3 on W is zero-order.

(f) The decomposition of N_2O on Au is first-order.

(g) The recombination of H atoms on Au is second-order.

(h) The decomposition rate of NH_3 on Pt is proportional to p_{NH_3}/p_{H_2}.

(i) The decomposition rate of NH_3 on Mo is strongly retarded by N_2 but does not approach zero as the surface becomes saturated with N_2.

(j) The rate of $2SO_2 + O_2 \rightarrow 2SO_3$ on Pt is $k_1[SO_2]/[SO_3]^{1/2}$ when O_2 is in excess.

[**Ans.** (a) HI is weakly adsorbed. (b) HI is strongly adsorbed. (c) SO_3 is strongly adsorbed. (d) CO_2 is weakly adsorbed at low *p*, strongly at high *p*. (e) NH_3 is strongly adsorbed on W, surface completely covered. (f) N_2O is weakly adsorbed on Au, linear region of Langmuir isotherm. (g) H atoms are weakly adsorbed and rate is proportional to collisions of two H atoms on the surface or of a gaseous H atom with surface H atom. (h) Product H_2 is strongly, and reactant NH_3 is weakly adsorbed. (i) Product N_2 is strongly adsorbed but adsorption coefficient decreases with surface coverage so that N_2 and NH_3 can compete for available surface when it is nearly covered with N_2. (j) The surface is covered to great extent by adsorbed oxygen so that the reaction is zero-order with respect to O_2. The SO_2 and SO_3 compete for remaining surface, with the SO_3 being adsorbed more strongly than SO_2 but less than O_2.]

2.24 Studies of the reaction $C_6H_6 + 3H_2 \rightleftharpoons C_6H_{12}$ show that the forward reaction is first-order with respect to each of C_6H_6 and H_2. What is the rate expression for the reverse reaction?

[**Ans.** $r_b = k_b\,[C_6H_{12}]/[H_2]^2$]

2.25 Given the following information:

$$C_2H_4 + H_2 \rightarrow C_2H_6 \qquad \Delta E^\circ = -\,125.52 \text{ kJ mol}^{-1}$$

$$r_f = k_f\,[H_2] \qquad \text{holds everywhere}$$

(a) Write the expression for the reverse rate at equilibrium.

(b) If the temperature is increased, does the forward rate constant k_f or the reverse rate constant k_b increase more percentagewise?

(c) If the activation energy is 117.16 kJ mol^{-1} for the forward reaction, what is the activation energy for the reverse reaction?

(d) If a catalyst is added, the activation energy for the forward direction drops to 44.77 kJ mol^{-1}. What is the activation energy for the reverse rate of the catalyzed reaction?

(e) The use of a catalyst speeds up forward rate by a factor of ten million. By what factor does the reverse rate increase?

(f) The equilibrium constant at 773 K is 10^5. What is it (approximately) at 873 K?

(g) What is the value of equilibrium constant at 773 K in the presence of the catalyst of part (c)?

[**Ans.** (b) k_b, (c) 242.68 kJ mol^{-1}, (d) 170.30 kJ mol^{-1}]

2.26 Work out the following problems on reaction mechanisms.

1. The following mechanism has been suggested for the pyrolysis of diborane:

$$B_2H_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2BH_3 \qquad \text{(fast)}$$

$$BH_3 + B_2H_6 \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \text{Intermediate hydride} + H_2$$

$$\text{Intermediate hydride} + B_2H_6 \xrightarrow{k_4} \text{Higher hydrides}$$

(a) Show that the above mechanism leads to the following rate law:

$$-\frac{d[B_2H_6]}{dt} = \frac{2k_2(k_4/k_3)K_1^{1/2}[B_2H_6]^{5/2}}{(k_4/k_3)[B_2H_6]+H_2}$$

(b) Initial rate law expression is

$$-\left(\frac{d[B_2H_6]}{dt}\right)_0 = k_2\,K_1^{1/2}\,[B_2H_6]^{3/2} = k'\,[B_2H_6]^{3/2}$$

The value of k' were found to be 8.6×10^{-5} and 5.8×10^{-2} $\text{dm}^{3/2}\,\text{mol}^{-1/2}\,\text{s}^{-1}$ at 358 K and 436.5 K, respectively. Calculate the apparent activation energy of the reaction.

(c) Show that the apparent activation energy is given by

$$E_a = E_2 + \frac{1}{2}\,\Delta H_1$$

where ΔH_1 is the dissociation energy of B_2H_6. If the latter has a value of 35 kcal mol^{-1}, what is the value of E_2?

[**Ans.** (b) 108.79 kJ mol^{-1}, (c) 35.57 kJ mol^{-1}]

2. The following mechanism has been suggested for the thermal decomposition of NO_2.

Overall reaction: $2NO_2 \rightarrow 2NO + O_2$

Mechanism

$$NO_2 + NO_2 \xrightarrow{k_1} NO + NO + O_2$$

$$NO_2 + NO_2 \xrightarrow{k_2} NO_3 + NO$$

$$NO_3 + NO \xrightarrow{k_3} 2NO_2$$

$$NO_3 + NO_2 \xrightarrow{k_4} NO + O_2 + NO_2$$

Show that the above mechanism leads to the following rate law:

$$-\frac{d[NO_2]}{dt} = 2\,k_d\,[NO_2]^2$$

where

$$k_d = k_1 + \frac{k_2 k_4\,[NO_2]}{k_3[NO] + k_4[NO_2]}$$

3. The thermal decomposition of H_2O_2 proceeds according to the reaction

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

and follows the rate law

$$\frac{d[H_2O_2]}{dt} = -\,k_{\text{homo}}\,[H_2O_2]$$

Show that the following mechanism accounts for the above rate law:

$$H_2O_2 + M \xrightarrow{k_1} 2OH + M$$

$$OH + H_2O_2 \xrightarrow[k_2]{\text{fast}} H_2O + HO_2$$

$$HO_2 + HO_2 \xrightarrow{k_3} H_2O_2 + O_2$$

$$HO_2 + OH \xrightarrow{k_4} H_2O + O_2$$

4. The following mechanism has been suggested for the pyrolysis of monosilane.

$$SiH_4 \xrightarrow{k_1} SiH_3 + H^\bullet$$

$$H^\bullet + SiH_4 \xrightarrow{k_2} SiH_3^\bullet + H_2$$

$$SiH_3^\bullet + SiH_4 \xrightarrow{k_3} Si_2H_6 + H^\bullet$$

$$2SiH_3^\bullet \xrightarrow{k_4} Si_2H_6$$

Show that

$$\frac{d[H_2]}{dt} = \frac{d[Si_2H_6]}{dt} = \left[k_3\left(\frac{k_1}{k_4}\right)^{1/2}[SiH_4]^{1/2} + k_1\right][SiH_4]$$

5. The reaction for the thermal decomposition of HNO_3 in the presence of NO is

$$2HNO_3 + NO \rightarrow 3NO_2 + H_2O$$

and the proposed mechanism is

$$HNO_3 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} OH + NO_2 + M$$

$$OH + HNO_3 \xrightarrow{k_2} H_2O + NO_3$$

$$NO_3 + NO_2 \xrightarrow{k_3} NO_2 + NO + O_2$$

$$NO_3 + NO \xrightarrow{k_4} 2NO_2$$

$$OH + NO + HNO_3 \xrightarrow{k_5} H_2O + 2NO_2$$

Show that the reaction scheme leads to the rate expression

$$-\frac{d[HNO_3]}{dt} = \frac{2\,k_1\,[M][HNO_3]^2\,(k_2 + k_5\,[NO])}{k_{-1}[NO_2][M] + k_2\,[HNO_3] + k_5\,[NO][HNO_3]}$$

Show that in the presence of excess of NO, the reaction is first order in HNO_3 and zero-order in NO.

6. (a) The following mechanism has been suggested for the reaction involving F_2, O_2 and H_2.

$$F_2 + M \xrightarrow{k_1} 2F^\bullet + M$$

$$F^\bullet + H_2 \xrightarrow{k_2} HF + H^\bullet$$

$$H^\bullet + F_2 \xrightarrow{k_3} HF + F^\bullet$$

$$H^\bullet + O_2 + M \xrightarrow{k_4} HO_2^\bullet + M$$

$$HO_2^\bullet + F_2 \xrightarrow{k_5} HF + O_2 + F^\bullet$$

$$HO_2^\bullet + F^\bullet \xrightarrow{k_6} HF + O_2$$

Assuming that $k_4\,[O_2] \gg k_1\,[F_2]$, show that

$$-\frac{d[F_2]}{dt} = \left(\frac{k_1\,k_2\,k_5}{k_6}\right)^{1/2}\left(\frac{k_3\,[F_2] + k_4\,[O_2][M]}{k_4\,[O_2][M]}\right)^{1/2}[F_2]\,[H_2]^{1/2}\,[M]^{1/2}$$

At large $[O_2]$, the above expression becomes

$$-\frac{d[F_2]}{dt} = \left(\frac{k_1k_2k_5}{k_6}\right)^{1/2}[M]^{1/2}\,[H_2]^{1/2}\,[F_2]$$

(b) An alternate mechanism suggested for the reaction involving F_2, O_2, and H_2 is

$$F_2 + M \xrightarrow{k_1} 2F + M$$

$$F + O_2 + M \xrightarrow{k_2} FO_2 + M$$

$$H_2 + FO_2 \xrightarrow{k_3} HF + O_2 + H$$

$$H + F_2 \xrightarrow{k_4} HF + F$$

$$H + O_2 + M \xrightarrow{k_5} HO_2 + M$$

$$\mathrm{HO_2 + F_2 \xrightarrow{k_6} HF + O_2 + F}$$
$$\mathrm{FO_2 + HO_2 \xrightarrow{k_7} HF + 2O_2}$$

Assuming $k_7\,[\mathrm{FO_2}] \ll k_6\,[\mathrm{F_2}]$, show that it leads to

$$-\frac{\mathrm{d}[\mathrm{F_2}]}{\mathrm{d}t} = \left(\frac{k_1k_3k_6}{k_7}\right)^{1/2}\left(\frac{k_4\,[\mathrm{F_2}] + k_5\,[\mathrm{O_2}][\mathrm{M}]}{k_5\,[\mathrm{O_2}][\mathrm{M}]}\right)^{1/2}[\mathrm{M}]^{1/2}\,[\mathrm{H_2}]^{1/2}\,[\mathrm{F_2}].$$

which in the limit of large $\mathrm{O_2}$ becomes

$$-\frac{\mathrm{d}[\mathrm{F_2}]}{\mathrm{d}t} = \left(\frac{k_1k_3k_6}{k_7}\right)^{1/2}[\mathrm{M}]^{1/2}\,[\mathrm{H_2}]^{1/2}\,[\mathrm{F_2}]$$

7. (a) The thermal decomposition of $\mathrm{N_2O_5}$ follows the mechanism:

$$\mathrm{N_2O_5 \xrightarrow{k_1} NO_2 + NO_3}$$
$$\mathrm{NO_3 + NO_2 \xrightarrow{k_2} N_2O_5}$$
$$\mathrm{NO_3 + NO_2 \xrightarrow{k_3} NO_2 + O_2 + NO}$$
$$\mathrm{NO + NO_3 \xrightarrow{k_4} 2NO_2}$$

Show that

$$-\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = \frac{2k_1k_3}{k_2 + 2k_3}\,[\mathrm{N_2O_5}]$$

If $k_2 \gg k_3$, then

$$-\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = 2k_3\,\frac{k_1}{k_2}\,[\mathrm{N_2O_5}]$$

(b) In the presence of NO, the mechanism is

$$\mathrm{N_2O_5 \xrightarrow{k_1} NO_3 + NO_2}$$
$$\mathrm{NO_3 + NO_2 \xrightarrow{k_2} N_2O_5}$$
$$\mathrm{NO_3 + NO \xrightarrow{k_3} 2NO_2}$$

Show that

$$-\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = \frac{k_1[\mathrm{N_2O_5}]}{1 + \{k_2[\mathrm{NO_2}]/k_3[\mathrm{NO}]\}}$$

In the presence of excess of NO the above expression becomes

$$-\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = k_1\,[\mathrm{N_2O_5}]$$

8. The conversion of $\mathrm{O_3}$ to $\mathrm{O_2}$ in the gas phase is catalyzed by $\mathrm{N_2O_5}$. The rate law is

$$-\frac{\mathrm{d}[\mathrm{O_3}]}{\mathrm{d}t} = k[\mathrm{N_2O_5}]^{2/3}[\mathrm{O_3}]^{2/3}$$

The proposed mechanism is

$$\mathrm{N_2O_5 \xrightarrow{k_1} NO_2 + NO_3}$$
$$\mathrm{NO_3 + NO_2 \xrightarrow{k_2} N_2O_5}$$
$$\mathrm{NO_2 + O_3 \xrightarrow{k_3} NO_3 + O_2}$$
$$\mathrm{2NO_3 \xrightarrow{k_4} NO_2 + O_2 + NO_2}$$

Applying steady-state approximation for NO_2 and NO_3, show that

$$-\frac{d[O_3]}{dt} = \left\{2\left(\frac{k_1}{k_2}\right)^2 k_3^2 k_4\right\}^{1/3} [N_2O_5]^{2/3} [O_3]^{2/3}$$

9. The following mechanisms were proposed for the reaction between Cl_2 and O_3 at 308 K and 323 K.

(a)

$$Cl_2 + O_3 \xrightarrow{k_1} ClO + ClO_2$$
$$ClO_2 + O_3 \xrightarrow{k_2} ClO_3 + O_2$$
$$ClO_3 + O_3 \xrightarrow{k_3} ClO_2 + 2O_2$$
$$2ClO_3 \xrightarrow{k_4} Cl_2 + 3O_2$$
$$2ClO \xrightarrow{k_5} Cl_2 + O_2$$

Applying steady-state approximation to ClO_2 and ClO_3, show that

$$-\frac{d[O_3]}{dt} = 2k_1 [Cl_2][O_3] + k_3 \left(\frac{2k_1}{k_4}\right)^{1/2} [Cl_2]^{1/2} [O_3]^{3/2}$$

(b)

$$Cl_2 + O_3 \xrightarrow{k_1} ClO + ClO_2$$
$$ClO_2 + O_3 \xrightarrow{k_2} ClO + 2O_2$$
$$ClO + O_3 \xrightarrow{k_3} ClO_2 + O_2$$
$$2ClO \xrightarrow{k_4} Cl_2 + O_2$$

Applying steady-state approximation to ClO and ClO_2, show that

$$-\frac{d[O_3]}{dt} = 2\,[O_3]\left\{k_1[Cl_2] + k_3\left(\frac{k_1}{k_4}[Cl_2][O_3]\right)^{1/2}\right\}$$

For the long chains, the expression reduces to

$$-\frac{d[O_3]}{dt} = 2k_3 \left(\frac{k_1}{k_4}\right)^{1/2} [Cl_2]^{1/2} [O_3]^{3/2}$$

(c)

$$Cl_2 + O_3 \xrightarrow{k_1} ClO + ClO_2$$
$$ClO_2 + O_3 \xrightarrow{k_2} ClO_3 + O_2$$
$$ClO_3 + O_3 \xrightarrow{k_3} ClO_2 + 2O_2$$
$$2ClO_3 \xrightarrow{k_4} 2ClO_2 + O_2$$
$$2ClO_3 \xrightarrow{k_5} ClO_4 + ClO_2$$
$$2ClO_3 \xrightarrow{k_6} Cl_2 + 3O_2$$
$$ClO_4 + ClO_3 \xrightarrow{k_7} Cl_2O_7$$
$$2ClO \xrightarrow{k_8} Cl_2 + O_2$$

Show that

$$-\frac{d[O_3]}{dt} = k_1[Cl_2][O_3]\left(2+\frac{2k_4+k_5}{2(k_5+k_6)}\right)$$

$$+\ 2k_3\left(\frac{k_1}{2(k_5+k_6)}\right)^{1/2}[Cl_2]^{1/2}[O_3]^{3/2}$$

For long chains, the expression reduces to

$$-\frac{d[O_3]}{dt} = k_3\left(\frac{2k_1}{k_5}\right)^{1/2}[Cl_2]^{1/2}[O_3]^{3/2}$$

10. The effect of adding N_2O_5 to the reaction

$$NOCl + O_3 = NO_2Cl + O_2$$

was studied and the mechanism proposed is

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$
$$NO_3 + NO_2 \xrightarrow{k_2} N_2O_5$$
$$NO_2 + O_3 \xrightarrow{k_3} NO_3 + O_2$$
$$NOCl + NO_3 \xrightarrow{k_4} NO_2Cl + NO_2$$

Show that it leads to

$$-\frac{d[NOCl]}{dt} = \left(\frac{k_1k_3k_4}{k_2}\right)^{1/2}[NOCl]^{1/2}[O_3]^{1/2}[N_2O_5]^{1/2}$$

11. For the reaction

$$H_2 + NO_2 \longrightarrow H_2O + NO$$

the suggested mechanism is

$$H_2 + NO_2 \xrightarrow{k_1} H + HNO_2$$
$$H + NO_2 \xrightarrow{k_2} NO + OH$$
$$OH + H_2 \xrightarrow{k_3} H_2O + H$$
$$OH + NO_2 + M \xrightarrow{k_4} HNO_3 + M$$
$$OH + NO + M \xrightarrow{k_5} HNO_2 + M$$

State the approximations at which the rate law would be given by

$$-\frac{d[NO_2]}{dt} = \frac{k_1k_3[NO_2][H_2]^2}{k_4[NO_2][M]+k_5[NO][M]}$$

12. The rate of attachment of gaseous electrons to NO_2 has been found to follow the rate law

$$-\frac{d[e^-]}{dt} = k[NO_2][e^-]$$

The proposed mechanism is

$$NO_2 + e^- \xrightarrow{k_1} (NO_2^-)^*$$
$$(NO_2^-)^* \xrightarrow{k_2} NO_2 + e^-$$

$$(NO_2^-)^* + M \xrightarrow{k_3} NO_2^- + M$$

$$(NO_2^-)^* + M \xrightarrow{k_4} NO_2 + M + e^-$$

Applying steady-state concentration to $(NO_2^-)^*$, show that

$$-\frac{d[e^-]}{dt} = \frac{k_1k_3[NO_2][M][e^-]}{k_2 + (k_3 + k_4)[M]}$$

Under what condition does the above expression reduce to the experimentally found rate law?

13. The thermal decomposition of NO at higher temperature is catalyzed by oxygen. The proposed mechanism is

$$2NO \xrightarrow{k_1} N_2 + O_2$$

$$O + NO \xrightarrow{k_2} O_2 + N$$

$$N + O_2 \xrightarrow{k_3} O + NO$$

$$NO + N \xrightarrow{k_4} N_2 + O$$

$$O + O \xrightarrow{k_5} O_2$$

$$O_2 \xrightarrow{k_6} O + O$$

Show that it leads to

$$-\frac{d[NO]}{dt} = k_1[NO]^2 + \frac{2k_2 K[NO_2][O]^{1/2}}{1 + (k_3[O_2]/k_4[NO])}$$

where $\quad K = \sqrt{k_6/k_5}$

14. For the thermal decomposition of N_2O, the proposed mechanism is

$$N_2O \xrightarrow{k_1} N_2 + O$$

$$O + O + M \xrightarrow{k_2} O_2 + M$$

$$O + N_2O \xrightarrow{k_3} N_2 + O_2$$

$$O + N_2O \xrightarrow{k_4} 2\,NO$$

Derive the rate law.

15. The reaction between H_2O_2 and nitrous acid in acidic medium follows the rate law

$$\frac{d[HOONO]}{dt} = \frac{K k_1[H^+][HNO_2]}{\{k_{-1}[H_2O]/k_2[H_2O_2]\} + 1}$$

Show that the following mechanism is consistent with the above rate law.

$$H^+ + HNO_2 \underset{}{\overset{K}{\rightleftharpoons}} H_2NO_2^+ \qquad \text{(fast)}$$

$$H_2NO_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO^+ + H_2O$$

$$NO^+ + H_2O_2 \xrightarrow{k_2} HOONO + H^+$$

16. The oxidation of hypophosphorus acid (H_3PO_2) and of phosphorous acid (H_3PO_3)

by $S_2O_8^{2-}$ have been studied. The reactions are

$$H_3PO_2 + S_2O_8^{2-} + H_2O \rightarrow H_3PO_3 + 2H^+ + 2SO_4^{2-}$$

$$H_3PO_3 + S_2O_8^{2-} + H_2O \rightarrow H_3PO_4 + 2H^+ + 2SO_4^{2-}$$

The chain mechanism has been proposed:

Initiation

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^-$$

$$S_2O_8^{2-} + H_2PO_2^- \xrightarrow{k_2} SO_4^{2-} + SO_4^- + H_2PO_2$$

Propagation

$$SO_4^- + H_2O \xrightarrow{k_3} HSO_4^- + OH$$

$$OH + H_2PO_2^- \xrightarrow{k_4} OH^- + H_2PO_2$$

$$\dot{H}_2PO_2 + S_2O_8^{2-} \xrightarrow{k_5} SO_4^{2-} + H_2PO_2^+ + SO_4^-$$

Termination

$$2H_2PO_2 \xrightarrow{k_6} H_2PO_2^+ + H_2PO_2^-$$

with the rapid reaction

$$H_2PO_2^+ + H_2O \longrightarrow H_3PO_3 + H^+$$

An analogous mechanism is applicable for H_3PO_3. Derive the expression for the rate law.

17. For the oxidation reaction

$$(CH_3)_2CHOH + S_2O_8^{2-} \longrightarrow (CH_3)_2C{=}O + 2H^+ + 2SO_4^{2-}$$

the proposed mechanism is

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^-$$

$$SO_4^- + (CH_3)_2CHOH \xrightarrow{k_2} (CH_3)_2\dot{C}OH + HSO_4^-$$

$$(CH_3)_2\dot{C}OH + S_2O_8^{2-} \xrightarrow{k_3} (CH_3)_2C{=}O + HSO_4^- + SO_4^-$$

$$(CH_3)_2\dot{C}OH + SO_4^- \xrightarrow{k_4} (CH_3)_2C{=}O + HSO_4^-$$

If it is assumed that k_1k_4 is very much smaller than $\sqrt{k_1k_2k_3k_4[(CH_3)_2CHOH]}$, show that the above mechanism leads to

$$-\frac{d[S_2O_8^{2-}]}{dt} = (k_1k_2k_3/k_4)^{1/2}\,[S_2O_8^{2-}]\,[(CH_3)_2CHOH]^{1/2}$$

18. For the reaction between CH_3OH and $S_2O_8^{2-}$, the following mechanism was proposed.

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^-$$

$$SO_4^- + CH_3OH \xrightarrow{k_2} \dot{C}H_2OH + HSO_4^-$$

$$\dot{C}H_2OH + S_2O_8^{2-} \xrightarrow{k_3} HCHO + HSO_4^- + SO_4^-$$

$$2\dot{C}H_2OH \xrightarrow{k_4} \text{products}$$

Derive the expression for the law.

19. For the oxidation of oxalic acid by $S_2O_8^{2-}$, the following mechanism was proposed.

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^-$$

$$SO_4^- + H_2O \xrightarrow{k_2} HSO_4^- + OH$$

$$OH + C_2O_4^{2-} \xrightarrow{k_3} CO_2 + CO_2^- + OH^-$$

$$OH^- + H^+ \xrightarrow{k_4} H_2O$$

$$CO_2^- + S_2O_8^{2-} \xrightarrow{k_5} CO_2 + SO_4^- + SO_4^{2-}$$

$$CO_2^- + SO_4^- \xrightarrow{k_6} CO_2 + SO_4^{2-}$$

If it be assumed that $4(k_1k_2/k_5k_6) \gg (k_1/k_5)^2$, show that the steady-state approximation applied to the concentration of the radical leads to the rate equation

$$-\frac{d[S_2O_8^{2-}]}{dt} = (k_1k_2k_5/k_6)^{1/2}[S_2O_8^{2-}].$$

20. The decomposition of $CHCl_3$ at 450–525 °C follows the rate law

$$-\frac{d[CHCl_3]}{dt} = \frac{k[CHCl_3]}{\{1 + b[HCl]\}^{1/2}}$$

where

$$k = (2k_1k_2k_4/k_3)^{1/2}$$

$$b = k_{-2}/k_4$$

Under what approximation will the following mechanism account for the above rate law?

$$CHCl_3 \xrightarrow{k_1} CHCl_2 + Cl$$

$$Cl + CHCl_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HCl + CCl_3$$

$$Cl + CCl_3 \xrightarrow{k_3} CCl_4$$

$$CCl_3 \xrightarrow{k_4} CCl_2 + Cl$$

$$CCl_2 + CHCl_3 \xrightarrow{k_5} C_2Cl_4 + HCl$$

21. The decomposition of dimethylether may be explained by means of RICE-HERZFELD mechanism with the following steps.

Initiation:	1	$CH_3OCH_3 \longrightarrow CH_3 + CH_3O$
Chain I:	2	$CH_3 + CH_3OCH_3 \longrightarrow CH_4 + CH_2OCH_3$
	3	$CH_2OCH_3 \longrightarrow CH_2O + CH_3$
Chain II:	4, 5	$CH_3O \overset{\text{fast}}{\rightleftharpoons} CH_2O + H$
	6	$H + CH_3OCH_3 \longrightarrow H_2 + CH_2OCH_3$
	7	$H + CH_2O \longrightarrow H_2 + CHO$
Chain III:	8	$CH_3 + CH_2O \longrightarrow CH_4 + CHO$
	9	$M + CHO \longrightarrow CO + H + M$
Termination:	10	$2CH_3 \longrightarrow C_2H_6$
Chain transfer:	11	$CH_3 + H_2 \longrightarrow CH_4 + H$

Show that

$$-\frac{d[CH_3OCH_3]}{dt} = k_2\left(\frac{k_1}{2k_{10}}\right)^{1/2}[CH_3OCH_3]^{3/2}\left(1+\frac{k_8[CH_2O]}{k_2[CH_3OCH_3]} + \frac{k_{11}}{k_2}\frac{[H_2]}{[CH_3OCH_3]}\right) + k_1[CH_3OCH_3]$$

Show that the initial rate law is given by

$$-\left(\frac{d[CH_3OCH_3]}{dt}\right)_0 = k_2\left(\frac{k_1}{k_{10}}\right)^{1/2}[CH_3OCH_3]_0^{3/2} + k_1[CH_3OCH_3]_0$$

22. The reaction between F_2 and ClO_2 follows the rate law

$$\frac{d[FClO_2]}{dt} = k_1[F_2][ClO_2]$$

The proposed mechanism is

$$F_2 + ClO_2 \xrightarrow{k_1} FClO_2 + F$$
$$F + ClO_2 \xrightarrow{k_2} FClO_2$$
$$F + F + M \xrightarrow{k_3} F_2 + M$$
$$F \xrightarrow[k_4]{\text{wall}} \frac{1}{2}F_2$$

What do you conclude about the relative speeds of elementary steps?

23. The following mechanism has been proposed for the reaction between NO_2^- and O_2.

$$NO_2^- + O_2 \xrightarrow{k_1} NO_3^- + O$$
$$O + NO_2^- \xrightarrow{k_2} NO_3^-$$
$$O + O \xrightarrow{k_3} O_2$$

Show that

$$\frac{d[NO_3^-]}{dt} = k_1[NO_2^-][O_2]\left\{1+\frac{k_2[NO_2^-]}{2k_3[O]+k_2[NO_2^-]}\right\}$$

24. The following mechanism has been proposed for the thermal decomposition of acetone

$CH_3COCH_3 \xrightarrow{k_1} \overset{\bullet}{C}H_3 + {\bullet}CH_3CO$ $\qquad E_1 = 351.47\ \text{kJ mol}^{-1}$

${\bullet}CH_3CO \xrightarrow{k_2} {\bullet}CH_3 + CO$ $\qquad E_2 = 41.84\ \text{kJ mol}^{-1}$

${\bullet}CH_3 + CH_3COCH_3 \xrightarrow{k_3} CH_4 + {\bullet}CH_2COCH_3$ $\qquad E_3 = 62.76\ \text{kJ mol}^{-1}$

${\bullet}CH_2COCH_3 \xrightarrow{k_4} {\bullet}CH_3 + {\bullet}CH_2CO$ $\qquad E_4 = 200.84\ \text{kJ mol}^{-1}$

${\bullet}CH_3 + {\bullet}CH_2COCH_3 \xrightarrow{k_5} C_2H_5COCH_3$ $\qquad E_5 = 20.92\ \text{kJ mol}^{-1}$

Express the overall rate in terms of the individual rate constants. Calculate the overall energy of activation.

25. Nitramide, O_2NNH_2, decomposes slowly in aqueous solution according to the reaction

$$O_2NNH_2 \longrightarrow N_2O + H_2O$$

The experimental rate law is

$$\frac{d[N_2O]}{dt} = k\,\frac{[O_2NNH_2]}{[H^+]}$$

(a) Which of the following mechanisms seems most appropriate?

(i) $O_2NNH_2 \xrightarrow{k_1} N_2O + H_2O$ (slow)

(ii) $O_2NNH_2 + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} O_2NNH_3^+$ (fast equilibrium)

$O_2NNH_3^+ \xrightarrow{k_3} N_2O + H_3O^+$ (slow)

(iii) $O_2NNH_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} O_2NNH^- + H^+$ (fast equilibrium)

$O_2NNH^- \xrightarrow{k_5} N_2O + OH^-$ (slow)

$H^+ + OH^- \xrightarrow{k_6} H_2O$ (fast)

26. The proposed mechanism for the decomposition of acetaldehyde catalyzed by iodine is

$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I^\bullet$$

$$I^\bullet + CH_3CHO \xrightarrow{k_2} HI + CH_3\dot{C}O$$

$$CH_3\dot{C}O \xrightarrow{k_3} \dot{C}H_3 + CO$$

$$\dot{C}H_3 + I_2 \xrightarrow{k_4} CH_3I + I^\bullet$$

$$\dot{C}H_3 + HI \xrightarrow{k_5} CH_4 + I^\bullet$$

$$CH_3I + HI \xrightarrow{k_6} CH_4 + I_2$$

Show that the rate equation for this reaction expressed as the formation of carbon monoxide is given by

$$\frac{d[CO]}{dt} = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[I_2]^{1/2}[CH_3CHO]$$

27. The aqueous oxidation of Cr^{3+} ions to CrO_4^{2-} can be accomplished in buffered H^+ solution with ceric ion, Ce^{4+}, as oxidizing agent. The rate of the reaction is found to depend upon concentrations as follows.

$$-\frac{d[Cr^{3+}]}{dt} = k\,\frac{[Ce^{4+}]^2[Cr^{3+}]}{[Ce^{3+}]}$$

(a) How is the rate of reaction expressed in terms of the production of Ce^{3+}(aq) related to the rate of consumption of Cr^{3+}(aq)?

(b) If all concentrations were diluted by a factor of ten, by what factor would the rate change?

(c) Which of the following reaction mechanisms are consistent with the observed rate law?

	Mech. A	Mech. B
$Ce^{4+} + Cr^{3+} \xrightarrow{k_1} Ce^{2+} + Cr^{5+}$	slow	fast
$Ce^{4+} + Ce^{2+} \xrightarrow{k_2} 2Ce^{3+}$	fast	fast
$Ce^{4+} + Cr^{5+} + 4H_2O \xrightarrow{k_3} Ce^{3+} + CrO_4^{2-} + 8H^+$	fast	slow

	Mech. C	Mech. D	Mech. E
$Ce^{4+} + Cr^{3+} \xrightarrow{k_1} Ce^{3+} + Cr^{4+}$	slow	fast	fast
$Ce^{4+} + Cr^{4+} \xrightarrow{k_2} Ce^{3+} + Cr^{5+}$	fast	fast	fast
$Ce^{4+} + Cr^{5+} + 4H_2O \xrightarrow{k_3} Ce^{2+} + CrO_4^{2-} + 8H^+$	fast	fast	slow

[**Ans.** Mech. D]

28. For the reaction $Cl_2 + CO(g) \longrightarrow COCl_2(g)$, the rate law is

$$-d[CO]/dt = k[Cl_2]^{3/2}[CO]$$

Which of the following mechanisms are consistent with the observed rate law?

	Mech. A	Mech. B	Mech. C
$Cl_2 + CO \xrightarrow{k_1} ClCO + Cl$	slow	fast	fast
$Cl + CO \xrightarrow{k_2} ClCO$	fast	slow	fast
$ClCO + Cl_2 \xrightarrow{k_3} Cl_2CO + Cl$	slow	fast	slow

	Mech. D	Mech. E	Mech. F
$Cl_2 \xrightarrow{k_1} 2Cl$	slow	fast	fast
$CO + Cl \xrightarrow{k_2} ClCO$	fast	slow	fast
$ClCO + Cl_2 \xrightarrow{k_3} Cl_2CO + Cl$	fast	fast	slow

	Mech. G	Mech. H	Mech. I
$Cl_2 \xrightarrow{k_1} 2Cl$	slow	fast	fast
$Cl + Cl_2 \xrightarrow{k_2} Cl_3$	fast	slow	fast
$Cl_3 + CO \xrightarrow{k_3} Cl_2CO + Cl$	fast	fast	slow

2.27 A substance decomposes according to a zero-order reaction with a rate constant k. (a) Derive the expression of half-life when the initial concentration is a. (b) How long will it take the reaction to go to completion?

2.28 Decomposition of a substance X to produce Y and Z can result by any of the following mechanisms:

(i) Simple first-order decomposition

$$X \xrightarrow{k_1} Y + Z$$

(ii) By parallel reaction

$$Z \xleftarrow{k_3} X \xrightarrow{k_2} Y$$

The decomposition reaction is followed by measuring the concentrations of Y and Z as a function of time. Prove that the above mechanisms can be distinguished from each other by measuring the ratio [Y]/[Z] as a function of time. Show that for these two mechanisms the ratio [Y]/[Z] will be independent of time.

2.29 The hypothetical reaction A → B is of the –1-order; that is

$$-d[A]/dt = k[A]^{-1}$$

(a) Obtain an equation for [A] as a function of t, k and the initial concentration $[A]_0$.

(b) Find the time required for the concentration to fall to 10 per cent of its initial value in terms of k and $[A]_0$.

(c) Does this reaction ever reach completion?

[Ans. $[A] = ([A]_0^2 - 2kt)^{1/2}$, $t = 0.99\,[A]_0^2/2k$, $t_{\text{completion}} = [A]_0^2/2k$]

2.30 The following mechanism has been proposed for the hydrogen-oxygen reaction:

		$\Delta H_{298\,K}/\text{kJ mol}^{-1}$
Initiation:	$H_2 + O_2 \xrightarrow{k_1} 2\,{}^\bullet OH$	72
Propagation:	${}^\bullet OH + H_2 \xrightarrow{k_2} H_2O + H^\bullet$	−62
Chain branching:	$H^\bullet + O_2 \xrightarrow{k_3} {}^\bullet OH + O^\bullet$	70
	$O^\bullet + H_2 \xrightarrow{k_4} {}^\bullet OH + H^\bullet$	8
Gas phase Termination:	$H^\bullet + O_2 + M \xrightarrow{k_5} HO_2^\bullet + M$	−196

Using the steady-state approximation of $[H^\bullet]$ and $[{}^\bullet OH]$, show that

$$\frac{d[H_2O]}{dt} = k_2[{}^\bullet OH][H_2]$$

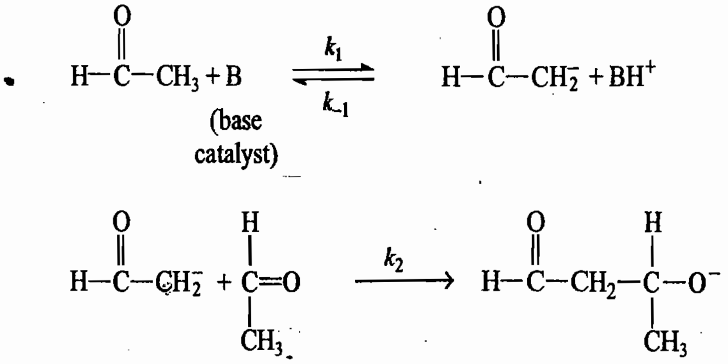
$$= \frac{2k_1k_5[H_2][O_2][M]}{k_5[M] - 2k_3}$$

Show that the second explosion limit occurs when $k_5[M] = 2k_3$.

2.31 Predict the effect of pressure on the rate constant of the following reactions:

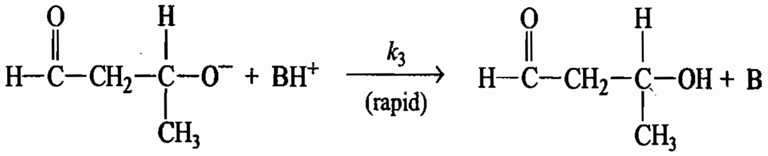
$Co(NH_3)_5Br^{2+} + OH^- \longrightarrow Co(NH_3)_5OH^{2+} + Br^-$	$\Delta^\ddagger V = 8.5\ \text{cm}^3\ \text{mol}^{-1}$
$\text{Sucrose} + H_2O \xrightarrow{H^+} \text{glucose} + \text{fructose}$	$\Delta^\ddagger V = 2.5\ \text{cm}^3\ \text{mol}^{-1}$
$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$	$\Delta^\ddagger V = -8.7\ \text{cm}^3\ \text{mol}^{-1}$
$C_6H_5CCl_3 \longrightarrow C_6H_5CCl_2^+ + Cl^-$	$\Delta^\ddagger V = -14.5\ \text{cm}^3\ \text{mol}^{-1}$

2.32 The following mechanism has been proposed for the aldol condensation.



$$H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + \underset{\text{(base catalyst)}}{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2^- + BH^+$$

$$H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2^- + \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{=}O \xrightarrow{k_2} H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}O^-$$



$$H-\overset{O}{\overset{\|}{C}}-CH_2-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-O^- + BH^+ \xrightarrow[\text{(rapid)}]{k_3} H-\overset{O}{\overset{\|}{C}}-CH_2-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH + B$$

Show that

$$\frac{d[\text{aldol}]}{dt} = \frac{k_1 k_2 [CH_3CHO]^2[B]}{k_2[CH_3CHO]+k_{-1}[BH^+]}$$

Deduce also the following reduced equations:

(i) When $k_2[CH_3CHO] \gg k_{-1}\,[BH^+]$

$$\frac{d[\text{aldol}]}{dt} = k_1[CH_3CHO]\,[B]; \qquad \text{(General basis catalysis)}$$

(ii) When $k_{-1} \gg k_2\,[CH_3CHO]$

$$\frac{d[\text{alchol}]}{dt} = \frac{k_1 k_2 [CH_3CHO]^2[B]}{k_{-1}[BH^+]}$$

$$= \frac{k_1 k_2}{k_{-1}K_b}[CH_3CHO]^2[OH^-]$$

(Specific catalysis by hydroxide ion)

NUMERICAL PROBLEMS

Order and Rate Constant of a Reaction

2.1 At 773 K dimethyl ether decomposes according to the equation

$$(CH_3)_2O \longrightarrow CH_4 + H_2 + CO$$

At this temperature the following data were obtained:

t/s	0	390	777	1 195	3 155
p_{total}/Torr	312	408	488	562	779

Determine the order of the reaction and calculate rate constant at 773 K. How much time will be required for the decomposition of half of the ether?

[**Ans.** First-order, 4.3×10^{-4} s^{-1}]

2.2 (a) The reaction $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ is a first-order gas reaction with $k_1 = 2.2 \times 10^{-5}$ s^{-1} at 573 K. What per cent of SO_2Cl_2 is decomposed on heating at 573 K for 90 min? [**Ans.** 11.2%]

(b) A first-order reaction is 40 per cent complete after 8 minutes. How long will it be before it is 90 per cent complete? What is the value of the first-order rate constant?

2.3 The half-life period and the initial concentration for a reaction are as follows. What is the order of the reaction? Calculate the rate constant.

$t_{0.5}$/s	425	275	941
a/mmHg	354	540	158

[**Ans.** $n = 2$, $k = 6.722 \times 10^{-6}$ mmHg^{-1} s^{-1}]

2.4 The radioactive decay follows the first-order kinetics. If half of a sample disintegrates in 1 590 years, what is the rate constant for the disintegration?

[**Ans.** 4.36×10^{-4} year^{-1}]

2.5 The conversion of acetochloroacetanilide (A) into *p*-chloroacetanilide (B) was followed by adding KI solution and titrating the iodine liberated with standardized thiosulphate solution. The KI reacts with A only.

Time/h	0	1	2	3	4	6	8
$V(0.1M\ S_2O_3^{2-})/cm^3$	49.3	35.6	25.74	18.5	14.0	7.3	4.6

Determine the order of the reaction and its rate constant.

[**Ans.** first, $8.5 \times 10^{-5}\ s^{-1}$]

2.6 The table given below gives kinetic data for the following reaction at 298 K.

$$OCl^- + I^- \rightarrow OI^- + Cl^-$$

$\frac{[OCl^-]}{mol\ dm^{-3}}$	$\frac{[I^-]}{mol\ dm^{-3}}$	$\frac{[OH^-]}{mol\ dm^{-3}}$	$\frac{\frac{d[IO^-]}{dt}\times 10^{-4}}{mol\ dm^{-3}\ s^{-1}}$
0.001 7	0.001 7	1.00	1.75
0.003 4	0.001 7	1.00	3.50
0.001 7	0.003 4	1.00	3.50
0.001 7	0.001 7	0.5	3.50

What is the rate law and what is the value rate constant?

$$\left[\textbf{Ans.}\ \frac{d[IO^-]}{dt} = \frac{(60\,s^{-1})[I^-][OCl^-]}{[OH^-]}\right]$$

2.7 The decomposition of NH_3 on tungsten wire at 856 °C gave the following results.

Total pressure/Torr	228	250	273	318
Time/s	200	400	600	1 000

Determine the order of the reaction and calculate its rate constant.

2.8 In a spectroscopic study for the first-order isomerization of *cis*-biethylenediaminedichlorocobalt(III) chloride in methanol, the rate of disappearance of the absorption peak at 540 nm was followed as a function of time.

Time/min	0	10	20	33	47	62
Absorbance	0.119	0.115	0.108	0.102	0.096	0.089
	80	93	107	121	140	∞
	0.081	0.075	0.071	0.066	0.058	0.005

Show that the reaction is first-order and calculate the half-life of the reaction.

[**Ans.** 8 050 s]

2.9 The solvolysis of cinnamyl chloride can be studied spectrophotometrically by observing the decrease in absorbance of the absorption maximum at 260 nm. The following observations were made in ethalonic sodium hydroxide at 298 K.

Time/min	0	10	31	74	133	∞
Absorbance at 260 nm	0.41	0.38	0.34	0.26	0.18	0

What are the order and rate constant of this reaction?

[**Ans.** First-order, $k = 1.01 \times 10^{-4}\ s^{-1}$]

(***Hint:*** Absorbance is directly proportional to the concentration of cinnamyl chloride.)

2.10 The overall reaction

$$CH_3CONH_2 + HCl + H_2O \rightarrow CH_3COOH + NH_4Cl$$

can be followed conductometrically. If the resistance of an equimolar mixture of acetamide and hydrochloric acid varies with time as follows.

Time/min	0	5	15	25	35	∞
Resistance/ohm	245	350	479	546	587	759

determine the order of the reaction.

[**Ans.** First-order with respect to both HCl and acetamide]

(***Hint:*** $[\mathrm{HCl}]_0 \propto \kappa_0 - \kappa_\infty$ and $[\mathrm{HCl}]_t \propto \kappa_t - \kappa_\infty$)

2.11 A solution of A is mixed with an equal volume of a solution of B containing the same amount and the reaction $A + B \rightarrow C$ occurs. At the end of one hour A is 75 per cent reacted. How much of A will be left unreacted at the end of two hours if the reaction is (a) first-order with respect to A and zero-order with respect to B, (b) first-order with respect to both A and B, and (c) zero-order with respect to both A and B?

2.12 A solution at 25 °C initially contains 0.063 mol dm^{-3} $FeCl_3$ and 0.031 5 mol dm^{-3} $SnCl_2$. After the elapsed time given, the concentration of the ferrous chloride produced is determined by a titration procedure:

t/min	1	3	7	17	40
$[Fe^{2+}]$/mol dm^{-3}	0.014 3	0.025 9	0.036 1	0.045 0	0.050 6

Determine the reaction order and the rate constant.

Consecutive Reaction

2.13 For the consecutive first-order reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

the values of k_1 and k_2 are 45 h^{-1} and 15 h^{-1}, respectively. If the reaction is carried out with pure A at a concentration of 1.0 mol dm^{-3}: (a) How much time will be required for the concentration of ~~B to~~ reach a maximum? (b) What will be the maximum concentration of B? (c) What will be the composition of the reacting system after a time interval of 10 min?

[**Ans.** (a) 132 s, (b) 0.58 mol dm^{-3}, (c) [A] = 0, [B] = 0.12 mol dm^{-3}, [C] = 0.88 mol dm^{-3}]

2.14 The following mechanism has been proposed for the reaction

$$S_2F_{10} = SF_6 + SF_4$$

$$S_2F_{10} \xrightarrow{k_1} 2SF_5$$

$$SF_5 + S_2F_{10} \xrightarrow{k_2} SF_6 + S_2F_9$$

$$S_2F_9 \xrightarrow{k_3} SF_4 + SF_5$$

$$S_2F_9 + SF_5 \xrightarrow{k_4} SF_6 + 2SF_4$$

(i) If $k_1/k_2 \ll (k_1k_3/k_2k_4)^{1/2}$, show that its differential rate law is given by

$$-\frac{d[S_2F_{10}]}{dt} = \left(\frac{k_1k_2k_3}{k_4}\right)^{1/2} [S_2F_{10}]$$

(ii) For the above reaction, the Arrhenius equation is

$$k/\mathrm{s}^{-1} = (4.98 \times 10^{18}) \exp\left(-\frac{205.85}{RT}\ \mathrm{kJ\ mol^{-1}}\right)$$

What are the values of E_a and $\Delta^{\ddagger}S$?

Collision Theory of Bimolecular Reaction

2.15 The bimolecular decomposition of hydrogen iodide is given by the equation

$$2HI \longrightarrow H_2 + I_2$$

Assuming a collision diameter of 0.35×10^{-8} cm and an activation energy of 183.90 kJ mol^{-1} for the reaction, calculate (a) the collision rate, (b) the rate of reaction, and (c) the rate constant for the above reaction at 500 K and one atmosphere pressure.

[**Ans.** (a) 1.686×10^{36} m^{-3} s^{-1}, (b) 1.71×10^{-7} mol m^{-3} s^{-1}, (c) 2.88×10^{-10} mol^{-1} m^{3} s^{-1}]

2.16 Using the expression from the collision theory, compute the rate constant for the reaction

$$H_2 + I_2 \longrightarrow 2HI$$

at 700 K. Use $\sigma_A + \sigma_B = 2 \times 10^{-8}$ cm and energy of activation as 167.4 kJ mol^{-1} The experimental value is 6.42×10^{-2} dm^3 mol^{-1} s^{-1}. Explain the discrepancy between the calculated and experimental values, if any.

Energy of Activation

2.17 At 300 K, a certain reaction is 50 per cent complete in 20 min. At 350 K, the same reaction is 50 per cent complete in 5.0 min. Calculate the activation energy for the reaction.

(***Hint:*** $k_{350K}/k_{300K} = 4$)

2.18 The half-life for a first-order decomposition reaction at 650 K is 363 min and its energy of activation is 217.58 kJ mol^{-1}. (a) What fraction of the molecules at 650 K have sufficient energy to react? (b) Calculate the time required for the compound to be 75 per cent decomposed at 723 K.

[**Ans.** (a) 4.0×10^{-18}, (b) 12.5 min]

Thermodynamic Parameters of a Reaction

2.19 For the decomposition of N_2O_5

T/K	298	308	318	328	338
$10^5 k_1/s^{-1}$	1.72	6.65	24.95	75	240

Calculate A and E for the reaction, in the equation $k_1 = A \exp(-E/RT)$. Calculate $\Delta^\ddagger G$, $\Delta^\ddagger H$ and $\Delta^\ddagger S$ for the reaction at 323 K.

[**Ans.** $E = 102.09$ kJ mol^{-1}, $A = 1.51 \times 10^{13}$ s^{-1}, $\Delta^\ddagger G = 101.68$ kJ mol^{-1}, $\Delta^\ddagger H = 99.17$ kJ mol^{-1} $\Delta^\ddagger S = -7.95$ J K^{-1} mol^{-1}]

2.20 (a) The rate constant of a first-order reaction is represented by the equation

$$k/\text{s} = 4.3 \times 10^{13} \exp\,(-104.6 \text{ kJ mol}^{-1}/RT)$$

Calculate (i) the value of rate constant at 373 K, and (ii) the entropy of activation.

(b) The reaction considered in part (a) can be carried out in the presence of a catalyst that lowers the entropy of activation by 8.368 J K^{-1} mol^{-1} and lowers the activation energy by 20.92 kJ mol^{-1}. Calculate the ratio of the rate constants of the catalyzed reaction to that of the uncatalyzed reaction at 373 K.

[**Ans.** 310]

2.21 The rate constant for the first order decomposition of 2-chloropropane into propylene and hydrogen chloride was found to vary with temperature as follows:

Rate constant $\times 10^3/s^{-1}$	0.162	0.238	0.311	0.475	0.706	0.901	1.225	1.593
Temperature/K	640.6	646.7	651.2	657.5	665.1	669.0	674.9	679.7

Calculate the energy of activation and the frequency factor.

[**Ans.** $\Delta^{\ddagger}E = 211$ kJ mol^{-1}, $A = 2.5 \times 10^{13}$ s^{-1}]

Effect of Ionic Strength on Ionic Reaction

2.22 The following data were obtained for the reaction

$$Co(NH_3)_5NO_2^{2+} + OH^- \longrightarrow Co(NH_3)_5OH^{2+} + NO_2^-$$

μ/M	2.34	5.61	8.10	11.73	16.90
$k \times 10^4$/mol^{-1} dm^3 s^{-1}	5.808	5.164	4.786	4.383	3.972

Evaluate k_0, the rate constant at zero ionic strength.

2.23 The rate determining step for the reaction

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

is $$S_2O_8^{2-} + I^- \longrightarrow [S_2O_8I^{3-}]$$

When the persulphate and iodide ion concentrations are 1×10^{-4} mol dm^{-3} and 2×10^{-4} mol dm^{-3}, respectively, the rate constant is 1.6×10^{-5} mol^{-1} dm^3 s^{-1}. What approximately is the rate constant if the reaction mixture is made 10^{-2} mol dm^{-3} with respect to KCl? [**Ans.** 2.33×10^{-5} mol^{-1} dm^3 s^{-1}]

2.24 For the reaction

$$NH_2SO_2OH + H_2O \rightarrow NH_4HSO_4$$

in aqueous solution at 30.35 °C, the following rate constants were observed at the indicated ionic strengths:

$\mu \times 10^3$ / M	5.06	11.21	15.85	22.94
k/mol^{-1} dm^3 h^{-1}	1.07	1.02	0.976	0.886

From these data ascertain (a) the valencies of reacting ions, and (b) the rate constant corrected for the primary salt effect. At this temperature the Debye-Hückel constant $A = 0.574$ mol$^{-1/2}$ dm$^{3/2}$.

Effect of Pressure on Rate Constant

2.25 The rate constant for the exchange reaction

$$Cr(H_2O)_6^{3+} + H_2^{18}O \longrightarrow [Cr(H_2O)_5(H_2^{18}O)]^{3+} + H_2O$$

is 5.0×10^{-5} mol^{-1} dm^3 s^{-1} at 298 K and 101.325 kPa pressure, and $\Delta^{\ddagger}V$ is -9.3 cm^3 mol^{-1}. Calculate the rate constant for 2 kbar pressure.

2.26 The data below relate to the first-order hydrolysis of 2-chloro-2-methylbut-3-yne in aqueous ethanol at 25 °C.

$$(CH_3)_2CCl\,C{\equiv}CH + H_2O \longrightarrow (CH_3)_2(OH)\,C{\equiv}CH + HCl$$

Rate constant $\times 10^6$/s^{-1}	0.23	0.38	0.74	1.27	2.04
Pressure/bar	0.0	10.7	21.3	31.7	42.1

Calculate the volume of activation. [**Ans.** $\Delta^{\ddagger}V = -13.1$ cm^3 mol^{-1}]

Catalytic Reaction

2.27 The initial rate of oxidation of sodium succinate to form sodium fumarate in the presence of the enzyme succinate dehydrogenase at different sodium succinate concentrations is given below:

Sodium succinate conc. $\times 10^3$/mol dm^{-3}	10	2.0	1.0	0.5	0.33
Initial rate $\times 10^6$ mol dm^{-3} s^{-1}	1.17	0.99	0.79	0.62	0.50

Determine the Michaelis constant and the limiting rate of equation.

[**Ans.** $r_{max} = 1.22 \times 10^{-6}$ mol dm^{-3} s^{-1}, $K_M = 4.8 \times 10^{-4}$ mol dm^{-3}]

2.28 The rate for the reaction, $H_2O_2 + 2H_3O^+ + 2Br^- \longrightarrow 4H_2O + Br_2$, is

$$-d[H_2O_2]/dt = k[H_2O_2][H_3O^+][Br^-]$$

At 298 K, k varies with the hydrogen bromide concentration as follows:

$[HBr]$/millimole dm^{-3}	13.5	22.0	28.8	43.2	67.7
$k \times 10^3/mol^{-2}\ dm^6\ min^{-1}$	377	347	338	318	297

Determine k_0, the rate constant for the uncatalyzed reaction.

[**Ans.** 0.467]

Homogeneous Catalyst

2.29 The hydrolysis of ethyl acetate

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

in aqueous solution is first-order with respect to ethyl acetate. Upon varying the pH of the solution the first-order rate constant varies as follows:

pH	3	2	1
$k_1/10^{-4}\ s^{-1}$	1.1	11	110

What is the order of the reaction with respect to H^+ and the value of the rate constant? [**Ans.** First order, $1.1 \times 10^{-1}\ dm^3\ mol^{-1}\ s^{-1}$]

Reversible Reaction

2.30 The formation of phosgene $COCl_2$ from CO and Cl_2 is a reversible reaction. The Arrhenius parameters are

$$\log\,(k_{form}/dm^3\ mol^{-1}s^{-1}) = 8.023 - \frac{(26\,300\,K)}{4.58}\frac{1}{T}$$

$$\log\,(k_{decomp}/s^{-1}) = 13.48 - \frac{(52\,400\,K)}{4.50}\frac{1}{T}$$

Answer the following

(i) What are the activation energies of forward and backward reactions at 298 K?

(ii) What is the value of ΔE at 298 K

(iii) What is the equilibrium constant of the reaction?

(iv) What are the values of $\Delta^{\ddagger}S_f$ and $\Delta^{\ddagger}S_b$?

3

Photochemistry

3.1 INTRODUCTION

Many reactions can be initiated by the absorption of radiation lying in the visible and ultraviolet regions (roughly from 800 nm to 200 nm). These reactions are called photochemical reactions. The science of photochemistry deals with the study of the effect of radiant energy on chemical reactions and with rates and mechanisms by which photochemical reactions proceed. The energy carried by the above mentioned region of radiation is sufficient to cause an electronic excitation in the molecule and thereby makes it more reactive which may result in a chemical reaction. Thus with the help of absorption of radiations, many reactions of different types, e.g. synthesis, decomposition, polymerization, isomeric change, oxidation and reduction, can be carried out.

Before we discuss the kinetics of photochemical reactions, a few definitions are in order.

3.2 TWO BASIC LAWS OF PHOTOCHEMISTRY

To all photochemical reactions, two basic laws hold good. These are:

The Grothuss-Draper Law

This law states that

Only those radiations which are absorbed by the reacting system are effective in producing chemical change.

This law can be easily accounted for as the molecules acquire energy for reaction by absorbing photons.

It should be clearly understood that though the law states that a photochemical reaction must have resulted because of the absorption of light, the reverse of this is not always true, i.e. the system on absorbing light may or may not result into a chemical reaction. In many cases, the absorbed light is converted into the kinetic energy of the absorbing molecules and thereby only heat effects are produced. In many cases, the absorbed light is re-emitted as fluorescence or phosphorescence.

The amount of light absorbed by a system is given by Lambert-Beer's law, a brief description of which is given in the next section.

Law of Photochemical Equivalence

The second law of photochemistry is the law of photochemical equivalence proposed by Stark and Einstein. According to this law, we have

Each light absorbing molecule in a photochemical reaction absorbs only one quantum of light which causes the activation.

If ν is the frequency of the absorbed light, its energy as given by the Planck's relation is

$$\Delta E = h\nu$$

Hence, energy absorbed per mol of the substance is

$$\Delta E = N_A h\nu$$

and is conventionally known as one *Einstein of energy*.

3.3 LAMBERT-BEER'S LAW

Statement of Lambert Law

The amount of light absorbed by a pure substance follows Lambert's law which states that:

Equal fractions of the incident radiation are absorbed by successive layers of equal thickness of the light absorbing substance.

Mathematically,

$$-\frac{dI}{I} \propto (dl) \quad \text{i.e.} \quad -\frac{dI}{I} = k(dl) \qquad (3.3.1)$$

where the constant k is known as *absorption coefficient* and is characteristic of the given material and the wavelength of the radiation. It has the unit of length^{-1}.

Alternative Definition

Alternatively, Lambert's law may be written as:

$$-\frac{dI}{dl} = kI$$

that is, the rate of decrease in intensity with thickness of the medium (i.e. $-dI/dl$) *is proportional to the intensity of the radiation.*

Integration Form of Lambert Law

Equation (3.3.1) on integration yields

$$-\int_{I_0}^{I} \frac{dI}{I} = k\int_0^l dl$$

i.e.

$$\ln\left(\frac{I}{I_0}\right) = -kl \qquad (3.3.2)$$

or

$$I = I_0\, e^{-kl} \qquad (3.3.3)$$

Equation (3.3.2) may be written as

$$\log\left(\frac{I}{I_0}\right) = -\frac{k}{2.303}\, l = -al$$

or

$$\frac{I}{I_0} = 10^{-al} \qquad (3.3.4)$$

The constant a which is equal to $k/2.303$ is known as absorption coefficient (formely as absorptivity or extinction coefficient). It has the unit of length^{-1}.

Extension of the Lambert Law to Solutions

The absorption of light by solutions of known concentration c is given by Beer's law, according to which, we have

$$-\frac{\mathrm{d}I}{I} \propto c$$

Combining the above equation with Eq. (3.3.1), we get

$$-\frac{\mathrm{d}I}{I} \propto (\mathrm{d}l)\,(c)$$

$$\text{or} \qquad -\frac{\mathrm{d}I}{I} = k(\mathrm{d}l)\,(c) \tag{3.3.5}$$

Equation (3.3.5) is known as Lambert-Beer's law which on integration gives

$$\ln\frac{I}{I_0} = -\,klc \tag{3.3.6a}$$

$$\text{or} \qquad I = I_0(10)^{-\varepsilon lc} \tag{3.3.6b}$$

where $\varepsilon = k/2{:}303$ and has the unit of (concentration)(length)$^{-1}$. It is knows as molar absorption coefficient (formerly as the *molar extinction coefficient* or *molar absorptivity*):

Beer's law is applicable for dilute solutions, deviations are observed for concentrated solutions. There is no exception of Lambert's law.

Absorbance of a Solution

The absolute value of the exponent in Eq. (3.3.6b) is defined as the *absorbance* A or (formerly as extinction or *optical density*).

$$A = \varepsilon lc \tag{3.3.7}$$

The terms absorptivity (for absorption coefficient) and molar absorptivity (for molar absorption coefficient) are to be avoided as these terms have been recommended for the absorptance per unit length. Also the terms extinction (for absorbance), extinction coefficient (for absorption coefficient) and molar extinction coefficient (for molar absorption coefficient) are to be avoided as the term extinction is now reserved for diffusion of radiation rather than absorption.

The ratio I/I_0 is called the *transmittance*. The amount of light absorbed is given by

$$I_0 - I = I_0 - I_0\,10^{-\varepsilon lc} = I_0\,(1 - 10^{-\varepsilon lc}) \tag{3.3.8}$$

Absorption of a Solution Containing more than one Absorbing Substance

For a solution containing more than one light absorbing substance, Lambert-Beer's law takes the form

$$-\frac{\mathrm{d}I}{I} = (\mathrm{d}l)\,(\textstyle\sum_i k_\mathrm{i} c_\mathrm{i}) \tag{3.3.9}$$

On integration the above expression yields

$$I = I_0 \exp\left(-l(\textstyle\sum_i k_\mathrm{i} c_\mathrm{i})\right) \tag{3.3.10a}$$

$$\text{or} \qquad I = I_0\,10^{-l(\Sigma_i \varepsilon_i c_i)} \tag{3.3.10b}$$

The absorbance of the solution in this case is given by

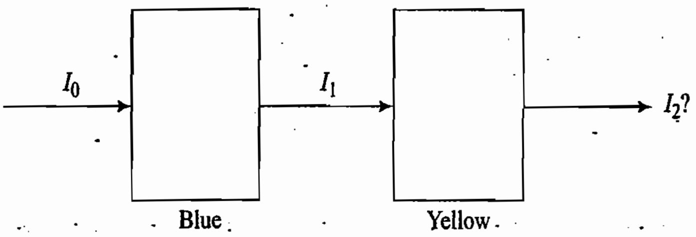
$$A = l\sum_i \varepsilon_i c_i = \sum_i \varepsilon_i c_i\, l = \sum_i A_i \qquad (3.3.11)$$

where A_i is the absorbance of the ith constituent.

Equation (3.3.11) indicates that the absorbance is additive, i.e. the absorbance of a solution is equal to the sum of absorbances of its constituents.

Example 3.3.1 At 460 nm a blue filter transmits 72.7% of the light and a yellow filter 40.7% of the light. What is the transmittance at the same wavelength of two filters in combination?

Solution We have



It is given that

$$\frac{I_1}{I_0} = 0.727 \quad \text{and} \quad \frac{I_2}{I_1} = 0.407$$

Hence, $$\frac{I_2}{I_0} = \frac{I_2}{I_1} \times \frac{I_1}{I_0} = 0.727 \times 0.407 = 0.296$$

Example 3.3.2 In a given absorption cell transmittance of 0.1 mol dm^{-3} of A is 0.75 and that of 0.1 mol dm^{-3} of B is 0.55 at a given wavelength. Calculate the transmittance of a solution that is simultaneous 0.1 mol dm^{-3} in A and 0.1 mol dm^{-3} in B.

Solution The absorbance of 0.1 mol dm^{-3} in A is

$$A_A = \varepsilon l c = -\log\frac{I}{I_0} = -\log(0.75) = 0.124\,9$$

Similarly, for 0.1 mol dm^{-3} in B is

$$A_B = \varepsilon l c = -\log\frac{I}{I_0} = -\log(0.55) = 0.259\,6$$

Now, the absorbance of the solution which is simultaneously 0.1 mol dm^{-3} in A and 0.1 mol dm^{-3} in B is

$$A = A_A + A_B = 0.124\,9 + 0.259\,6 = 0.384\,5$$

Since $A = -\log\left(\dfrac{I}{I_0}\right)$

therefore

$$\frac{I}{I_0} = \text{antilog}(-A) = \text{antilog}(-0.384\,5) = \text{antilog}(\bar{1}.6165) = 0.412\,5$$

(**Note:** Since absorbance is additive, transmittance will be multiplicative. Hence, $I/I_0 = 0.55 \times 0.75 = 0.412\,5$.)

Example 3.3.3 A certain substance in a cell of length l absorbs 10 per cent of the incident light. What fraction of the incident light will be absorbed in a cell five times as long?

Solution We have

$$\log\left(\frac{I}{I_0}\right)_1 = -\varepsilon c l, \qquad \text{where} \qquad \left(\frac{I}{I_0}\right)_1 = 0.9$$

$$\log\left(\frac{I}{I_0}\right)_2 = \varepsilon c(5l)$$

Hence,
$$\frac{\log(I/I_0)_2}{\log(I/I_0)_1} = 5$$

or $\log(I/I_0)_2 = 5 \times \log(I/I_0)_1 = 5 \times \log(0.9) = 5 \times \bar{1}.954\,2 = \bar{1}.771$

Thus $I/I_0 = 0.590\,2$

Hence, light absorbed is 40.98 per cent.

Example 3.3.4 In a cell of a certain length and at a pressure of 100 mmHg, gaseous acetone transmits 25.1 per cent of the incident radiation of wavelength 265 nm. Assuming Beer's law to apply, calculate the pressure at which 98 per cent of the incident radiation will be absorbed by acetone in the same cell at the same temperature.

Solution For gaseous system, c in the Lambert-Beer's law may be replaced by p. Thus, we have

$$\log\left(\frac{I}{I_0}\right) = -\varepsilon l p$$

Since at 100 mmHg transmittance is 0.251, we have

$$\log(0.251) = -\varepsilon l(100\text{ mmHg})$$

or
$$(\varepsilon l) = -\frac{\log(0.251)}{100\,\text{mmHg}} = 0.006\,003\ \text{mmHg}^{-1}$$

For 98 per cent absorption or 2 per cent transmittance, we have

$$\log(0.02) = -(\varepsilon l)p = -(0.006\,003\ \text{mmHg}^{-1})p$$

or
$$p = -\frac{\log(0.02)}{0.006\,003\,\text{mmHg}^{-1}} = 283.0\ \text{mmHg}$$

Example 3.3.5 In an experiment to determine the concentrations of the two substances A and B in a certain solution spectrophotometrically, the following data were obtained.

Solution	[A] mol dm^{-3}	[B] mol dm^{-3}	*Per cent Transmittance at* 400 nm	*Per cent Transmittance at* 500 nm
1	0.001	0	10	60
2	0	0.005	80	20
3	unknown	unknown	40	50

Determine the concentrations of A and B in solution 3.

Solution The relation between absorbance and transmittance is

$$A = \varepsilon l c = -\log\left(\frac{I}{I_0}\right)$$

For solution 1, we have

$$A_\mathrm{A} \text{ at } 400 \text{ nm} = \varepsilon_\mathrm{A} l c_\mathrm{A} = -\log(10/100) = 1$$

$$A_\mathrm{A} \text{ at } 500 \text{ nm} = \varepsilon_\mathrm{A} l c_\mathrm{A} = -\log(60/100) = 0.22$$

Since $c_\mathrm{A} = 0.001 \text{ mol dm}^{-3}$, we have

$$(\varepsilon_\mathrm{A} l)_{400\text{ nm}} = \frac{1}{0.001 \text{ mol dm}^{-3}} = 1000 \text{ mol}^{-1} \text{ dm}^3$$

$$(\varepsilon_\mathrm{A} l)_{500\text{ nm}} = \frac{0.22}{0.001 \text{ mol dm}^{-3}} = 220 \text{ mol}^{-1} \text{ dm}^3$$

For solution 2, we have

$$A_\mathrm{B} \text{ at } 400 \text{ nm} = \varepsilon_\mathrm{B} l c_\mathrm{B} = -\log(80/100) = 0.097$$

$$A_\mathrm{B} \text{ at } 500 \text{ nm} = \varepsilon_\mathrm{B} l c_\mathrm{B} = -\log(20/100) = 0.699$$

Since $c_\mathrm{B} = 0.005 \text{ mol dm}^{-3}$, we have

$$(\varepsilon_\mathrm{B} l)_{400\text{ nm}} = \frac{0.097}{0.005 \text{ mol dm}^{-3}} = 19.4 \text{ mol}^{-1} \text{ dm}^3$$

$$(\varepsilon_\mathrm{B} l)_{500\text{ nm}} = \frac{0.669}{0.005 \text{ mol dm}^{-3}} = 139.8 \text{ mol}^{-1} \text{ dm}^3$$

For solution 3, we have

At 400 nm: $(\varepsilon_\mathrm{A} l)_{400\text{ nm}}\, c_\mathrm{A} + (\varepsilon_\mathrm{B} l)_{400\text{ nm}}\, c_\mathrm{B} = -\log(40/100) = 0.398$

At 500 nm: $(\varepsilon_\mathrm{A} l)_{500\text{ nm}}\, c_\mathrm{A} + (\varepsilon_\mathrm{B} l)_{500\text{ nm}}\, c_\mathrm{B} = -\log(50/100) = 0.301$

Substituting the values, we have

$$(1000 \text{ mol}^{-1} \text{ dm}^3)\, c_\mathrm{A} + (19.4 \text{ mol}^{-1} \text{ dm}^3)\, c_\mathrm{B} = 0.398$$

$$(220 \text{ mol}^{-1} \text{ dm}^3)\, c_\mathrm{A} + (139.8 \text{ mol}^{-1} \text{ dm}^3)\, c_\mathrm{B} = 0.301$$

Solving for c_A and c_B, we get

$$c_\mathrm{A} = 0.000\,368 \text{ mol dm}^{-3} \quad \text{and} \quad c_\mathrm{B} = 0.001\,57 \text{ mol dm}^{-3}$$

Spectrophotometric Determination of Equilibrium Constant

Lambert-Beer's law has been used to determine the equilibrium constant of the reaction

$$\mathrm{AB}_n \rightleftharpoons \mathrm{A} + n\mathrm{B}$$

First of all, a wavelength is chosen where only complex AB_n absorbs appreciably. The absorbance of the solution is entirely due to AB_n and we may write it as

$$A = \{l \cdot \varepsilon(\mathrm{AB}_n)\}[\mathrm{AB}_n]$$

The value of the expression within the bracket can be determined by taking a known concentration of A (say, c) to which a very large excess of B is added so that the equilibrium is shifted to left and thus

$$[AB_n] \simeq [A]$$

For the above solution, $A_{\max}$ is determined experimentally and thus, we have

$$\{l \cdot \varepsilon(AB_n)\} = \frac{A_{\max}}{c}$$

Now the absorbance of a solution containing, respectively, the concentrations c and nc of A and B, is determined. Let it be represented by A_s. At these concentrations, the concentrations of various species at equilibrium are

$$[A] = \alpha c$$

$$[B] = n\alpha c$$

$$[AB_n] = (1-\alpha)\, c$$

Thus $\quad A_s = \{l \cdot \varepsilon(AB_n)\}(1-\alpha)\, c = \dfrac{A_{\max}}{c}\,(1-\alpha)\, c = A_{\max}(1-\alpha)$

Hence, $\quad \alpha = \dfrac{A_{\max} - A_s}{A_{\max}}$

Knowing α, K_c can be determined from the expression

$$K_c = \frac{[A][B]^n}{[AB_n]} = \frac{(\alpha c)(n\alpha c)^n}{(1-\alpha)c}$$

Alternative Procedure

We may proceed as follows.

Let two solutions containing different amounts of A and B be prepared in such a way that they have the same absorbance. Since absorbance is due to the absorption of AB_n only, we have

$$\{l \times \varepsilon(AB_n)\}[AB_n]_1 = \{l \cdot \varepsilon(AB_n)\}[AB_n]_2 = A$$

or $\quad [AB_n]_1 = [AB_n]_2 = \dfrac{A}{\{l \cdot \varepsilon(AB_n)\}} = x$

where x is an unknown parameter.

Now the concentrations of A and B in the two solutions at equilibrium will be

$$[A]_1 = a_1 - [AB_n] = a_1 - x$$

$$[B]_1 = b_1 - n[AB_n] = b_1 - nx$$

$$[A]_2 = a_2 - [AB_n] = a_2 - x$$

$$[B]_2 = b_2 - n[AB_n] = b_2 - nx$$

Substituting these in the expression of equilibrium constant

$$K_c = \frac{[A][B]^n}{[AB_n]}$$

we get

$$K_c = \frac{(a_1 - x)(b_1 - nx)^n}{x}$$

$$K_c = \frac{(a_2 - x)(b_2 - nx)^n}{x}$$

which may be solved by eliminating x.

Example 3.3.6 The complex between ferric and trion ions dissociates following the equation

$$FeR_3^{3-} \rightleftharpoons Fe^{3+} + 3R^{2-}$$

The absorbance of a solution in which the initial concentration of Fe^{3+} was 6×10^{-5} mol dm^{-3} and that of R^{2-} was 18×10^{-5} mol dm^{-3}, was found to be 0.25. By adding a large excess of R^{2-}, the absorbance changes to 0.35. All measurements were made at the wavelength where only FeR_3^{3-} absorbs appreciably. Determine the values of α and K_c.

Solution We have

$$\alpha = \frac{A_{max} - A_s}{A_{max}}$$

Substituting the values, we get

$$\alpha = \frac{0.35 - 0.25}{0.35} = \frac{0.10}{0.35} = 0.286$$

Now $$K_c = \frac{[Fe^{3+}][R^{2-}]^3}{[FeR_3^{3-}]} = \frac{(\alpha c)(n\alpha c)^n}{(1-\alpha)c}$$

where $c = 6.0 \times 10^{-5}$ mol dm^{-3} and $n = 3$. Substituting the value of α, c and n, we get

$$K_c = \frac{(0.286 \times 6.0 \times 10^{-5}\ \text{mol dm}^{-3})(3 \times 0.286 \times 6.0 \times 10^{-5}\ \text{mol dm}^{-3})^3}{(1 - 0.286)(6.0 \times 10^{-5}\ \text{mol dm}^{-3})}$$

$$= 5.465 \times 10^{-14}\ (\text{mol dm}^{-3})^3$$

Example 3.3.7 (a) A solution containing 2.5×10^{-5} mol dm^{-3} Bi^{3+} ions and a large excess of SCN^- was found to have an absorbance 0.417 when placed in a cell of 2.0 cm thick and exposed to 360 nm light where only $Bi(SCN)_6^{3-}$ absorbs appreciably. The equilibrium reaction setup is $Bi(SCN)_6^{3-} \rightleftharpoons Bi(SCN)_4^- + 2SCN^-$. Calculate the extinction coefficient of $Bi(SCN)_6^{3-}$.

(b) If the initial concentrations of Bi^{3+} and SCN^- were 2.5×10^{-5} mol dm^{-3} and 0.50 mol dm^{-3}, respectively, the absorbance was found to be 0.280. Calculate K for the reaction

$$Bi(SCN)_6^{3-} \rightleftharpoons Bi(SCN)_4^- + 2SCN^-$$

Solution (a) Since $= \varepsilon cl$, we have

$$\varepsilon\{Bi(SCN)_6^{3-}\} = \frac{A}{cl} = \frac{0.417}{(2.5 \times 10^{-5}\ \text{mol dm}^{-3})(2\ \text{cm})} = 8\ 340\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$$

(b) Let c_s be the concentration of complex $Bi(SCN)_6^{3-}$ when the initial concentrations of Bi^{3+} and SCN^- are 2.5×10^{-5} mol dm^{-3} and 0.50 mol dm^{-3}, respectively. Since A is proportional to c, we have

$$A_{max} \propto c_{max}; \quad \text{where} \quad c_{max} = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$$

$$A_s \propto c_s$$

Hence, $$\frac{c_s}{c_{max}} = \frac{A_s}{A_{max}}$$

or $$c_s = \frac{A_s}{A_{max}} c_{max} = \frac{0.280}{0.417} \times 2.5 \times 10^{-5} \text{ mol dm}^{-3}$$

$$= 1.68 \times 10^{-5} \text{ mol dm}^{-3}$$

Thus, the concentrations of various species at equilibrium are

$$[Bi(SCN)_4^-] = 2.5 \times 10^{-5} \text{ mol dm}^{-3} - 1.68 \times 10^{-5} \text{ mol dm}^{-3}$$

$$= 0.82 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[SCN^-] = 0.5 \text{ mol dm}^{-3} - 6\,(1.68 \times 10^{-5} \text{ mol dm}^{-3})$$

$$- 4\,(0.82 \times 10^{-5} \text{ mol dm}^{-3})$$

$$\simeq 0.50 \text{ mol dm}^{-3}$$

Hence, $$K_c = \frac{[Bi(SCN)_4^-][SCN^-]^2}{[Bi(SCN)_6^{3-}]}$$

$$= \frac{(0.82 \times 10^{-5} \text{ mol dm}^{-3})(0.5 \text{ mol dm}^{-3})^2}{(1.68 \times 10^{-5} \text{ mol dm}^{-3})}$$

$$= 0.122 \text{ (mol dm}^{-3})^2$$

Example 3.3.8

A solution of *m*-nitrophenol indicator of concentration 6.36×10^{-4} mol dm^{-3} was prepared and the following spectrophotometric measurements were made.

Condition	*Form of indicator*	*Absorbance*
strongly acidic	HIn	0.142
strongly alkaline	In^-	0.943
pH = 8.321	$HIn + In^-$	0.527

Determine the equilibrium constant of the reaction

$$HIn \rightleftharpoons H^+ + In^-$$

Solution

The absorbance is given by

$$= \varepsilon lc$$

Hence, $$\{l\varepsilon(HIn)\} = \frac{(A)_{acidic}}{c} = \frac{0.142}{6.36 \times 10^{-4} \text{ mol dm}^{-3}} = 223 \text{ mol}^{-1} \text{ dm}^3$$

$$\{l\varepsilon(In^-)\} = \frac{(A)_{alkaline}}{c} = \frac{0.943}{6.36 \times 10^{-4} \text{ mol dm}^{-3}} = 1\,483 \text{ mol}^{-1} \text{ dm}^3$$

At any other H^+, we will have

$$A = \{l\varepsilon(\text{HIn})\}\, c_{\text{HIn}} + \{l\varepsilon(\text{In}^-)\}\, c_{\text{In}^-}$$

Since $c_{\text{HIN}} + c_{\text{In}^-} = 6.36 \times 10^{-4}$ mol dm^{-3}

we have $A = \{l\varepsilon(\text{HIn})\}\,(6.36 \times 10^{-4} \text{ mol dm}^{-3} - c_{\text{In}^-}) + \{l\varepsilon(\text{In}^-)\}\, c_{\text{In}^-}$

or $A = \{l\varepsilon(\text{HIn})\}\,(6.36 \times 10^{-4} \text{ mol dm}^{-3}) + c_{\text{In}^-}\,[\{l\varepsilon(\text{In}^-)\} - \{l\varepsilon(\text{HIn})\}]$

$$c_{\text{In}^-} = \frac{A - \{l\varepsilon(\text{HIn})\}(6.36 \times 10^{-4} \text{ mol dm}^{-3})}{\{l\varepsilon(\text{In}^-)\} - \{l\varepsilon(\text{HIn})\}}$$

Substituting the given value of A and those of $\{l\varepsilon(\text{HIn})\}$ and $\{l\varepsilon(\text{In}^-)\}$, we get

$$c_{\text{In}^-} = \frac{0.527 - 223 \times 6.36 \times 10^{-4}}{1483 \text{ mol}^{-1}\text{dm}^3 - 223 \text{ mol}^{-1}\text{dm}^3} \doteq 3.057 \times 10^{-4} \text{ mol dm}^{-3}$$

Hence, $c_{\text{Hin}} = 6.36 \times 10^{-4} \text{ mol dm}^{-3} - 3.057 \times 10^{-4} \text{ mol dm}^{-3}$

$= 3.303 \times 10^{-4}$ mol dm^{-3}

Since pH = 8.321, we have

$[H^+] = 4.775 \times 10^{-9}$ mol dm^{-3}

Now
$$K = \frac{[H^+][\text{In}^-]}{[\text{HIn}]} = \frac{(4.775 \times 10^{-9} \text{ mol dm}^{-3})(3.057 \times 10^{-4} \text{ mol dm}^{-3})}{(3.303 \times 10^{-4} \text{ mol dm}^{-3})}$$

$= 4.419 \times 10^{-9}$ mol dm^{-3}

Example 3.3.9 The per cent transmittance of a solution of bromophenol blue were determined at 590 nm under the following conditions.

At pH = 4.39, transmittance is 20%.

At strongly basic conditions, transmittance is 5.4%.

At the given wavelength, only the base form In^- absorbs appreciably. Determine K_{HIn}.

Solution Since $A = -\log (I/I_0)$

we get
$$A_{\max} = -\log \left(\frac{I}{I_0}\right)_{\text{strongly alkaline}} = -\log\left(\frac{5.4}{100}\right) = 1.267\,6$$

$$A_s = -\log \left(\frac{I}{I_0}\right)_{\text{given pH}} = -\log\left(\frac{20}{100}\right) = 0.699$$

If α is the degree of dissociation of the indicator, we have

$$\begin{array}{ccc} \text{HIn} & \rightleftharpoons & H^+ + \text{In}^- \\ c(1-\alpha) & & c\alpha \end{array}$$

Now $A_{\max} = l\varepsilon(\text{In}^-)\cdot c$

$A_s = l\varepsilon(\text{In}^-)(c\alpha)$

Hence,
$$\alpha = \frac{A_s}{A_{\max}} = \frac{0.699}{1.267\,6} = 0.551$$

Now $$K_{\text{HIn}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} = \frac{[\text{H}^+](c\alpha)}{c(1-\alpha)} = \frac{[\text{H}^+]\alpha}{1-\alpha}$$

Since pH = 4.39, we will have

$$[\text{H}^+] = 4.074 \times 10^{-5}\ \text{mol dm}^{-3}$$

Hence, $$K_{\text{HIn}} = \frac{(4.074\times10^{-5}\ \text{mol dm}^{-3})(0.551)}{(0.449)}$$

$$= 5.0 \times 10^{-5}\ \text{mol dm}^{-3}$$

Example 3.3.10

In studying the dissociation of the complex between Cu^{2+} and sulphosalicylate ions, i.e.

$$\text{CuR} \rightleftharpoons \text{Cu}^{2+} + \text{R}^{2-}$$

it was found that a solution in which the initial concentrations of Cu^{2+} and R^{2-} were 0.016 mol dm^{-3} and 0.026 3 mol dm^{-3}, respectively, has the same absorbance as a solution in which initial concentrations were Cu^{2+} = 0.019 mol dm^{-3} and R^{2-} = 0.019 mol dm^{-3}. The wavelength used is such that only CuR absorbs appreciably. Determine K_c of the reaction.

Solution

We will have

$$K_c = \frac{[\text{Cu}^{2+}][\text{R}^{2-}]}{[\text{CuR}]} = \frac{(0.016\ \text{mol dm}^{-3} - x)(0.0263\ \text{mol dm}^{-3} - x)}{x}$$

$$= \frac{(0.019\ \text{mol dm}^{-3} - x)(0.019\ \text{mol dm}^{-3} - x)}{x}$$

nm

where x is the amount per dm^3 of complex CuR that has formed.

Hence, $$(0.016\ \text{mol dm}^{-3} - x)(0.026\ 3\ \text{mol dm}^{-3} - x) = (0.019\ \text{mol dm}^{-3} - x)^2$$

or $$x = \frac{(0.016\ \text{mol dm}^{-3})(0.026\ 3\ \text{mol dm}^{-3}) - (0.019\ \text{mol dm}^{-3})^2}{(0.042\ 3\ \text{mol dm}^{-3} - 0.038\ \text{mol dm}^{-3})}$$

$$= 0.013\ 9\ \text{mol dm}^{-3}$$

Now $$K_c = \frac{[\text{Cu}^{2+}][\text{R}^{2-}]}{[\text{CuR}]} = \frac{(0.019\ \text{mol dm}^{-3} - x)(0.019\ \text{mol dm}^{-3} - x)}{x}$$

$$= \frac{(0.019\ \text{mol dm}^{-3} - 0.013\ 9\ \text{mol dm}^{-3})^2}{(0.013\ 9\ \text{mol dm}^{-3})} = 0.001\ 870\ \text{mol dm}^{-3}$$

Determination of Composition of the Complex AB_n

The value of n in the complex AB_n can be determined spectrophotometrically. Considering the equilibrium expression

$$\text{AB}_n \rightleftharpoons \text{A} + n\text{B}$$

we have

$$K_c = \frac{[\text{A}][\text{B}]^n}{[\text{AB}_n]}$$

Taking logarithm, we have

$$\log K_c^\circ = \log \{[\text{A}]/c^\circ\} + n \log \{[\text{B}]/c^\circ\} - \log \{[\text{AB}_n]/c^\circ\}$$

A wavelength is chosen where only AB_n absorbs appreciably. We will have

$$A = l\varepsilon(AB_n)[AB_n]$$

or

$$[AB_n] = \frac{A}{l\varepsilon(AB_n)}$$

Substituting the above expression in the previous expression, we get

$$\log K_c^\circ = \log\{[A]/c^\circ\} + n\log\{[B]/c^\circ\} - \log A + \log\{l\varepsilon(AB_n)/c^\circ\}$$

or

$$\log A = [\log\{l\varepsilon(AB_n)/c^\circ\} + \log\{[A]/c^\circ\} - \log K_c^\circ] + n\log\{[B]/c^\circ\}$$

Hence when [A] is kept constant, a plot of log A versus log $\{[B]/c^\circ\}$ gives a straight line whose slope is equal to n.

Alternatively, from the two readings, n may be calculated from the expression

$$n = \frac{\log A_1 - \log A_2}{\log\{[B]_1/c^\circ\} - \log\{[B]_2/c^\circ\}}$$

Example 3.3.11 For the determination of the value of n in $Fe(SCN)_n^{3-n}$, two experiments were done whose data are recorded below.

Experiment No.	*Initial concentrations of* $\frac{Fe^{3+}}{mol\ dm^{-3}}$	$\frac{SCN^-}{mol\ dm^{-3}}$	*Absorbance*
1	3.582×10^{-3}	8.28×10^{-3}	3.0
2	3.582×10^{-3}	3.05×10^{-4}	0.127

What is the value of n?

Solution Using the expression

$$n = \frac{\log A_1 - \log A_2}{\log\{[B]_1/c^\circ\} - \log\{[B]_2/c^\circ\}}$$

we get

$$n = \frac{\log(3.0) - \log(0.127)}{\log(0.008\,28) - \log(0.000\,305)} = \frac{0.4771 - \bar{1}.1038}{\bar{3}.9180 - \bar{4}.4843} = \frac{1.3763}{1.4337}$$

$$= 0.96 \simeq 1$$

3.4 PRIMARY AND SECONDARY PROCESSES

Photochemical reactions can be classified as primary and secondary processes.

Primary Process The primary process of the reaction is the light absorbing process which follows the law of photochemical equivalence. As stated earlier, the photon absorbed by a molecule causes the electronic excitation. The electronic transitions follow the Franck-Condon rule, according to which, the time required for the electronic excitation is so small that the internuclear distance remains unchanged during the excitation.

Based on the relationship between the lower and the upper electronic levels, four types of primary processes are possible. A brief discussion on these four processes is in order.[†]

[†] For detail, see chapter 4 of volume 4 of the book.

Type I In this case, the vibrational energy of the molecule in the upper electronic state exceeds the maximum value, which leads to the dissociation of molecule in its first oscillation. The electronic spectrum consists of a series of discrete vibration-rotation bands converging to a limit and followed by a region of continuous absorption.

Type II In this case, the molecule is simply excited to the upper electronic state. The electronic spectrum consists of a series of bands with no continuous region.

Type III The molecule is again dissociated as the upper level represents an unstable state. The electronic spectrum is continuous throughout.

Type IV In this case, stable and unstable upper levels overlap each other. Transition occurs from the lower level to the stable upper level. During the course of vibration, the molecule is switched over to the unstable one at the point where two levels cross each other; and the molecule then dissociates. This behaviour is referred to as *predissociation*. The electronic spectrum consists of a banded region. In the predissociation region, the rotational lines are absent and the vibrational bands have diffuse appearance.

Secondary Processes

The products of primary process may involve in subsequent thermal reactions. These processes are known as secondary processes. The secondary process may involve only one step or more than one step. Sometimes, the secondary processes represent the chain reaction.

For example, the photochemical decomposition of HI involves the following processes:

Primary process $HI \xrightarrow{h\nu} H + I$

Secondary Processes $H + HI \longrightarrow H_2 + I$

$I + I \longrightarrow I_2$

3.5 QUANTUM EFFICIENCY

Definition An important parameter of a photochemical reaction is the quantum efficiency or quantum yield which is defined as

$$\Phi = \frac{\text{Rate of conversion}}{\text{Rate of photon absorption}} = \frac{d\xi/dt}{dn_\gamma/dt}$$

For a finite time, this may be expressed as

$$\Phi = \frac{\text{Amount of the substance reacted}}{\text{Amount of photons absorbed}}$$

In terms of number of substance reacted, we have

$$\Phi = \frac{\text{Number of molecules reacted}}{\text{Number of photons absorbed}}$$

According to the law of photochemical equivalence, the quantum efficiency will always be equal to one. But reactions of low and high quantum yields (as low as 0.04 and as high as 10^5) are known.

For a primary process, the quantum yield is always one, it is the secondary processes which alter the overall quantum yield of the reaction. Therefore, the determination of quantum yield helps understanding the nature of secondary processes.

Determination of Number of Photons Absorbed

The amount of photons absorbed are counted either with a *thermopile* or a *chemical actinometer.*

The **thermopile** is made up of a large number of junctions of two dissimilar metals. The radiation falling on it is converted into thermal energy. The increase in temperature is a measure of the intensity of radiation. The instrument is calibrated with standard lamps.

A **chemical actinometer** depends on the use of a photochemical reaction of known quantum yield. A common reaction used in actinometers is the decomposition of oxalic acid, sensitized by uranyl ion. The uranyl ion UO_2^{2+} absorbs light in the wavelength region from 250 nm to 440 nm. The excited UO_2^{2+} transfers the absorbed energy to the oxalic acid which is decomposed. The reactions are

$$UO_2^{2+} + h\nu \longrightarrow (UO_2^{2+})^*$$

$$(UO_2^{2+})^* + (COOH)_2 \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The amount of oxalic acid decomposed can be determined by titrating undecomposed oxalic acid against $KMnO_4$ solution. The quantum efficiency of the above reaction is 0.57. Hence, knowing the amount of oxalic acid decomposed, the amount of photons absorbed can be determined.

The radiation used for the photochemical reaction must be monochromatic. These are usually obtained by using discharge tubes which give atomic line spectra; the line of desired wavelength is isolated by means of a filter or by passage through a prism in a spectrograph. A device of this kind is called a monochromator.

Experimental set up of Photochemical Reactions

A schematic diagram of the apparatus used for the study of a photochemical reaction is shown in Fig. 3.5.1, where A represents a light source emitting radiation of suitable intensity in the desired spectral ~~range,~~ B is the lens, C is the monochromator or filter, D photochemical cell which contains the reaction mixture, and E is the recorder where its intensity is measured.

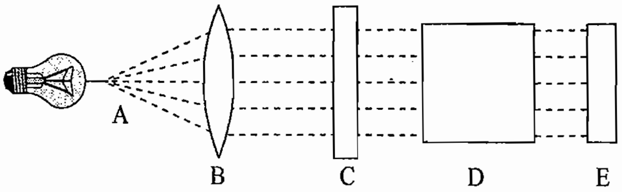


Fig. 3.5.1 Experimental set up to study photochemical reactions

First of all, the cell filled with the solvent is exposed to the radiation and the reading is recorded. This gives the total energy incident upon the system in a given interval of time. Next the cell is filled with the reacting mixture and is exposed to the radiation over the same interval of time and the reading is recorded. This gives the total energy transmitted. The difference between the two readings gives the total energy absorbed by the reacting mixture in the given interval of time.

Reasons of Low and High Quantum Efficiency

The quantum efficiency of a reaction helps understanding the nature of secondary processes and hence the mechanism of chemical reactions. If the absorption of radiation lies in the banded region, the electron is excited to the upper level without causing decomposition of the molecule. The excited molecule may deactivate itself by any one of the following steps.

- The excited molecule may simply emit the radiation of the frequency which it absorbed. The emitted radiation is called *resonance radiation.*
- The absorbed energy may be re-emitted as fluorescence or phosphorescence. The intensity of fluorescence depends on the concentration or pressure of the system. The frequency of fluorescent light is different from that of the absorbed light.
- The molecule may collide with other molecules and pass on them some or all of its excitation energy. This energy either can cause a reaction in the other molecule or can gradually be degraded into heat.
- The excited molecule may react with other molecules.
- The excited molecule may decompose through predissociation.

On the other side, if the absorption lies in the continuous region, the molecule dissociates to produce active species which react with the reactant molecules or other molecules in the secondary processes.

With the above facts, it is easy to understand the reasons for obtaining the low and high quantum efficiency. Some of the reasons are as follows.

Low Quantum Yield

A few reasons are:

1. The excited molecule is deactivated through fluorescence or phosphorescence.
2. The excited molecule is deactivated by converting its energy into the kinetic energy of other molecules (heating effects are produced).
3. The secondary process may involve a step which produces the reactant molecule as one of the products.
4. The energy absorbed might not be sufficient to cause any fruitful excitation of the molecule.

High Quantum Yield

The high quantum yield is attributed to the chain reactions caused by the generation of atoms or free radicals in the primary process. The quantum yield depends on the length of the chain propagating steps.

Example 3.5.1

In the photochemical decomposition of ethylene iodide

$$C_2H_4I_2 + h\nu \longrightarrow C_2H_4 + I_2$$

with radiation of 424 nm, the iodine formed after 20 minutes required 41.14 cm^3 of 0.002 5 mol dm^{-3} solution of $Na_2S_2O_3$. The intensity of the light source was 9.15×10^{-4} J s^{-1}. Calculate the quantum yield assuming absorption of the energy was complete.

Solution

The quantity of energy consumed in 20 minutes

$$= (9.15 \times 10^{-4}\ \mathrm{J\ s^{-1}})\ (20 \times 60\ \mathrm{s}) = 1.098\ \mathrm{J}$$

Energy associated with 1 mol of photons of wavelength 424 nm

$$= \frac{N_A hc}{\lambda} = \frac{(6.022\times10^{23}\,\mathrm{mol^{-1}})(6.626\times10^{-34}\,\mathrm{J\,s})(3\times10^{8}\,\mathrm{m\,s^{-1}})}{(424\times10^{-9}\,\mathrm{m})}$$

$$= 2.823 \times 10^5\ \mathrm{J\,mol^{-1}}$$

Amount of radiation consumed

$$= \frac{1.098\,\mathrm{J}}{(2.823\times10^{5}\,\mathrm{J\,mol^{-1}})} = 3.890 \times 10^{-6}\ \mathrm{mol}$$

Amount of $S_2O_3^{2-}$ consumed

$$= (0.002\,5\ \mathrm{mol\,dm^{-3}})\,(0.041\,14\ \mathrm{dm^3}) = 1.028 \times 10^{-4}\ \mathrm{mol}$$

From the reaction $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$, we get

Amount of ethylene iodide reacted = amount of iodine formed

$$= \frac{1.028\times10^{-4}\,\mathrm{mol}}{2} = 0.514 \times 10^{-4}\ \mathrm{mol}$$

Hence, $\quad \text{Quantum yield} = \dfrac{\text{Amount of ethylene iodide reacted}}{\text{Amount of radiation absorbed}}$

$$= \frac{(0.514\,5\times10^{-4}\,\mathrm{mol})}{(3.890\times10^{-6}\,\mathrm{mol})} = 13.225$$

Example 3.5.2 The photochemical dissociation of gaseous HI to form hydrogen and iodine atoms requires radiation of 404 nm or less. (a) Determine the molar energy of dissociation of HI. (b) If radiation of 253.7 nm is used, how much energy will appear as kinetic energy of atoms?

Solution (a) On absorbing one photon of wavelength 404 nm, one molecule of HI is dissociated. For the decomposition of one mole of HI, we will require N_A photons. Hence, energy carried by these photons is

$$E = \frac{N_A hc}{\lambda} = \frac{(6.022\times10^{23}\,\mathrm{mol^{-1}})\,(6.626\times10^{-34}\,\mathrm{J\,s})\,(3\times10^{8}\,\mathrm{m\,s^{-1}})}{(404\times10^{-9}\,\mathrm{m})}$$

$$= 2.963 \times 10^5\ \mathrm{J\,mol^{-1}}$$

which is molar energy of dissociation of HI.

(b) If the wavelength of the incident light is less than 404 nm, the atoms after dissociating will fly apart with the total kinetic energy equivalent to the excessive energy. One mole of radiation of wavelength 253.7 nm will carry an energy

$$\frac{N_A hc}{\lambda} = \frac{(6.022\times10^{23}\,\mathrm{mol^{-1}})(6.626\times10^{-34}\,\mathrm{J\,s})(3\times10^{8}\,\mathrm{m\,s^{-1}})}{(253.7\times10^{-9}\,\mathrm{m})}$$

$$= 4.719 \times 10^5\ \mathrm{J\,mol^{-1}}$$

Hence, extra energy which appears as kinetic energy

$$= (4.719 \times 10^5 - 2.963 \times 10^5)\ \mathrm{J\,mol^{-1}} = 1.756 \times 10^5\ \mathrm{J\,mol^{-1}}$$

Example 3.5.3 When acetone vapour is irradiated with light of wavelength 313 nm it decomposes to form ethane and carbon monoxide.

$$(CH_3)_2CO + h\nu \longrightarrow C_2H_6 + CO$$

Using a reaction cell of 60.3 cm^3 capacity and a temperature of 329 K irradiation for 23 000 s at the rate of 8.52×10^{-3} J s^{-1} produced a change in pressure from 760.0 to 790.4 mmHg. Calculate (a) the number of molecules of acetone decomposed, and (b) the quantum yield.

Solution **(a)** Change in pressure = 790.4 mmHg – 760.0 mmHg = 30.4 mmHg. This increase in pressure is due to the increase in the number of gaseous molecules. There is an increase of one molecule per molecule of acetone dissociated. Hence, number of molecules of acetone dissociated as given by ideal gas law is

$$\frac{(\Delta p)V}{RT} N_A = \frac{\left(\dfrac{1.013\times10^5}{760}\times30.4\ \mathrm{N\,m^{-2}}\right)\left(\dfrac{60.3}{10^6}\ \mathrm{m^3}\right)}{(8.314\ \mathrm{N\,m\,K^{-1}\,mol^{-1}})(329\ \mathrm{K})} \times (6.022\times10^{23}\ \mathrm{mol^{-1}})$$

$$= 5.38 \times 10^{19}$$

(b) Quantity of energy absorbed

$$= (8.52\times10^{-3}\ \mathrm{J\,s^{-1}})\,(23\,000\ \mathrm{s}) = 195.96\ \mathrm{J}$$

Number of photons absorbed

$$= \frac{(195.96\ \mathrm{J})}{hc/\lambda} = \frac{(195.96\ \mathrm{J})(313\times10^{-9}\ \mathrm{m})}{(6.626\times10^{-34}\ \mathrm{J\,s})(3\times10^{8}\ \mathrm{m\,s^{-1}})}$$

$$= 3.086 \times 10^{20}$$

Hence, $\Phi = \dfrac{5.38\times10^{19}}{3.086\times10^{20}} = 0.174$

Example 3.5.4 In the photochemical combination of H_2(g), and Cl_2(g), a quantum efficiency of about 1×10^6 is obtained with a wavelength of 480 nm. What amount of HCl(g) would be produced under these conditions per calories of radiant energy absorbed?

Solution Energy associated with 1 mol of photons of wavelength 480 nm

$$= \frac{N_A hc}{\lambda} = \frac{(6.022\times10^{23}\ \mathrm{mol^{-1}})(6.626\times10^{-34}\ \mathrm{J\,s})(3\times10^{8}\ \mathrm{m\,s^{-1}})}{(480\times10^{-9}\ \mathrm{m})}$$

$$= 2.494 \times 10^{5}\ \mathrm{J\,mol^{-1}}$$

Amount of photons in 1 cal (i.e. 4.184 J)

$$= \frac{(4.184\ \mathrm{J})}{2.494\times10^{5}\ \mathrm{J\,mol^{-1}}} = 1.677\times10^{-5}\ \mathrm{mol}$$

Since $\Phi = \dfrac{\text{Amount of substance reacted}}{\text{Amount of photons absorbed}}$, we have

$$1\times10^{6} = \frac{\text{Amount of } Cl_2 \text{ reacted}}{1.677\times10^{-5}\ \mathrm{mol}}$$

Hence,

Amount of Cl_2 reacted = $(1 \times 10^6)(1.677 \times 10^{-5}$ mol) = 16.77 mol

1 mol of Cl_2 on reacting produces 2 mol of HCl. Hence, amount of HCl produced is 33.54 mol.

Example 3.5.5 In 10 cm^3 of a solution of 0.049 5 mol dm^{-3} oxalic acid and 0.01 mol dm^{-3} uranyl sulphate was passed a radiation of 254 nm. After the mixture had absorbed 88.1 J, the concentration of the oxalic acid was found to be 0.038 3 mol dm^{-3}. What is the quantum yield at this wavelength for the decomposition of oxalic acid?

Solution 1 mol of photons of wavelength 254 nm carries energy

$$= \frac{N_A hc}{\lambda} = \frac{(6.022 \times 10^{23}\ \text{mol}^{-1})(6.626 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{(254 \times 10^{-9}\ \text{m})}$$

$$= 4.714 \times 10^{5}\ \text{J mol}^{-1}$$

Amount of photons absorbed

$$= \frac{(88.1\ \text{J})}{(4.714 \times 10^{5}\ \text{J mol}^{-1})} = 1.869 \times 10^{-4}\ \text{mol}$$

Amount of oxalic acid reacted in 10 cm^3 of the solution

$$= \left(\frac{0.049\,5\ \text{mol} - 0.038\,3\ \text{mol}}{1\,000\ \text{cm}^3}\right)(10\ \text{cm}^3)$$

$$= 1.12 \times 10^{-4}\ \text{mol}$$

Hence, $\Phi = \dfrac{\text{Amount of oxalic acid reacted}}{\text{Amount of photons absorbed}} = \dfrac{1.12 \times 10^{-4}\ \text{mol}}{1.869 \times 10^{-4}\ \text{mol}} = 0.599$

Example 3.5.6 Absorption of UV radiation decomposes acetone according to the reaction

$$(CH_3)_2CO \xrightarrow{h\nu} C_2H_6 + CO$$

The quantum yield of the reaction at 280 nm is 0.2. A sample of acetone absorbs monochromatic radiation at 280 nm at the rate of 7.50 × 10^{-3} J s^{-1}. Calculate the rate of formation of CO.

Solution Energy carried by 1 mol of photons

$$= \frac{N_A hc}{\lambda} = \frac{(6.022 \times 10^{23}\ \text{mol}^{-1})(6.626 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{(280 \times 10^{-9}\ \text{m})}$$

$$= 4.275 \times 10^{5}\ \text{J mol}^{-1}$$

Amount of photons absorbed per second

$$= \frac{7.50 \times 10^{-3}\ \text{J s}^{-1}}{4.275 \times 10^{5}\ \text{J mol}^{-1}} = 1.754 \times 10^{-8}\ \text{mol s}^{-1}$$

Since 1 mol of acetone of decomposing produces 1 mol of CO, therefore

Amount of CO produced in one second

$$= \text{(Amount of photon absorbed) (Quantum yield)}$$

$$= (1.754 \times 10^{-8}\ \text{mol s}^{-1})\ (0.2)$$

$$= 3.508 \times 10^{-9}\ \text{mol s}^{-1}$$

3.6 KINETICS OF PHOTOCHEMICAL REACTIONS

As indicated earlier, a photochemical reaction includes two types of processes, namely primary and secondary processes. In the primary process, the radiation is absorbed by the light absorbing substance. The quantum efficiency of this process is always equal to one (law of photochemical equivalence). Hence, the number of molecules of light absorbing substance removed per unit time (i.e. the rate at which light absorbing substance is removed) in the primary process is equal to the intensity of the light.

To be specific, let us take an example of the following light absorbing primary process;

$$Br_2 \xrightarrow{h\nu} 2Br$$

Now $$\Phi = \frac{\text{Amount of } Br_2 \text{ decomposed per unit time}}{\text{Amount of radiation absorbed per unit time}}$$

$$= \frac{-d[Br_2]/dt}{I_{abs}}$$

Now since $\Phi = 1$, we will have

$$\frac{-d[Br_2]}{dt} = I_{abs}$$

If the amount of Br formed in primary step is required, we will have

$$\frac{d[Br]}{dt} = 2I_{abs}$$

The nature of products formed in the primary process depends on the obtained absorption spectrum. If the spectrum includes only a series of lines (i.e. banded), then the product formed is an excited molecule. If it also includes a continuum, then the molecule on absorption dissociates and thus active atoms of radicals are produced.

The secondary processes represent the thermal reactions which also include the reaction (or reactions) between the products of primary process and other substances. The rate at which these reactions proceed can be represented as usual by the differential rate law.

The steady-state approximation can be applied to the reactive intermediates. Thus, the differential rate law of a photochemical reaction can be worked out as for any other thermal reaction. The only difference that appears is while writing the differential rate law of the primary process.

In general, the rate of photochemical reactions depends on the intensity of absorbed light.

To illustrate the procedure, we describe below a few photochemical reactions.

Decomposition of HI

The decomposition of HI has been studied with wavelengths of 207, 253 and 282 nm. The electronic spectrum of hydrogen iodide is continuous in the region from about 332 nm to below 200 nm wavelength, hence the dissociation of HI is involved in the primary process. Thus the mechanism of the reaction is:

$$\textit{Primary process} \qquad \mathrm{HI} \xrightarrow{h\nu} \mathrm{H + I}$$

$$\textit{Secondary processes} \qquad \mathrm{H + HI} \xrightarrow{k_2} \mathrm{H_2 + I}$$

$$\mathrm{I + I} \xrightarrow{k_3} \mathrm{I_2}$$

The rate of disappearance of HI

$$-\frac{d[\mathrm{HI}]}{dt} = I_{\mathrm{abs}} + k_2\,[\mathrm{H}]\,[\mathrm{HI}] \qquad (3.6.1)$$

Applying the steady-state approximation to hydrogen atoms, we get

$$\frac{d[\mathrm{H}]}{dt} = 0 = I_{\mathrm{abs}} - k_2\,[\mathrm{H}]\,[\mathrm{HI}] \qquad (3.6.2)$$

Hence, $k_2\,[\mathrm{H}]\,[\mathrm{HI}] = I_{\mathrm{abs}}$ (3.6.3)

Substituting Eq. (3.6.3) in Eq. (3.6.2), we get

$$-\frac{d[\mathrm{HI}]}{dt} = 2I_{\mathrm{abs}} \qquad (3.6.4)$$

The quantum efficiency is

$$\Phi = \frac{\text{Rate of disappearance of HI}}{\text{Rate at which photon is absorbed}} = \frac{d[\mathrm{HI}]/dt}{I_{\mathrm{abs}}}$$

$$= \frac{2I_{\mathrm{abs}}}{I_{\mathrm{abs}}} = 2 \qquad (3.6.5)$$

As the reaction proceeds, the quantum efficiency decreases. The reason behind this is that as iodine accumulates, the thermal reaction

$$\mathrm{H + I_2} \xrightarrow{k_4} \mathrm{HI + I}$$

becomes appreciable. With the inclusion of this reaction, the steady-state approximation as applied to H atoms gives

$$\frac{d[\mathrm{H}]}{dt} = 0 = I_{\mathrm{abs}} - k_2\,[\mathrm{H}][\mathrm{HI}] - k_4\,[\mathrm{H}][\mathrm{I_2}]$$

Hence, $[\mathrm{H}] = \dfrac{I_{\mathrm{abs}}}{k_2[\mathrm{HI}] + k_4[\mathrm{I_2}]}$

Substituting this in the expression

$$-\frac{d[\mathrm{HI}]}{dt} = I_{\mathrm{abs}} + k_2[\mathrm{H}][\mathrm{HI}] - k_4[\mathrm{H}]\,[\mathrm{I_2}]$$

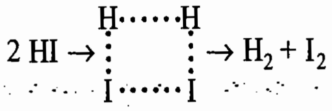
we get $-\dfrac{d[\mathrm{HI}]}{dt} = I_{\mathrm{abs}} + (k_2[\mathrm{HI}] - k_4[\mathrm{I_2}])\,\dfrac{I_{\mathrm{abs}}}{k_2[\mathrm{HI}] + k_4[\mathrm{I_2}]}$

or $-\dfrac{d[\mathrm{HI}]}{dt} = I_{\mathrm{abs}}\left(\dfrac{2}{1 + k_4[\mathrm{I_2}]/k_2[\mathrm{HI}]}\right)$

Hence, $$\Phi = \frac{2}{1 + k_4[\mathrm{I_2}]/k_2[\mathrm{HI}]} \qquad (3.6.6)$$

With time, the concentration of I_2 increases and that of HI decreases, with the result the Φ decreases from its original value of 2.

The mechanism of thermal decomposition of HI is quite different, where we have



$$2\,\mathrm{HI} \rightarrow \begin{array}{ccc} \mathrm{H} & \cdots\cdots & \mathrm{H} \\ \vdots & & \vdots \\ \mathrm{I} & \cdots\cdots & \mathrm{I} \end{array} \rightarrow \mathrm{H_2} + \mathrm{I_2}$$

and the rate law is

$$-\frac{1}{2}\,\frac{\mathrm{d[HI]}}{\mathrm{d}t} = k\,[\mathrm{HI}]^2$$

Reaction between Hydrogen and Bromine

The mechanism of photochemical reaction between H_2 and Br_2 is similar to that established for the thermal reaction. The mechanism is

(i) $\mathrm{Br_2} \xrightarrow{h\nu} 2\mathrm{Br}$

(ii) $\mathrm{Br} + \mathrm{H_2} \xrightarrow{k_2} \mathrm{HBr} + \mathrm{H}$

(iii) $\mathrm{H} + \mathrm{Br_2} \xrightarrow{k_3} \mathrm{HBr} + \mathrm{Br}$

(iv) $\mathrm{H} + \mathrm{HBr} \xrightarrow{k_4} \mathrm{H_2} + \mathrm{Br}$

(v) $\mathrm{Br} + \mathrm{Br} \xrightarrow{k_5} \mathrm{Br_2}$

The rate of formation of HBr is given by

$$\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = k_2[\mathrm{H_2}][\mathrm{Br}] + k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] \qquad (3.6.7)$$

The steady-state approximation applied to H and Br atoms gives

$$\frac{\mathrm{d[H]}}{\mathrm{d}t} = 0 = k_2[\mathrm{H_2}][\mathrm{Br}] - k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{HBr}][\mathrm{H}] \qquad (3.6.8)$$

$$\frac{\mathrm{d[Br]}}{\mathrm{d}t} = 2I_{\mathrm{abs}} - k_2[\mathrm{H_2}][\mathrm{Br}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_4[\mathrm{HBr}][\mathrm{H}] - 2k_5[\mathrm{Br}]^2 \qquad (3.6.9)$$

(**Note** the factor of 2 in the first term and in last term; in the first term it is due to the fact that 2 atoms of Br are produced per bromine molecule decomposed; in the last term, it is due to the fact that the rate expression of reaction (v) is $-(1/2)\mathrm{d[Br]}/\mathrm{d}t = k_5\,[\mathrm{Br}]^2$, hence $-\mathrm{d[Br]}/\mathrm{d}t = 2k_5\,[\mathrm{Br}]^2$.)

On adding Eqs (3.6.8) and (3.6.9), we get

$$2I_{\mathrm{abs}} - 2k_5\,[\mathrm{Br}]^2 = 0$$

or $$[\mathrm{Br}] = \left(\frac{I_{\mathrm{abs}}}{k_5}\right)^{1/2} \qquad (3.6.10)$$

Substituting Eq. (3.6.10) in Eq. (3.6.8), we get

$$[\mathrm{H}] = \frac{k_2\,(I_{\mathrm{abs}}/k_5)^{1/2}[\mathrm{H_2}]}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} \qquad (3.6.11)$$

Now substituting Eqs (3.6.10) and (3.6.11) in Eq. (3.6.7), we get

$$\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = k_2\,[\mathrm{H_2}]\left(\frac{I_{\mathrm{abs}}}{k_5}\right)^{1/2} + \frac{k_2(I_{\mathrm{abs}}/k_5)^{1/2}[\mathrm{H_2}]}{k_3[\mathrm{Br_2}]+k_4[\mathrm{HBr}]}\,(k_3[\mathrm{Br_2}] - k_4[\mathrm{HBr}])$$

$$= k_2[\mathrm{H_2}]\left(\frac{I_{\mathrm{abs}}}{k_5}\right)^{1/2}\left[1+\frac{k_3[\mathrm{Br_2}]-k_4[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]+k_4[\mathrm{HBr}]}\right]$$

$$= \frac{2k_2(I_{\mathrm{abs}}/k_5)^{1/2}[\mathrm{H_2}]}{1+(k_4[\mathrm{HBr}]/k_3[\mathrm{Br_2}])} \qquad (3.6.12)$$

While evaluating the quantum efficiency, we require $-\,\mathrm{d[Br_2]}/\mathrm{d}t$, which is given as

$$-\frac{\mathrm{d[Br_2]}}{\mathrm{d}t} = I_{\mathrm{abs}} + k_3[\mathrm{H}][\mathrm{Br_2}] - k_5[\mathrm{Br}]^2$$

Substituting [Br] and [H] from Eqs (3.6.10) and (3.6.11), we get

$$-\frac{\mathrm{d[Br_2]}}{\mathrm{d}t} = I_{\mathrm{abs}} + k_3[\mathrm{Br_2}]\left(\frac{k_2(I_{\mathrm{abs}}/k_5)^{1/2}[\mathrm{H_2}]}{k_3[\mathrm{Br_2}]+k_4[\mathrm{HBr}]}\right) - k_5\left(\frac{I_{\mathrm{abs}}}{k_5}\right)$$

or

$$-\frac{\mathrm{d[Br_2]}}{\mathrm{d}t} = \frac{k_2(I_{\mathrm{abs}}/k_5)^{1/2}[\mathrm{H_2}]}{1+(k_4[\mathrm{HBr}]/k_3[\mathrm{Br_2}])} \qquad (3.6.13)$$

(Note that $\mathrm{d\,[HBr]/d}t = 2\,(-\,\mathrm{d\,[Br_2]/d}t)$. This follows immediately from the fact that 1 mol of $\mathrm{Br_2}$ on reacting with 1 mol of $\mathrm{H_2}$ will produce 2 mol of HBr.)

Hence,

$$\Phi = \frac{-\mathrm{d[Br_2]/d}t}{I_{\mathrm{abs}}} = \frac{1}{I_{\mathrm{abs}}^{1/2}}\,\frac{k_2(1/k_5)^{1/2}[\mathrm{H_2}]}{1+(k_4[\mathrm{HBr}]/k_3[\mathrm{Br_2}])} \qquad (3.6.14)$$

The activation energy for the reaction (ii), i.e. between Br and $\mathrm{H_2}$ is about 75 kJ mol^{-1}. Consequently, the reaction (ii) is slow at room temperature and thus k_2 has a small value. From Eq. (3.6.14), it follows that the quantum efficiency will have a small value in spite of the fact that the HBr is formed in a chain reaction. On increasing the temperature, k_2 increases (k_5 is nearly independent of temperature as it involves the reaction between two atoms) and thus Φ is also increased.

Reaction between CO and $\mathrm{Cl_2}$

The proposed mechanism of photochemical reaction between CO and $\mathrm{Cl_2}$ is

(i) $\mathrm{Cl_2} \xrightarrow{h\nu} 2\,\mathrm{Cl}$

(ii) $\mathrm{Cl + CO} \xrightarrow{k_2} \mathrm{COCl}$

(iii) $\mathrm{COCl} \xrightarrow{k_3} \mathrm{CO + Cl}$

(iv) $\mathrm{COCl + Cl_2} \xrightarrow{k_4} \mathrm{COCl_2 + Cl}$

(v) $\mathrm{COCl + Cl} \xrightarrow{k_5} \mathrm{CO + Cl_2}$

The rate of formation of phosgene is given by

$$\frac{d[COCl_2]}{dt} = k_4[COCl][Cl_2] \tag{3.6.15}$$

Applying the steady-state approximation to Cl and COCl, we get

$$\frac{d[Cl]}{dt} = 0 = 2\,I_{abs} - k_2[Cl][CO] + k_3[COCl] + k_4[COCl][Cl_2] - k_5[COCl][Cl] \tag{3.6.16}$$

$$\frac{d[COCl]}{dt} = 0 = k_2[Cl][CO] - k_3[COCl] - k_4[COCl][Cl_2] - k_5[COCl][Cl] \tag{3.6.17}$$

Adding Eqs (3.6.16) and (3.6.17), we get

$$2I_{abs} - 2k_5\,[COCl][Cl] = 0$$

or

$$[COCl] = \frac{I_{abs}}{k_5[Cl]} \tag{3.6.18}$$

Reactions (ii) and (iii) together constitute a reversible reaction system. Hence applying the principle of microscopic reversibility (the rates of forward and backward reactions are equal), we get

$$k_2[Cl][CO] = k_3[COCl]$$

Hence,

$$[Cl] = \frac{k_3}{k_2[CO]}\,[COCl]$$

Making use of Eq. (3.6.18), we get

$$[Cl] = \frac{k_3}{k_2[CO]} \cdot \frac{I_{abs}}{k_5[Cl]}$$

or

$$[Cl] = \left(\frac{k_3\,I_{abs}}{k_2k_5[CO]}\right)^{1/2} \tag{3.6.19}$$

Substituting Eq. (3.6.19) in Eq. (3.6.18), we get

$$[COCl] = \frac{I_{abs}}{k_5}\left(\frac{k_2k_5[CO]}{k_3I_{abs}}\right)^{1/2} = \left(\frac{k_2[CO]I_{abs}}{k_3k_5}\right)^{1/2}$$

which on substituting in Eq. (3.6.15) gives

$$\frac{d[COCl_2]}{dt} = k_4\left(\frac{k_2[CO]I_{abs}}{k_3k_5}\right)^{1/2}[Cl_2] \tag{3.6.20}$$

$$= kI_{abs}^{1/2}\,[CO]^{1/2}\,[Cl_2]$$

where $k = k_4(k_2/k_3k_5)^{1/2}$.

The rate of disappearance of Cl_2 is given by

$$-\frac{d[Cl_2]}{dt} = I_{abs} + k_4[COCl][Cl_2] - k_5[COCl][Cl]$$

Substituting the expressions of [COCl] and [COCl] [Cl], we get

$$-\frac{\mathrm{d}[\mathrm{Cl_2}]}{\mathrm{d}t} = I_{\mathrm{abs}} + k_4\left(\frac{k_2[\mathrm{CO}]I_{\mathrm{abs}}}{k_3k_5}\right)^{1/2}[\mathrm{Cl_2}] - I_{\mathrm{abs}}$$

$$= k_4\left(\frac{k_2[\mathrm{CO}]I_{\mathrm{abs}}}{k_3k_5}\right)^{1/2}[\mathrm{Cl_2}] \tag{3.6.21}$$

which is the same as given by Eq. (3.6.20). Hence

$$\Phi = \frac{-\mathrm{d}[\mathrm{Cl_2}]/\mathrm{d}t}{I_{\mathrm{abs}}} = k_4\left(\frac{k_2[\mathrm{CO}]}{k_3k_5I_{\mathrm{abs}}}\right)^{1/2}[\mathrm{Cl_2}] \tag{3.6.22}$$

Photolysis of Acetaldehyde

The proposed mechanism is

$$\mathrm{CH_3CHO} \xrightarrow{h\nu} \mathrm{CH_3 + CHO}$$

$$\mathrm{CH_3 + CH_3CHO} \xrightarrow{k_2} \mathrm{CH_4 + CH_3CO}$$

$$\mathrm{CH_3CO} \xrightarrow{k_3} \mathrm{CO + CH_3}$$

$$\mathrm{CH_3 + CH_3} \xrightarrow{k_4} \mathrm{C_2H_6}$$

The rate of formation of CO is

$$\frac{\mathrm{d}[\mathrm{CO}]}{\mathrm{d}t} = k_3[\mathrm{CH_3CO}] \tag{3.6.23}$$

Applying the steady-state approximation to CH_3CO and CH_3, we get

$$\frac{\mathrm{d}[\mathrm{CH_3CO}]}{\mathrm{d}t} = 0 = k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}] - k_3[\mathrm{CH_3CO}] \tag{3.6.24}$$

$$\frac{\mathrm{d}[\mathrm{CH_3}]}{\mathrm{d}t} = 0 = I_{\mathrm{abs}} - k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}] + k_3[\mathrm{CH_3CO}] - 2k_4[\mathrm{CH_3}]^2 \tag{3.6.25}$$

Adding Eqs (3.6.24) and (3.6.25), we get

$$[\mathrm{CH_3}] = \left(\frac{I_{\mathrm{abs}}}{2k_4}\right)^{1/2} \tag{3.6.26}$$

Substituting Eq. (3.6.26) in Eq. (3.6.24), we have

$$k_2\left(\frac{I_{\mathrm{abs}}}{2k_4}\right)^{1/2}[\mathrm{CH_3CHO}] - k_3[\mathrm{CH_3CO}] = 0$$

or

$$[\mathrm{CH_3CO}] = \frac{k_2}{k_3}\left(\frac{I_{\mathrm{abs}}}{2k_4}\right)^{1/2}[\mathrm{CH_3CHO}] \tag{3.6.27}$$

Substituting Eq. (3.6.27) in Eq. (3.6.23), we get

$$\frac{\mathrm{d}[\mathrm{CO}]}{\mathrm{d}t} = k_2\left(\frac{I_{\mathrm{abs}}}{2k_4}\right)^{1/2}[\mathrm{CH_3CHO}] \tag{3.6.28}$$

Decomposition of H_2O_2 in the Presence of CO

The proposed mechanism is

$$H_2O_2 \xrightarrow{h\nu} 2OH$$

$$OH + CO \xrightarrow{k_2} COOH$$

$$COOH + H_2O_2 \xrightarrow{k_3} CO_2 + H_2O + OH$$

$$H_2O_2 + OH \xrightarrow{k_4} H_2O + HO_2$$

$$2HO_2 \xrightarrow{k_5} O_2 + H_2O_2$$

The rate of formation of O_2 is given by

$$\frac{d[O_2]}{dt} = k_5[HO_2]^2 \tag{3.6.29}$$

Applying the steady-state approximation to HO_2, OH and COOH, we get

$$\frac{d[HO_2]}{dt} = 0 = k_4[H_2O_2][OH] - 2k_5[HO_2]^2 \tag{3.6.30}$$

$$\frac{d[OH]}{dt} = 0 = 2I_{abs} - k_2[OH][CO] + k_3[COOH][H_2O_2] - k_4[H_2O_2][OH] \tag{3.6.31}$$

$$\frac{d[COOH]}{dt} = 0 = k_2[OH][CO] - k_3[COOH][H_2O_2] \tag{3.6.32}$$

Adding Eqs (3.6.31) in (3.6.32), we get

$$2I_{abs} - k_4[H_2O_2][OH] = 0$$

or $$[OH] = \frac{2I_{abs}}{k_4[H_2O_2]} \tag{3.6.33}$$

Substituting Eqs (3.6.33) in (3.6.30), we get

$$k_4[H_2O_2]\left(\frac{2I_{abs}}{k_4[H_2O_2]}\right) - 2k_5[HO_2]^2 = 0$$

or $$[HO_2] = \left(\frac{I_{abs}}{k_5}\right)^{1/2} \tag{3.6.34}$$

which on substituting in Eq. (3.6.29) gives

$$\frac{d[O_2]}{dt} = I_{abs}$$

For calculating Φ, we have to evaluate $-\,d[H_2O_2]/dt$. From the given mechanism, we have

$$-\frac{d[H_2O_2]}{dt} = I_{abs} + k_3[COOH][H_2O_2] + k_4[H_2O_2][OH] - k_5[HO_2]^2 \tag{3.6.35}$$

From Eq. (3.6.32), we get

$$[COOH] = \frac{k_2[OH][CO]}{k_3[H_2O_2]}$$

which on making use of Eq. (3.6.33) becomes

$$[COOH] = \frac{2k_2 I_{abs}[CO]}{k_3 k_4 [H_2O_2]^2} \tag{3.6.36}$$

Substituting for [OH], $[HO_2]$ and [COOH] from Eqs (3.6.33), (3.6.34) and (3.6.36) in Eq. (3.6.35), we get

$$-\frac{d[H_2O_2]}{dt} = I_{abs} + k_3\left(\frac{2k_2 I_{abs}[CO]}{k_3k_4[H_2O_2]^2}\right)[H_2O_2] + k_4[H_2O_2]\left(\frac{2I_{abs}}{k_4[H_2O_2]}\right) - k_5\left(\frac{I_{abs}}{k_5}\right)$$

$$= 2I_{abs}\left(1+\frac{k_2[CO]}{k_4[H_2O_2]}\right) \qquad (3.6.37)$$

Hence, $$\Phi = \frac{-d[H_2O_2]/dt}{I_{abs}} = 2\left(1+\frac{k_2[CO]}{k_4[H_2O_2]}\right) \qquad (3.6.38)$$

Chlorination of Chloroform

For the gaseous reaction

$$Cl_2 + CHCl_3 \xrightarrow{h\nu} CCl_4 + HCl$$

the proposed mechanism is

$$Cl_2 \xrightarrow{h\nu} 2Cl$$

$$Cl + CHCl_3 \xrightarrow{k_2} CCl_3 + HCl$$

$$CCl_3 + Cl_2 \xrightarrow{k_3} CCl_4 + Cl$$

$$2CCl_3 + Cl_2 \xrightarrow{k_4} 2CCl_4$$

The rate of formation of CCl_4 is

$$\frac{d[CCl_4]}{dt} = k_3[CCl_3][Cl_2] + 2k_4[CCl_3]^2[Cl_2] \qquad (3.6.39)$$

Applying the steady-state approximation to CCl_3 and Cl, we get

$$\frac{d[CCl_3]}{dt} = 0 = k_2[Cl][CHCl_3] - k_3[CCl_3][Cl_2] - 2k_4[CCl_3]^2[Cl_2] \qquad (3.6.40)$$

$$\frac{d[Cl]}{dt} = 0 = 2I_{abs} - k_2[Cl][CHCl_3] + k_3[CCl_3][Cl_2] \qquad (3.6.41)$$

Adding Eqs (3.6.40) and (3.6.41), we get

$$2I_{abs} - 2k_4[CCl_3]^2[Cl_2] = 0$$

or $$[CCl_3] = \left(\frac{I_{abs}}{k_4[Cl_2]}\right)^{1/2} \qquad (3.6.42)$$

Substituting Eq. (3.6.42) in Eq. (3.6.39), we get

$$\frac{d[CCl_4]}{dt} = k_3\left(\frac{I_{abs}}{k_4[Cl_2]}\right)^{1/2}[Cl_2] + 2k_4\frac{I_{abs}}{k_4[Cl_2]}[Cl_2]$$

$$= 2I_{abs} + k_3\left(\frac{I_{abs}[Cl_2]}{k_4}\right)^{1/2} \qquad (3.6.43)$$

For the quantum yield, we determine $-\,\mathrm{d}[Cl_2]/\mathrm{d}t$. From the given mechanism, we have

$$-\frac{\mathrm{d}[Cl_2]}{\mathrm{d}t} = I_{abs} + k_3[CCl_3][Cl_2] + k_4[CCl_3]^2[Cl_2]$$

Substituting for $[CCl_3]$ from Eq. (3.6.42), we get

$$-\frac{\mathrm{d}[Cl_2]}{\mathrm{d}t} = I_{abs} + k_3\left(\frac{I_{abs}}{k_4[Cl_2]}\right)^{1/2}[Cl_2] + k_4\left(\frac{I_{abs}}{k_4[Cl_2]}\right)[Cl_2]$$

$$= 2I_{abs} + k_3\left(\frac{I_{abs}[Cl_2]}{k_4}\right)^{1/2} \tag{3.6.44}$$

Equation (3.6.44) follows from Eq: (3.6.43), since $-\,\mathrm{d}[Cl_2]/\mathrm{d}t = \mathrm{d}[CCl_4]/\mathrm{d}t$.

Hence, $$\Phi = \frac{-\mathrm{d}[Cl_2]/\mathrm{d}t}{I_{abs}} = 2 + k_3\left(\frac{[Cl_2]}{I_{abs}\,k_4}\right)^{1/2} \tag{3.6.45}$$

3.7 EFFECT OF TEMPERATURE ON PHOTOCHEMICAL REACTIONS

The effect of temperature on photochemical reactions is primarily due to the type and nature of secondary processes. The primary process of light absorption is practically independent of temperature.

If the secondary process involves the active atom or radical produced in the primary process, its activation energy is usually very small and thus very small temperature coefficient of the overall process is observed. If one or more of the secondary processes possess a large activation energy, then the photochemical reaction exhibits a larger value of temperature coefficient. If the secondary processes involve a reversible reaction of appreciable energy of reaction and if its equilibrium constant appears in the final rate expression, then obviously, a large temperature coefficient is expected. The effect of temperature on the photochemical reaction between CO and Cl_2 may be described here. The rate of formation of $COCl_2$ as given by Eq. (3.6.20) is

$$\frac{\mathrm{d}[COCl_2]}{\mathrm{d}t} = k\,I_{abs}^{1/2}\,[CO]^{1/2}\,[Cl_2]$$

where $$k = k_4\left(\frac{k_2}{k_3}\right)^{1/2}\left(\frac{1}{k_5}\right)^{1/2} = k_4\,K^{1/2}\left(\frac{1}{k_5}\right)^{1/2}$$

We write the above expression as

$$\frac{k}{\mathrm{mol^{-1}\,dm^3\,s^{-1/2}}} = \left(\frac{k_4}{\mathrm{mol^{-1}\,dm^3\,s^{-1/2}}}\right)\left(\frac{k_2/k_3}{\mathrm{mol^{-1}\,dm^3}}\right)\left(\frac{\mathrm{mol^{-1}\,dm^3\,s^{-1}}}{k_5}\right)^{1/2}$$

that is

$$\frac{k}{k^\circ} = \left(\frac{k_4}{k_4^\circ}\right)(Kc^\circ)\left(\frac{k_5^\circ}{k_5}\right)^{1/2}$$

Taking logarithm and then differentiating with respect to temperature, we get

$$\frac{\mathrm{d}\ln(k/k^{\circ})}{\mathrm{d}T} = \frac{\mathrm{d}\ln(k_4/k_4^{\circ})}{\mathrm{d}T} + \frac{1}{2}\frac{\mathrm{d}\ln(Kc^{\circ})}{\mathrm{d}T} - \frac{1}{2}\frac{\mathrm{d}\ln(k_5/k_5^{\circ})}{\mathrm{d}T}$$

$$= \frac{1}{RT^2}\left[\left(E_4 + \frac{1}{2}\Delta H - \frac{1}{2}E_5\right)\right]$$

where E_4 and E_5 are the activation energies of reactions

$$\mathrm{COCl} + \mathrm{Cl_2} \longrightarrow \mathrm{COCl_2} + \mathrm{Cl}$$

$$\mathrm{COCl} + \mathrm{Cl} \longrightarrow \mathrm{CO} + \mathrm{Cl_2}$$

and ΔH is the enthalpy change of the reaction

$$\mathrm{Cl} + \mathrm{CO} \rightleftharpoons \mathrm{COCl}$$

Hence, the variation of the overall rate constant of the reaction depends on E_4, E_5 and ΔH values.

In many cases, a negative temperature coefficient is observed. This is again due to a reversible reaction in secondary processes with a large negative value of ΔH.

If a photochemical reaction has a quantum efficiency of one and shows no temperature dependence, it is very likely that the reaction involves only primary process, i.e. the reaction proceeds in one step with the absorption of radiation. Thus, the determination of temperature coefficient of a photochemical reaction helps establishing the mechanism of a reaction.

3.8 THE PHOTOSTATIONARY STATE

Explanation of the Photostationary State

Absorption of radiation by reactants of a reaction at equilibrium increases the rate of forward reaction without directly affecting the rate of the reverse reaction. The latter is, however, increased due to the increase in the concentration of products. Thus, a new state called the photostationary state (or photochemical equilibrium) is established when the increase in the rate of forward reaction (due to the absorption of light) becomes equal to the increase in the rate of reverse reaction (due to the enhanced concentration of the products).

Dimerization of Anthracene

One of the well-known examples exhibiting photostationary state is the dimerization of anthracene. This example also illustrates another interesting feature of photochemical reactions, namely, the *quenching of fluorescence.*

When a dilute solution of anthracene in benzene or other intert solvent, is exposed to ultraviolet light, the system exhibits fluorescence with a small quantum efficiency of dimerization reaction. As the concentration of anthracene is increased, the fluorescence falls off and the quantum efficiency of dimerization increases towards a limiting value where fluorescence is practically eliminated (Fig. 3.8.1). In other words, the fluorescence is said to be quenched as the concentration of light absorbing substance is increased. The explanation of the above phenomenon is straight forward. The natural life-time of an excited state in a molecule undisturbed by collisions is about 10^{-8} second. At higher concentrations, a molecule experiences a large number of collisions in 10^{-8} second. Consequently, the excited molecule loses its energy by collisions with other molecules before it has a chance to exhibit fluorescence. As the concentration is decreased, the collision frequency decreases and the chance for the fluorescence is increased.

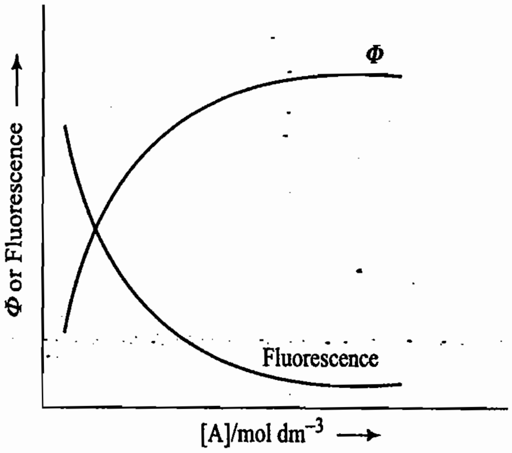


Fig. 3.8.1 Quenching of fluorescence exhibited by anthracene in solution

For gaseous reactions, the fluorescence is quenched even at ordinary pressures. This is because of the fact that the excited molecules in gaseous systems at ordinary pressures usually lose their energies by collision before they have a chance to fluoresce (there are about 100 collisions in 10^{-8} second at a pressure of 1 atm). The fluorescence can, however, be observed if the pressure of the system is reduced significantly.

Kinetics of Quenching of Fluorescence

A kinetic expression for the quenching of fluorescence is obtained by considering the following scheme.

Absorption $\quad M + h\nu \xrightarrow{I_{abs}} M^*$

Fluorescence $\quad M^* \xrightarrow{k_f} M + h\nu'$

Quenching $\quad M^* + Q \xrightarrow{k_q} M + Q + \text{kinetic energy}$

Applying steady-state approximation to M*, we get

$$\frac{d[M^*]}{dt} = I_{abs} - k_f[M^*] - k_q[M^*][Q] = 0$$

or $\quad I_{abs} = k_f[M^*] + k_q[M^*][Q]$

The intensity of fluorescence I_f will be given by

$$I_f = k_f[M^*]$$

The fraction of excited molecules that fluoresce, called the fluorescence yield, is given by

$$\frac{I_f}{I_{abs}} = \frac{k_f[M^*]}{k_f[M^*]+k_q[M^*][Q]} = \frac{1}{1+(k_q/k_f)[Q]}$$

or $$\frac{1}{I_f} = \frac{1}{I_{abs}} + \frac{(k_q/k_f)}{I_{abs}}[Q]$$

The above relationship is known as *Stern-Volmer relation*. According to this, a plot between $1/I_f$ and [Q] will be linear of slope $(k_q/k_f)/I_{abs}$ and intercept $1/I_{abs}$. Hence, (k_q/k_f) can be determined. If k_f is known from an independent determination of the life-time τ of excited state in the absence of quencher Q, the constant k_q can be evaluated.

Mechanism of Dimerization of Anthracene

Coming back to the photostationary state as exhibited by dimerization of anthracene, the following mechanism has been proposed.

Primary Process	(i) $A \xrightarrow{h\nu} A^*$;	rate = I_{abs}
Secondary Processes	(ii) $A^* + A \xrightarrow{k_2} A_2$;	rate = $k_2\,[A^*][A]$
	(iii) $A_2 \xrightarrow{k_3} 2A$;	rate = $k_3\,[A_2]$
	(iv) $A^* \xrightarrow{k_4} A + h\nu'$;	rate = $k_4\,[A^*]$

The rate of formation of A_2 is

$$\frac{d[A_2]}{dt} = k_2[A^*][A] - k_3[A_2] \tag{3.8.1}$$

Applying the steady-state approximation to A*, we get

$$\frac{d[A^*]}{dt} = 0 = I_{abs} - k_2[A^*][A] - k_4[A^*]$$

Hence,
$$[A^*] = \frac{I_{abs}}{k_2[A]+k_4} \tag{3.8.2}$$

Substituting Eq. (3.8.2) in Eq. (3.8.1), we get

$$\frac{d[A_2]}{dt} = k_2 \frac{I_{abs}}{k_2[A]+k_4}[A] - k_3\,[A_2] \tag{3.8.3}$$

In the photostationary state, the reactions (ii) and (iii) represent an equilibrium reaction for which $d[A_2]/dt = 0$. Thus, from Eq. (3.8.3), we get

$$[A_2] = \frac{k_2[A]I_{abs}}{k_3(k_2[A]+k_4)} = \frac{I_{abs}}{k_3(1+k_4/k_2[A])} \tag{3.8.4}$$

If the concentration of monomer is very large, Eq. (3.8.4) reduces to

$$[A_2] = \frac{I_{abs}}{k_3} \tag{3.8.5}$$

that is, when the reaction is at photostationary state the concentration of dimer is independent of the concentration of monomer. This is in contrast to the reaction at the thermal equilibrium state where the concentration of dimer depends on the monomer concentration through the equilibrium constant expression $[A_2] = K\,[A]^2$.

The system at photostationary state, unlike a thermal equilibrium state, is unaffected by the change in temperature of the system.

The system reverts back to the normal equilibrium state as soon as the source of radiation is removed.

3.9 PHOTOSENSITIZED REACTIONS

In many photochemical reactions, the reacting substance does not absorb radiation directly, but acquires the energy from some other light absorbing foreign substance. The latter is known as a *sensitizer*. Thus, in the absence of photosensitized no reaction can take place as the reacting substance cannot absorb radiation of its own. Processes in which photosensitizer is used are known as photosensitizer reactions. Mercury or cadmium vapour are often used as the sensitizer.

Many mercury-photosensitized reactions are known. One of the examples is the combination of carbon monoxide and hydrogen. The proposed mechanism is

$$Hg + h\nu \longrightarrow Hg^*$$

$$Hg^* + H_2 \longrightarrow Hg + 2H$$

$$H + CO \longrightarrow HCO$$

$$HCO + H_2 \longrightarrow HCHO + H$$

$$2HCO \longrightarrow HCHO + CO$$

$$2HCO \longrightarrow HCOCHO \text{ (glyoxal)}$$

In uranyl actinometer, uranyl is used as photosensitizer.

Many other photosensitized reactions of practical importance are known. One of the most important examples is the photosynthesis of carbohydrates in plants where chlorophyll acts as the sensitizer.

3.10 CHEMILUMINESCENCE

Many reactions are accompanied by the emission of visible radiation. This phenomenon is known as chemiluminescence. The explanation of chemiluminescence is very easy to understand; one of the products formed is in the electronically excited state which emits radiation of appropriate wavelength in the visible region of the spectrum.

Examples exhibiting chemiluminescence include phosphorus and its trioxide in air, oxidation by air oxygen of many of the Grignard reagents and oxidation of alkaline aqueous solutions of 5-aminophthalic hydrazide. The light of the firefly, the light emitted by some micro-organisms in the course of metabolism, bioluminescence are other examples of chemiluminescence.

REVISIONARY PROBLEMS

3.1 What are photochemical reactions? How do they differ from thermal reactions?

3.2 Define the following two laws of photochemistry.
  (i) The Grotthuss-Draper law.
  (ii) Law of photochemical equivalence.
  Is there any exception to the above laws?

3.3 Define Lambert-Beer's law. Does it hold good in a concentrated solution of light absorbing substance?

3.4 Define the following terms.
  (i) Absorption coefficient.
  (ii) Molar absorptivity or extinction coefficient.
  (iii) Extinction or absorbance or optical density.
  (iv) Transmittance.
  (v) Absorption.
  (vi) One einstein of energy.
  (vii) Primary and secondary processes.
  (viii) Photosensitizers.
  (ix) Actinometer.

3.5 Illustrate, how Lambert-Beer's law can be employed to determine (i) equilibrium constant of a complex compound, (ii) composition of the complex AB_m, and (iii) the concentrations of A and B in a solution.

3.6 Illustrate with diagrams, the four types of primary processes classified on the basis of electronic excitation in the molecule.

3.7 Define the term 'Quantum efficiency'. Justify the statement that the quantum efficiency of a primary process is always one.

3.8 Elaborate the reasons for obtaining low and high quantum efficiencies.

3.9 Explain the effect of temperature on the photochemical reactions.

3.10 Explain the term, 'quenching of fluorescence'. On what factors does it depend?

3.11 Explain the phenomenon of photostationary state. Given below is the mechanism of photochemical dimerization of anthracene (A):

$$A \xrightarrow{h\nu} A^*$$

$$A^* + A \longrightarrow A_2$$

$$A_2 \longrightarrow 2A$$

$$A^* \longrightarrow A + h\nu'$$

  (a) Derive the expression for the rate of formation of the dimer.
  (b) Deduce from the latter the expression for the concentration of dimer at photochemical equilibrium.
  (c) How does this concentration depend upon the intensity of absorbed light?

3.12 The intensity of fluorescence and phosphorescence from an excited molecule M will depend on the efficiency of any competitive chemical quenching process. Consider the following mechanism:

$$M + h\nu_i \xrightarrow{k_a} M^*$$

$$M^* + Q \xrightarrow{k_q} M + Q; \text{ second-order reaction}$$

$$M^* \xrightarrow{k_f} M + h\nu_f$$

If I_f is the fluorescence intensity, show that

$$\frac{1}{I_f} = \frac{1}{I_a}\left\{1+\frac{k_q}{k_f}[Q]\right\}$$

Explain, how does the above expression help determining the value of k_f.

3.13 Given below are mechanisms of a few photochemical reactions. Derive the corresponding differential rate law and the expression of quantum yield.

(i) *Decomposition of* HI

$$HI \xrightarrow{h\nu} H + I$$

$$H + HI \xrightarrow{k_2} H_2 + I$$

$$I + I \xrightarrow{k_3} I_2$$

$$-\frac{d[HI]}{dt} = 2I_{abs}$$

$$\Phi = 2$$

(ii) *Reaction between hydrogen and bromine*

$$Br_2 \xrightarrow{h\nu} 2Br$$

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br$$

$$H + HBr \xrightarrow{k_4} H_2 + Br$$

$$Br + Br \xrightarrow{k_5} Br_2$$

$$\frac{d[HBr]}{dt} = \frac{2k_2(I_{abs}/k_5)^{1/2}[H_2]}{1+(k_4[HBr]/k_3[Br_2])}$$

$$\Phi = \frac{1}{2I_{abs}}\frac{d[HBr]}{dt}$$

(iii) *Reaction between* CO *and* Cl_2

$$Cl_2 \xrightarrow{h\nu} 2Cl$$

$$Cl + CO \xrightarrow{k_2} COCl$$

$$COCl \xrightarrow{k_3} CO + Cl$$

$$COCl + Cl_2 \xrightarrow{k_4} COCl_2 + Cl$$

$$COCl + Cl \xrightarrow{k_5} CO + Cl_2$$

$$\frac{d[COCl_2]}{dt} = k_4\left(\frac{k_2}{k_3k_5}\right)^{1/2} I_{abs}^{1/2}\,[CO]^{1/2}\,[Cl_2]$$

$$\Phi = \frac{1}{I_{abs}^{1/2}}\frac{d[COCl_2]}{dt}$$

(iv) *Photolysis of acetaldehyde*

$$CH_3CHO \xrightarrow{h\nu} CH_3 + CHO$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$$

$$CH_3CO \xrightarrow{k_3} CO + CH_3$$

$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$$

$$\frac{d[CO]}{dt} = k_3\left(\frac{I_{abs}}{2k_4}\right)^{1/2}[CH_3CHO]$$

(v) *Decomposition of* H_2O_2 *in the presence of* CO

$$H_2O_2 \xrightarrow{h\nu} 2OH$$

$$OH + CO \xrightarrow{k_2} COOH$$

$$COOH + H_2O_2 \xrightarrow{k_3} CO_2 + H_2O + OH$$

$$H_2O_2 + OH \xrightarrow{k_4} H_2O + HO_2$$

$$2HO_2 \xrightarrow{k_5} O_2 + H_2O_2$$

$$-\frac{d[H_2O_2]}{dt} = 2\,I_{abs}\left(1+\frac{k_2[CO]}{k_4[H_2O_2]}\right)$$

$$\Phi = \frac{-d[H_2O_2]/dt}{I_{abs}} = 2\left(1+\frac{k_2[CO]}{k_4[H_2O_2]}\right)$$

(vi) *Chlorination of chloroform*

$$Cl_2 \xrightarrow{h\nu} 2Cl$$

$$Cl + CHCl_3 \xrightarrow{k_2} CCl_3 + HCl$$

$$CCl_3 + Cl_2 \xrightarrow{k_3} CCl_4 + Cl$$

$$2CCl_3 + Cl_2 \xrightarrow{k_4} 2CCl_4$$

$$\frac{d[CCl_4]}{dt} = I_{abs} + k_3\left(\frac{I_{abs}[Cl_2]}{k_4}\right)^{1/2}$$

$$\Phi = 2 + k_3\left(\frac{[Cl_2]}{I_{abs}k_4}\right)^{1/2}$$

TRY YOURSELF PROBLEMS

3.1 For the photochemical decomposition of ammonia

$$2NH_3(g) \xrightarrow{h\nu} N_2(g) + 3H_2(g)$$

The following mechanism has been proposed:

$$NH_3 \xrightarrow{h\nu} NH_2 + H$$

$$NH_2 + H \xrightarrow{k_2} NH_3$$

$$H + H \xrightarrow{k_3} H_2$$

$$NH_2 + NH_2 \xrightarrow{k_4} N_2H_4$$

$$N_2H_4 + H \xrightarrow{k_5} NH_3 + NH_2$$

$$NH_2 + NH_2 \xrightarrow{k_6} N_2 + 2H_2$$

show that

$$\frac{d[N_2]}{dt} = \frac{k_6 I_{abs}}{2k_6 + k_4 + k_2(k_6/k_3)^{1/2}}$$

$$\Phi = 1 - \frac{1}{1 + 2k_6/\{k_2(k_6/k_3)^{1/2} + k_4\}}$$

3.2 For the photochemical reaction

$$A_2 \xrightarrow{hv} 2A$$

the following mechanism has been proposed:

$$A_2 \xrightarrow{hv} A_2^*$$

$$A_2^* \xrightarrow{k_2} 2A$$

$$A_2^* + A_2 \xrightarrow{k_3} 2A_2$$

show that

$$\frac{d[A]}{dt} = \frac{2k_2 I_{abs}}{k_2 + k_3[A_2]}$$

3.3 Derive the expression for the quantum efficiency of decomposition of chloroacetic acid which follows the mechanism

$$ClCH_2COOH + hv \longrightarrow ClCH_2COOH^*$$

$$ClCH_2COOH^* + H_2O \longrightarrow HOCH_2COOH + HCl$$

3.4 (a)Using the mechanism for the formation of dianthracene in Section 3.8, write the expression for the quantum yield in the initial stage of the reaction when $[A_2] = 0$. (b) The observed value of Φ is one. What conclusion can be reached regarding the fluorescence of A* ?

[**Ans.** (a) $\Phi = k_2 [A]/(k_2 [A] + k_3)$, (b) Fluorescence is weak]

3.5 The following mechanism has been proposed for the photochlorination of trichloroethylene:

$$Cl_2 + hv \longrightarrow 2Cl$$

$$Cl + C_2HCl_3 \longrightarrow \bullet C_2HCl_4$$

$$\bullet C_2HCl_4 + Cl_2 \longrightarrow C_2HCl_5 + Cl$$

$$2\bullet C_2HCl_4 \longrightarrow \text{inert products}$$

Derive the rate law. [**Ans.** $d[C_2HCl_5]/dt = k\, I_{abs}^{1/2}\, [Cl_2]$]

3.6 The photolysis of $COBr_2$ is found to have quantum efficiency of 1 with no temperature coefficient. What do you conclude about its mechanism?

3.7 Formaldehyde can be synthesized by irradiating a mixture of CO and H_2 containing a trace of Hg with light of wavelength 253.7 nm. Show that the reaction mechanism

$$Hg \xrightarrow{I_{abs}} Hg^*$$

$$Hg^* + H_2 \xrightarrow{k_2} 2H + Hg$$

$$\mathrm{H + CO \xrightarrow{k_3} HCO}$$

$$\mathrm{HCO + H_2 \xrightarrow{k_4} HCHO + H}$$

$$\mathrm{2\,HCO \xrightarrow{k_5} HCHO + CO}$$

$$\mathrm{2\,HCO \xrightarrow{k_6} \begin{array}{c} CHO \\ | \\ CHO \end{array}}$$

leads to the rate equation

$$\frac{d[\mathrm{HCHO}]}{dt} = \frac{k_5 I_{\mathrm{abs}}}{k_5 + k_6} + k_4 [\mathrm{H_2}] \left(\frac{I_{\mathrm{abs}}}{k_5 + k_6} \right)^{1/2}$$

3.8 The mechanism for the photochemical reaction between H_2 and Cl_2 is

(i) $\mathrm{Cl_2 \xrightarrow{h\nu} 2Cl}$

(ii) $\mathrm{Cl + H_2 \xrightarrow{k_2} HCl + H}$

(iii) $\mathrm{H + Cl_2 \xrightarrow{k_3} HCl + Cl}$

(iva) $\mathrm{Cl \xrightarrow{k_4} (1/2)\, Cl_2}$ (on wall)

or

(ivb) $\mathrm{Cl + Cl \longrightarrow Cl_2}$ (in gas)

Show that

$$\frac{d[\mathrm{HCl}]}{dt} = k\,[\mathrm{H_2}] I_{\mathrm{abs}} \qquad \text{for (iva) termination reaction}$$

or

$$\frac{d[\mathrm{HCl}]}{dt} = k'\,[\mathrm{H_2}] I_{\mathrm{abs}}^{1/2} \qquad \text{for (ivb) termination reaction}$$

3.9 (a) The mechanisms of thermal and photochemical reactions of $H_2 + Cl_2$ and $H_2 + Br_2$ are of similar nature but those of $H_2 + I_2$ are altogether different. From the following data, explain why it is so.

$\mathrm{Cl + H_2 \longrightarrow HCl + H}$ $E_a = 20.92\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{Br + H_2 \longrightarrow HBr + H}$ $E_a = 73.64\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{I + H_2 \longrightarrow HI + H}$ $E_a = 139.75\ \mathrm{kJ\ mol^{-1}}$

(b) The quantum efficiency of $H_2 + Cl_2$ reaction is very large (10^4–10^6) whereas that of $H_2 + Br_2$ is low. Explain why it is so.

[**Ans.** (a) because of high E_a, (b) comparatively larger E_a.]

3.10 The photolysis of O_3 in liquid Ar solution at 87 K by wavelength 353.7 nm and 313 nm follows the mechanism given below:

$$\mathrm{O_3 + h\nu \longrightarrow O_2 + O^*}$$

$$\mathrm{O^* + O_3 \xrightarrow{k_2} 2O_2}$$

$$\mathrm{O^* \xrightarrow{k_3} O}$$

$$\mathrm{O + O_2 + M \xrightarrow{k_4} O_3 + M}$$

(a) If ϕ is the quantum yield of the first step and Φ is the overall quantum yield, show that

$$\Phi^{-1} = \phi^{-1} \left[\frac{1}{2} + \frac{k_3}{2k_2[\mathrm{O_3}]} \right]$$

(b) The experimental results for Φ at 353.7 nm fit the equation

$$\Phi^{-1} = 0.538 + 0.81\,[O_3]^{-1}$$

Show that

$$\phi = 0.93 \text{ and } k_3/k_2 = 1.51 \text{ mol dm}^{-3}$$

(***Hint:*** For the first step $-\,d\,[O_3]/dt = \phi\, I_a$ and for the overall $-\,d[O_3]/dt = \Phi\, I_a$)

NUMERICAL PROBLEMS

Lambert-Beer's Law

3.1 At 360 nm a blue filter transmits 37.0 per cent and a yellow filter 19.0 per cent of a radiation. What is the transmittance at the same wavelength of the two filters in combination? [**Ans.** 0.07]

3.2 In a certain cell 10^{-3} mol dm^{-3} solution of a substance absorbs 10% of incident radiation. What concentration of the same solute in the same cell will absorb 90% of incident radiation? [**Ans.** 0.022 mol dm^{-3}]

3.3 An 0.03 mol dm^{-3} solution of a substance has an absorbance of 2.0 at 660 nm using a 1-cm cell. Calculate (a) the value of absorption coefficient, (b) the value of I/I_0; and (c) the per cent absorption for an 0.015 mol dm^{-3} solution in the same cell. [**Ans.** 66.7 mol^{-1} dm^3 cm^{-1} 0.01, 90%]

3.4 A cell of 5.5 cm length and 125 cm^3 capacity contains a gas of molar absorptivity 2.5 dm^3 mol^{-1} cm^{-1} at a pressure of 10 cmHg and a temperature 300 K. If the radiation of wavelength 400 nm and intensity 9.05×10^{-3} J s^{-1} is passed through the gas, what per cent of it will be absorbed? [**Ans.** 15.75]

3.5 In a given cell, solution I transmits 42.0 per cent and solution II 85.0 per cent of radiation having a certain wavelength. What is the transmittance at the same wavelength of a solution made by mixing 35.0 cm^3 solution I and 55.0 cm^3 solution II, if no reaction occurs? [**Ans.** 0.646]

3.6 The concentrations of two solutes were estimated in the same solution of absorption spectroscopy at the two wavelengths. At λ_1, the molar absorptivities were 300 and 30 dm^3 mol^{-1} cm^{-1}; at λ_2, 10 and 200 dm^3 mol^{-1} cm^{-1} (respectively). When measured in a cell 2.0 cm in length, the percentage transmitted was 1.77% at λ_1 and 20.3% at λ_2, calculate the concentrations of the two solutes. [**Ans.** 0.002 76 mol dm^{-3}, 0.001 59 mol dm^{-3}]

3.7 The absorbance of a solution in which Bi^{3+} was very large and SCN$^-$ was 5.0×10^{-5} mol dm^{-3} in a cell of 1.0 cm thickness was found to be 0.286. The reaction which occurs is

$$Bi(SCN)^{2+} \rightleftharpoons Bi^{3+} + SCN^-$$

What was the absorption coefficient of Bi(SCN)$^{2+}$? In an another experiment, absorbance was found to be 0.24 when the initial [Bi^{3+}] was 0.50 mol dm^{-3}. What is the value of K_c of the above equilibrium?

[**Ans.** 5 720 dm^3 mol^{-1} cm^{-1}, 9.5×10^{-2} mol dm^{-3}]

Quantum Yield

3.8 When propanal is irradiated at 200 Torr and 30 °C with radiation of wavelength 302 nm the quantum yield for CO production is found to be 0.54. If the incident radiation intensity is 15×10^{-4} J s^{-1}, calculate the rate of CO formation. What is the radiation intensity in einstein per second?

[**Ans.** 2.04×10^{-9} mol s^{-1}; 3.78×10^{-9}]

3.9 $[Cr(NH_3]_5(NCS)]^{2+}$ reacts photochemically in the following manner.

$$[Cr(NH_3]_5(NCS)]^{2+} + H_2O \xrightarrow{hv} [Cr(NH_3)_4(H_2O)(NCS)]^{2+} + NH_3$$

In an experiment, a beam of monochromatic radiation of intensity 6×10^{-9} einstein/second is incident on a cell containing 20 cm^3 of 0.01 mol dm^{-3} solution of $[Cr(NH_3)_5(NCS)]^{2+}$. It is estimated that 80% of incident light is absorbed and after 10 minutes exposure, analysis showed that 0.6% of the reactant had undergone the change. Calculate the quantum yield and the molar absorption coefficient if the path length for the beam is 1 cm.

[**Ans.** 4.16, 69.9 $dm^3\ mol^{-1}\ cm^{-1}$]

3.10 An actinometer using the following reaction

$$HN_3 + H_2O + hv \longrightarrow N_2 + NH_2OH.$$

was used to find the number of quanta absorbed by a sample of HX(g). The concentrations of nitrogen in the actinometer after 30.0 min of light absorption were 43.1×10^{-5} mol dm^{-3} and 51.2×10^{-5} mol dm^{-3}, respectively, for the transmitted and the incident beam. (i) Find the quanta absorbed by the HX(g) sample if the actinometer had a volume of 1 dm^3. (ii) If 0.158×10^{-3} mol of HX decomposed upon absorption of these quanta, find the quantum yield of the reaction. [**Ans.** 4.5×10^{-8} mol s^{-1}, 1.94]

3.11 An uranyl oxalate actinometer is irradiated for 15 minutes with the radiation of 435 nm. At the end of this time, it is found that oxalic acid equivalent to 12 cm^3 of 0.001 molar $KMnO_4$ has been decomposed by the radiation. At this wavelength, the quantum efficiency is 0.58. Find the average intensity of the radiation used. [**Ans.** 0.015 8 J s^{-1}]

4

Statistical Thermodynamics

4.1 INTRODUCTION TO STATISTICAL THERMODYNAMICS

A thermodynamic system is a macrosystem consisting of a large number of molecules. In establishing the various thermodynamic functions, the structural model of the system is no where required. In fact, all thermodynamic properties of a system can be derived without knowing whether the system is composed of atoms or molecules and how these are moving or interacting with each other. By treating the molecules on a statistical formalism, it is possible to develop the subject of statistical thermodynamics where the thermodynamic properties of a system can be expressed in terms of molecular properties. In establishing the expressions for the computation, one is not concerned with the motion of individual molecules but only with the number of ways the molecules are distributed over the available quantum mechanical energy states subject to the constancy of the energy of the system. The various distributions are known as the various *complexions* or the *microstates* of the system.

Throughout the chapter, we restrict to a system containing noninteracting particles. Example of such a system is an ideal gas.

4.2 BOLTZMANN STATISTICS

In Boltzmann statistics, we deal with the distribution of distinguishable particles amongst energy levels with no restriction on the number of particles in any energy level.

A Typical Example of Distribution

Let five distinguishable particles be distributed over the five energy levels with energies 0, ε, 2ε, 3ε and 4ε, respectively. Let the total energy of the system in any one distribution be 4ε. Assuming equal accessibility of all energy levels to all particles, the possible microstates are shown in Table 4.2.1, which also includes the number of ways of achieving the microstates and the corresponding mathematical probabilities of their occurrence in the system.

Analysis of Distribution

The following comments regarding the microstates of a system may be made.

- The number of microstates in a distribution is given by

$$W = \frac{N!}{\Pi_i N_i} \tag{4.2.1}$$

where N is the total number of particles and N_is are the number of particles in various energy levels.

Table 4.21 Number of Ways of Distributing Five Distinguishable Particles

Distribution	*Number of Particles in the Energy Levels*					*Procedure of Distribution*	*Number of Microstates*	*Mathematical Probability of Occurrence*
	0	ε	2ε	3ε	4ε			
I	4	0	0	0	1	Any one of the 5 molecules can be placed in the 4ε level	5	$\frac{5}{70} = 0.071$
II	3	1	0	1	0	5 ways of placing 1st molecule 4 ways of placing 2nd molecule	$5 \times 4 = 20$	$\frac{20}{70} = 0.286$
III	3	0	2	0	0	5 ways of placing 1st molecule 4 ways of placing 2nd molecule Since the molecules are placed in the same energy level, the distribution containing the same molecules is counted twice, hence division by two.	$\frac{5 \times 4}{2} = 10$	$\frac{10}{70} = 0.143$
IV	2	2	1	0	0	5 ways of placing 1st molecule 4 ways of placing 2nd molecule 3 ways of placing 3rd molecule In the energy level ε, each distribution is counted twice, hence divison by two.	$\frac{5 \times 4 \times 3}{2} = 30$	$\frac{30}{70} = 0.429$
V	1	4	0	0	0	5 ways of placing 1st molecule 4 ways of placing 2nd molecule 3 ways of placing 3rd molecule 2 ways of placing 4th molecule In the energy level ε, each distribution is counted $4 \times 3 \times 2$ ways, hence division by 4!	$\frac{5 \times 4 \times 3 \times 2}{4 \times 3 \times 2} = 5$	$\frac{5}{70} = 0.071$
						Total Number of Distributions	70	

- The total number of microstates in all distributions may be computed by using the expression

$$W_{\text{total}} = \frac{(N+E-1)!}{(N-1)!E!} \tag{4.2.2}$$

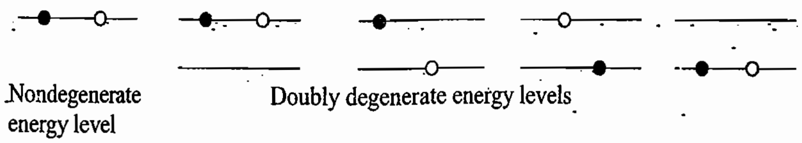
where E is the number of quanta of energy in the maximum energy level.

- The mathematical probability of occurrence of a distribution is given by

$$p = \frac{W}{W_{\text{total}}} = \frac{W}{\sum_i W_i} \tag{4.2.3}$$

- The most probable distribution corresponds to the maximum probability of occurrence.

- With the increase in the number of particles, the probability of the most probable distribution increases towards the maximum value of unity (e.g. for $N = 10$, $P = 0.503$; $N = 20$, $P = 0.547$; $N = 50$, $P = 0.786$ and $N = 100$, $P = 0.887$). In a real system where very large number of particles (e.g. 10^{23}) is involved, the probability of the most probable distribution will be almost equal to one.
- The macroscopic properties of a system depend upon the various microscopic states of the system. The fact that the probability of the most probable distribution is nearly unity, the macroscopic properties of a system at equilibrium is largely governed by the most probable distribution.
- In a real system, energy levels may involve degeneracy (i.e. more than one energy state is involved in an energy level). In such a case, the number of ways of distributing the particles is enhanced. For example, the number of ways of distributing two distinguishable particles is increased from **one** in a nondegenerate energy level to **four** in a doubly degenerate energy levels, as shown in the following.



The general expression for computing the number of microstates for distinguishable particles occupying degenerate energy levels with no restriction on the number of particles in any energy level is given by

$$W = (N!)\left(\Pi_i \frac{g_i^{N_i}}{N_i!}\right) \qquad (4.2.4)^{\dagger}$$

where g_i is the degeneracy of ith energy level.

- The quantity W is frequently called the thermodynamic probability, which is not the same as mathematical probability which for a given distribution is defined as $W_i / \sum_i W_i$.

The Equilibrium Distribution

As stated earlier, out of many distributions of a large number of particles over the available energy levels in a system at equilibrium, the probability of occurrence of the most probable distribution is nearly unity, the contributions from other distributions are vanishingly small. In this section, we derive the expression to compute the number of particles in various energy levels corresponding to the most probable distribution.

- In deriving the expression, the principle of *equal a priori probabilities* is assumed to be applicable. This implies that the system at any instant may be present in any one of the possible microstates but the contribution from the most probable distribution has a maximum value. So, we maximize the number of microstates W, or more conveniently $\ln W$, associated with the most probable distribution subject to the following two conditions.

[†] For indistinguishable particles, $W = \Pi_i (g_i^{N_i}/N_i!)$

1. The total number of particles in a system has a constant value, i.e.

$$N = \sum_i N_i = \text{constant} \tag{4.2.5}$$

or equivalently,

$$dN = \sum_i dN_i = 0 \tag{4.2.6}$$

2. The total energy of the system has a constant value, i.e.

$$U = \sum_i N_i \varepsilon_i = \text{constant} \tag{4.2.7}$$

Comment All energies ε_i are measured with respect to the lowest available energy at $T = 0$ K. For translational and rotational motions, $\varepsilon_0 = 0$, but for vibrational motion, $\varepsilon_0 = (1/2)h\nu_0$. Correctly speaking, the internal energy of a system is given by

$$U' = U_0 + \sum_i N_i \varepsilon_i$$

Throughout this chapter, we represent $U' - U_0$ as U.

The condition of constant U implies that

$$dU = \sum_i \varepsilon_i \, dN_i = 0 \tag{4.2.8}$$

The expression of ln W is

$$\ln W = \ln \left[(N)! \left(\Pi_i \frac{g_i^{N_i}}{N_i!} \right) \right]$$

$$= \ln N! + \sum_i (N_i \ln g_i - \ln N_i!)$$

For a large value of x, one can simplify ln x! by using Stirling approximation

$$\ln x! = x \ln x - x$$

Hence, $\ln W = (N \ln N - N) + \sum_i [N_i \ln g_i - (N_i \ln N_i - N_i)]$

The condition of maximizing ln W is

$$d \ln W = \sum_i \left(\frac{\partial \ln W}{\partial N_i} \right) dN_i = 0 \tag{4.2.9}$$

Now $$\frac{\partial \ln W}{\partial N_i} = \left[\left(\frac{\partial N}{\partial N_i} \right) \ln N + N \cdot \frac{1}{N} \frac{\partial N}{\partial N_i} - \frac{\partial N}{\partial N_i} \right] + \left[\ln g_i - \ln N_i - N_i \frac{1}{N_i} + 1 \right]$$

Since $\dfrac{\partial N}{\partial N_i} = \dfrac{\partial \sum_i N_i}{\partial N_i} = 1$, we have

$$\frac{\partial \ln W}{\partial N_i} = \ln N + \ln g_i - \ln N_i = -\ln \left(\frac{N_i}{N g_i} \right)$$

With this, Eq. (4.2.9) becomes

$$\sum_i -\ln\left(\frac{N_i}{Ng_i}\right)\mathrm{d}N_i = 0 \tag{4.2.10}$$

The constancy of number of particles (Eq. 4.2.6) and energy of the system (Eq. 4.2.8) are introduced in Eq. (4.2.10) by the method of Lagrange multipliers. In this method, Eqs (4.2.6) and (4.2.8) are multiplied by undetermined multipliers and added in Eq. (4.2.10). Hence, we can write

$$\sum_i \left[-\ln\left(\frac{N_i}{Ng_i}\right)+\alpha-\beta\varepsilon_i\right]\mathrm{d}N_i = 0 \tag{4.2.11}$$

where α and $-\beta$ are the undetermined multipliers.

Boltzmann Distribution Law

For the sum to be equal to zero, each coefficient of $\mathrm{d}N_i$ is set equal to zero. Hence, we write

$$-\ln\left(\frac{N_i}{Ng_i}\right)+\alpha-\beta\,\varepsilon_i = 0 \tag{4.2.12}$$

or

$$N_i = Ng_i\mathrm{e}^{\alpha}\mathrm{e}^{-\beta\varepsilon_i} \tag{4.2.13}$$

Equation (4.2.13) is known as *Boltzmann distribution law*. This specifies the most probable distribution of particles among the energy levels.

Identification of the Constant α

The constant α may be eliminated by using the relation

$$N = \sum_i N_i$$

Substituting N_i from Eq. (4.2.13), we get

$$N = \sum_i Ng_i\mathrm{e}^{\alpha}\mathrm{e}^{-\beta\varepsilon_i}$$

This gives

$$\mathrm{e}^{\alpha} = \frac{1}{\sum_i g_i\,\mathrm{e}^{-\beta\varepsilon_i}}$$

Molecular Partition Function

With this, Eq. (4.2.13) becomes

$$N_i = N\,\frac{g_i\,\mathrm{e}^{-\beta\varepsilon_i}}{\sum_i g_i\,\mathrm{e}^{-\beta\varepsilon_i}} = \frac{N}{q}\,g_i\,\mathrm{e}^{-\beta\varepsilon_i} \tag{4.2.14}$$

where q, known as *molecular partition function*, is given by

$$q = \sum_i g_i\mathrm{e}^{-\beta\varepsilon_i} \tag{4.2.15}$$

The degeneracy of the energy levels is taken care of by the term g_i. However, if we take summation over quantum states, Eq. (4.2.15) may be written as

$$q = \sum_{\substack{i \\ \text{(states)}}} \mathrm{e}^{-\beta\varepsilon_i}$$

It is for this reason, the molecular partition function is sometimes referred to as a 'sum over states'.

Equation (4.2.14) indicates that the fraction of particles in any energy state is equal to the term $\exp(-\beta\,\varepsilon_i)$ divided by the sum of all such terms for all the energy states. Since the physical quantity q governs the partition of molecules in the energy states, it is called the molecular partition function.

The importance of molecular partition function is that it contains all the information needed to calculate the thermodynamic properties of a system of independent particles.

Identification of the Constant β

The constant β may be identified by equating the internal energy of a monatomic gas with that obtained from the kinetic theory of gases.

Since the atoms of a monatomic gas have only translational energy, the expression of internal energy is given by

$$U = \sum_i N_i \varepsilon_i \tag{4.2.16}$$

Using the Boltzmann distribution expression, we get

$$U = \underset{\text{(level)}}{\frac{N}{q}\sum_i g_i\,\varepsilon_i \exp(-\beta\varepsilon_i)} = \underset{\text{(state)}}{\frac{N}{q}\sum_i \varepsilon_i \exp(-\beta\varepsilon_i)} \tag{4.2.17}$$

The expression of ε_i in terms of velocity components of a molecule is

$$\varepsilon_i = \frac{1}{2}m(v_{xi}^2 + v_{yi}^2 + v_{zi}^2) \tag{4.2.18}$$

Substituting this expression along with the expression of molecular partition function in Eq. (4.2.17), we get

$$U = \frac{N\sum_i \frac{1}{2}m(v_{xi}^2 + v_{yi}^2 + v_{zi}^2)\exp\left\{-\frac{\beta m}{2}(v_{xi}^2 + v_{yi}^2 + v_{zi}^2)\right\}}{\sum_i \exp\left\{-\frac{\beta m}{2}(v_{xi}^2 + v_{yi}^2 + v_{zi}^2)\right\}} \tag{4.2.19}$$

The summation i in the above expression may be considered as the summation over all possible values of velocity components. Since the translational energies are very closely spaced, the velocity components may be considered continuous variables, with the summations replaced by integrals.

$$U = \frac{\frac{1}{2}mN\int\int_{-\infty}^{+\infty}\int (v_x^2 + v_y^2 + v_z^2)\exp\left\{-\frac{\beta m}{2}(v_x^2 + v_y^2 + v_z^2)\right\}dv_x\,dv_y\,dv_z}{\int\int_{-\infty}^{+\infty}\int \exp\left\{-\frac{\beta m}{2}(v_x^2 + v_y^2 + v_z^2)\right\}dv_x\,dv_y\,dv_z} \tag{4.2.20}$$

i.e.
$$U = \frac{1}{2}mN\left[\frac{\int_{-\infty}^{+\infty} v_x^2 \exp(-\beta m v_x^2/2)\,\mathrm{d}v_x}{\int_{-\infty}^{+\infty} \exp(-\beta m v_x^2/2)\,\mathrm{d}v_x} + \frac{\int_{-\infty}^{+\infty} v_y^2 \exp(-\beta m v_y^2/2)\,\mathrm{d}v_y}{\int_{-\infty}^{+\infty} \exp(-\beta m v_y^2/2)\,\mathrm{d}v_y} + \frac{\int_{-\infty}^{+\infty} v_z^2 \exp(-\beta m v_z^2/2)\,\mathrm{d}v_z}{\int_{-\infty}^{+\infty} \exp(-\beta m v_z^2/2)\,\mathrm{d}v_z}\right]$$

Since v_x, v_y and v_z are independent, and each of the three terms has the same form, we can write

$$U = \frac{3}{2}mN\,\frac{\int_{-\infty}^{+\infty} v^2 \exp(-\beta m v^2/2)\,\mathrm{d}v}{\int_{-\infty}^{+\infty} \exp(-\beta m v^2/2)\,\mathrm{d}v} = \frac{3}{2}mN\left[\frac{(1/2)\sqrt{8\pi/\beta^3 m^3}}{\sqrt{2\pi/\beta m}}\right]$$

$$= \frac{3N}{2\beta}$$

The expression of average kinetic energy becomes

$$\overline{U} = \frac{U}{N} = \frac{3}{2\beta} \tag{4.2.21}$$

From the kinetic theory of gases, we have

$$\overline{U} = \frac{3}{2}kT$$

Hence, $$\frac{3}{2\beta} = \frac{3}{2}kT$$

This gives

$$\beta = \frac{1}{kT} \tag{4.2.22}$$

Although, the above expression has been derived for a monatomic gas, it is valid for all types of system.

Comment on the Molecular Partition Function

- The expression of molecular partition function is

$$q = \textstyle\sum_i g_i \exp(-\varepsilon_i/kT)$$

At temperature T close to zero, the value of each of the term $\exp(-\varepsilon_i/kT)$ will be close to zero. If $\varepsilon_0 = 0$, then leaving the first term, for which $\exp(-\varepsilon_0/kT)$ will have a value of one, the partition function will have a value close to g_0, i.e.

$$\lim_{T\to 0} q = g_0$$

At very high temperature, the value of each of the term $\exp(-\varepsilon_i/kT)$ will be close to one, and the value of partition function will be close to the number of available energy states.

Thus, the molecular partition function gives an idea about the average number of states that are thermally accessible to a particle at the temperature of the system. At $T = 0$ K, only the lowest energy state will be accessible while at very high temperature, a large number of higher energy states are accessible.

4.3 BOSE-EINSTEIN STATISTICS

In Bose-Einstein statistics, we deal with the distribution of indistinguishable particles among the energy levels with no limit on the number of particles in any of the energy state.

Expression to Compute the Arrangements

Let N indistinguishable identical particles (p_1, p_2, ..., p_N) be distributed over g distinguishable degenerate energy states ($E_1, E_2, ..., E_g$) with no limit on the number of particles in any of the energy states.

Let we represent a particular distribution in the following way.

$$E_1\ p_1\ p_5\ p_7\ E_2\ p_2\ p_9\ E_3\ E_4\ p_4\ p_8\ \ldots$$

This implies that the energy state

E_1 is occupied by the particles p_1, p_5 and p_7,

E_2 is occupied by the particles p_2 and p_9,

E_3 is unoccupied, and,

E_4 is occupied by the particles p_4 and p_8, ... and so on.

Leaving the energy state E_1, the number of ways of arranging the remaining $N + g - 1$ energy states and particles is equal to $(N + g - 1)!$.

In the above arrangement, the interchange of two energy states along with their occupied particles leads to the same distribution. There will be $(g - 1)!$ arrangements which correspond to the same numbered particles in the same order placed in the same numbered energy states. Thus, the total arrangements $(N + g - 1)!$ are reduced by the factor $(g - 1)!$.

Since all the particles are identical and indistinguishable, and we are concerned with no specific order in any energy state, the total number of arrangement is further reduced by a factor $N!$. Hence, the number of ways of placing N indistinguishable particles in g distinguishable energy states with no restriction on the number per energy state is given by

$$W = \frac{(g+N-1)!}{(g-1)!N!} \tag{4.3.1}$$

The thermodynamic probability of a given distribution of particles over the energy levels is the product of number of arrangements of all energy levels, i.e.

$$W = \Pi_i \frac{(g_i+N_i-1)!}{(g_i-1)!N_i!} \tag{4.3.2}$$

A Typical Example Let five identical indistinguishable particles be distributed over five energy levels with energies 0, ε, 2ε, 3ε and 4ε, each one is fivefold degenerate. Let the total energy of the system be 4ε. The possible distribution along with their thermodynamic probabilities are shown in Table 4.3.1.

Table 4.3.1 Distributions of Five Bosons Amongst Energy Levels

Distribution	*Number of Particles in Energy Levels*					*Thermodynamic Probability* $W = \Pi_i \dfrac{(N_i+g_i-1)!}{(g_i-1)!N_i!}$
	0	ε	2ε	3ε	4ε	
I	4	0	0	0	1	$\left(\dfrac{8!}{4!4!}\right)\left(\dfrac{4!}{4!0!}\right)\left(\dfrac{4!}{4!0!}\right)\left(\dfrac{4!}{4!0!}\right)\left(\dfrac{5!}{4!1!}\right)=350$
II	3	1	0	1	0	$\left(\dfrac{7!}{4!3!}\right)\left(\dfrac{5!}{4!1!}\right)\left(\dfrac{4!}{4!0!}\right)\left(\dfrac{5!}{4!1!}\right)\left(\dfrac{4!}{4!0!}\right)=875$
III	3	0	2	0	0	$\left(\dfrac{7!}{4!3!}\right)\left(\dfrac{4!}{4!0!}\right)\left(\dfrac{6!}{4!2!}\right)\left(\dfrac{4!}{4!0!}\right)\left(\dfrac{4!}{4!0!}\right)=525$
IV	2	2	1	0	0	$\left(\dfrac{6!}{4!2!}\right)\left(\dfrac{6!}{4!2!}\right)\left(\dfrac{5!}{4!1!}\right)\left(\dfrac{4!}{4!0!}\right)\left(\dfrac{4!}{4!0!}\right)=1\,125$
V	1	4	0	0	0	$\left(\dfrac{5!}{4!1!}\right)\left(\dfrac{8!}{4!4!}\right)\left(\dfrac{4!}{4!0!}\right)\left(\dfrac{4!}{4!0!}\right)\left(\dfrac{4!}{4!0!}\right)=350$

The Equilibrium Distribution The system to which Bose-Einstein statistics is applicable is found to have the characteristics of $g_i \gg 1$. In such a situation, the number 1 appearing in the numerator and denominator of thermodynamic probability (Eq. 4.3.2) can be neglected. The expression is reduced to

$$W = \Pi_i \frac{(N_i+g_i)!}{g_i!N_i!} \tag{4.3.3}$$

The expression of ln W becomes

$$\ln W = \sum_i [\ln (N_i+g_i)! - \ln g_i! - \ln N_i!] \tag{4.3.4}$$

For a system containing very large values of g_i and N_i, one can use Stirling approximation to eliminate factorials. Hence, we get

$$\begin{aligned}\ln W &= \sum_i [\{(N_i+g_i)\ln (N_i+g_i) - (N_i+g_i)\} - \{g_i \ln g_i - g_i\} \\ &\qquad - \{N_i \ln N_i - N_i\}] \\ &= \sum_i (N_i+g_i)\ln(N_i+g_i) - g_i \ln g_i - N_i \ln N_i\end{aligned}$$

The condition of maximizing ln W is

$$\mathrm{d}\ln W = \sum_i \left(\frac{\partial \ln W}{\partial N_i}\right)\mathrm{d}N_i = 0 \tag{4.3.5}$$

Now $$\frac{\partial \ln W}{\partial N_i} = \ln (N_i + g_i) + 1 - \ln N_i - 1 = -\ln \frac{N_i}{N_i + g_i}$$

With this, Eq. (4.3.5) becomes

$$\mathrm{d} \ln W = \sum_i \left[-\ln\left(\frac{N_i}{N_i + g_i}\right) \mathrm{d}N_i \right] = 0 \tag{4.3.6}$$

The constancy of number of particles (Eq. 4.2.6) and energy of the system (Eq. 4.2.8) are introduced in Eq. (4.3.6) to give

$$\sum_i \left[-\ln\left(\frac{N_i}{N_i + g_i}\right) + \alpha - \beta\varepsilon_i \right] \mathrm{d}N_i = 0$$

For the sum to be equal to zero, each coefficient of $\mathrm{d}N_i$ is set equal to zero. Hence, we write

$$-\ln\left(\frac{N_i}{N_i + g_i}\right) + \alpha - \beta\varepsilon_i = 0 \tag{4.3.7}$$

or $$\frac{N_i}{N_i + g_i} = \mathrm{e}^{\alpha}\, \mathrm{e}^{-\beta\varepsilon_i}$$

Inverting this equation, we get

$$1 + \frac{g_i}{N_i} = \mathrm{e}^{-\alpha}\, \mathrm{e}^{\beta\varepsilon_i} \tag{4.3.8}$$

or $$N_i = \frac{g_i}{\mathrm{e}^{-\alpha}\mathrm{e}^{\beta\varepsilon_i} - 1} \tag{4.3.9}$$

Reduction to the Boltzmann Distribution Law

For a system in which $g_i/N_i \gg 1$, Eq. (4.3.8) may be approximated as

$$\frac{g_i}{N_i} = \mathrm{e}^{-\alpha}\, \mathrm{e}^{\beta\varepsilon_i}$$

or $$N_i = g_i\, \mathrm{e}^{\alpha}\, \mathrm{e}^{-\beta\varepsilon_i}$$

We can eliminate e^{α} by using the fact that

$$N = \sum_i N_i = \sum_i g_i\, \mathrm{e}^{\alpha}\, \mathrm{e}^{-\beta\varepsilon_i}$$

or $$\mathrm{e}^{\alpha} = \frac{N}{\sum_i g_i\, \mathrm{e}^{-\beta\varepsilon_i}}$$

Hence, $$N_i = N \frac{g_i\, \mathrm{e}^{-\beta\varepsilon_i}}{\sum_i g_i\, \mathrm{e}^{-\beta\varepsilon_i}} = \frac{N}{q} g_i\, \mathrm{e}^{-\beta\varepsilon_i} \tag{4.3.10}$$

which is identical to Boltzmann distribution law (Eq. 4.2.14), i.e. the Bose-Einstein statistics predicts the same distribution of particles among energy level as does Boltzmann statistics.

Under the approximation $g_i \gg N_i$, the thermodynamic probability also reduces to a form identical to that of Boltzmann statistics, since one can write

$$\frac{(g_i+N_i-1)!}{(g_i-1)!} = g_i(g_i+1)(g_i+2)\ldots(g_i+N_i-1) \simeq g_i^{N_i} \qquad (4.3.11)$$

In an atom or molecule, the number of translational energy states alone is sufficient to guarantee the number of energy states available to any atom/molecule much greater than the number of atoms/molecules in the system.

4.4 FERMI-DIRAC STATISTICS

Expression to Compute the Arrangements

In Fermi-Dirac statistics, we deal with the distribution of indistinguishable particles among the energy levels with only one particle in any of the energy state.

Let N indistinguishable identical particles be distributed over g distinguishable degenerate energy states with the restriction of only one particle in any of energy state. The latter condition requires that $N \le g$.

For distinguishable particles, we will have

g choices for the 1st particle

$g - 1$ choices for the 2nd particle

....

$g - N + 1$ choices for the Nth particle

The total choices or arrangements will be

$$(g)(g-1)\ldots(g-N+1) = \frac{g!}{(g-N)!}$$

Since the particles are indistinguishable, the above arrangement has to be divided by $N!$ permutations of the N particles. Hence, the number of ways of placing N indistinguishable particles in g distinguishable degenerate energy states with a limit of no more than one particle per energy state is

$$W = \frac{g!}{(g-N)!N!} \qquad (4.4.1)$$

The thermodynamic probability of a given distribution of particles over energy levels is the product of number of arrangements of all energy levels, i.e.

$$W = \Pi_i \frac{g_i!}{(g_i-N_i)!N_i!} \qquad (4.4.2)$$

A Typical Example

Let five identical indistinguishable particles be distributed over five energy levels with energies 0, ε, 2ε, 3ε and 4ε, each one is fivefold degenerate. Let the total energy of the system be 4ε. The possible distributions along with their thermodynamic probabilities are shown in Table 4.4.1.

Table 4.4.1 Distributions of Five Fermions Amongst Energy Levels

Distribution	*Number of Particles in Energy Levels*					*Thermodynamic Probability* $W = \Pi_i \frac{g_i!}{(g_i - N_i)!N_i!}$
	0	ε	2ε	3ε	4ε	
I	4	0	0	0	1	$\left(\frac{5!}{1!4!}\right)\left(\frac{5!}{5!0!}\right)\left(\frac{5!}{5!0!}\right)\left(\frac{5!}{5!0!}\right)\left(\frac{5!}{4!1!}\right) = 25$
II	3	1	0	1	0	$\left(\frac{5!}{2!3!}\right)\left(\frac{5!}{4!1!}\right)\left(\frac{5!}{5!0!}\right)\left(\frac{5!}{4!1!}\right)\left(\frac{5!}{5!0!}\right) = 250$
III	3	0	2	0	0	$\left(\frac{5!}{2!3!}\right)\left(\frac{5!}{5!0!}\right)\left(\frac{5!}{3!2!}\right)\left(\frac{5!}{5!0!}\right)\left(\frac{5!}{5!0!}\right) = 100$
IV	2	2	1	0	0	$\left(\frac{5!}{3!2!}\right)\left(\frac{5!}{3!2!}\right)\left(\frac{5!}{4!1!}\right)\left(\frac{5!}{5!0!}\right)\left(\frac{5!}{5!0!}\right) = 500$
V	1	4	0	0	0	$\left(\frac{5!}{4!1!}\right)\left(\frac{5!}{1!4!}\right)\left(\frac{5!}{5!0!}\right)\left(\frac{5!}{5!0!}\right)\left(\frac{5!}{5!0!}\right) = 25$

The Equilibrium Distribution

The expression of ln W is

$$\ln W = \ln \left[\Pi_i \frac{g_i!}{(g_i - N_i)!N_i!}\right]$$

$$= \sum_i \left[\ln g_i! - \ln (g_i - N_i)! - \ln N_i!\right] \qquad (4.4.3)$$

Using Stirling approximation, we get

$$\ln W = \sum_i \left[(g_i \ln g_i - g_i) - \{(g_i - N_i) \ln (g_i - N_i) - (g_i - N_i)\} - (N_i \ln N_i - N_i)\right]$$

$$= \sum_i \left[g_i \ln g_i - (g_i - N_i) \ln (g_i - N_i) - N_i \ln N_i\right]$$

The condition of maximizing ln W is

$$\mathrm{d} \ln W = \sum_i \left(\frac{\partial \ln W}{\partial N_i}\right) \mathrm{d}N_i = 0 \qquad (4.4.4)$$

Now $\frac{\partial \ln W}{\partial N_i} = 0 - \{-\ln (g_i - N_i) - 1\} - \{\ln N_i + 1\}$

$$= -\ln \left(\frac{N_i}{g_i - N_i}\right) \qquad (4.4.5)$$

With this, Eq. (4.4.4) becomes

$$\mathrm{d} \ln W = \sum_i \left[-\ln \left(\frac{N_i}{g_i - N_i}\right) \mathrm{d}N_i\right] = 0 \qquad (4.4.6)$$

The constancy of number of particles (Eq. 4.2.6) and energy of the system (Eq. 4.2.8) are introduced in Eq. (4.4.6) to give

$$\sum_i \left[-\ln\left(\frac{N_i}{g_i - N_i}\right) + \alpha - \beta\varepsilon_i \right] \mathrm{d}N_i = 0 \tag{4.4.7}$$

For the sum to be equal to zero, each coefficient of $\mathrm{d}N_i$ is set equal to zero. Hence, we write

$$-\ln\left(\frac{N_i}{g_i - N_i}\right) + \alpha - \beta\,\varepsilon_i = 0 \tag{4.4.8}$$

or $$\frac{N_i}{g_i - N_i} = \mathrm{e}^{\alpha}\,\mathrm{e}^{-\beta\varepsilon_i} \tag{4.4.9}$$

Inverting this equation, we get

$$\frac{g_i}{N_i} - 1 = \mathrm{e}^{-\alpha}\,\mathrm{e}^{\beta\varepsilon_i}$$

or $$N_i = \frac{g_i}{\mathrm{e}^{-\alpha}\mathrm{e}^{\beta\varepsilon_i} + 1} \tag{4.4.10}$$

Reduction to the Boltzmann Distribution Law

For a system in which $g_i / N_i \gg 1$, Eq. (4.4.10) may be approximated as

$$\frac{g_i}{N_i} = \mathrm{e}^{-\alpha}\,\mathrm{e}^{\beta\varepsilon_i}$$

or $$N_i = g_i\,\mathrm{e}^{\alpha}\,\mathrm{e}^{-\beta\varepsilon_i}$$

We can eliminate e^{α} by using the fact that

$$N = \sum_i N_i = \sum_i g_i\,\mathrm{e}^{\alpha}\,\mathrm{e}^{-\beta\varepsilon_i}$$

or $$\mathrm{e}^{\alpha} = \frac{N}{\sum_i g_i\,\mathrm{e}^{-\beta\varepsilon_i}}$$

Hence, $$N_i = N\frac{g_i\,\mathrm{e}^{-\beta\varepsilon_i}}{\sum_i g_i\,\mathrm{e}^{-\beta\varepsilon_i}} = \frac{N}{q}\,g_i\,\mathrm{e}^{-\beta\varepsilon_i} \tag{4.4.11}$$

which is identical to Boltzmann distribution law (Eq. 4.2.14), i.e. the Fermi-Dirac statistics predicts the same distribution of particles among energy levels as does Boltzmann statistics.

Under the approximation $g_i \gg N_i$, the thermodynamic probability also reduces to a form identical to that of Boltzmann statistics, since we can write

$$\frac{g_i!}{(g_i - N_i)!} = g_i\,(g_i - 1)\,\dots\,(g_i - N_i + 1) \simeq g_i^{N_i} \tag{4.4.12}$$

• In an atom or molecule, the number of translational energy states alone is sufficient to guarantee the number of energy states available to any atom/molecule much greater than the number of atoms/molecules in the system.

4.5 THERMODYNAMIC PROPERTIES IN TERMS OF MOLECULAR PARTITION FUNCTION

In this section, we express some of the properties of a system in terms of molecular partition function.

Internal Energy

The expression of internal energy is

$$U = \sum_i N_i \varepsilon_i$$

From the Boltzmann expression, we have

$$N_i = \frac{N}{q} g_i \,\mathrm{e}^{-\beta\varepsilon_i}; \qquad \text{(where } \beta = 1/kT\text{)}$$

Hence, $U = \left(\sum_i \frac{N}{q} g_i \,\mathrm{e}^{-\beta\varepsilon_i}\right)\varepsilon_i$

From the fact that

$$\left(\frac{\partial \mathrm{e}^{-\beta\varepsilon_i}}{\partial\beta}\right)_V = -\varepsilon_i \,\mathrm{e}^{-\beta\varepsilon_i}$$

we can write the above expression as

$$U = -\frac{N}{q}\sum_i g_i\left(\frac{\partial \mathrm{e}^{-\beta\varepsilon_i}}{\partial\beta}\right)_V = -\frac{N}{q}\frac{\partial}{\partial\beta}\left(\sum_i g_i \,\mathrm{e}^{-\beta\varepsilon_i}\right)_V = -\frac{N}{q}\left(\frac{\partial q}{\partial\beta}\right)_V$$

$$= -N\left(\frac{\partial \ln q}{\partial\beta}\right)_V \qquad (4.5.1)$$

In terms of T, we have

$$U = -N\left(\frac{\partial \ln q}{\partial T}\right)_V\left(\frac{\mathrm{d}T}{\mathrm{d}\beta}\right)$$

Since $T = 1/k\beta$, we have

$$\frac{\mathrm{d}T}{\mathrm{d}\beta} = -\frac{1}{k\beta^2} = -\frac{1}{k(1/kT)^2} = -kT^2$$

Thus $U = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V \qquad (4.5.2)$

Identification of the Terms Heat and Work in the First Law of Thermodynamics

From the first law of thermodynamics, we have

$$\mathrm{d}U = \mathrm{d}q' + \mathrm{d}w \qquad (4.5.3)$$

where q' and w stand for heat and work, respectively.

Since $U = \sum_i N_i \varepsilon_i$, we also have

$$\mathrm{d}U = \sum_i \varepsilon_i \,\mathrm{d}N_i + \sum_i N_i \,\mathrm{d}\varepsilon_i \qquad (4.5.4)$$

The first term of Eq. (4.5.4) expresses the change in internal energy due to the change in population of particles in the energy levels. This fact may be attributed to the term $\mathrm{d}q'$ of Eq. (4.5.3). Hence, we write

$$\mathrm{d}q' = \sum_i \varepsilon_i \,\mathrm{d}N_i \qquad (4.5.5)$$

The second term of Eq. (4.5.4) expresses the change in internal energy due to the change in the magnitude of energy levels. This fact may be attributed to the term $\mathrm{d}w$ of Eq. (4.5.3) as the magnitude of energy level is affected by the change in the boundary parameters (say, volume) of the system. Hence, we write

$$\mathrm{d}w = \sum_i N_i \,\mathrm{d}\varepsilon_i \tag{4.5.6}$$

Expression of Pressure

The expression of mechanical work is

$$\mathrm{d}w = -p\,\mathrm{d}V$$

Using Eq. (4.5.6), this becomes

$$-p\,\mathrm{d}V = \sum_i N_i \,\mathrm{d}\varepsilon_i$$

Using the Boltzmann expression, we get

$$-p\,\mathrm{d}V = \frac{N}{q} \sum_i (g_i\,\mathrm{e}^{-\beta\varepsilon_i}\,\mathrm{d}\varepsilon_i)\,; \qquad \text{(where } \beta = 1/kT) \tag{4.5.7}$$

The differential change in the molecular partition function q at fixed temperature is

$$\mathrm{d}q = \sum_i g_i\,\mathrm{e}^{-\beta\varepsilon_i}\,(-\beta)\,\mathrm{d}\varepsilon_i$$

With this, Eq. (4.5.7) becomes

$$p\,\mathrm{d}V = \frac{N}{q}\,\frac{1}{\beta}\,\mathrm{d}q = \frac{N}{\beta}\,\mathrm{d}\ln q$$

Hence, $$p = \frac{N}{\beta}\left(\frac{\partial \ln q}{\partial V}\right)_T \tag{4.5.8}$$

Since $\beta = 1/kT$, we have

$$p = NkT\left(\frac{\partial \ln q}{\partial V}\right)_T \tag{4.5.9}$$

Expression of Entropy

By definition,

$$\mathrm{d}S = \frac{\mathrm{d}q'_{\text{rev}}}{T} \tag{4.5.10}$$

Using Eq. (4.5.5), this becomes

$$\mathrm{d}S = \frac{1}{T}\sum_i \varepsilon_i\,\mathrm{d}N_i \tag{4.5.11}$$

Since $\beta = 1/kT$, we get

$$\mathrm{d}S = \beta k \sum_i \varepsilon_i\,\mathrm{d}N_i = k\sum_i (\beta\varepsilon_i)\,\mathrm{d}N_i \tag{4.5.12}$$

From the Boltzmann expression

$$\frac{\partial \ln W}{\partial N_i} + \alpha - \beta\varepsilon_i = 0 \qquad \text{(Eq. 4.2.12)}$$

we get $$\beta\varepsilon_i = \frac{\partial \ln W}{\partial N_i} + \alpha$$

With this, Eq. (4.5.12) becomes

$$dS = k\sum_i \left(\frac{\partial \ln W}{\partial N_i}\right) dN_i + k\alpha \sum_i dN_i \qquad (4.5.13)$$

But $\sum_i dN_i = 0$. Hence

$$dS = k\sum_i \left(\frac{\partial \ln W}{\partial N_i}\right) dN_i = k\,(d \ln W)$$

or $$S = k \ln W \qquad (4.5.14)$$

Equation (4.5.14) is known as *Botlzmann-Planck equation.*

Entropy of Distinguishable Particles

Since $W = N!\,\Pi_i \dfrac{g_i^{N_i}}{N_i!}$, we get

$$\ln W = \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i!$$

Using Stirling approximation, we get

$$\ln W = (N \ln N - N) + \sum_i N_i \ln g_i - \sum_i (N_i \ln N_i - N_i)$$

$$= N \ln N + \sum_i N_i \ln g_i - \sum_i N_i \ln N_i$$

$$= -\sum_i N_i \ln\left(\frac{N_i}{Ng_i}\right) \qquad (4.5.15)$$

From the Boltzmann expression $N_i = (N/q)\,g_i \exp(-\beta\varepsilon_i)$, we get

$$\frac{N_i}{Ng_i} = \frac{e^{-\beta\varepsilon_i}}{q}$$

or $$\ln\left(\frac{N_i}{Ng_i}\right) = -\beta\varepsilon_i - \ln q$$

With this, Eq. (4.5.15) becomes

$$\ln W = \sum_i N_i(\beta\varepsilon_i + \ln q) = \beta\left(\sum_i N_i\varepsilon_i\right) + \left(\sum_i N_i\right)\ln q$$

$$= \beta U + N \ln q \qquad (4.5.16)$$

Hence, the expression of entropy is

$$S = k \ln W = k\beta U + kN \ln q$$

$$= \frac{U}{T} + kN \ln q \qquad (4.5.17a)$$

Substituting the expression of U from Eq. (4.5.2), we get

$$S = NkT\left(\frac{\partial \ln q}{\partial T}\right)_V + Nk \ln q$$

$$= Nk\left[T\left(\frac{\partial \ln q}{\partial T}\right)_V + \ln q\right] \qquad (4.5.18a)$$

Entropy of Indistinguishable Particles

For indistinguishable particles

$$W = \Pi_i \frac{g_i^{N_i}}{N_i!}$$

Hence, $\ln W = \sum_i (N_i \ln g_i - \ln N_i!)$

Using Stirling approximation, we get

$$\ln W = \sum_i (N_i \ln g_i - N_i \ln N_i + N_i)$$

$$= \sum_i N_i \ln \frac{g_i}{N_i} + N$$

From Boltzmann expression $N_i = (N/q)\, g_i \exp(-\beta\varepsilon_i)$, we get

$$\frac{g_i}{N_i} = \frac{q}{N}\, \mathrm{e}^{\beta\varepsilon_i}$$

or $$\ln\left(\frac{g_i}{N_i}\right) = \ln\left(\frac{q}{N}\right) + \beta\varepsilon_i$$

Hence, $$\ln W = \sum_i N_i \left[\ln\left(\frac{q}{N}\right) + \beta\varepsilon_i\right] + N$$

$$= N \ln\left(\frac{q}{N}\right) + \beta\left(\sum_i N_i\varepsilon_i\right) + N$$

$$= N \ln\left(\frac{q}{N}\right) + \beta U + N$$

The expression of entropy is

$$S = k \ln W$$

$$= k\left[N \ln\left(\frac{q}{N}\right) + \beta U + N\right]$$

$$= Nk\left[\ln\left(\frac{q}{N}\right) + T\left(\frac{\partial \ln q}{\partial T}\right)_V + 1\right] \tag{4.5.17b}$$

Enthalpy

Since $H = U + pV$, the expression of H is

$$H = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V + pV \tag{4.5.18b}$$

Heat Capacities

Since $C_V = (\partial U/\partial T)_V$, the expression of C_V is

$$C_V = \left[\frac{\partial}{\partial T} NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V\right]_V = Nk\left[\frac{\partial}{\partial T} T^2\left(\frac{\partial \ln q}{\partial T}\right)_V\right]_V \tag{4.5.19}$$

Since $C_p = (\partial H/\partial T)_p$, the expression of C_p is

$$C_p = \left[\frac{\partial}{\partial T}\left\{NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V + pV\right\}\right]_p \tag{4.5.20}$$

Helmholtz Free Energy

Since $A = U - TS$, the expression of A for distinguishable particles is

$$A = U - T\left(\frac{U}{T} + kN\ln q\right)$$

$$= -NkT\ln q \qquad (4.5.21a)$$

For indistinguishable particles, the expression is

$$A' = -NkT\left(\ln\frac{q}{N} + 1\right) \qquad (4.5.21b)$$

Gibbs Free Energy

Since $G = H - TS$, the expression of G for distinguishable particles is

$$G = (U + pV) - TS = (U - TS) + pV = A + pV$$

$$= -NkT\ln q + pV \qquad (4.5.22a)$$

For indistinguishable particles, the expression is

$$G' = -NkT\left(\ln\frac{q}{N} + 1\right) + pV$$

Since $pV = NkT$, we get

$$G' = -NkT\ln\left(\frac{q}{N}\right) \qquad (4.5.22b)$$

4.6 MOLECULAR PARTITION FUNCTION OF A DIATOMIC MOLECULE

A diatomic molecule has various kinds of energy, viz., translational, rotational, vibrational, electronic and nuclear energies. All these energies are quantized. Since the nuclear energy levels are not involved in chemical reactions, these are simply ignored.

Factorization of Partition Function

If the molecules of a system are considered independent molecules (say, molecules in an ideal gas), the energy of a diatomic molecule, under the assumption that there exists no interactions amongst different modes of energies, can be written as the sum of its translational, rotational, vibrational and electronic energies (Born-Oppenheimer approximation), i.e.

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e \qquad (4.6.1)$$

The degeneracy of energy ε is equal to the product of degeneracies of ε_t, ε_r, ε_v and ε_e energy levels.

The molecular partition function is given by

$$q = \sum_{t,r,v,e} g_t\, g_r\, g_v\, g_e \exp(-\beta\varepsilon)$$

$$= \sum_{t,r,v,e} g_t\, g_r\, g_v\, g_e \exp\{-\beta(\varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e)\} \qquad (4.6.2)$$

Since a sum of independent products can be written as a product of sums, the above expression can be written as

$$q = \left[\sum_t g_t \exp(-\beta\varepsilon_t)\right]\left[\sum_r g_r \exp(-\beta\varepsilon_r)\right]\left[\sum_v g_v \exp(-\beta\varepsilon_v)\right]\left[\sum_e g_e \exp(-\beta\varepsilon_e)\right]$$

$$= q_t\, q_r\, q_v\, q_e \qquad (4.6.3)$$

that is, *molecular partition function is equal to the product of translational, rotational, vibrational, and electronic molecular partition functions.*

Additive Nature of Thermodynamic Functions

Taking logarithm of Eq. (4.6.3), we get

$$\ln q = \ln q_t + \ln q_r + \ln q_v + \ln q_e$$

Since the thermodynamic functions of distinguishable independent molecules involve $\ln q$ or the differentials $(\partial \ln q/\partial V)_T$ and $(\partial \ln q/\partial T)_V$, the expression of overall thermodynamic function will be equal to the sum of thermodynamic functions of different modes of motion. For example, the internal energy is given by

$$U = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V = NkT^2\left\{\frac{\partial \ln(q_t q_r q_v q_e)}{\partial T}\right\}_V$$

$$= NkT^2\left\{\frac{\partial(\ln q_t + \ln q_r + \ln q_v + \ln q_e)}{\partial T}\right\}_V$$

$$= NkT^2\left(\frac{\partial \ln q_t}{\partial T}\right)_V + NkT^2\,\frac{\mathrm{d}\ln q_r}{\mathrm{d}T} + NkT^2\,\frac{\mathrm{d}\ln q_v}{\mathrm{d}T} + NkT^2\,\frac{\mathrm{d}\ln q_e}{\mathrm{d}T}$$

$$= U_t + U_r + U_v + U_e \tag{4.6.4}$$

Note: For rotational, vibrational and electronic modes, the notation of partial derivative is not used, because the corresponding molecular partition functions are independent of volume.

The expression of entropy (also those of Helmholtz and Gibbs functions) for indistinguishable particles is different from that of distinguishable particles.

$$S_{\text{dis}} = Nk\ln q + \frac{U}{T} \qquad \text{(Eq. 4.5.17a)}$$

$$S_{\text{indis}} = Nk\ln\frac{q}{N} + \frac{U}{T} + Nk \qquad \text{(Eq. 4.5.17b)}$$

Since the translational motion makes the particles indistinguishable, all extra terms in entropy of indistinguishable particles are attributed to translational entropy. The expression of entropy of indistinguishable diatomic molecules is given by

$$S = Nk\ln\frac{q}{N} + \frac{U}{T} + Nk$$

$$= Nk\ln\frac{q_t q_r q_v q_e}{N} + \frac{U_t + U_r + U_v + U_e}{T} + Nk$$

Hence, we have

$$S_t = Nk\ \ln\left(\frac{q_t}{N}\right) + \frac{U_t}{T} + Nk \tag{4.6.5}$$

$$S_r = Nk\ \ln q_r + \frac{U_r}{T} \tag{4.6.6}$$

$$S_v = Nk\ \ln q_v + \frac{U_v}{T} \tag{4.6.7}$$

$$S_e = Nk\ \ln q_e + \frac{U_e}{T} \tag{4.6.8}$$

In a similar manner, the expressions of Helmholtz and Gibbs functions for indistinguishable particles are given by

$$A_t = -NkT\left(\ln\frac{q_t}{N}+1\right) \tag{4.6.9}$$

$$A_r = -NkT\ln q_r \tag{4.6.10}$$

$$A_v = -NkT\ln q_v \tag{4.6.11}$$

$$A_e = -NkT\ln q_e \tag{4.6.12}$$

$$G_t = -NkT\ln\left(\frac{q_t}{N}\right) \tag{4.6.13}$$

$$G_r = -NkT\ln q_r \tag{4.6.14}$$

$$G_v = -NkT\ln q_v \tag{4.6.15}$$

and

$$G_e = -NkT\ln q_e \tag{4.6.16}$$

4.7 THERMODYNAMIC PROPERTIES OF A MONATOMIC IDEAL GAS

Translational Partition Function

An atom has two kinds of energy, viz., translational and electronic energies. The partition function can be written as

$$q = q_t\, q_e \tag{4.7.1}$$

In this section, we derive the expressions of q_t and q_e and then proceed to compute the thermodynamic properties of monatomic ideal gases.

The translational energy of an atom in a volume V is given by

$$\varepsilon = \frac{h^2}{8mV^{2/3}}(n_1^2+n_2^2+n_3^2) \tag{4.7.2}$$

where n_1, n_2 and n_3 are quantum numbers, each having values of 1, 2, 3, ...

The partition function written as a sum over quantum states is

$$q_t = \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\exp(-\beta\varepsilon) \qquad \text{(where } \beta = 1/kT)$$

$$= \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty}\exp\left\{-\frac{h^2\beta}{8mV^{2/3}}(n_1^2+n_2^2+n_3^2)\right\}$$

$$= \left[\sum_{n_1=1}^{\infty}\exp\left(-\frac{h^2\beta}{8mV^{2/3}}n_1^2\right)\right]\left[\sum_{n_2=1}^{\infty}\exp\left(-\frac{h^2\beta}{8mV^{2/3}}n_2^2\right)\right]$$

$$\times\left[\sum_{n_3=1}^{\infty}\exp\left(-\frac{h^2\beta}{8mV^{2/3}}n_3^2\right)\right]$$

Since the three exponential functions and summation over n_1, n_2 and n_3 are identical, we can write the above expression as

$$q_\mathrm{t} = \left[\sum_{n=1}^{\infty} \exp\left(-\frac{h^2\beta}{8mV^{2/3}}n^2\right)\right]^3 \tag{4.7.3}$$

Equation (4.7.3) may be written as

$$q_\mathrm{t} = \left[\sum_{n=0}^{\infty} \exp\left(-\frac{h^2\beta}{8mV^{2/3}}n^2\right) - 1\right]^3 \tag{4.7.4}$$

Neglecting one in comparison to the summation term, we get

$$q_\mathrm{t} = \left[\sum_{n=0}^{\infty} \exp\left(-\frac{h^2\beta}{8mV^{2/3}}n^2\right)\right]^3 \tag{4.7.5}$$

Since the translational energy levels are very close to each other, the summation in the above expression may be replaced by integration. Hence

$$q_\mathrm{t} = \left[\int_0^{\infty} \exp\left(-\frac{h^2\beta}{8mV^{2/3}}n^2\right)\mathrm{d}n\right]^3 \tag{4.7.6}$$

which on integrating gives

$$q_\mathrm{t} = \left[\frac{1}{2}\sqrt{\pi}\left(\frac{8mV^{2/3}}{h^2\beta}\right)^{1/2}\right]^3 = V\left(\frac{2\pi m}{h^2\beta}\right)^{3/2}$$

$$= V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{4.7.7†}$$

Equation (4.7.7) may be written as

$$q_\mathrm{t} = \frac{V}{\Lambda^3} \tag{4.7.8}$$

where $\Lambda = (h^2/2\pi mkT)^{1/2}$ and is called the *thermal de Broglie wavelength.*

Example 4.7.1 Evaluate translational partition function for oxygen atoms at 300 K contained in a volume of 22.414 dm^3.

Solution The expression of thermal de Broglie wavelength is

$$\Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$

Substituting the data, we get

$$\Lambda = \left[\frac{(6.626\times10^{-34}\ \mathrm{J\ s})^2}{2(3.14)(16\times1.66\times10^{-27}\mathrm{kg})(1.38\times10^{-23}\ \mathrm{J\ K^{-1}})(300\ \mathrm{K})}\right]^{1/2}$$

$$= 2.52\times10^{-11}\ \mathrm{m}$$

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† See Annexure I at the end of the chapter for the alternative method of computing translational partition function.

The value of translational partition function is

$$q_t = \frac{V}{\Lambda^3} = \frac{22.414\times10^{-3}\ \text{m}^3}{(2.52\times10^{-11}\ \text{m})^3} = 1.40\times10^{30}$$

Variation of q_t with T and V

Taking logarithm of Eq. (4.7.7), we get

$$\ln q_t = \ln(V/\text{m}^3) + \frac{3}{2}\ln\left(\frac{2\pi mk}{h^2}\Big/\text{m}^{-2}\,\text{K}^{-1}\right) + \frac{3}{2}\ln(T/\text{K}) \tag{4.7.9}$$

Hence,

$$\left(\frac{\partial \ln q_t}{\partial V}\right)_T = \frac{1}{V} \quad \text{and} \quad \left(\frac{\partial \ln q_t}{\partial T}\right)_V = \frac{3}{2T} \tag{4.7.10}$$

Internal Energy

From Eq. (4.5.2), we have

$$U = NkT^2\left(\frac{\partial \ln q_t}{\partial T}\right)_V$$

Hence,

$$U = NkT^2\left(\frac{3}{2T}\right) = \frac{3}{2}NkT \tag{4.7.11}$$

In terms of amount of gas, we have

$$U = \frac{3}{2}(nN_A)kT = \frac{3}{2}n\,(N_Ak)T = \frac{3}{2}nRT \tag{4.7.12}$$

Pressure

From Eq. (4.5.9), we get

$$p = NkT\left(\frac{\partial \ln q_t}{\partial V}\right)_T$$

Hence,

$$p = NkT\left(\frac{1}{V}\right) = \frac{NkT}{V} \tag{4.7.13}$$

In terms of amount of gas, we have

$$p = \frac{(nN_A)kT}{V} = \frac{n(N_Ak)T}{V} = \frac{nRT}{V} \tag{4.7.14}$$

Heat Capacity at Constant Volume

Since $C_V = (\partial U/\partial T)_V$, we get

$$C_V = \frac{\text{d}}{\text{d}T}\left(\frac{3}{2}nRT\right) = \frac{3}{2}nR$$

and

$$C_{V,\text{m}} = \frac{C_V}{n} = \frac{3}{2}R \tag{4.7.15}$$

Enthalpy

Since $H = U + pV$, we get

$$H = \frac{3}{2}nRT + nRT = \frac{5}{2}nRT \tag{4.7.16}$$

Heat Capacity at Constant Pressure

Since $C_p = (\partial H/\partial T)_p$, we get

$$C_p = \frac{\text{d}}{\text{d}T}\left(\frac{5}{2}nRT\right) = \frac{5}{2}nR$$

and

$$C_{p,\text{m}} = \frac{5}{2}R \tag{4.7.17}$$

Entropy

Since the molecules in a gaseous phase are indistinguishable, the entropy of monatomic gas is given by

$$S = Nk\left[\ln\frac{q_t}{N} + T\left(\frac{\partial \ln q_t}{\partial T}\right)_V + 1\right] \qquad \text{(Eq. 4.5.17b)}$$

$$= Nk\left[\ln\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + T\left(\frac{3}{2T}\right) + 1\right]$$

$$= Nk\left[\ln\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}\right] \qquad (4.7.18)$$

In terms of pressure of the gas, we have

$$S_t = Nk\left[\ln\left\{\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}\right] \qquad (4.7.19)$$

Sackur-Tetrode Equation

The atomic mass is given by

$$m = A_r\, m_u \qquad (4.7.20)$$

where A_r is the relative atomic mass and m_u is the atomic mass unit ($= 1.66 \times 10^{-27}$ kg). Substituting Eq. (4.7.20) in Eq. (4.7.19) and expressing T and p as dimensionless quantities, we get

$$S_t = Nk\left[\ln\left\{\frac{k^{5/2}\{\mathrm{K}(T/\mathrm{K})\}^{5/2}}{p^\circ(p/p^\circ)}\left(\frac{2\pi A_r m_u}{h^2}\right)^{3/2}\right\} + \frac{5}{2}\right]$$

or

$$S_t = Nk\left[\ln\left\{\frac{k^{5/2}(1\,\mathrm{K})^{5/2}}{(1\,p^\circ)}\left(\frac{2\pi m_u}{h^2}\right)^{3/2}\right\} + \frac{3}{2}\ln A_r + \frac{5}{2}\ln\left(\frac{T}{\mathrm{K}}\right) - \ln\left(\frac{p}{p^\circ}\right) + \frac{5}{2}\right] \qquad (4.7.21)$$

The numerical value of the constant terms within the brackets is

$$\ln\left[\frac{(1.38\times10^{-23}\,\mathrm{J\,K^{-1}})^{5/2}(1\,\mathrm{K})^{5/2}}{(10^5\,\mathrm{Pa})}\left\{\frac{2(3.14)(1.66\times10^{-27}\,\mathrm{kg})}{(6.626\times10^{-34}\,\mathrm{J\,s})^2}\right\}^{3/2}\right] + \frac{5}{2}$$

$$= \ln(0.025\,88) + \frac{5}{2} = -3.654\,1 + 2.5 = -1.154\,1$$

With this, Eq. (4.7.21) can be written as

$$S_m^\circ = \frac{S_t^\circ}{n} = R\left[-1.154\,1 + \frac{3}{2}\ln A_r + \frac{5}{2}\ln\left(\frac{T}{\mathrm{K}}\right) - \ln\left(\frac{p}{p^\circ}\right)\right] \qquad (4.7.22)$$

Equation (4.7.22) is known as *Sackur-Tetrode equation.*

Helmholtz Free Energy

Since $A = U - TS$, we get

$$A = \frac{3}{2}\,NkT - NkT\left[\ln\left\{\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}\right]$$

i.e.
$$A = -NkT\left[\ln\left\{\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + 1\right] \tag{4.7.23}$$

Gibbs Free Energy

Since $G = H - TS$, we get

$$G = \frac{5}{2}\,NkT - NkT\left[\ln\left\{\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}\right]$$

$$= -NkT\ln\left\{\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} \tag{4.7.24}$$

Example 4.7.2 Calculate the translational contributions to U°_m, H°_m, S°_m, A°_m and G°_m for helium at 25 °C.

Solution We have

$$U^\circ_\mathrm{m} = (3/2)\,RT = (3/2)(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K}) = 3\ 716.4\ \mathrm{J\ mol^{-1}}$$

$$H^\circ_\mathrm{m} = (5/2)\,RT = (5/2)(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K}) = 6\ 193.9\ \mathrm{J\ mol^{-1}}$$

$$S^\circ_\mathrm{m} = R\left[-1.1541 + \frac{3}{2}\ln A_r + \frac{5}{2}\ln\left(\frac{T}{\mathrm{K}}\right) - \ln\left(\frac{p}{p^\circ}\right)\right]$$

$$= (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\left[-1.1541 + \frac{3}{2}\ln 4 + \frac{5}{2}\ln 298 - \ln 1\right]$$

$$= 126.1\ \mathrm{J\ K^{-1}\ mol^{-1}}.$$

$$A^\circ_\mathrm{m} = U^\circ_\mathrm{m} - T\,S^\circ_\mathrm{m} = (3\ 716.4\ \mathrm{J\ mol^{-1}}) - (298\ \mathrm{K})\,(126.1\ \mathrm{J\ K^{-1}\ mol^{-1}})$$

$$= -\,33\ 861.4\ \mathrm{J\ mol^{-1}}$$

$$G^\circ_\mathrm{m} = H^\circ_\mathrm{m} - T\,S^\circ_\mathrm{m} = (6\ 193.9\ \mathrm{J\ mol^{-1}}) - (298\ \mathrm{K})\,(126.1\ \mathrm{J\ K^{-1}\ mol^{-1}})$$

$$= -\,31\ 382.9\ \mathrm{J\ mol^{-1}}$$

Electronic Partition Function

By convention, the energy of the ground electronic level is taken as the reference state and assign its value equal to zero. The electronic partition function is given by

$$q_\mathrm{e} = g_0 + g_1\,\mathrm{e}^{-\varepsilon_1/kT} + g_2\,\mathrm{e}^{-\varepsilon_2/kT} + \dots \tag{4.7.25}$$

The summation is carried out by direct addition of different terms.

Using the following definitions

$$q'_\mathrm{e} = T\left(\frac{\mathrm{d}q_\mathrm{e}}{\mathrm{d}T}\right) = T\left[\sum\nolimits_i g_i\left(\frac{\varepsilon_i}{kT^2}\right)\mathrm{e}^{-\varepsilon_i/kT}\right]$$

$$= \sum\nolimits_i g_i\left(\frac{\varepsilon_i}{kT}\right)\mathrm{e}^{-\varepsilon_i/kT} \tag{4.7.26}$$

and
$$q''_{\mathrm{e}} = T\,\frac{\mathrm{d}q'_{\mathrm{e}}}{\mathrm{d}T} = T\left[\frac{\mathrm{d}}{\mathrm{d}T}\left(T\,\frac{\mathrm{d}q_{\mathrm{e}}}{\mathrm{d}T}\right)\right] = T\,\frac{\mathrm{d}q_{\mathrm{e}}}{\mathrm{d}T} + T^2\,\frac{\mathrm{d}^2q_{\mathrm{e}}}{\mathrm{d}T^2}$$

$$= T\left[\sum\nolimits_i g_i\left(\frac{\varepsilon_i}{kT^2}\right)\mathrm{e}^{-\varepsilon_i/kT}\right] + T^2\left[\sum\nolimits_i g_i\left\{-\frac{2\varepsilon_i}{kT^3}+\left(\frac{\varepsilon_i}{kT^2}\right)^2\right\}\mathrm{e}^{-\varepsilon_i/kT}\right]$$

$$= -\sum\nolimits_i g_i\left(\frac{\varepsilon_i}{kT}\right)\mathrm{e}^{-\varepsilon_i/kT} + \sum\nolimits_i g_i\left(\frac{\varepsilon_i}{kT}\right)^2\mathrm{e}^{-\varepsilon_i/kT}$$

$$= -q' + \sum\nolimits_i g_i\left(\frac{\varepsilon_i}{kT}\right)^2\mathrm{e}^{-\varepsilon_i/kT} \tag{4.7.27}$$

we can write the expressions of thermodynamic molar quantities as

$$U_{\mathrm{e}} = H_{\mathrm{e}} = RT^2\,\frac{\mathrm{d}\ln q_{\mathrm{e}}}{\mathrm{d}T} = \frac{RT^2}{q_{\mathrm{e}}}\,\frac{\mathrm{d}q_{\mathrm{e}}}{\mathrm{d}T} = RT\,\frac{q'_{\mathrm{e}}}{q_{\mathrm{e}}} \tag{4.7.28}$$

$$S_{\mathrm{e}} = R\ln q_{\mathrm{e}} + \frac{U_{\mathrm{e}}}{T} = R\left[\ln q_{\mathrm{e}} + \frac{q'_{\mathrm{e}}}{q_{\mathrm{e}}}\right] \tag{4.7.29}$$

$$A_{\mathrm{e}} = G_{\mathrm{e}} = -RT\ln q_{\mathrm{e}} \tag{4.7.30}$$

$$(C_p)_{\mathrm{e}} = (C_V)_{\mathrm{e}} = \frac{\mathrm{d}}{\mathrm{d}T}\left(RT\,\frac{q'_{\mathrm{e}}}{q_{\mathrm{e}}}\right) = R\,\frac{q'_{\mathrm{e}}}{q_{\mathrm{e}}} + R\,\frac{q''_{\mathrm{e}}}{q_{\mathrm{e}}} - R\,\frac{(q'_{\mathrm{e}})^2}{q_{\mathrm{e}}^2}$$

$$= R\left[\frac{q'_{\mathrm{e}}+q''_{\mathrm{e}}}{q_{\mathrm{e}}} - \left(\frac{q'_{\mathrm{e}}}{q_{\mathrm{e}}}\right)^2\right] \tag{4.7.31}$$

Comment For an atom where only the ground electronic state is of significance, the partition function q_{e} reduces to the degeneracy of the ground level, and both q'_{e} and q''_{e} are zero. Consequently, the electronic contributions to U, H, C_p and C_V are all zero, while those of S, G and A are zero only if the degeneracy of ground level is unity.

Equations (4.7.26) – (4.7.31) are also applicable to rotational and vibrational motions.

Example 4.7.3

The following first three electronic energy levels of atomic fluorine are available.

$(1s)^2(2s)^2(2p)^5$	$^2P_{3/2}$	0;	$^2P_{1/2}$	404 cm^{-1}
$(1s)^2(2s)^2(2p)^4(3s)$	$^4P_{5/2}$	102 406 cm^{-1}		

Calculate:

(a) The fraction of atoms in each of the first three electronic levels at 1 000 K.

(b) The internal energy, heat capacity at constant volume, enthalpy, heat capacity at constant pressure, entropy and Gibbs free energy at 1 000 K and 1 bar pressure.

Solution

We have

$$\frac{\varepsilon_1}{kT} = \frac{hc\tilde{\nu}_1}{kT} = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})(3\times10^8\ \mathrm{m\,s^{-1}})(404\times10^2\ \mathrm{m^{-1}})}{(1.38\times10^{-23}\ \mathrm{J\,K^{-1}})(1\,000\ \mathrm{K})}$$
$$= 0.582$$

$$\frac{\varepsilon_2}{kT} = \frac{hc\tilde{\nu}_2}{kT} = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})(3\times10^8\ \mathrm{m\,s^{-1}})(102\,406\times10^2\ \mathrm{m^{-1}})}{(1.38\times10^{-23}\ \mathrm{J\,K^{-1}})(1\,000\ \mathrm{K})}$$
$$= 147.51$$

The value of electronic partition function is

$$q_e = g_0 + g_1\, e^{-\varepsilon_1/kT} + g_2\, e^{-\varepsilon_2/kT}$$

$$= \left(2\times\frac{3}{2}+1\right) + \left(2\times\frac{1}{2}+1\right) e^{-0.582} + \left(2\times\frac{5}{2}+1\right) e^{-147.51}$$

$$= 4 + 2\,(0.559) + 0 = 5.118$$

(a) The fractions of fluorine atoms in the first three electronic levels are

$$\frac{N_0}{N} = \frac{g_0}{q_e} = \frac{4}{5.118} = 0.782$$

$$\frac{N_1}{N} = \frac{g_1\, e^{-\varepsilon_1/kT}}{q_e} = \frac{2\times 0.559}{5.118} = 0.218$$

$$\frac{N_2}{N} = \frac{g_2\, e^{-\varepsilon_2/kT}}{q_e} = \frac{6\times 0}{5.118} = 0$$

(b) The translational contributions to thermodynamic properties of fluorine atoms are as follows.

$$(U^\circ_\mathrm{m})_\mathrm{t} = \frac{3}{2}\, RT = \frac{3}{2}\,(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\,(1\,000\ \mathrm{K}) = 12{\cdot}471\ \mathrm{J\,mol^{-1}}$$

$$(C_{V,\mathrm{m}})_\mathrm{t} = \frac{3}{2}\, R = \frac{3}{2}\,(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}) = 12.471\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$(H^\circ_\mathrm{m})_\mathrm{t} = \frac{5}{2}\, RT = \frac{5}{2}\,(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\,(1\,000\ \mathrm{K}) = 20\,785\ \mathrm{J\,mol^{-1}}$$

$$(C_{p,\mathrm{m}})_\mathrm{t} = \frac{5}{2}\, R = \frac{5}{2}\,(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}) = 20.785\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$(S^\circ_\mathrm{m})_\mathrm{t} = R\left[-1.1541 + \frac{3}{2}\ln A_\mathrm{r} + \frac{5}{2}\ln\left(\frac{T}{\mathrm{K}}\right) - \ln\left(\frac{p}{p^\circ}\right)\right]$$

$$= (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\left[-1.1541 + \frac{3}{2}\ln 19 + \frac{5}{2}\ln 1000 - \ln 1\right]$$

$$= (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\,(-\,1.1541 + 4.4167 + 17.2694 - 0)$$

$$= (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\,(20.5320) = 170.70\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$(G^\circ_\mathrm{m})_\mathrm{t} = (H^\circ_\mathrm{m})_\mathrm{t} - T(S^\circ_\mathrm{m})_\mathrm{t} = (20\,785\ \mathrm{J\,mol^{-1}}) - (1\,000\ \mathrm{K})\,(170.70\ \mathrm{J\,K^{-1}\,mol^{-1}})$$

$$= -\,149\,915\ \mathrm{J\,mol^{-1}}$$

The electronic contributions to thermodynamic properties of fluorine atoms can be computed by considering the first two electronic levels as the population in the third and higher electronic energy levels are negligible.

$$q'_e = \sum\nolimits_i g_i \left(\frac{\varepsilon_i}{kT}\right) e^{-\varepsilon_i/kT}$$

$$= 4(0)\,(1) + 2\,(0.582)\,(0.559) = 0.651$$

$$q''_e = \sum\nolimits_i g_i \left(\frac{\varepsilon_i}{kT}\right)^2 e^{-\varepsilon_i/kT} - q'_e$$

$$= 4(0)\,(1) + 2\,(0.582)^2\,(0.559) - 0.651 = -\,0.272$$

Hence, $$(U_\mathrm{m})_\mathrm{e} = (H_\mathrm{m})_\mathrm{e} = RT\,\frac{q'_\mathrm{e}}{q_\mathrm{e}} = (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\,(1\ 000\ \mathrm{K})\left(\frac{0.651}{5.118}\right)$$

$$= 1\ 057.5\ \mathrm{J\,mol^{-1}}$$

$$(C_{p,\mathrm{m}})_\mathrm{e} = (C_{V,\mathrm{m}})_\mathrm{e} = R\left[\frac{q'_\mathrm{e} + q''_\mathrm{e}}{q_\mathrm{e}} - \left(\frac{q'_\mathrm{e}}{q_\mathrm{e}}\right)^2\right]$$

$$= (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\left[\frac{0.651 - 0.272}{5.118} - \left(\frac{0.651}{5.118}\right)^2\right]$$

$$= (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\,(0.0741 - 0.0162)$$

$$= 0.481\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$(S^\circ_\mathrm{m})_\mathrm{e} = R\left[\ln q_\mathrm{e} + \frac{q'_\mathrm{e}}{q_\mathrm{e}}\right]$$

$$= (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\left[\ln 5.118 + \frac{0.651}{5.118}\right]$$

$$= (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\,(1.633 + 0.127)$$

$$= 14.63\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$(G^\circ_\mathrm{m})_\mathrm{e} = (H^\circ_\mathrm{m})_\mathrm{e} - T\,(S^\circ_\mathrm{m})_\mathrm{e} = 1\ 057.5\ \mathrm{J\,mol^{-1}} - (1\ 000\ \mathrm{K})(14.63\ \mathrm{J\,K^{-1}\,mol^{-1}})$$

$$= -\ 13\ 572.5\ \mathrm{J\,mol^{-1}}$$

The values of thermodynamic properties of fluorine at 1 000 K and 1 bar pressure are as follows:

$$U_\mathrm{m} = (U_\mathrm{m})_\mathrm{t} + (U_\mathrm{m})_\mathrm{e} = (12\ 471 + 1\ 057.5)\ \mathrm{J\,mol^{-1}} = 13\ 528.5\ \mathrm{J\,mol^{-1}}$$

$$H_\mathrm{m} = (H_\mathrm{m})_\mathrm{t} + (H_\mathrm{m})_\mathrm{e} = (20\ 785 + 1\ 057.5)\ \mathrm{J\,mol^{-1}} = 21\ 842.5\ \mathrm{J\,mol^{-1}}$$

$$C_{p,\mathrm{m}} = (C_{p,\mathrm{m}})_\mathrm{t} + (C_{p,\mathrm{m}})_\mathrm{e} = (20.79 + 0.48)\ \mathrm{J\,K^{-1}\,mol^{-1}} = 21.27\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$C_{V,\mathrm{m}} = (C_{V,\mathrm{m}})_\mathrm{t} + (C_{V,\mathrm{m}})_\mathrm{e} = (12.47 + 0.48)\ \mathrm{J\,K^{-1}\,mol^{-1}} = 12.95\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$S_\mathrm{m} = (S_\mathrm{m})_\mathrm{t} + (S_\mathrm{m})_\mathrm{e} = (170.70 + 14.63)\ \mathrm{J\,K^{-1}\,mol^{-1}} = 185.33\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$G_\mathrm{m} = (G_\mathrm{m})_\mathrm{t} + (G_\mathrm{m})_\mathrm{e} = (-\ 149\ 915 - 13\ 572.5)\ \mathrm{J\,mol^{-1}} = -\ 163\ 487.5\ \mathrm{J\,mol^{-1}}$$

4.8 THERMODYNAMIC PROPERTIES OF A DIATOMIC IDEAL GAS

Expression of Molecular Partition Function

A diatomic molecule has all the four kinds of energy, i.e. translation, rotational, vibrational and electronic. Assuming no interactions amongst different modes of energies, we can write

$$\varepsilon = \varepsilon_\mathrm{t} + \varepsilon_\mathrm{r} + \varepsilon_\mathrm{v} + \varepsilon_\mathrm{e} \tag{4.8.1}$$

The expression of its partition function is

$$q = q_\mathrm{t}\,q_\mathrm{r}\,q_\mathrm{v}\,q_\mathrm{e} \tag{4.8.2}$$

Contribution from Translational Motion

The translational contributions towards the various thermodynamic properties of a molecule are the same as those of atoms. Hence, the expressions derived in Section 4.7 are also applicable to diatomic gases.

Contribution from Rotational Motion

Expression of Rotational Energy

The rotational energy of a diatomic molecule assuming it to be rigid rotator is given by

$$\varepsilon_r = BhcJ(J+1)\,; \qquad J = 0, 1, 2, \ldots \tag{4.8.3}$$

where B, rotational constant, is given by

$$B = \frac{h}{8\pi^2 Ic} \tag{4.8.4}$$

In the above expression, I is moment of inertia ($I = \mu r^2$, $\mu = m_1m_2/(m_1 + m_2)$) and c is the speed of light.

The degeneracy of energy levels is given by

$$g_r = 2J + 1 \tag{4.8.5}$$

Expression of Partition Function

The rotational partition function is given by

$$q_r = \sum_{J=0}^{\infty} (2J+1)\exp\{-BhcJ(J+1)/kT\} \tag{4.8.6}$$

If it is assumed that the rotational energy levels are spaced sufficiently close together, then the summation in Eq. (4.8.6) may be replaced by integration to give

$$q_r = \int_0^{\infty} (2J+1)\exp\{-BhcJ(J+1)/kT\}\,dJ \tag{4.8.7}$$

Let $J(J+1) = y^2$ such that $(2J+1)\,dJ = 2y\,dy$. With this, the above integration becomes

$$q_r = 2\int_0^{\infty} y\,e^{-(Bhc/kT)y^2}\,dy = 2\left(\frac{1}{2Bhc/kT}\right) = \frac{kT}{Bhc} = \frac{kT}{(h/8\pi^2 Ic)hc}$$

$$= \left(\frac{8\pi^2 Ik}{h^2}\right)T \tag{4.8.8}$$

The above expression is usually written as

$$q_r = \frac{T}{\theta_r} \tag{4.8.9}$$

where θ_r, known as *characteristic rotational temperature*, is given by

$$\theta_r = \frac{h^2}{8\pi^2 Ik} \tag{4.8.10}$$

Example 4.8.1 Calculate the characteristic rotational temperature for N_2 molecule. Given: The internuclear distance of N_2 is 109.76 pm.

Solution The reduced mass of N_2 is

$$\mu = \frac{m_N m_N}{m_N + m_N} = \frac{m_N}{2} = \frac{14 \times 1.66 \times 10^{-27}\,\text{kg}}{2} = 1.162 \times 10^{-26}\ \text{kg}$$

The moment of inertia of N_2 is

$$I = \mu r^2 = (1.162 \times 10^{-26}\ \text{kg})\ (109.76 \times 10^{-12}\ \text{m})^2$$
$$= 1.40 \times 10^{-46}\ \text{kg m}^2$$

The characteristic rotational temperature is

$$\theta_r = \frac{h^2}{8\pi^2 I k} = \frac{(6.626 \times 10^{-34}\ \text{J s})^2}{8(3.14)^2(1.40 \times 10^{-46}\,\text{kg m}^2)(1.38 \times 10^{-23}\ \text{J K}^{-1})}$$
$$= 2.88\ \text{K}$$

Symmetry Number

Symmetry number (symbol: σ) of a molecule is the number of indistinguishable configurations the molecule assumes when it is rotated once by an angle 360°.[†]

For a homonuclear molecule (e.g. H_2, O_2, N_2, ...), $\sigma = 2$ as the rotation by 180° produces indistinguishable configuration from its original configuration.

For a heteronuclear molecule (e.g. HCl, HBr, ...), $\sigma = 1$.

To avoid more than one counting of indistinguishable configurations of a molecule during the rotation by 360°, the partition function is divided by its symmetry number to give

$$q_r = \frac{T}{\sigma \theta_r} \tag{4.8.11}$$

Expressions of Thermodynamic Functions

The expression of $\ln q_r$ is

$$\ln q_r = \ln (T/\text{K}) - \ln \sigma - \ln (\theta_r/\text{K}) \tag{4.8.12}$$

Hence,
$$\frac{\mathrm{d} \ln q_r}{\mathrm{d}T} = \frac{1}{T} \tag{4.8.13}$$

The thermodynamic properties of diatomic gases are given by the following expressions.

$$(U_m)_r = (H_m)_r = RT^2 \frac{\mathrm{d} \ln q_r}{\mathrm{d}T} = RT^2 \left(\frac{1}{T}\right) = RT \tag{4.8.14}$$

$$(C_{p,m})_r = (C_{V,m})_r = R \tag{4.8.15}$$

$$(S_m)_r = R \ln q_r + \frac{U_r}{T} = R\left[\ln\left(\frac{T}{\sigma\theta_r}\right) + 1\right] \tag{4.8.16}$$

$$(A_m)_r = (G_m)_r = -RT \ln q_r = -RT \ln \left(\frac{T}{\sigma\theta_r}\right) \tag{4.8.17}$$

Example 4.8.2 Calculate the rotational contributions to internal energy, entropy and Gibbs free energy for

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[†] See Annexure II at the end of the chapter for the quantum mechanical explanation of symmetry number.

diatomic oxygen at 500 K. Given: Internuclear distance of O_2 = 121 pm.

Solution We have

Reduced mass

$$\mu = \frac{m_O m_O}{m_O + m_O} = \frac{m_O}{2} = \frac{M_O}{2N_A}$$

$$= \frac{16 \times 10^{-3}\ \text{kg mol}^{-1}}{2(6.022 \times 10^{23}\ \text{mol}^{-1})} = 1.33 \times 10^{-26}\ \text{kg}$$

Moment of inertia

$$I = \mu r^2 = (1.33 \times 10^{-26}\ \text{kg})\,(121 \times 10^{-12}\ \text{m})^2$$

$$= 1.95 \times 10^{-46}\ \text{kg m}^2$$

Characteristic rotational temperature

$$\theta_r = \frac{h^2}{8\pi^2 Ik} = \frac{(6.626 \times 10^{-34}\ \text{J s})^2}{8(3.14)^2(1.95 \times 10^{-46}\ \text{kg m}^2)(1.38 \times 10^{-23}\ \text{J K}^{-1})} = 2.07\ \text{K}$$

Rotational partition function

$$q_r = \frac{T}{\sigma\theta_r} = \frac{(500\ \text{K})}{2(2.07\ \text{K})} = 120.77$$

The values of thermodynamic properties are as follows.

$$(U_m)_r = (H_m)_r = RT = (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (500\ \text{K}) = 4\ 157\ \text{J mol}^{-1}$$

$$(S_m)_r = R\,(\ln q_r + 1) = (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ \{\ln (120.77) + 1\}$$

$$= (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (4.79 + 1) = 48.17\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$(G_m)_r = -RT \ln q_r = -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (500\ \text{K})\ (\ln 120.77)$$

$$= -19\ 928.2\ \text{J mol}^{-1}$$

Comment on the Replacement of Summation by Integration in the Expression of Rotational Partition Function

The replacement of summation in Eq. (4.8.6) by integration is found to be valid provided $T/\theta_r \geq 100$. For a low T or high θ_r (i.e. low I), the value of T/θ_r may be less than 100. In such a situation, the value of rotational partition function should be evaluated by term-by-term summation. Using the Euler-Maclaurin summation theorem, it can be shown that the rotational partition function is given by

$$q_r = \frac{T}{\sigma\theta_r}\left[1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots\right] \tag{4.8.18}$$

The various thermodynamic molar properties may be evaluated by using Eqs (4.7.28) to (4.7.31), where

$$q'_r = T\left(\frac{\mathrm{d}q_r}{\mathrm{d}T}\right) = \frac{T}{\sigma\theta_r}\left[1 - \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 - \frac{8}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots\right] \tag{4.8.19}$$

and

$$q''_r = \left(\frac{\mathrm{d}q'_r}{\mathrm{d}T}\right) = \frac{T}{\sigma\theta_r}\left[1 + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{16}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots\right] \tag{4.8.20}$$

Contribution from Vibrational Motion

Expression of Vibrational Energy

Assuming diatomic molecule as a harmonic oscillator, its vibrational energy is given by

$$\varepsilon_\upsilon = \left(\upsilon + \frac{1}{2}\right) h\nu_0 ; \qquad \upsilon = 0, 1, 2, \ldots \qquad (4.8.21)$$

where ν_0, the classical frequency of oscillation, is given by

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k_f}{\mu}} \qquad (4.8.22)$$

In Eq. (4.8.22), k_f represents force constant and μ represents reduced mass of the molecule.

The molecule has a ground state energy of $(1/2)h\nu_0$ where vibrational quantum number $\upsilon = 0$. The vibrational energy with reference to the ground-state energy is given by

$$\varepsilon_\upsilon - \varepsilon_0 = h\nu_0\,\upsilon ; \qquad \upsilon = 0, 1, 2, \ldots \qquad (4.8.23)$$

For convenience (though it is not necessary, see Example 4.8.4) the vibrational contribution to the partition function is considered by using Eq. (4.8.23).

Expression of Partition Function

Since the vibrational energy levels are nondegenerate, the expression of vibrational partition function is given by

$$q_v = \sum_{\upsilon=0}^{\infty} \exp\{-(\varepsilon_\upsilon - \varepsilon_0)/kT\} \qquad (4.8.24)$$

Using Eq. (4.8.23), this becomes

$$q_v = \sum_{\upsilon=0}^{\infty} \exp(-h\nu_0\upsilon/kT) \qquad (4.8.25)$$

For $\exp(-h\nu_0/kT) < 1$, the above summation is given by

$$q_v = \frac{1}{1-\exp(-h\nu_0/kT)} \qquad (4.8.26)$$

Equation (4.8.26) is usually written as

$$q_v = \frac{1}{1-\exp(-\theta_v/T)} \qquad (4.8.27)$$

where θ_v, known as the *characteristic vibrational temperature*, is given by

$$\theta_v = \frac{h\nu_0}{k} \qquad (4.8.28)$$

Example 4.8.3

Calculate the characteristic vibrational temperature of N_2 molecule. Given: $\tilde{\nu}_0 = 2\,357.6\ \text{cm}^{-1}$ for N_2 molecule.

Solution

The characteristic vibrational temperature is given by

$$\theta_v = \frac{h\nu}{k} = \frac{hc\tilde{\nu}}{k}$$

Substituting the values, we get

$$\theta_\mathrm{v} = \frac{hc\tilde{\nu}}{k} = \frac{(6.626\times10^{-34}\ \mathrm{J\ s})(3\times10^{8}\ \mathrm{m\ s^{-1}})(2357.6\times10^{2}\ \mathrm{m^{-1}})}{(1.38\times10^{-23}\ \mathrm{J\ K^{-1}})}$$

$$= 3\,396\ \mathrm{K}$$

Expressions of Thermodynamic Properties

Since the partition function (Eq. 4.8.27) is evaluated with respect to the ground vibrational state energy ε_0, the expression of internal energy due to the vibrational mode will be given by

$$U = U' - U_0 = NkT^2\left(\frac{\mathrm{d}\ln q_\mathrm{v}}{\mathrm{d}T}\right) \tag{4.8.29}$$

Taking logarithm of Eq. (4.8.27), we get

$$\ln q_\mathrm{v} = -\ln\left(1 - \mathrm{e}^{-\theta\mathrm{v}/T}\right)$$

Hence, $$\frac{\mathrm{d}\ln q_\mathrm{v}}{\mathrm{d}T} = -\left(\frac{1}{1-\mathrm{e}^{-\theta_\mathrm{v}/T}}\right)\left(-\mathrm{e}^{-\theta_\mathrm{v}/T}\right)\left(\frac{\theta_\mathrm{v}}{T^2}\right) = \frac{1}{T^2}\,\frac{\theta_\mathrm{v}}{\mathrm{e}^{\theta_\mathrm{v}/T}-1} \tag{4.8.30}$$

Substituting Eq. (4.8.30) in Eq. (4.8.29), we get

$$U_\mathrm{v} = U'_\mathrm{v} - \frac{1}{2}Nh\nu_0 = \frac{Nk\theta_\mathrm{v}}{\mathrm{e}^{\theta_\mathrm{v}/T}-1} \tag{4.8.31}$$

Since $H_\mathrm{int} = U_\mathrm{int}$ for the internal motions, we also have

$$H_\mathrm{v} = H'_\mathrm{v} - \frac{1}{2}Nh\nu_0 = \frac{Nk\theta_\mathrm{v}}{\mathrm{e}^{\theta_\mathrm{v}/T}-1} \tag{4.8.32}$$

The expression of heat capacities is

$$C_p = C_V = \frac{\mathrm{d}U}{\mathrm{d}T} = \frac{Nk(\theta_\mathrm{v}/T)^2\mathrm{e}^{\theta_\mathrm{v}/T}}{(\mathrm{e}^{\theta_\mathrm{v}/T}-1)^2} \tag{4.8.33}$$

The entropy contribution is given by

$$S_\mathrm{v} = Nk\ln q_\mathrm{v} + \frac{U_\mathrm{v}}{T} \tag*{(Eq. 4.6.7)}$$

$$= Nk\left[-\ln(1-\mathrm{e}^{-\theta_\mathrm{v}/T}) + \frac{\theta_\mathrm{v}/T}{\mathrm{e}^{\theta_\mathrm{v}/T}-1}\right] \tag{4.8.34}$$

The expressions of Helmholtz and Gibbs free energies are

$$A_\mathrm{v} - U_0 = G_\mathrm{v} - U_0 = NkT\ln\left(1-\mathrm{e}^{-\theta_\mathrm{v}/T}\right) \tag{4.8.35}$$

It is important to point out here that the zero-point vibrational energy is involved in the expressions of U, H, A and G and not in S, C_p and C_V of the molecule.

Example 4.8.4

Taking the zero reference as the bottom of potential energy diagram to express vibrational energies of a diatomic molecule (executing harmonic oscillations), derive the expressions of molecular partition function and various thermodynamic properties.

The expression of vibrational energies is

Solution

$$\varepsilon_\upsilon = \left(\upsilon + \frac{1}{2}\right) h\nu_0; \qquad \upsilon = 0, 1, 2, \ldots$$

The expression of molecular partition function is

$$q_v = \sum_\upsilon \exp[-(\upsilon + 1/2)h\nu_0/kT]$$

$$= \exp(-h\nu_0/2kT)\ [\textstyle\sum_\upsilon \exp(-\upsilon h\nu_0/kT)]$$

$$= \frac{\exp(-h\nu_0/2kT)}{1-\exp(-h\nu_0/kT)} = \frac{\exp(-\theta_v/2T)}{1-\exp(-\theta_v/T)}$$

The expression of $\ln q_v$ is

$$\ln q_v = -\frac{\theta_v}{2T} - \ln[1-\exp(-\theta_v/T)]$$

Hence, $$\frac{d\ln q_v}{dT} = \frac{\theta_v}{2T^2} + \frac{\theta_v}{T^2}\left[\frac{1}{\exp(\theta_v/T)-1}\right]$$

The expression of internal energy is

$$U_v = NkT^2\frac{d\ln q}{dT} = Nk\left[\frac{\theta_v}{2} + \frac{\theta_v}{\exp(\theta_v/T)-1}\right]$$

For internal motion, $H_v = U_v$.

The expression of entropy is

$$S_v = Nk\ln q_v + \frac{U_v}{T}$$

$$= Nk\left[-\ln\{1-\exp(-\theta_v/T)\} + \frac{\theta/T}{\exp(\theta_v/T)-1}\right] \qquad \text{(Eq. 4.8.34)}$$

$$G_v = H_v - TS_v = \frac{Nk\theta_v}{2} + NkT\ln[1-\exp(-\theta_v/T)] \qquad \text{(Eq. 4.8.35)}$$

Example 4.8.5 Calculate the vibrational contributions to internal energy, enthalpy, entropy and Gibbs free energy for 1 mol of diatomic oxygen at 298 K. Given: The vibrational frequency of O_2 corresponds to 1 580 cm^{-1}.

Solution We have

Characteristic vibrational temperature

$$\theta_v = \frac{h\nu}{k} = \frac{hc\tilde{\nu}}{k} = \left[\frac{(6.626\times10^{-34}\ \text{J s})(3\times10^{8}\ \text{m s}^{-1})(1580\times10^{2}\ \text{m}^{-1})}{(1.38\times10^{-23}\ \text{J mol}^{-1})}\right]$$

$$= 2\,275.9\ \text{K}$$

Value of $\exp(\theta_v/T)$

$$e^{\theta v/T} = e^{(2\,275.9/298)} = e^{7.637\,2} = 2\,074.0$$

Values of thermodynamic properties

$$U_m = \frac{N_A k\theta_v}{e^{\theta_v/T}-1} = \frac{R\theta_v}{e^{\theta_v/T}-1} = \frac{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(2\,275.9\ \text{K})}{(2074.0-1)}$$

$$= 9.123\ \text{J mol}^{-1}$$

$$H_m = U_m = 9.123\ \text{J mol}^{-1}$$

$$S_\mathrm{m} = R\left[-\ln(1-\mathrm{e}^{-\theta_\mathrm{v}/T}) + \frac{\theta_\mathrm{v}/T}{\mathrm{e}^{\theta_\mathrm{v}/T}-1}\right]$$

$$= (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\left[-\ln\{1-(1/2\,074.0)\} + \frac{2\,275.9/298}{2\,074.0-1}\right]$$

$$= (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ (4.823 \times 10^{-4} + 3.684 \times 10^{-3})$$

$$= 0.034\,6\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$G_\mathrm{m} = RT \ln(1 - \mathrm{e}^{-\theta_\mathrm{v}/T})$$

$$= (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ (298\ \mathrm{K})\ \ln\{1 - 1/2\,074.0\}$$

$$= -\ 1.195\ \mathrm{J\ mol^{-1}}$$

The zero-point vibrational energy is

$$U_0 = N_\mathrm{A}\left(\frac{1}{2}h\nu\right) = (6.023 \times 10^{23}\ \mathrm{mol^{-1}})\left(\frac{1}{2}\right)(6.626 \times 10^{-34}\ \mathrm{J\ s})$$

$$\times \{(3 \times 10^{8}\ \mathrm{m\ s^{-1}})\ (1\,580 \times 10^{2}\ \mathrm{m^{-1}})\}$$

$$= 9.46 \times 10^{3}\ \mathrm{J\ mol^{-1}}.$$

This value is to be added in the values of U_m, H_m and G_m. Hence,

$$U'_\mathrm{m} = (9.123 + 9.46 \times 10^{3})\ \mathrm{J\ mol^{-1}} = 9.47 \times 10^{3}\ \mathrm{J\ mol^{-1}}$$

$$H'_\mathrm{m} = U'_\mathrm{m} = 9.47 \times 10^{3}\ \mathrm{J\ mol^{-1}}$$

$$G'_\mathrm{m} = (-1.195 + 9.46 \times 10^{3})\ \mathrm{J\ mol^{-1}} = 9.46 \times 10^{3}\ \mathrm{J\ mol^{-1}}$$

Contribution from Electronic Energy Levels

In most cases, the molecules are present in the ground electronic state unless temperature is very high. Since the electronic energy in the ground electronic level is, by convention, assigned a value of zero, only the ground level degeneracy is involved in the determination of electronic contributions to various thermodynamic properties. Exception to this statement are nitric oxide and the monatomic halogens, where the energy of the first excited state is not far away from that of the ground state.

Since the degeneracy of the ground electronic level is independent of temperature (i.e. d ln $q_\mathrm{e}/\mathrm{d}T = 0$), the electronic contributions to U, H, C_V and C_p are all zero. However, entropy, helmholtz free energy and Gibbs free energy do include contributions as they involve ln q_e. Hence

$$(S_\mathrm{m})_\mathrm{e} = R \ln g_0 \tag{4.8.36}$$

$$(A_\mathrm{m})_\mathrm{e} = (G_\mathrm{m})_\mathrm{e} = -\,RT \ln g_0 \tag{4.8.37}$$

Contribution from the Chemical Energy of a Molecule

The chemical energy of a molecule is the energy released when the molecule is formed from the gaseous atoms. This is equal to the minus of the dissociation energy (symbol: D_0) of the molecule (Fig. 4.8.1).

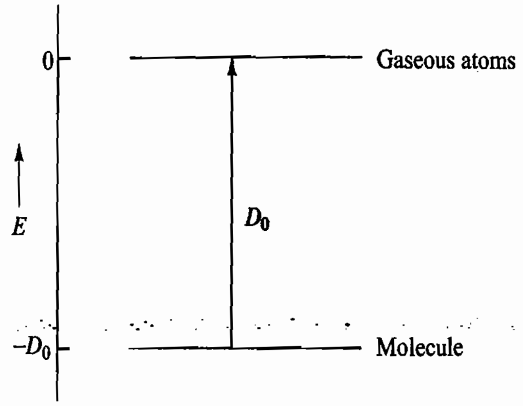


Fig. 4.8.1 Electronic energy of a molecule relative to its dissociated gaseous atoms

The thermodynamic contributions of the molecule relative to those of gaseous atoms are obtained by taking the ground state electronic energy of the molecule equal to $-D_0$. Hence, we have

$$q_e = g_0\, e^{D_0/kT} \tag{4.8.38}$$

$$(U^\circ_m)_e = (H^\circ_m)_e = -D_0 \tag{4.8.39}$$

$$(C^\circ_p)_e = 0 \tag{4.8.40}$$

$$(S^\circ_m)_e = R \ln g_0 \tag{4.8.41}$$

$$(G^\circ_m)_e = -D_0 - RT \ln g_0 \tag{4.8.42}$$

Contribution from Nuclear Energy Levels

Since the nuclear excited levels are energetically very far away from the ground level (assumed to have zero energy), only the degeneracy of ground nuclear energy contributes towards the nuclear partition function unless the temperature is exceedingly high.

The degeneracy of the ground level in atom is determined by the nuclear spin quantum number I, which is equal to $2I + 1$. The nuclear degeneracy of the molecule is given by

$$g_n = \Pi_i\,(2\,I_i + 1)$$

where the multiplication is carried over the number of atoms in the molecule. Since the ground nuclear level is considered to have zero energy, the nuclear partition function is given by

$$q_n = g_n$$

The nuclear partition function does not contribute towards the thermodynamic properties in a given chemical reaction, since nuclear energy levels of reactants and products are not affected.

Summary of Expressions

- At the end, we summarize the expressions of partition function and thermodynamic properties for an ideal diatomic gas under the harmonic oscillator-rigid rotator approximation.

$$q = \left[\left\{\frac{2\pi(m_1+m_2)kT}{h^2}\right\}^{3/2} V\right]\left[\frac{8\pi^2 IkT}{\sigma h^2}\right]\left[\frac{1}{1-\exp(-h\nu/kT)}\right][g_e \exp(D_0/kT)]$$

$$\frac{U}{NkT} = \frac{3}{2} + 1 + \left[\frac{h\nu}{2kT} + \frac{h\nu/kT}{\exp(h\nu/kT)-1}\right] - \frac{D_0}{kT}$$

$$\frac{C_V}{Nk} = \frac{3}{2} + 1 + \left(\frac{h\nu}{kT}\right)^2 \frac{\exp(h\nu/kT)}{[\exp(h\nu/kT)-1]^2}$$

$$\frac{S}{Nk} = \ln\left[\left(\frac{2\pi(m_1+m_2)kT}{h^2}\right)^{3/2} \frac{V\exp(5/2)}{N}\right] + \ln\frac{8\pi^2 IkTe}{\sigma h^2}$$

$$+ \left[\frac{h\nu/kT}{\exp(h\nu/kT)-1} - \ln[1-\exp(-h\nu/kT)]\right] + \ln g_e$$

$$pV = NkT$$

$$\frac{G_m^\circ}{NkT} = -\ln\left[\left(\frac{2\pi(m_1+m_2)kT}{h^2}\right)^{3/2} \frac{kT}{p}\right] - \ln\frac{8\pi^2 IkT}{\sigma h^2}$$

$$+ \left[\frac{h\nu}{2kT} + \ln\{1-\exp(-h\nu/kT)\}\right] - \frac{D_0}{kT} - \ln g_e$$

Comment The values of thermodynamic properties calculated by using the above expressions agree more or less with the values determined experimentally. The agreement can be made more perfect by invoking nonrigid rotation and anharmonic oscillation. The necessary data are determined spectroscopically. It may be pointed here that the above expressions are strictly valid only when $T \gg \theta_r$. At this condition, the molecules are in states with large enough rotational quantum numbers. Consequently, the coupling between the angular momenta due to the rotation of molecules ~~and~~ electronic ~~state~~ does not take place. This results into the separation of rotational-electronic partition function into the product of partition functions of the individual components.

4.9 THERMODYNAMIC PROPERTIES OF A POLYATOMIC IDEAL GAS

Introduction Assuming the different modes of energy independent of each other, the energy of a polyatomic molecule can be written as

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e \tag{4.9.1}$$

The molecular partition function is given by

$$q = q_t\, q_r\, q_v\, q_e \tag{4.9.2}$$

Translational Contribution The translational contributions towards the various thermodynamic properties of a molecule are given by the expressions derived earlier for a monatomic gas (see Section 4.7).

LINEAR MOLECULE

Rotational Contribution For a linear molecule, the expression of the rotational partition function and those of various thermodynamic properties are the same as those of a diatomic molecule. The moment of inertia of the molecule is given by

$$I = \sum_i m_i r_i^2 \tag{4.9.3}$$

where the summation is over the atoms of the molecule. The distances r_i s are measured from the centre of mass of the molecule which can be located by using the expression

$$\sum_i m_i r_i = 0 \tag{4.9.4}$$

The value of symmetric number σ depends upon the structure of the molecule. For symmetrical molecules, $\sigma = 2$ while for asymmetric molecules, $\sigma = 1$.

Vibrational Contribution

A linear molecule has $3N - 5$ independent modes of vibration. Assuming no interactions amongst these modes of vibration, we will have $3N - 5$ characteristic vibrational temperatures $\theta_v (= h\nu_0/k)$. For each vibrational mode, the contributions to thermodynamic properties can be computed by using Eqs (4.8.31) to (4.8.35).

Electronic Contribution

The electronic contributions to thermodynamic properties can be computed by using Eqs (4.8.38) to (4.8.42).

Example 4.9.1

Calculate the values of translational, rotational and vibrational molecular partition functions for carbon dioxide at 1 200 K and 1 atm pressure. Also calculate the contributions made by these motions toward the molar internal energy and molar entropy. Given: Vibrational frequencies of CO_2 are 4.03×10^{13} Hz, 2.00×10^{13} Hz (doubly degenerate) and 7.05×10^{13} Hz. The distance between C and O in CO_2 is 116.2 pm.

Solution

Translational molecular partition function

The mass of CO_2 molecule is

$$m = m_C + 2m_O = (12.0 + 2 \times 16.0)\,(1.66 \times 10^{-27}\ \text{kg})$$

$$= 7.30 \times 10^{-26}\ \text{kg}$$

The molar volume of CO_2 at 1200 K and 1 atm pressure is

$$V_m = \frac{RT}{p} = \frac{(8.314\ \text{J K}^{-1}\text{mol}^{-1})(1\,200\ \text{K})}{(101325\ \text{Pa})} = 9.85 \times 10^{-2}\ \text{m}^3\ \text{mol}^{-1}$$

Hence, $$q_t = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$= (9.85 \times 10^{-2}\ \text{m}^3\ \text{mol}^{-1})$$

$$\times \left[\frac{2(3.14)(7.30\times10^{-26}\ \text{kg})(1.38\times10^{-23}\ \text{J K}^{-1})(1\,200\ \text{K})}{(6.626\times10^{-34}\ \text{J s})^2}\right]^{3/2}$$

$$= 2.34 \times 10^{32}\ \text{mol}^{-1}$$

Rotational molecular partition function

Taking the centre of C atom as a centre of mass, we have

$$I = \sum_i m_i r_i^2 = 2\,(16.0 \times 1.66 \times 10^{-27}\ \text{kg})\,(116.2 \times 10^{-12}\ \text{m})^2$$

$$= 7.17 \times 10^{-46}\ \text{kg m}^2$$

Hence, $$\theta_r = \frac{h^2}{8\pi^2 Ik} = \frac{(6.626\times10^{-34}\ \text{J s})^2}{8(3.14)^2(7.17\times10^{-46}\ \text{kg m}^2)(1.38\times10^{-23}\ \text{J K}^{-1})} = 0.563\ \text{K}$$

$$q_r = \frac{T}{\sigma\theta_r} = \frac{1200\ \text{K}}{2(0.563\ \text{K})} = 1066$$

Vibrational molecular partition function

$$\theta_{v1} = \frac{h\nu_1}{k} = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})(4.03\times10^{13}\ \mathrm{s^{-1}})}{(1.38\times10^{-23}\ \mathrm{J\,K^{-1}})} = 1\,935\ \mathrm{K}$$

$$\theta_{v2} = \frac{h\nu_2}{k} = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})(2.00\times10^{13}\ \mathrm{s^{-1}})}{(1.38\times10^{-23}\ \mathrm{J\,K^{-1}})} = 960.3\ \mathrm{K}$$

(doubly degenerate)

$$\theta_{v3} = \frac{h\nu_3}{k} = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})(7.05\times10^{13}\ \mathrm{s^{-1}})}{(1.38\times10^{-23}\ \mathrm{J\,K^{-1}})} = 3\,385\ \mathrm{K}$$

Hence, $q_{v1} = \frac{1}{1-\exp(-\theta_{v1}/T)} = \frac{1}{1-\exp(-1935\,\mathrm{K}/1\,200\,\mathrm{K})} = \frac{1}{1-\exp(-1.613)}$

$= 1.249$

$$q_{v2} = \frac{1}{1-\exp(-\theta_{v2}/T)} = \frac{1}{1-\exp(-960.3\,\mathrm{K}/1\,200\,\mathrm{K})} = \frac{1}{1-\exp(-0.800)}$$

$= 1.816$

$$q_{v3} = \frac{1}{1-\exp(-\theta_{v3}/T)} = \frac{1}{1-\exp(-3\,385\,\mathrm{K}/1\,200\,\mathrm{K})} = \frac{1}{1-\exp(-2.821)}$$

$= 1.063$

Contribution towards molar internal energy

Since $U_t = NkT^2\left(\frac{\partial \ln q_t}{\partial T}\right)_V = NkT^2\left(\frac{3}{2T}\right) = \frac{3}{2}NkT$

we have $U_{m,t} = \frac{3}{2}RT = \frac{3}{2}(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(1\,200\ \mathrm{K})$

$= 1.497\times10^4\ \mathrm{J\,mol^{-1}}$

Since $U_r = NkT^2\frac{\mathrm{d}\ln q_r}{\mathrm{d}T} = NkT^2\left(\frac{1}{T}\right) = NkT$

we have $U_{m,r} = RT = (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(1\,200\ \mathrm{K})$

$= 9.98\times10^3\ \mathrm{J\,mol^{-1}}$

Since $U_v = NkT^2\frac{\mathrm{d}\ln q_v}{\mathrm{d}T} = NkT^2\left(\frac{1}{T^2}\frac{\theta_v}{e^{\theta_v/T}-1}\right)$

we have $U_{m,v1} = \frac{R\theta_{v1}}{e^{\theta_{v1}/T}-1} = \frac{(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(1\,935\ \mathrm{K})}{(e^{1.613}-1)}$

$= 4.00\times10^3\ \mathrm{J\,mol^{-1}}$

$$U_{m,v2} = \frac{(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(960.3\ \mathrm{K})}{(e^{0.80}-1)} = 6.52\times10^3\ \mathrm{J\,mol^{-1}}$$

(doubly degenerate)

$$U_{\text{m, v3}} = \frac{(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})(3385\ \text{K})}{(e^{2.821}-1)} = 1.78 \times 10^3\ \text{J mol}^{-1}$$

The sum of internal energies is

$$U_\text{m} = (14.97 + 9.98 + 4.00 + 2 \times 6.52 + 1.78) \times 10^3\ \text{J mol}^{-1}$$
$$= 43.77 \times 10^3\ \text{J mol}^{-1}$$

The above internal energy is with reference to zero energy of the ground vibrational state. The actual internal energy is obtained by adding ground vibrational energies, which, respectively, are

$$U_{01} = N_\text{A}\left(\frac{1}{2}h\nu_1\right)$$
$$= (6.023 \times 10^{23}\ \text{mol}^{-1})\ (1/2)\ (6.626 \times 10^{-34}\ \text{J s})\ (4.03 \times 10^{13}\ \text{s}^{-1})$$
$$= 8\,041.5\ \text{J mol}^{-1}$$
$$U_{02} = (6.023 \times 10^{23}\ \text{mol}^{-1})\ (1/2)\ (6.626 \times 10^{-34}\ \text{J s})\ (2.00 \times 10^{13}\ \text{s}^{-1})$$

(doubly degenerate)

$$= 3\,990.8\ \text{J mol}^{-1}$$
$$U_{03} = (6.023 \times 10^{23}\ \text{mol}^{-1})\ (1/2)\ (6.626 \times 10^{-34}\ \text{J s})\ (7.05 \times 10^{13}\ \text{s}^{-1})$$
$$= 14\,067.7\ \text{J mol}^{-1}$$

Hence, the molar internal energy including zero-point vibrational energies is

$$U = (43.77 + 8.04 + 3.99 \times 2 + 14.07) \times 10^3\ \text{J mol}^{-1}$$
$$= 73.86 \times 10^3\ \text{J mol}^{-1}$$

Contribution towards molar entropy

Since $S_\text{t} = Nk \ln\left(\frac{q_\text{t}}{N}\right) + \frac{U_\text{m,t}}{T} + Nk$, we have.

$$S_\text{m, t} = R \ln\left(\frac{q_\text{t}}{N_\text{A}}\right) + \frac{3}{2}R + R$$
$$= (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\left[\ln\left(\frac{2.34\times10^{32}\,\text{mol}^{-1}}{6.023\times10^{23}\,\text{mol}^{-1}}\right)+\frac{5}{2}\right]$$
$$= (164.43 + 20.79)\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$= 185.22\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$S_\text{m, r} = R \ln q_\text{r} + \frac{U_\text{m,r}}{T}$$
$$= (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \ln (1\,066) + \frac{9\,977\ \text{J mol}^{-1}}{1\,200\ \text{K}}$$
$$= (57.96 + 8.31)\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$= 66.27\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Since $S_\text{m, v} = R \ln q_\text{v} + \frac{U_\text{m, v}}{T}$, we have

$$S_\text{m, v1} = (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \ln (1.249) + \frac{4\,000\ \text{J mol}^{-1}}{1\,200\ \text{K}}$$
$$= (1.85 + 3.33)\ \text{J K}^{-1}\ \text{mol}^{-1} = 5.18\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$S_{\mathrm{m,\,v2}} = (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ \ln(1.816) + \frac{6\,520\ \mathrm{J\ mol^{-1}}}{1\,200\ \mathrm{K}}$$

$$= (4.96 + 5.43)\ \mathrm{J\ K^{-1}\ mol^{-1}} = 10.39\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$S_{\mathrm{m,\,v3}} = (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ \ln(1.063) + \frac{1\,780\ \mathrm{J\ mol^{-1}}}{1\,200\ \mathrm{K}}$$

$$= (0.51 + 1.48)\ \mathrm{J\ K^{-1}\ mol^{-1}} = 1.99\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

The sum of entropies is

$$S_{\mathrm{m}} = S_{\mathrm{m,\,t}} + S_{\mathrm{m,\,r}} + S_{\mathrm{m,\,v1}} + 2\,S_{\mathrm{m,\,v2}} + S_{\mathrm{m,\,v3}}$$

$$= (185.22 + 66.27 + 5.18 + 2 \times 10.39 + 1.99)\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$= 279.44\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

NONLINEAR MOLECULE

Rotational Contribution

For a nonlinear molecule, the rotational partition function is given by

$$q_{\mathrm{r}} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 I_x kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_y kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_z kT}{h^2}\right)^{1/2}$$

$$= \frac{8\pi^2}{\sigma h^3}\,(I_x I_y I_z)\,(2\pi\,kT)^{3/2} \qquad (4.9.5)$$

where I_x, I_y and I_z are the three principal moments of inertia of the molecule along the three principal Cartesian-coordinate axes with the centre of mass of molecule as the origin. The latter is defined by the expressions

$$\textstyle\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i = 0 \qquad (4.9.6)$$

In the principal set of axes, we have

$$I_x = \textstyle\sum_i m_i(y_i^2 + z_i^2) \qquad (4.9.7)$$

$$I_y = \textstyle\sum_i m_i(z_i^2 + x_i^2) \qquad (4.9.8)$$

$$I_z = \textstyle\sum_i m_i(x_i^2 + y_i^2) \qquad (4.9.9)$$

and the products of inertia are zero, i.e.

$$I_{xy} = I_{yx} = \textstyle\sum_i m_i\, x_i\, y_i = 0 \qquad (4.9.10)$$

$$I_{yz} = I_{zy} = \textstyle\sum_i m_i\, y_i\, z_i = 0 \qquad (4.9.11)$$

$$I_{zx} = I_{xz} = \textstyle\sum_i m_i\, z_i\, x_i = 0 \qquad (4.9.12)$$

The principal set of axes can be conveniently selected by letting any one of the coordinate directions x, y and z to coincide with a line of symmetry in the molecule.

Comment on the Moment of Inertia

In general, the expressions given by Eqs (4.9.7) to (4.9.9) are represented as I_{xx}, I_{yy} and I_{zz}, respectively. It is found that the values of I_{xx}, I_{yy}, I_{zz}, I_{xy}, I_{yz} and I_{zx} depend upon the orientations of the three Cartesian axes keeping the origin at the centre of mass of the molecule. However, in one particular orientation, the value of each of I_{xy}, I_{yz} and I_{zx} is zero. This particular orientation is called the principal set of axes.

For any orientation, the product $I_x I_y I_z$ is given by

$$I_x I_y I_z = \begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{yx} & I_{yy} & -I_{yz} \\ -I_{zx} & -I_{zy} & I_{zz} \end{vmatrix} \tag{4.9.13}$$

and for the principal set of axes,

$$I_x I_y I_z = \begin{vmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & 0 \\ 0 & 0 & I_{zz} \end{vmatrix} = I_{xx} I_{yy} I_{zz} \tag{4.9.14}$$

Classification of a Molecule

A given molecule may be classified based on the values of the principal moments of inertia as described in Table 4.9.1.

Table 4.9.1 Classification of Rotating Molecules

Characteristics	*Name*	*Example*
$I_x = I_y = I_z$	Spherical top	CCl_4
$I_x = I_y \neq I_z$	Symmetric top	NH_3
$I_x \neq I_y \neq I_z$	Asymmetric top	CH_2Cl_2
$I_x = 0, I_y = I_z = I$	Linear	$HC{\equiv}CH$
$I_x + I_y = I_z$	Planar	C_6H_6

Comment on the Evaluation of Moment of Inertia

It is not necessary to locate the centre of mass of the molecule to determine the moment of inertia I of a linear molecule or the product $I_x I_y I_z$ of a nonlinear molecule. The following procedure may be adopted.

Linear Molecule Take any point on the molecular axis (labelled as x axis) as the origin and determine the x_i coordinate of each atom. The expression of moment of inertia is then given by

$$I = \sum_i m_i x_i^2 - \left(\frac{1}{M}\right) \left(\sum_i m_i x_i\right)^2 \tag{4.9.15}$$

where M is the molar mass of the molecule. Alternatively, the following expression may be used

$$I = \left(\frac{1}{2M}\right) \sum_i \sum_j m_i m_j r_{ij}^2 = \left(\frac{1}{M}\right) \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} m_i m_j r_{ij}^2 \tag{4.9.16}$$

where r_{ij} is the distance between ith and jth atoms.

Nonlinear Molecule Take any one point as the origin (preferably on the symmetry axis or symmetry plane if existed). Determine the coordinates x_i, y_i and z_i of every atom with reference to a convenient rectangular coordinate system. Evaluate the terms given below.

$$A = \sum_i m_i\,(y_i^2 + z_i^2) - \left(\frac{1}{M}\right)\left(\sum_i m_i y_i\right)^2 - \left(\frac{1}{M}\right)\left(\sum_i m_i z_i\right)^2$$

$$B = \sum_i m_i\,(x_i^2 + z_i^2) - \left(\frac{1}{M}\right)\left(\sum_i m_i x_i\right)^2 - \left(\frac{1}{M}\right)\left(\sum_i m_i z_i\right)^2$$

$$C = \sum_i m_i\,(x_i^2 + y_i^2) - \left(\frac{1}{M}\right)\left(\sum_i m_i x_i\right)^2 - \left(\frac{1}{M}\right)\left(\sum_i m_i y_i\right)^2$$

$$D = \sum_i m_i x_i y_i - \left(\frac{1}{M}\right)\left(\sum_i m_i x_i\right)\left(\sum_i m_i y_i\right)$$

$$E = \sum_i m_i x_i z_i - \left(\frac{1}{M}\right)\left(\sum_i m_i x_i\right)\left(\sum_i m_i z_i\right)$$

$$F = \sum_i m_i y_i z_i - \left(\frac{1}{M}\right)\left(\sum_i m_i y_i\right)\left(\sum_i m_i z_i\right)$$

and evaluate $I_x I_y I_z$ by using the following determinant.

$$I_x I_y I_z = \begin{vmatrix} A & -D & -E \\ -D & B & -F \\ -E & -F & C \end{vmatrix}$$

Vibrational Contribution A nonlinear molecule has $3N-6$ independent modes of vibration. Assuming no interactions amongst these modes of vibration, we will have $3N-6$ characteristic vibrational temperatures θ_v ($= h\nu/k$). For each vibrational mode, the contributions to thermodynamic properties can be computed by using Eqs (4.8.31) to (4.8.35).

Example 4.9.2 Calculate the values of translational, rotational and vibrational molecular partition functions for gaseous H_2O molecules at 1 200 K and 1 bar pressure. Also, calculate the contributions made by these motions toward the molar internal energy and molar entropy. Given: Vibrational frequencies of H_2O are 1.10×10^{14} Hz, 4.78×10^{13} Hz and 1.13×10^{14} Hz. The distance O—H is 95.8 pm and the angle HOH is 104.5°.

Solution ***Translational molecular partition function***

The mass of H_2O molecule is

$$m = m_O + 2m_H = (16.0 + 2 \times 1.0)\,(1.66 \times 10^{-27}\ \text{kg}) = 2.99 \times 10^{-26}\ \text{kg}$$

The molar volume of $H_2O(g)$ at 1 200 K and 1 bar pressure is

$$V_m = \frac{RT}{p} = \frac{(8.314\ \text{J K}^{-1}\text{mol}^{-1})(1200\ \text{K})}{(10^5\ \text{Pa})} = 9.98 \times 10^{-2}\ \text{m}^3\ \text{mol}^{-1}$$

$$q_t = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$= (9.98 \times 10^{-2}\ \text{m}^3\ \text{mol}^{-1})$$

$$\times \left[\frac{2(3.14)(2.99\times10^{-26}\ \text{kg})(1.38\times10^{-23}\ \text{J K}^{-1})^{3/2}(1\ 200\ \text{K})}{(6.626\times10^{-34}\ \text{J s})^2}\right]^{3/2}$$

$$= 5.95 \times 10^{31}\ \text{mol}^{-1}$$

Rotational molecular partition function

To calculate the rotational partition function, we need the moment of inertia of water. Let the water molecule may be represented as shown in Fig. 4.9.1.

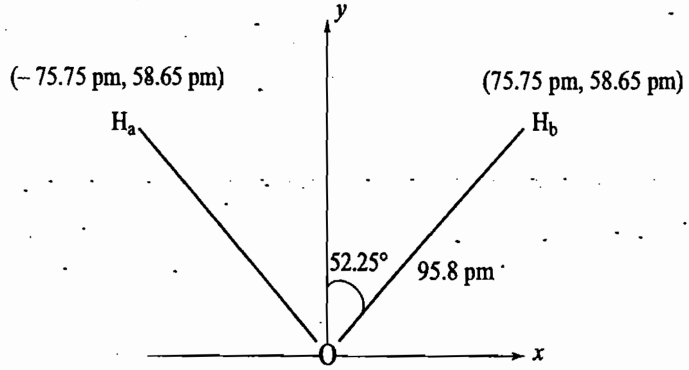


Fig. 4.9.1 Orientation of H_2O molecule

Let (x_c, y_c) be the coordinates of the centre of mass of the molecule. To calculate (x_c, y_c), we set

$$m_O\,(x_c - 0) + m_H\,(x_c - 75.75\ \text{pm}) + m_H\,(x_c + 75.75\ \text{pm}) = 0$$

$$m_O\,(y_c - 0) + m_H\,(y_c - 58.65\ \text{pm}) + m_H\,(y_c - 58.65\ \text{pm}) = 0$$

where $m_O = 16 \times 1.66 \times 10^{-27}\ \text{kg} = 2.66 \times 10^{-26}\ \text{kg}$

$m_H = 1 \times 1.66 \times 10^{-27}\ \text{kg} = 1.66 \times 10^{-27}\ \text{kg}$

This gives

$$x_c = 0$$

$$y_c = \frac{(2m_H)(58.68\ \text{pm})}{(m_O + 2m_H)} = \frac{2(58.65\ \text{pm})}{(16+2)} = 6.52\ \text{pm}$$

Taking (x_c, y_c) as the origin and the y-axis along the line of symmetry, the coordinates of atoms are

$x_O = 0$	$y_O = -6.52$ pm
$x_{H_a} = -75.75$ pm	$y_{H_a} = (58.65 - 6.52)$ pm $= 52.13$ pm
$x_{H_b} = +75.75$ pm	$y_{H_b} = (58.65 - 6.52)$ pm $= 52.13$ pm

$$I_{xx} = \sum_i m_i(y_i^2 + z_i^2) = \sum_i m_i y_i^2 \qquad \text{(as } z_i\text{s are zero)}$$

$$= [(2.66 \times 10^{-26})(-6.52)^2 + (1.66 \times 10^{-27})(52.13)^2 + (1.66 \times 10^{-27}) \times (52.13)^2]\ \text{kg pm}^2$$

$$= 1.02 \times 10^{-23}\ \text{kg pm}^2$$

$$I_{yy} = \sum_i m_i(z_i^2 + x_i^2) = \sum_i m_i x_i^2 \qquad \text{(as } z_i\text{s are zero)}$$

$$= [(2.66 \times 10^{-26})\,(0)^2 + (1.66 \times 10^{-27})\,(-75.75)^2 + (1.66 \times 10^{-27}) \times (75.75)^2]\ \text{kg pm}^2$$

$$= 1.91 \times 10^{-23}\ \text{kg pm}^2$$

$$I_{zz} = \sum_i m_i(x_i^2 + y_i^2)$$

$$= [(2.66 \times 10^{-26})\,[0^2 + (-6.52)^2] + (1.66 \times 10^{-27})\,[(-75.75)^2 + (52.13)^2] + (1.66 \times 10^{-27})\,[(75.75)^2 + (52.13)^2]]\ \text{kg pm}^2$$

$$= 2.92 \times 10^{-23}\ \text{kg pm}^2$$

$$I_{xy} = \sum_i m_i\, x_i\, y_i$$

$$= [(2.66 \times 10^{-26})\,(0)\,(-6.52) + (1.66 \times 10^{-27})\,(-75.75)\,(52.13) + (1.66 \times 10^{-27})\,(75.75)\,(52.13)]\ \text{kg pm}^2$$

$$= 0$$

$$I_{xz} = I_{yz} = 0 \qquad \text{(as } z_i\text{s are zero)}$$

Hence, the principal moments of inertia are

$$I_x = 1.02 \times 10^{-23}\ \text{kg pm}^2 = 1.02 \times 10^{-47}\ \text{kg m}^2$$

$$I_y = 1.91 \times 10^{-23}\ \text{kg pm}^2 = 1.91 \times 10^{-47}\ \text{kg m}^2$$

$$I_z = 2.92 \times 10^{-23}\ \text{kg pm}^2 = 2.92 \times 10^{-47}\ \text{kg m}^2$$

The value of rotational partition function is

$$q_r = \frac{8\pi^2}{\sigma h^3}\,(I_x\, I_y\, I_z)^{1/2}\,(2\pi kT)^{3/2} \qquad \text{(where } \sigma = 2 \text{ for } H_2O)$$

$$= \frac{8(3.14)^2}{2(6.626\times10^{-34}\,\text{J s})^3}\,[(1.02 \times 10^{-47}\ \text{kg m}^2)\,(1.91 \times 10^{-47}\ \text{kg m}^2) \times (2.92 \times 10^{-47}\ \text{kg m}^2)]^{1/2}\,[2(3.14)\,(1.38 \times 10^{-23}\ \text{J K}^{-1})\,(1200\ \text{K})]^{3/2}$$

$$= 343$$

Vibrational molecular partition function

$$\theta_{v1} = \frac{h\nu_1}{k} = \frac{(6.626\times10^{-34}\,\text{J s})(1.10\times10^{14}\,\text{s}^{-1})}{(1.38\times10^{-23}\,\text{J K}^{-1})} = 5\,281.6\ \text{K}$$

$$\theta_{v2} = \frac{h\nu_2}{k} = \frac{(6.626\times10^{-34}\,\text{J s})(4.78\times10^{13}\,\text{s}^{-1})}{(1.38\times10^{-23}\,\text{J K}^{-1})} = 2\,295.1\ \text{K}$$

$$\theta_{v3} = \frac{h\nu_3}{k} = \frac{(6.626\times10^{-34}\,\text{J s})(1.13\times10^{14}\,\text{s}^{-1})}{(1.38\times10^{-23}\,\text{J K}^{-1})} = 5\,425.6\ \text{K}$$

$$q_{v1} = \frac{1}{1-\exp(-\theta_{v1}/T)} = \frac{1}{1-\exp(-5\,281.6/1\,200)} = \frac{1}{1-\exp(-4.401)}$$

$$= 1.012$$

$$q_{v2} = \frac{1}{1-\exp(-\theta_{v2}/T)} = \frac{1}{1-\exp(-2\,295.1/1\,200)} = \frac{1}{1-\exp(-1.913)}$$

$$= 1.173$$

$$q_{v3} = \frac{1}{1-\exp(-\theta_{v3}/T)} = \frac{1}{1-\exp(-5\,425.6/1\,200)} = \frac{1}{1-\exp(-4.521)}$$

$$= 1.011$$

Contribution towards molar internal energy

Since $\quad U_{\mathrm{t}} = NkT^2\left(\dfrac{\partial \ln q_t}{\partial T}\right)_V = NkT^2\left(\dfrac{3}{2T}\right) = \dfrac{3}{2}\,NkT$

we have $\quad U_{\mathrm{m,\,t}} = \dfrac{3}{2}\,RT = \dfrac{3}{2}\,(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\,(1\ 200\ \mathrm{K}) = 1.50 \times 10^4\ \mathrm{J\ mol^{-1}}$

Since $\quad U_{\mathrm{r}} = NkT^2\,\dfrac{\mathrm{d}\ln q_{\mathrm{r}}}{\mathrm{d}T} = NkT^2\left(\dfrac{3}{2T}\right) = \dfrac{3}{2}\,NkT$

we have $\quad U_{\mathrm{m,\,r}} = \dfrac{3}{2}\,RT = \dfrac{3}{2}\,(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\,(1200\ \mathrm{K}) = 1.50 \times 10^4\ \mathrm{J\ mol^{-1}}$

Since $\quad U_{\mathrm{v}} = NkT^2\,\dfrac{\mathrm{d}\ln q_{\mathrm{v}}}{\mathrm{d}T} = NkT^2\left(\dfrac{1}{T^2}\,\dfrac{\theta_{\mathrm{v}}}{\mathrm{e}^{\theta_{\mathrm{v}}/T}-1}\right)$

we have $\quad U_{\mathrm{m,\,v1}} = \dfrac{R\theta_{\mathrm{v1}}}{\mathrm{e}^{\theta_{\mathrm{v1}}/T}-1} = \dfrac{(8.314\ \mathrm{J\,K^{-1}\ mol^{-1}})(5\,281.6\,\mathrm{K})}{(\mathrm{e}^{4.401}-1)} = 545.3\ \mathrm{J\ mol^{-1}}$

$$U_{\mathrm{m,\,v2}} = \frac{R\theta_{\mathrm{v2}}}{\mathrm{e}^{\theta_{\mathrm{v2}}/T}-1} = \frac{(8.314\ \mathrm{J\,K^{-1}\ mol^{-1}})(2\,295.1\,\mathrm{K})}{(\mathrm{e}^{1.913}-1)} = 3\,305.1\ \mathrm{J\ mol^{-1}}$$

$$U_{\mathrm{m,\,v3}} = \frac{R\theta_{\mathrm{v3}}}{\mathrm{e}^{\theta_{\mathrm{v3}}/T}-1} = \frac{(8.314\ \mathrm{J\,K^{-1}\ mol^{-1}})(5\,425.6\,\mathrm{K})}{(\mathrm{e}^{4.521}-1)} = 496.1\ \mathrm{J\ mol^{-1}}$$

The sum of internal energies is

$$U_{\mathrm{m}} = U_{\mathrm{m,\,t}} + U_{\mathrm{m,\,r}} + U_{\mathrm{m,\,v1}} + U_{\mathrm{m,\,v2}} + U_{\mathrm{m,\,v3}}$$

$$= (15.0 + 15.0 + 0.543 + 3.305 + 0.496) \times 10^3\ \mathrm{J\ mol^{-1}}$$

$$= 34.34 \times 10^3\ \mathrm{J\ mol^{-1}}$$

The above internal energy refers to zero energy of the ground vibrational state. The actual internal energy is obtained by adding ground-state vibrational energies, which, respectively, are

$$U_{01} = N_{\mathrm{A}}\left(\frac{1}{2}h\nu_1\right) = (6.022 \times 10^{23}\ \mathrm{mol^{-1}})\left(\frac{1}{2}\right)(6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (1.10 \times 10^{14}\ \mathrm{s^{-1}})$$

$$= 21.95 \times 10^3\ \mathrm{J\ mol^{-1}}$$

$$U_{02} = (6.022 \times 10^{23}\ \mathrm{mol^{-1}})\left(\frac{1}{2}\right)(6.626 \times 10^{-34}\ \mathrm{J\ s})\,(4.78 \times 10^{13}\ \mathrm{s^{-1}})$$

$$= 9.54 \times 10^3\ \mathrm{J\ mol^{-1}}$$

$$U_{03} = (6.022 \times 10^{23}\ \mathrm{mol^{-1}})\left(\frac{1}{2}\right)(6.626 \times 10^{-34}\ \mathrm{J\ s})\,(1.13 \times 10^{14}\ \mathrm{s^{-1}})$$

$$= 22.55 \times 10^3\ \mathrm{J\ mol^{-1}}$$

Hence, the molar internal energy including zero-point vibrational energies is

$$U = (34.34 + 21.95 + 9.54 + 22.55) \times 10^3\ \text{J mol}^{-1}$$

$$= 88.38 \times 10^3\ \text{J mol}^{-1}$$

Contribution towards molar entropy

Since $S_t = N k \ln\left(\frac{q_t}{N}\right) + \frac{U_{m,t}}{T} + Nk$, we have

$$S_{m,t} = R \ln\left(\frac{q_t}{N_A}\right) + \frac{3}{2} R + R$$

$$= (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \left[\ln\left(\frac{5.95 \times 10^{31}\ \text{mol}^{-1}}{6.023 \times 10^{23}\ \text{mol}^{-1}}\right) + \frac{5}{2}\right]$$

$$= 173.83\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$S_{m,r} = R \ln q_r + \frac{U_{m,r}}{T}$$

$$= (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \ln (343) + \frac{1.50 \times 10^4\ \text{J mol}^{-1}}{1\,200\ \text{K}}$$

$$= (48.53 + 12.5)\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$= 61.03\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Since $S_{m,v} = R \ln q_v + \frac{U_{m,v}}{T}$, we have

$$S_{m,v1} = (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \ln (1.012) + \frac{545.3\ \text{J mol}^{-1}}{1\,200\ \text{K}}$$

$$= (0.099 + 0.453)\ \text{J K}^{-1}\ \text{mol}^{-1} = 0.552\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$S_{m,v2} = (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \ln (1.173) + \frac{3\,305.1\ \text{J mol}^{-1}}{1\,200\ \text{K}}$$

$$= (1.327 + 2.754)\ \text{J K}^{-1}\ \text{mol}^{-1} = 4.081\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$S_{m,v3} = (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \ln (1.011) + \frac{496.1\ \text{J mol}^{-1}}{1\,200\ \text{K}}$$

$$= (0.091 + 0.413)\ \text{J K}^{-1}\ \text{mol}^{-1} = 0.504\ \text{J K}^{-1}\ \text{mol}^{-1}$$

The sum of entropies is

$$S_m = S_{m,t} + S_{m,r} + S_{m,v1} + S_{m,v2} + S_{m,v3}$$

$$= (173.83 + 61.03 + 0.552 + 4.081 + 0.504)\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$= 239.95\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Note: The total entropy of the system can be evaluated by using the expression

$$S_t = R \ln\left(\frac{q_t q_r q_{v1} q_{v2} q_{v3}}{N_A}\right) + \frac{U_{m,t} + U_{m,r} + U_{m,v1} + U_{m,v2} + U_{m,v3}}{T} + R$$

$$= \left[8.314\ln\left\{\left(\frac{5.95\times10^{31}}{6.022\times10^{23}}\right)(343)(1.012)(1.173)(1.011)\right\}\right.$$

$$\left. + \left(\frac{1.50\times10^4+1.50\times10^4+545.3+3\,305.1+496.1}{1\,200}\right)+8.314\right] \text{ J K}^{-1}\text{ mol}^{-1}$$

$$= (203.10 + 28.62 + 8.314) \text{ J K}^{-1}\text{ mol}^{-1}$$

$$= 240.0 \text{ J K}^{-1}\text{ mol}^{-1}$$

4.10 STANDARD EQUILIBRIUM CONSTANT OF A REACTION INVOLVING IDEAL GASES

The thermodynamic relation for a reaction at equilibrium is

$$0 = \sum_i \nu_i \mu_i \qquad \begin{bmatrix} \nu_i \text{ is +ve for products} \\ \nu_i \text{ is −ve for reactants} \end{bmatrix} \tag{4.10.1}$$

The expression of chemical potential, μ_i, in terms of molecular partition function is given by

$$\mu_i = \frac{G_i}{n_i} = \frac{-N_i kT\ln(q_i/N_i)}{n_i} \tag{4.10.2}$$

Since $N_i = n_i N_A$, we get

$$\mu_i = -(N_A k)\,T\ln\left(\frac{q_i}{N_i}\right) = -RT\ln\left(\frac{q_i}{N_i}\right)$$

Using ideal gas equation

$$p_i V = n_i RT = \left(\frac{N_i}{N_A}\right)RT = N_i kT$$

the above expression becomes

$$\mu_i = -RT\ln\left(\frac{q_i kT}{p_i V}\right)$$

$$= -RT\ln\left(\frac{q_i kT}{p^\circ V}\right) - RT\ln\left(\frac{p^\circ}{p_i}\right) \tag{4.10.3}$$

where $p^\circ = 1$ bar.

Substituting Eq. (4.10.3) in Eq. (4.10.1), we get

$$0 = \sum_i\left[-RT\nu_i\ln\left(\frac{q_i kT}{p^\circ V}\right) + RT\,\nu_i\ln\left(\frac{p_i}{p^\circ}\right)\right]$$

or

$$RT\ln \Pi_i\left(\frac{p_i}{p^\circ}\right)^{\nu_i} = RT\ln \Pi_i\left(\frac{q_i kT}{p^\circ V}\right)^{\nu_i} \tag{4.10.4}$$

By definition, the standard equilibrium constant of a reaction is given by

$$K_p^\circ = \Pi_i\left(\frac{p_i}{p^\circ}\right)^{\nu_i} \tag{4.10.5}$$

With this, Eq. (4.10.4) gives

$$K_p^\circ = \Pi_i \left(\frac{q_i\, kT}{p^\circ V}\right)^{\nu_i} = \left(\frac{kT}{p^\circ}\right)^{\Sigma_i \nu_i} \Pi_i \left(\frac{q_i}{V}\right)^{\nu_i} \tag{4.10.6}$$

While computing the various molecular partition functions, it is essential to use the same reference of zero energy for all species. For this purpose, the zero of energy is assigned to the dissociated atoms of each species. This reference affects the expressions of electronic partition function. The expression of the latter with respect to the ground electronic state of the molecule is

$$q_i = g_0 + g_1\, e^{-\varepsilon_1/kT} + g_2\, e^{-\varepsilon_2/kT} + \cdots$$

This is changed to

$$q_i' = e^{D_0/kT}\, q_i \tag{4.10.7}$$

when the reference of zero energy is shifted to ground-state dissociated atoms (Fig 4.10.1).

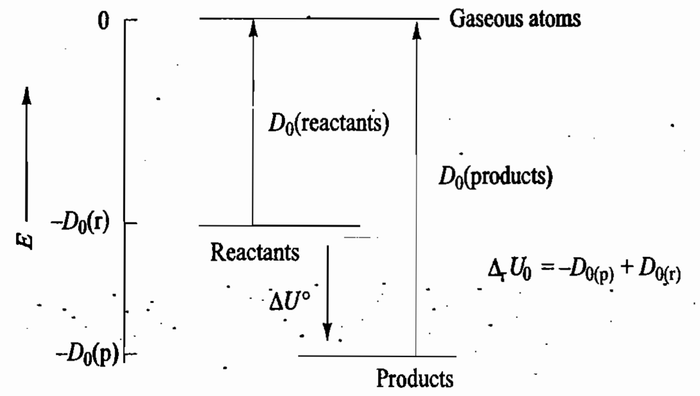


Fig. 4.10.1 Energy change in a reaction in terms of dissociation energies of reactants and products

The expression of the standard equilibrium constant with this shift of reference of energy is

$$K_p^\circ = \left(\frac{kT}{p^\circ}\right)^{\Sigma_i \nu_i} \exp\left(\frac{\Sigma_i \nu_i D_{0i}}{RT}\right) \Pi_i \left(\frac{q_i}{V}\right)^{\nu_i}$$

$$= \left[\left(\frac{kT}{p^\circ}\right)^{\Sigma_i \nu_i}\right] \left[e^{-\Delta_r U_0/RT}\right] \left[\Pi_i \left(\frac{q_i}{V}\right)^{\nu_i}\right] \tag{4.10.8}$$

Example 4.10.1

Determine the standard equilibrium constant for the reaction

$$N_2(g) \rightleftharpoons 2N(g)$$

at 5000 K. Given: r_{eq} = 110 pm for N_2, classical frequency of vibration of $N_2(g) = 7.07 \times 10^{13}\ s^{-1}$, dissociation energy of $N_2(g)$ = 940.3 kJ mol^{-1} and degeneracy of ground electronic level of N_2 is 1 while that of N(g) is 4.

Solution ***Partition function of*** N(g)

For monatomic species

$$q = q_t\, q_e$$

The expression of translational partition function is

$$q_t = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \qquad \text{(Eq. 4.7.7)}$$

Thus

$$\frac{q_t}{V} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$= \left[\frac{2(3.14)(14\times1.66\times10^{-27}\ \text{kg})(1.38\times10^{-23}\ \text{J K}^{-1})(5\,000\ \text{K})}{(6.626\times10^{-34}\ \text{J s})^2}\right]^{3/2}$$

$$= 3.474 \times 10^{33}\ \text{m}^{-3}$$

The electronic partition function is

$$q_e = g_0 = 4$$

Hence, $q_N = q_t\, q_e = \{(3.474 \times 10^{33}\ \text{m}^{-3})\ V\}\ (4) = (1.390 \times 10^{34}\ \text{m}^{-3})\ V$

Partition function of N_2(g)

For diatomic species, we have

$$q = q_t\, q_r\, q_v\, q_e$$

For N_2 the value of translational partition function is

$$\frac{q_t}{V} = \frac{(2\pi mkT)^{3/2}}{h^2}$$

$$= \left[\frac{2(3.14)(28\times1.66\times10^{-27}\text{kg})(1.38\times10^{-23}\ \text{J K}^{-1})(5\,000\text{K})}{(6.626\times10^{-34}\ \text{J s})^2}\right]^{3/2}$$

$$= 9.826 \times 10^{33}\ \text{m}^{-3}$$

The value of rotational partition function is calculated as follows:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m^2}{2m} = \frac{m}{2} = \frac{14\times1.66\times10^{-27}\text{kg}}{2} = 1.16 \times 10^{-26}\text{kg}$$

$$I = \mu r^2 = (1.16 \times 10^{-26}\ \text{kg})\ (110 \times 10^{-12}\ \text{m})^2$$

$$= 1.40 \times 10^{-46}\ \text{kg m}^2$$

$$q_r = \left(\frac{8\pi^2 Ik}{h^2}\right)\frac{T}{\sigma} \qquad \text{(Eq. 4.8.8)}$$

$$= \frac{8(3.14)^2(1.40\times10^{-46}\ \text{kg m}^2)(1.38\times10^{-23}\ \text{J K}^{-1})(5\,000\ \text{K})}{(6.626\times10^{-34}\ \text{J s})^2(2)} = 867.7$$

The value of vibrational partition function is calculated as follows.

$$\theta_v = \frac{h\nu}{k} = \frac{(6.626\times10^{-34}\text{J s})(7.07\times10^{13}\ \text{s}^{-1})}{(1.38\times10^{-23}\text{J K}^{-1})} = 3\,395\ \text{K}$$

$$q_v = \frac{1}{1-e^{-\theta_v/T}} = \frac{1}{1-e^{-3395/5000}} = \frac{1}{1-0.507} = 2.029$$

The value of electronic partition function is

$$q_e = g_e = 1$$

The partition function of N_2 is

$$\begin{aligned} q_{N_2} &= q_t\, q_r\, q_v\, q_e \\ &= \{(9.826 \times 10^{33}\ \mathrm{m^{-3}})\ V\}\ (867.7)\ (2.029)\ (1) \\ &= (1.73 \times 10^{-37}\ \mathrm{m^{-3}})\ V \end{aligned}$$

Equilibrium constant of the reaction

The value of equilibrium constant is

$$K_p^\circ = \left(\frac{kT}{p^\circ}\right)^{\Sigma_i \nu_i} \mathrm{e}^{-\Delta_r U/RT}\ \Pi_i \left(\frac{q_i}{V}\right)^{\nu_i}$$

$$= \left[\frac{(1.38\times10^{-23}\ \mathrm{J\,K^{-1}})(5\,000\ \mathrm{K})}{10^5\ \mathrm{Pa}}\right]^{2-1} \exp\left[-\frac{(940\,300\ \mathrm{J\,mol^{-1}})}{(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(5\,000\ \mathrm{K})}\right] \times \left[\frac{(1.39\times10^{34}\ \mathrm{m^{-3}})^2}{(1.73\times10^{37}\ \mathrm{m^{-3}})}\right]$$

$$= (6.9 \times 10^{-25}\ \mathrm{m^3})\ (1.50 \times 10^{-10})\ (1.12 \times 10^{31}\ \mathrm{m^{-3}})$$

$$= 0.001\ 16$$

Alternative Solution Alternatively, we may compute molar values of G_N° and $G_{N_2}^\circ$ by using partition functions and determine

$$\Delta_r G^\circ = 2G_N^\circ - G_{N_2}^\circ$$

and use $\Delta_r G^\circ = -RT \ln K_p^\circ$ to determine the equilibrium constant.

For N(g), we have

$$q_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \left(\frac{NkT}{p^\circ}\right)$$

Hence,

$$\frac{q_t}{N} = \frac{(kT)^{5/2}}{p^\circ} \left(\frac{2\pi m}{h^2}\right)^{3/2}$$

$$= \frac{[(1.38\times10^{-23}\ \mathrm{J\,K^{-1}})(5\,000\ \mathrm{K})]^{5/2}}{(10^5\ \mathrm{Pa})} \left[\frac{2(3.14)(14\times1.66\times10^{-27}\ \mathrm{kg})}{(6.626\times10^{-34}\ \mathrm{J\,s})^2}\right]^{3/2}$$

$$= (1.25 \times 10^{-53})\ (1.92 \times 10^{62}) = 2.40 \times 10^9$$

$$G_t^\circ = -RT \ln\left(\frac{q_t}{N}\right) = -(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\ (5\ 000\ \mathrm{K})\ \ln(2.40 \times 10^9)$$

$$= -8.98 \times 10^5\ \mathrm{J\,mol^{-1}}$$

$$q_e = 4$$

$$G_e^\circ = -RT \ln q_e = -(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\ (5\ 000\ \mathrm{K})\ \ln 4$$

$$= -5.76 \times 10^4\ \mathrm{J\,mol^{-1}}$$

Hence, $G^\circ_{\text{N}} = G^\circ_{\text{t}} + G^\circ_{\text{e}}$

$= (-\,8.98 \times 10^5 - 5.76 \times 10^4)\ \text{J mol}^{-1}$

$= -\,9.556 \times 10^5\ \text{J mol}^{-1}$

For N_2(g), we have

$$\frac{q_{\text{t}}}{N} = \frac{(kT)^{5/2}}{p^\circ}\left(\frac{2\pi m}{h^2}\right)^{3/2}$$

$$= \frac{[(1.38\times10^{-23}\,\text{J K}^{-1})(5\,000\,\text{K})]^{5/2}}{10^5\,\text{Pa}}\left[\frac{2(3.14)(28\times1.66\times10^{-27}\,\text{kg})}{(6.626\times10^{-34}\,\text{J s})^2}\right]^{3/2}$$

$= (1.25 \times 10^{-53})\ (5.42 \times 10^{62})$

$= 6.78 \times 10^9$

$$G^\circ_{\text{t}} = -\,RT \ln\left(\frac{q_{\text{t}}}{N}\right) = -\,(8.314\ \text{J K}^{-1}\,\text{mol}^{-1})\ (5\,000\ \text{K})\ \ln\,(6.78 \times 10^9)$$

$= -\,9.41 \times 10^5\ \text{J mol}^{-1}$

$q_{\text{r}} = 867.7$

$G^\circ_{\text{r}} = -\,RT \ln q_{\text{r}} = -\,(8.314\ \text{J K}^{-1}\,\text{mol}^{-1})\ (5\,000\ \text{K})\ \ln\,(867.7)$

$= -\,2.81 \times 10^5\ \text{J mol}^{-1}$

$q_{\text{v}} = 2.029$

$G^\circ_{\text{v}} - U_0 = -\,RT \ln q_{\text{v}} = -\,(8.314\ \text{J K}^{-1}\,\text{mol}^{-1})\ (5\,000\ \text{K})\ \ln\,(2.029)$

$= -\,2.94 \times 10^4\ \text{J mol}^{-1}$

$q_{\text{e}} = 1$

$G^\circ_{\text{e}} = -\,RT \ln q_{\text{e}} = 0$

$G^\circ_{\text{chem}} = -\,D_0 = -\,940\ 300\ \text{J mol}^{-1}$

Thus, for N_2 we have

$G^\circ_{N_2} = G^\circ_{\text{t}} + G^\circ_{\text{r}} + (G^\circ_{\text{v}} - U_0) + G^\circ_{\text{e}} + G^\circ_{\text{chem}}$

$= (-\,9.41 \times 10^5 - 2.81 \times 10^5 - 2.94 \times 10^4 + 0 - 940\,300)\ \text{J mol}^{-1}$

$= -\,2.192 \times 10^6\ \text{J mol}^{-1}$

The standard free energy change of the given reaction is

$\Delta_{\text{r}}G^\circ = 2G^\circ_{\text{N}} - G^\circ_{N_2} = 2(-\,9.556 \times 10^5\ \text{J mol}^{-1}) - (-\,2.192 \times 10^6\ \text{J mol}^{-1})$

$= 2.81 \times 10^5\ \text{J mol}^{-1}$

Finally, the standard equilibrium constant of the reaction is

$$\ln K^\circ_p = -\,\frac{\Delta_{\text{r}}G^\circ}{RT} = -\,\frac{(2.81\times10^5\,\text{J mol}^{-1})}{(8.314\,\text{J K}^{-1}\text{mol}^{-1})\,(5\,000\,\text{K})}$$

$= -\,6.76$

Hence, $K^\circ_p = \text{e}^{-6.76} = 0.001\ 16$

Example 4.10.2 Show that the standard equilibrium constant at 400 K for the reaction

$$H_2 + D_2 \rightleftharpoons 2HD$$

is equal to 3.54. Given:

	$I \times 10^{46}/\text{kg m}^2$	θ_v/K	$D_0/\text{kJ mol}^{-1}$
H_2	4.60	5 986	431.8
D_2	9.20	4 308	439.2
HD	6.13	5 226	435.2

Solution The standard equilibrium constant is given by

$$K_p^\circ = \left(\frac{kT}{p^\circ}\right)^{\sum_i \nu_i} \Pi_i \left(\frac{q_i}{V}\right)^{\nu_i} \mathrm{e}^{-\Delta_r U^\circ/RT}$$

For the given reaction, $\sum_i \nu_i = \nu_{HD} + \nu_{H_2} + \nu_{D_2} = 2 - 1 - 1 = 0$.
Hence,

$$K_p^\circ = \left(\frac{q_{HD}}{V}\right)^2 \left(\frac{q_{H_2}}{V}\right)^{-1} \left(\frac{q_{D_2}}{V}\right)^{-1} \mathrm{e}^{-\Delta_r U^\circ/RT}$$

$$= \frac{(q_t q_r q_v)_{HD}^2}{(q_t q_r q_v)_{H_2} (q_t q_r q_v)_{D_2}} \mathrm{e}^{-\Delta_r U^\circ/RT}$$

$$= \left[\frac{(q_t)_{HD}^2}{(q_t)_{H_2}(q_t)_{D_2}}\right] \left[\frac{(q_r)_{HD}^2}{(q_r)_{H_2}(q_r)_{D_2}}\right] \left[\frac{(q_v)_{HD}^2}{(q_v)_{H_2}(q_v)_{D_2}}\right] \mathrm{e}^{-\Delta_r U^\circ/RT}$$

$$= \left[\frac{m_{HD}^3}{(m_{H_2})^{3/2}(m_{D_2})^{3/2}}\right] \left[\left\{\frac{I_{HD}^2}{(I_{H_2})(I_{D_2})}\right\} \frac{\sigma_{H_2}\sigma_{D_2}}{\sigma_{HD}^2}\right] \left[\frac{\left(1 - \mathrm{e}^{-\theta_v/T}\right)_{HD}^{-2}}{\left(1 - \mathrm{e}^{-\theta_v/T}\right)_{H_2}^{-1} \left(1 - \mathrm{e}^{-\theta_v/T}\right)_{D_2}^{-1}}\right]$$

$$\times \exp(-\Delta_r U^\circ/RT)$$

$$\Delta_r U^\circ = -2D_{HD}^\circ + D_{H_2} + D_{D_2} = (-2 \times 435.2 + 431.8 + 439.2)\ \text{kJ mol}^{-1}$$

$$= 0.60\ \text{kJ mol}^{-1}$$

Substituting the given values, we get

$$K_p^\circ = \left(\frac{3^3}{2^{3/2}\, 4^{3/2}}\right) \left\{\left(\frac{6.13^2}{4.60 \times 9.20}\right)\left(\frac{2 \times 2}{1^2}\right)\right\} \left[\frac{(1 - \mathrm{e}^{-5226/400})^{-2}}{(1 - \mathrm{e}^{-5986/400})^{-1}(1 - \mathrm{e}^{-4308/400})^{-1}}\right]$$

$$\times [\mathrm{e}^{-600/(8.314 \times 400)}]$$

$$= (1.193)\ (0.888 \times 4) \left(\frac{1 \times 1}{1^2}\right) (0.835) = 3.54$$

4.11 TRANSITION-STATE THEORY

In the transition-state theory, the reaction between the reactants A and B is visualized as follows.

$$A + B \rightleftharpoons X^\ddagger \rightarrow \text{Products} \qquad (4.11.1)$$

where $X^\ddagger$ is the activated complex (Fig. 4.11.1).

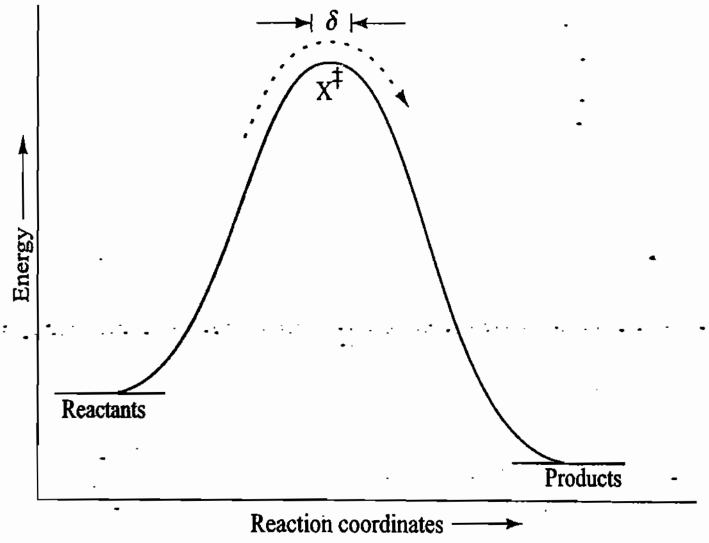


Fig. 4.11.1 A schematic potential-energy profile of converting reactants into products via the transition-state complex

The rate of reaction A + B → products depends on two factors, namely, the concentration of activated complex and the frequency of decomposition of the complex, i.e.

$$r = \begin{pmatrix}\text{concentration of}\\ \text{activated complex}\end{pmatrix}\begin{pmatrix}\text{frequency of decomposition}\\ \text{of activated complex}\end{pmatrix} \qquad (4.11.2)^\dagger$$

Since the reactants are in equilibrium with the activated complex, we can write

$$K_c^\ddagger = \frac{[X^\ddagger]}{[A][B]} \qquad (4.11.3)$$

The equilibrium constant K_c in terms of molecular partition function is given by

$$K_c^\ddagger = \left(\frac{1}{N_A}\right)^{\sum_i \nu_i} e^{-\Delta_r U^\circ/RT}\left[\Pi_i\left(\frac{q_i}{V}\right)^{\nu_i}\right] \qquad (4.11.4)^\ddagger$$

Since $\sum_i \nu_i = -1$ for the reaction $A + B \rightleftharpoons X^\ddagger$, we will have

$$K_c^\ddagger = (N_A)\, e^{-\Delta_r U^\circ/RT}\frac{(q^\ddagger/V)}{(q_A/V)(q_B/V)} \qquad (4.11.5)$$

Since the activated complex is in a process of decomposing, one of its vibrational degree of freedom is in a process of becoming a translation degree of freedom. This fact in terms of vibrational partition function is expressed as

$$\lim_{\nu\to 0} q_v = \lim_{\nu\to 0}\frac{1}{1-\exp(-h\nu/kT)}$$

[†] For a reaction reactants $\rightleftharpoons X^\ddagger \rightleftharpoons$ products, Eq. (4.11.2) is given by $r = ([X^\ddagger]/2)\,(2\nu)$, i.e. the first term is halved as only half of the activated complex is converted into products and the second term is doubled as the activated complex takes only half of time period for the conversion into products.

[‡] The conversion expressions involving equilibrium constant are $K_p = K_p^\circ(p^\circ)^{\Delta\nu_g}$; $K_c = K_c^\circ(c^\circ)^{\Delta\nu_g}$; $K_p = K_c(RT)^{\Delta\nu_g}$; $K_p^\circ = K_c^\circ(c^\circ RT/p^\circ)^{\Delta\nu_g}$.

Expanding the exponential and retaining only the first two terms, we get

$$\lim_{\nu \to 0} q_\mathrm{v} = \frac{1}{1-(1-h\nu/kT)} = \frac{kT}{h\nu} \tag{4.11.6}$$

The complete partition function of the activated complex is written as

$$\frac{q^{\ddagger}}{V} = \left(\lim_{\nu \to 0} q_\mathrm{v}\right)\left(\frac{q_{\ddagger}}{V}\right) = \frac{kT}{h\nu}\left(\frac{q_{\ddagger}}{V}\right) \tag{4.11.7}$$

where $(q_{\ddagger}/V)$ is the remaining portion of partition function which includes the contribution from $3(N_\mathrm{A} + N_\mathrm{B}) - 7$ (for a nonlinear molecule) or $3(N_\mathrm{A} + N_\mathrm{B}) - 6$ (for a linear molecule) modes of vibration of the activated complex.

Substituting Eq. (4.11.7) in Eq. (4.11.5), we get

$$K_c^{\ddagger} = (N_\mathrm{A})\, \mathrm{e}^{-\Delta_\mathrm{r} U/kT} \left[\frac{(kT/h\nu)(q_{\ddagger}/V)}{(q_\mathrm{A}/V)(q_\mathrm{B}/V)}\right] \tag{4.11.8}$$

The concentration of activated complex as given by Eq. (4.11.3) is

$$[\mathrm{X}^{\ddagger}] = K_c^{\ddagger}[\mathrm{A}]\,[\mathrm{B}] = (N_\mathrm{A})\, \mathrm{e}^{-\Delta_\mathrm{r} U/kT} \left[\frac{(kT/h\nu)(q_{\ddagger}/V)}{(q_\mathrm{A}/V)(q_\mathrm{B}/V)}\right][\mathrm{A}]\,[\mathrm{B}]$$

Substituting the above expression in Eq. (4.11.2), we get

$$r = \left[(N_\mathrm{A})\mathrm{e}^{-\Delta_\mathrm{r} U/RT}\left\{\left(\frac{kT}{h\nu}\right)\frac{(q_{\ddagger}/V)}{(q_\mathrm{A}/V)(q_\mathrm{B}/V)}\right\}[\mathrm{A}][\mathrm{B}]\right](\nu)$$

$$= \left[\left(\frac{RT}{h}\right)\left(\mathrm{e}^{-\Delta_\mathrm{r} U/RT}\right)\left\{\frac{q_{\ddagger}/V}{(q_\mathrm{A}/V)(q_\mathrm{B}/V)}\right\}\right][\mathrm{A}]\,[\mathrm{B}] \tag{4.11.9}$$

The expression of rate constant is given by

$$k = \left(\frac{RT}{h}\right)\left(\mathrm{e}^{-\Delta_\mathrm{r} U/RT}\right)\left\{\frac{q_{\ddagger}/V}{(q_\mathrm{A}/V)(q_\mathrm{B}/V)}\right\} \tag{4.11.10}$$

The expression of pre-exponential is

$$A = \left(\frac{RT}{h}\right)\left\{\frac{(q_{\ddagger}/V)}{(q_\mathrm{A}/V)(q_\mathrm{B}/V)}\right\} \tag{4.11.11}$$

Example 4.11.1 On the basis of transition-state theory, calculate the rate constant at 300 K for the reaction

$$\mathrm{H} + \mathrm{HBr} \rightarrow \mathrm{H_2} + \mathrm{Br}$$

Given are the following data.

Barrier height from zero-point level = 5.0 kJ mol^{-1}

H—Br internuclear distance = 141.4 pm

H—Br vibrational frequency = 7.95×10^{13} Hz

The activated complex is linear with H—H distance = 150 pm, H—Br distance = 142 pm, vibrational frequency for the symmetrical stretch = 7.02×10^{13} Hz and that of bending modes is 1.38×10^{13} Hz. The antisymmetrical stretching mode is converted into translational degree of freedom of the products. Assume electronic contribution to molecular partition functions to be negligible.

Solution The expression of rate constant is

$$k = \left(\frac{RT}{h}\right)\left(e^{-\Delta_r U/RT}\right)\left\{\frac{q_{\ddagger}/V}{(q_A/V)(q_B/V)}\right\}$$

Evaluation of q_A/V Let A represent H atom. We will have

$$\frac{q_t}{V} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$= \left[\frac{2(3.14)(1.67\times10^{-27}\ \text{kg})(1.38\times10^{-23}\ \text{J K}^{-1})(300\ \text{K})}{(6.626\times10^{-34}\ \text{J s})^2}\right]^{3/2}$$

$$= 9.83 \times 10^{29}\ \text{m}^{-3}$$

Evaluation of q_B/V Let B represent HBr molecule. We will have

$$m_{HBr} = \frac{M_{HBr}}{N_A} = \frac{80.90\times10^{-3}\ \text{kg mol}^{-1}}{6.023\times10^{23}\ \text{mol}^{-1}} = 1.34 \times 10^{-25}\ \text{kg}$$

$$\frac{q_t}{V} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$= \left[\frac{2(3.14)(1.34\times10^{-25}\ \text{kg})(1.38\times10^{-23}\ \text{J K}^{-1})(300\ \text{K})}{(6.626\times10^{-34}\ \text{J s})^2}\right]^{3/2}$$

$$= 7.07 \times 10^{32}\ \text{m}^{-3}$$

The reduced mass of HBr is

$$\mu = \frac{m_H m_{Br}}{m_H + m_{Br}} = \left(\frac{M_H M_{Br}}{M_H + M_{Br}}\right)\frac{1}{N_A}$$

$$= \left[\frac{(1.0\times10^{-3}\ \text{kg mol}^{-1})(79.9\ \text{kg mol}^{-1})}{(1.0\times10^{-3} + 79.9\times10^{-3})\ \text{kg mol}^{-1}}\right]\left[\frac{1}{(6.022\times10^{23}\ \text{mol}^{-1})}\right]$$

$$= 1.64 \times 10^{-27}\ \text{kg}$$

$$I = \mu r^2 = (1.64 \times 10^{-27}\ \text{kg})\ (141.4 \times 10^{-12}\ \text{m})^2$$

$$= 3.28 \times 10^{-47}\ \text{kg m}^2$$

$$q_r = \frac{8\pi^2 IkT}{h^2} = \frac{8(3.14)^2(3.28\times10^{-47}\ \text{kg m}^2)(1.38\times10^{-23}\ \text{J K}^{-1})(300\ \text{K})}{(6.626\times10^{-34}\ \text{J s})^2}$$

$$= 24.40$$

Finally, $$\frac{h\nu}{kT} = \frac{(6.626\times10^{-34}\ \text{J s})(7.95\times10^{13}\ \text{s}^{-1})}{(1.38\times10^{-23}\ \text{J K}^{-1})(300\ \text{K})} = 12.72$$

$$q_v = \frac{1}{1-\exp(-h\nu/kT)} = \frac{1}{1-\exp(-12.72)} \simeq 1.0$$

The complete partition function of HBr is

$$\frac{q_B}{V} = \left(\frac{q_t}{V}\right) q_r\, q_v = (6.99 \times 10^{32}\ \mathrm{m^{-3}})\ (24.40)\ (1)$$

$$= 1.71 \times 10^{34}\ \mathrm{m^{-3}}$$

Evaluation of $q_{\ddagger}/V$ The mass of activated complex is

$$m^{\ddagger} = 2\,m_{\mathrm{H}} + m_{\mathrm{Br}} = \frac{2M_{\mathrm{H}} + M_{\mathrm{Br}}}{N_{\mathrm{A}}}$$

$$= \frac{2 \times 10^{-3}\ \mathrm{kg\ mol^{-1}} + 79.9 \times 10^{-3}\ \mathrm{kg\ mol^{-1}}}{6.022 \times 10^{23}\ \mathrm{mol^{-1}}}$$

$$= 1.35 \times 10^{-25}\ \mathrm{kg}$$

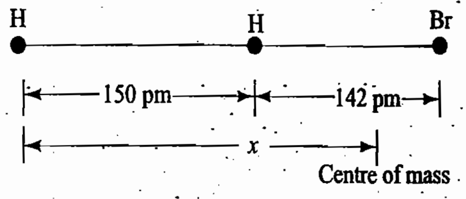
$$\frac{q_t}{V} = \left(\frac{2\pi m kT}{h^2}\right)^{3/2}$$

$$= \left[\frac{2(3.14)(1.35 \times 10^{-25}\ \mathrm{kg})(1.38 \times 10^{-23}\ \mathrm{J\ K^{-1}})(300\ \mathrm{K})}{(6.626 \times 10^{-34}\ \mathrm{J\ s})^2}\right]^{3/2}$$

$$= 7.15 \times 10^{32}\ \mathrm{m^{-3}}$$

To calculate q_r, we first determine the moment of inertia of H—H—Br.

We have



For the location of centre of mass, we write

$$m_{\mathrm{H}}\, x + m_{\mathrm{H}}\, (x - 150\ \mathrm{pm}) = m_{\mathrm{Br}}\, (292\ \mathrm{pm} - x)$$

This gives

$$x = \frac{m_{\mathrm{H}}(150\ \mathrm{pm}) + m_{\mathrm{Br}}(292\ \mathrm{pm})}{(2m_{\mathrm{H}} + m_{\mathrm{Br}})} = \frac{M_{\mathrm{H}}(150\ \mathrm{pm}) + M_{\mathrm{Br}}(292\ \mathrm{pm})}{(2M_{\mathrm{H}} + M_{\mathrm{Br}})}$$

$$= \frac{(150\ \mathrm{pm}) + (79.9)(292\ \mathrm{pm})}{81.9} = 286.7\ \mathrm{pm}$$

The expression of moment of inertia is

$$I = \sum_i m_i r_i^2\,; \qquad (r_i \text{ is measured from the centre of mass})$$

$$= (1.67 \times 10^{-27}\ \mathrm{kg})\ (286.7\ \mathrm{pm})^2 + (1.67 \times 10^{-27}\ \mathrm{kg})\ (136.7\ \mathrm{pm})^2$$

$$+ (1.33 \times 10^{-25}\ \mathrm{kg})\ (5.3\ \mathrm{pm})^2$$

$$= (1.37 \times 10^{-22} + 3.12 \times 10^{-23} + 3.74 \times 10^{-24})\ \text{kg pm}^2$$

$$= 1.69 \times 10^{-22}\ \text{kg pm}^2 = 1.69 \times 10^{-46}\ \text{kg m}^2$$

$$q_r = \frac{8\pi^2 IkT}{h^2} = \frac{8(3.14)^2(1.69 \times 10^{-46}\ \text{kg m}^2)(1.38 \times 10^{-23}\ \text{J K}^{-1})(300\ \text{K})}{(6.626 \times 10^{-34}\ \text{J s})^2}$$

$$= 125.7$$

$$\frac{h\nu_1}{kT} = \frac{(6.626 \times 10^{-34}\ \text{J s})(7.02 \times 10^{13}\ \text{s}^{-1})}{(1.38 \times 10^{-23}\ \text{J K}^{-1})(300\ \text{K})} = 11.2$$

$$\frac{h\nu_2}{kT} = \frac{(6.626 \times 10^{-34}\ \text{J s})(1.38 \times 10^{13}\ \text{s}^{-1})}{(1.38 \times 10^{-23}\ \text{J K}^{-1})(300\ \text{K})} = 2.21$$

$$q_{v1} = \frac{1}{1 - \exp(-h\nu_1/kT)} = \frac{1}{1 - \exp(-11.2)} = 1.000$$

$$q_{v2} = \frac{1}{1 - \exp(-h\nu_2/kT)} = \frac{1}{1 - \exp(-2.21)} = 1.123$$

(doubly degenerate)

Hence, $$\frac{q_\ddagger}{V} = \left(\frac{q_t}{V}\right) q_r\, q_{v1}\, q_{v2}\, q_{v2}$$

$$= (7.15 \times 10^{32}\ \text{m}^{-3})\ (125.7)\ (1.000)\ (1.123)\ (1.123)$$

$$= 1.13 \times 10^{35}\ \text{m}^{-3}$$

Rate constant of the reaction Finally, the rate constant is

$$k = \left(\frac{RT}{h}\right)\left(e^{-\Delta_r U/RT}\right)\left\{\frac{(q_\ddagger/V)}{(q_A/V)(q_B/V)}\right\}$$

$$= \left[\frac{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}{6.626 \times 10^{-34}\ \text{J s}}\right]\left[e^{-5\times10^3/(8.314\times300)}\right]$$

$$\times \left[\frac{1.13 \times 10^{35}\ \text{m}^{-3}}{(9.83 \times 10^{29}\ \text{m}^{-3})(1.70 \times 10^{34}\ \text{m}^{-3})}\right]$$

$$= (3.76 \times 10^{36}\ \text{mol}^{-1}\ \text{s}^{-1})\ (0.135)\ (6.68 \times 10^{-30}\ \text{m}^3)$$

$$= 3.39 \times 10^6\ \text{mol}^{-1}\ \text{m}^3\ \text{s}^{-1}$$

$$= 3.39 \times 10^9\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

4.12 MONATOMIC SOLIDS

The atoms in a crystalline solid vibrate about their mean positions. They may be treated as distinguishable harmonic oscillators by virtue of their fixed positions in the solid.

The vibrational energy of a harmonic oscillator is given by

$$\varepsilon_\upsilon = h\nu_0\left(\upsilon+\frac{1}{2}\right); \qquad \upsilon = 0, 1, 2, \ldots \tag{4.12.1}$$

where ν_0 is the classical frequency of oscillator and is given by

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k_\mathrm{f}}{m}} \tag{4.12.2}$$

The term k_f in Eq. (4.12.2) is known as force constant.

The vibrational energy relative to that of the ground state is given by

$$\varepsilon_\upsilon - \varepsilon_0 = h\nu_0\upsilon; \qquad \upsilon = 0, 1, 2, \ldots \tag{4.12.3}$$

The vibrational partition function with energies given by Eq. (4.12.3) is

$$q_\mathrm{v} = \sum_{\upsilon=0}^{\infty} \exp\{-(h\nu_0/kT)\upsilon\} \tag{4.12.4}$$

The above summation has to be carried out term-by-term as the energy levels are not close to each other to permit the replacement of summation by integration.

Equation (4.12.4) is

$$q_\mathrm{v} = 1 + \mathrm{e}^{-h\nu_0/kT} + \mathrm{e}^{-2h\nu_0/kT} + \cdots$$

$$= 1 + x + x^2 + \cdots \quad ; \qquad \{\text{where } x = \exp(-h\nu_0/kT)\}$$

$$= \frac{1}{1-x} = \frac{1}{1-\mathrm{e}^{-h\nu_0/kT}} \tag{4.12.5}$$

Equation (4.12.5) is usually written as

$$q_\mathrm{v} = \frac{1}{1-\mathrm{e}^{-\theta_\mathrm{v}/T}} \tag{4.12.6}$$

where $\theta_\mathrm{v} = h\nu_0/k$, and is known as characteristic vibrational temperature.

The contributions towards the thermodynamic properties are as follows.

$$U_\mathrm{v} - U_0 = NkT^2\,\frac{\mathrm{d}\ln q_\mathrm{v}}{\mathrm{d}T}$$

$$= NkT^2\,\frac{\mathrm{d}}{\mathrm{d}T}\left(\ln\frac{1}{1-\mathrm{e}^{-\theta_\mathrm{v}/T}}\right) = -NkT^2\,\frac{\mathrm{d}}{\mathrm{d}T}\left[\ln\left(1-\mathrm{e}^{-\theta_\mathrm{v}/T}\right)\right]$$

$$= -NkT^2\left[-\frac{\mathrm{e}^{-\theta_\mathrm{v}/T}}{1-\mathrm{e}^{-\theta_\mathrm{v}/T}}\left(\frac{\theta_\mathrm{v}}{T^2}\right)\right]$$

$$= Nk\left[\frac{\theta_\mathrm{v}}{\mathrm{e}^{\theta_\mathrm{v}/T}-1}\right] \tag{4.12.7}$$

$$H_\mathrm{v} - U_0 = U_\mathrm{v} - U_0 = \frac{Nk\theta_\mathrm{v}}{\mathrm{e}^{\theta_\mathrm{v}/T}-1} \tag{4.12.8}$$

The expressions of heat capacity is

$$C_p = C_V = \frac{\mathrm{d}}{\mathrm{d}T}\left[\frac{Nk\theta_\mathrm{v}}{\mathrm{e}^{\theta_\mathrm{v}/T}-1}\right] = \frac{Nk(\theta_\mathrm{v}/T)^2\,\mathrm{e}^{\theta_\mathrm{v}/T}}{(\mathrm{e}^{\theta_\mathrm{v}/T}-1)^2} \tag{4.12.9}$$

The expression of entropy is

$$S_\mathrm{v} = Nk\ln q_\mathrm{v} + \frac{U_\mathrm{v}-U_0}{T}$$

$$= -Nk\ln(1-\mathrm{e}^{-\theta_\mathrm{v}/T}) + \frac{\theta_\mathrm{v}/T}{\mathrm{e}^{\theta_\mathrm{v}/T}-1} \tag{4.12.10}$$

The expression of Helmholtz and Gibbs free energies is

$$A_\mathrm{v} - U_0 = G_\mathrm{v} - U_0 = -NkT\ln q_\mathrm{v}$$

$$= NkT\ln(1-\mathrm{e}^{-\theta_\mathrm{v}/T}) \tag{4.12.11}$$

The Einstein Solids

In Einstein model of a solid, it is assumed that the atoms vibrate about their mean positions without being affected by their neighbours in spite of the fact that there exist forces of attraction between them and a continued exchange of energy. The overall vibration of an atom is considered to be three dimensional. It may be considered as the superposition of three one-dimensional oscillators, each vibrating with the same frequency. The properties of such a solid are $3N$ times those of a single oscillator. The expression of heat capacity will be three times the heat capacity as given by Eq. (4.12.9), that is

$$C_V = \frac{3Nk(\theta_\mathrm{E}/T)^2\,\mathrm{e}^{\theta_\mathrm{E}/T}}{(\mathrm{e}^{\theta_\mathrm{E}/T}-1)^2} \tag{4.12.12}$$

where θ_E ($= h\nu_0/k$) is called the *Einstein temperature*. The expression of molar heat capacity is

$$C_{V,\mathrm{m}} = \frac{3R(\theta_\mathrm{E}/T)^2\,\mathrm{e}^{\theta_\mathrm{E}/T}}{(\mathrm{e}^{\theta_\mathrm{E}/T}-1)^2} \tag{4.12.13}$$

The plot of $C_{V,\mathrm{m}}$ versus T/θ_E is shown in Fig. 4.12.1

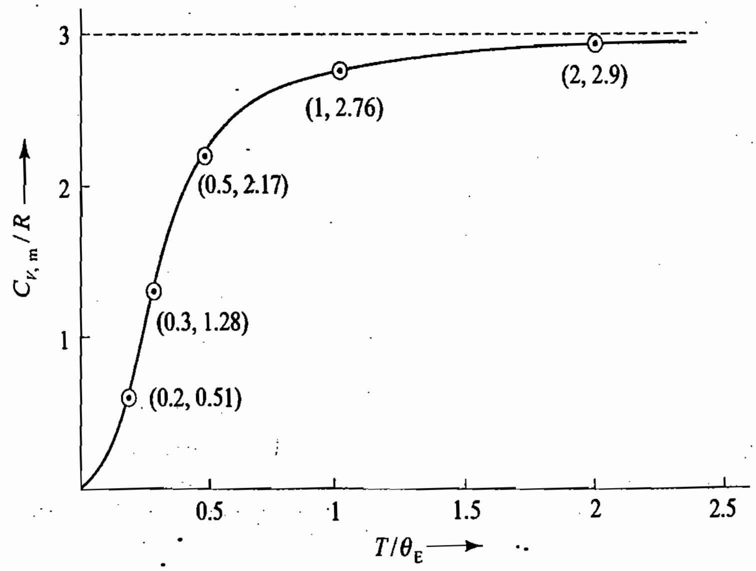


Fig. 4.12.1 The variation of $C_{V,\mathrm{m}}/R$ versus T/θ_E for an Einstein solid

Limiting Value of $C_{V,m}$ as $T \to \infty$

When T assumes a large value, one can write Eq. (4.12.13) as

$$C_{V,\,\mathrm{m}} = \frac{3R(\theta_{\mathrm{E}}/T)^2\,\mathrm{e}^{\theta_{\mathrm{E}}/T}}{\left[1+\dfrac{\theta_{\mathrm{E}}/T}{1!}+\dfrac{(\theta_{\mathrm{E}}/T)^2}{2!}+\cdots-1\right]^2}$$

Cancelling one in the denominator and taking $(\theta_{\mathrm{E}}/T)^2$ of the numerator in the denominator, we get

$$C_{V,\,\mathrm{m}} = \frac{3R\,\mathrm{e}^{\theta_{\mathrm{E}}/T}}{\left[1+\dfrac{\theta_{\mathrm{E}}/T}{2!}+\cdots\right]^2}$$

Now as $T \to \infty$, $\exp(\theta_{\mathrm{E}}/T) \to 1$ and $\theta_{\mathrm{E}}/T \to 0$. With this, the above expression reduces to

$$C_{V,\,\mathrm{m}} = 3R \qquad (4.12.14)$$

The above expression is in agreement with the experimental data on molar heat capacity of most solids. The limiting value of $3R$ was observed by Dulong and Petit and is known as Dulong and Petit rule.

Limiting Value of $C_{V,\,m}$ as $T \to 0$

As $T \to 0$, the value $\theta_{\mathrm{E}}/T \to \infty$. In such a situation, one in the denominator of Eq. (4.12.13) may be ignored in comparison to $\exp(\theta_{\mathrm{E}}/T)$. With this, Eq. (4.12.13) reduces to

$$C_{V,\,\mathrm{m}} = 3R(\theta_{\mathrm{E}}/T)^2\,\mathrm{e}^{-\theta_{\mathrm{E}}/T} \qquad (4.12.15)$$

and approaches zero as the temperature approaches zero kelvin. This fact is found to be correct experimentally. However, the quantitative agreement with experimental values is poor. The calculated values are considerably smaller than the experimental values which are very closely proportional to T^3. This disagreement is attributed to the assumption that all the atoms in solid oscillate with the same frequency.

Comment According to Eq. (4.12.13), two monatomic solids have the same value of molar heat capacity if they have the same value of θ_{E}/T. For example, lead and diamond solids will have the same value of molar heat capacity, provided

$$\left(\frac{\theta_{\mathrm{E}}}{T}\right)_{\mathrm{Pb}} = \left(\frac{\theta_{\mathrm{E}}}{T}\right)_{\mathrm{diamond}}$$

But $(\theta_{\mathrm{E}})_{\mathrm{Pb}} < (\theta_{\mathrm{E}})_{\mathrm{diamond}}$, it follows that

$$T_{\mathrm{Pb}} < T_{\mathrm{diamond}}$$

for the two solids to have the same molar heat capacity.

In general, the increase in the value of molar heat capacity with increase in temperature is more gradual for the elements having lower atomic masses.

Debye Contribution

Debye explained the disagreement between molar heat capacity at lower temperatures and the experimental values by the atoms with a continuous varying frequencies instead of a single frequency. His theory being more involved is not described here. The Debye equation of molar heat capacity is

$$C_{V,\mathrm{m}} = 3R\left[4D - \frac{3x_{\mathrm{D}}}{\mathrm{e}^{x_{\mathrm{D}}} - 1}\right] \tag{4.12.16}$$

where $x_{\mathrm{D}} = \dfrac{h\nu_{\mathrm{D}}}{kT} = \dfrac{\theta_{\mathrm{D}}}{T}$; (θ_{D} is called the Debye temperature) (4.12.17)

and $D = \dfrac{3}{x_{\mathrm{D}}^3} \displaystyle\int_0^{x_{\mathrm{D}}} \frac{x^3}{\mathrm{e}^x - 1}\,\mathrm{d}x$; (D is called the Debye function) (4.12.18)

The value of D has to be evaluated numerically. At high temperature, the Debye function approaches unity and the molar heat capacity approaches a limiting value of $3R$.

At very low temperature, the Debye function reduces to the form

$$D = \frac{\pi^4}{5}\,\frac{1}{x_{\mathrm{D}}^3}$$

so that, at low temperature

$$C_{V,\mathrm{m}} = \frac{12\pi^4}{5}\,R\left(\frac{T}{\theta_{\mathrm{D}}}\right)^3 \tag{4.12.19}$$

Thus, the value of $C_{V,\mathrm{m}}$ is proportional to T^3. Its value approaches zero as T approaches zero.

4.13 STATISTICAL TREATMENT OF THE BLACK-BODY RADIATIONS

The Photon Gas

The radiation emitted by a black body may be regarded as an ideal gas consisting of photons, known as photon gas. The behaviour of a body can be analysed in terms of radiant field which is considered to be in equilibrium with the body.

The photons in the radiant field are bosons and thus follow Bose-Einstein statistics with only one constraint of constant radiant energy, i.e.

$$U = \textstyle\sum_i N_i\,\varepsilon_i = \text{constant} \tag{4.13.1}$$

where N_i is the number of photons carrying energy ε_i. The constraint of constant number of photons is not necessary since the body can absorb or emit photons of different energies without changing its energy. For example, two photons of energy ε may be absorbed and at the same time one photon of energy 2ε may be emitted.

Most Probable Distribution in the Photon Gas

The most probable distribution of number of photons N_i having energy ε_i in the photon gas emitted by a black body may be obtained by setting the Lagrange multiplier α in Eq. (4.3.9) equal to zero. This gives

$$N_i = \frac{g_i}{\exp(\varepsilon_i/kT) - 1} = \frac{g_i}{\exp(h\nu_i/kT) - 1} \tag{4.13.2}$$

where g_i represents the number of degenerate quantum states in the frequency range ν_i to $\nu_i + \mathrm{d}\nu$.

Degeneracy of Energy Levels

Considering the black body to be a cube of edge-length l and the emitted photons as the de Broglie particles, we may write

$$\varepsilon = \frac{p^2}{2m} = \frac{(h/\lambda)^2}{2m}$$

Also $\quad \varepsilon = \dfrac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)$

Equating the two expressions, we get

$$\frac{h^2}{2m\lambda^2} = \frac{h^2}{8ml^2}\,(n_x^2 + n_y^2 + n_z^2)$$

or $\quad \dfrac{1}{\lambda^2} = \dfrac{1}{4l^2}\,(n_x^2 + n_y^2 + n_z^2)$

or $\quad \nu = \dfrac{c}{2l}\,(n_x^2 + n_y^2 + n_z^2)^{1/2} \qquad (4.13.3)$

Representing quantum states of photons by points in a three-dimensional space of coordinates n_x, n_y, n_z as described in Annexure I, we can write

$$\nu = \frac{cr}{2l} \qquad (4.13.4)$$

where $r \left(= \sqrt{n_x^2 + n_y^2 + n_z^2}\right)$ is the distance of the point, representing quantum state n_x, n_y, n_z, from the origin.

The number of quantum states in the portion of spherical shell from r to $r + \mathrm{d}r$ and lying in the first quadrant of the space coordinates derived in Eq. (AI.4) is given by

$$g_i = \frac{1}{8}\,(4\pi r^2\,\mathrm{d}r) \qquad (4.13.5)$$

From Eq. (4.13.4), we get

$$r = \left(\frac{2l}{c}\right)\nu$$

Hence, $\quad \mathrm{d}r = \left(\dfrac{2l}{c}\right)\mathrm{d}\nu$

With these two expressions, Eq. (4.13.5) becomes

$$g_\nu = \frac{1}{8}\,(4\pi)\left(\frac{2l\nu}{c}\right)^2\left(\frac{2l}{c}\mathrm{d}\nu\right)$$

$$= \frac{4\pi l^3}{c^3}\,\nu^2\,\mathrm{d}\nu = \frac{4\pi V}{c^3}\,\nu^2\,\mathrm{d}\nu \qquad (4.13.6)$$

Equation (4.13.6) gives the number of quantum states in the frequency range ν and $\nu + \mathrm{d}\nu$. However, this equation needs to be multiplied by 2 since the radiation has two planes of polarization normal to the direction of propagation of photons.

Thus

$$g_\nu = \frac{8\pi V}{c^3}\nu^2\,\mathrm{d}\nu \tag{4.13.7}$$

When the above equation is made use in Eq. (4.13.2), we get

$$\mathrm{d}N_\nu = \frac{8\pi V}{c^3}\,\frac{\nu^2}{\exp(h\nu/kT)-1}\,\mathrm{d}\nu \tag{4.13.8}$$

where $\mathrm{d}N_\nu$ is the number of photons having frequency in the range ν and $\nu + \mathrm{d}\nu$.

Radiant Energy Emitted by the Black Body

The radiant energy emitted per unit volume of the black body in the frequency range ν and $\nu + \mathrm{d}\nu$ is given by

$$\begin{aligned}\frac{\varepsilon_\nu \mathrm{d}N_\nu}{V} &= \frac{8\pi h}{c^3}\,\frac{\nu^3}{\exp(h\nu/kT)-1}\,\mathrm{d}\nu \\ &= E_\nu\,\mathrm{d}\nu\end{aligned} \tag{4.13.9}$$

Equation (4.13.9) is known as Planck's distribution expression. Figure 4.13.1 displays the variation of E_ν versus ν at two temperatures. The area under the curve gives the energy density emitted by a black body at the indicated temperature.

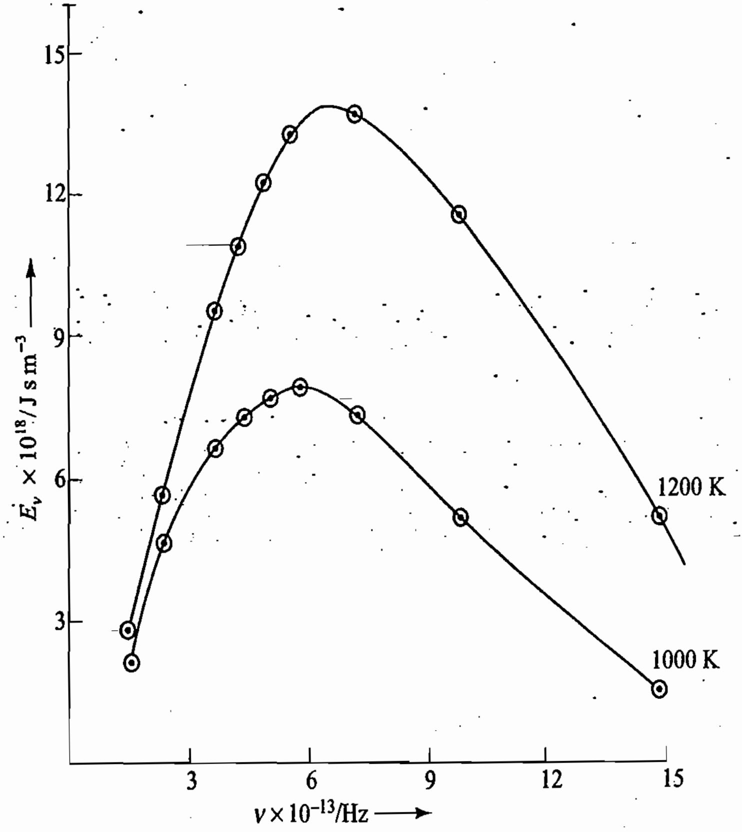


Fig. 4.13.1 Variation of E_ν versus ν

Frequency Corresponding to Maximum E_ν

The frequency at which E_ν has a maximum value is obtained by setting $\mathrm{d}E_\nu/\mathrm{d}\nu$ equal to zero. Starting with the simpler expression obtained by ignoring 1 in comparison to the exponential term, we get

$$\frac{\mathrm{d}}{\mathrm{d}\nu}\left(\frac{8\pi h}{c^3}\nu^3 \mathrm{e}^{-h\nu/kT}\right) = 0$$

i.e. $$\frac{8\pi h}{c^3}[3\nu^2 - \nu^3(h/kT)]\mathrm{e}^{-h\nu/kT} = 0$$

This gives

$$\nu_{\max} = \frac{3kT}{h} \tag{4.13.10}$$

From Eq. (4.13.10), it follows that

$$\nu_{\max}/T = \text{constant} \tag{4.13.11}$$

This implies that $\nu_{\max}$ increases with increase in temperature.

Maximum Value of E_ν

The approximate value of $E_{\nu,\max}$ is

$$E_{\nu,\max} = \frac{8\pi h}{c^3}\left(\frac{3kT}{h}\right)^3 \mathrm{e}^{-3} \tag{4.13.12}$$

From this, we find that $E_{\nu,\max} \propto T^3$.

Radiant Energy in Terms of Wavelength

In terms of wavelength, Eq. (4.13.9) becomes

$$\frac{\varepsilon_\lambda \mathrm{d}N_\lambda}{V} = \frac{8\pi h}{c^3}\frac{(c/\lambda)^3}{\exp(hc/\lambda kT)-1}\left(-\frac{c}{\lambda^2}\mathrm{d}\lambda\right)$$

$$= -\frac{8\pi hc}{\lambda^5}\frac{1}{\exp(hc/\lambda kT)-1}\mathrm{d}\lambda$$

$$= E_\lambda\,\mathrm{d}\lambda \tag{4.13.13}$$

Figure 4.13.2 displays the variation of E_λ versus λ at two temperatures. The area under the curve gives the energy density emitted by a black body at the indicated temperature.

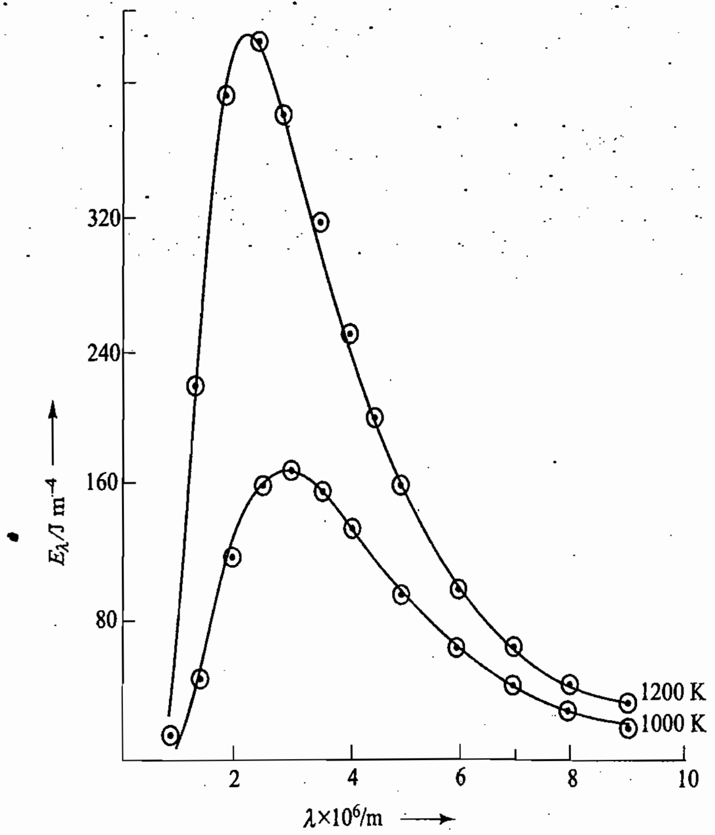


Fig. 4.13.2 **Variation of E_λ versus λ**

Wavelength Corresponding to Maximum E_λ

The wavelength at which E_λ has a maximum value is obtained by setting $\mathrm{d}E_\lambda/\mathrm{d}\lambda$ equal to zero. Starting with the simpler expression obtained by ignoring 1 in comparison to the exponential term, we get

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\frac{8\pi hc}{\lambda^5}\mathrm{e}^{-hc/\lambda kT}\right)=0$$

i.e. $\quad 8\pi hc\,[(-5)\lambda^{-6} + (1/\lambda^5)\,(hc/\lambda^2 kT)]\,\mathrm{e}^{-hc/\lambda kT} = 0$

This gives

$$\lambda_{\max} = hc/5kT \tag{4.13.14}$$

From Eq. (4.13.14), it follows that

$$\lambda_{\max}\,T = \text{constant} \tag{4.13.15}$$

This is, in fact, *Wien's displacement law*. This implies that $\lambda_{\max}$ decreases with increasing temperature.

Maximum Value of E_λ

The approximate value of $E_{\lambda,\,\max}$ is

$$E_{\lambda,\,\max} = \frac{8\pi(5kT)^5}{(hc)^4}\,\mathrm{e}^{-5} \tag{4.13.16}$$

From Eq. (4.13.16), it follows that $E_{\lambda,\,\max} \propto T^5$.

Note: From Eqs (4.13.10) and (4.13.14) and also from Eqs (4.13.12) and (4.13.16), it seems that the behaviour of a black body depends whether it is treated in terms of wavelength λ or frequency ν ($= c/\lambda$). In fact, it is not so. The black body has the same value of $E_\nu\,\mathrm{d}N_\nu/V$ and $E_\lambda\,\mathrm{d}N_\lambda/V$ when evaluated by using Eqs (4.13.9) and (4.13.13), respectively, for known values of λ (or $\nu = c/\lambda$) and $\mathrm{d}\lambda$ (or $\mathrm{d}\nu = -c\,\mathrm{d}\lambda/\lambda^2$).

Limiting Case in the Low Frequency Range

In the low frequency range, we may write

$$\frac{h\nu}{kT} \ll 1$$

Hence, $\quad \exp\left(\dfrac{h\nu}{kT}\right) - 1 = \left(1+\dfrac{h\nu}{kT}+\cdots\right) - 1 \simeq \dfrac{h\nu}{kT}$

With this, Eq. (4.13.9) reduces to

$$\frac{\varepsilon_\nu \mathrm{d}N_\nu}{V} = \frac{8\pi kT\nu^2}{c^3}\,\mathrm{d}\nu \tag{4.13.17}$$

Equation (4.13.17) is known as *Rayleigh-Jean distribution expression*. In terms of wavelength, Eq. (4.13.17) is given by

$$\frac{\varepsilon_\lambda \mathrm{d}N_\lambda}{V} = \frac{8\pi kT(c/\lambda)^2}{c^3}\left(-\frac{c}{\lambda^2}\mathrm{d}\lambda\right) = -\frac{8\pi kT}{\lambda^4}\,\mathrm{d}\lambda \tag{4.13.18}$$

Limiting Case in the High Frequency Range

In the high frequency range, we may write

$$\frac{h\nu}{kT} \gg 1$$

Hence, $\quad e^{h\nu/kT} - 1 \simeq e^{h\nu/kT}$

With this, Eq. (4.13.9) reduces to

$$\frac{\varepsilon_\nu \mathrm{d}N_\nu}{V} = \frac{8\pi h}{c^3}\nu^3\, e^{-h\nu/kT}\mathrm{d}\nu \tag{4.13.19}$$

Equation (4.13.19) is known as *Wien's relation.* In terms of wavelength, Eq. (4.13.19) is given by

$$\frac{E_\lambda \mathrm{d}N_\lambda}{V} = \frac{8\pi h}{c^3}\left(\frac{c}{\lambda}\right)^3 \exp(-hc/\lambda kT)\left\{-\frac{c}{\lambda^2}\mathrm{d}\lambda\right\}$$

$$= -\frac{8\pi hc}{\lambda^5}\exp(-hc/\lambda kT) \tag{4.13.20}$$

Total Energy Emitted per Unit Volume

The total energy emitted per unit volume of black body is given by

$$\frac{U}{V} = \int_0^\infty \left(\frac{\varepsilon_\nu \mathrm{d}N_\nu}{V}\right)\mathrm{d}\nu$$

Making use of Eq. (4.13.9), this becomes

$$\frac{U}{V} = \int_0^\infty \left(\frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/kT}-1}\right)\mathrm{d}\nu = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3}{e^{h\nu/kT}-1}\mathrm{d}\nu$$

Let $x = h\nu/kT$, such that $\mathrm{d}x = (h/kT)\,\mathrm{d}\nu$. With these, the above expression becomes

$$\frac{U}{V} = \frac{8\pi(kT)^4}{(hc)^3}\int_0^\infty \frac{x^3}{e^x - 1}\mathrm{d}x$$

$$= \frac{8\pi(kT)^4}{(hc)^3}\left(\frac{\pi^4}{15}\right) = \frac{8\pi^5}{15}\frac{(kT)^4}{(hc)^3} \tag{4.13.21}$$

Hence, the energy density is found to be proportional to T^4. The rate of flow of radiant field from the black body will also be proportional to the energy density and hence to the fourth power of the temperature. This fact is known as *Stefan-Boltzmann radiation law.*

4.14 MAXWELL-BOLTZMANN PROBABILITY DISTRIBUTION OF MOLECULAR VELOCITIES AND SPEEDS

For a gas involving noninteracting molecules, the fraction N_i/N of molecules in the energy state i with energy ε_i is given by

$$\frac{N_i}{N} = \frac{e^{-\varepsilon_i/kT}}{q} \tag{4.14.1}$$

where q, the molecular partition function, is given by

$$q = \sum_{\substack{i \\ \text{(state)}}} e^{-\varepsilon_i/kT} \tag{4.14.2}$$

Restricting only to the translational motion, we know that the energy of a molecule moving in a three-dimensional box with sides l_x, l_y and l_z is given by

$$\varepsilon_i = \frac{h^2}{8m}\left[\frac{n_x^2}{l_x^2}+\frac{n_y^2}{l_y^2}+\frac{n_z^2}{l_z^2}\right] \tag{4.14.3}$$

where n_x, n_y and n_z are the quantum numbers, each having values of 1, 2, 3, ... We also know that the translational energy levels are closely spaced for a macroscopic box. This permit us to replace the summation in Eq. (4.14.2) by integration. In other words, the numbers n_x, n_y and n_z may be considered to vary in a continuous manner.

Equation (4.14.3) may be written in terms of components of momentum as

$$\varepsilon_i = \frac{1}{2m}\left(p_x^2+p_y^2+p_z^2\right) \tag{4.14.4}$$

where $p_x^2 = n_x^2h^2/4l_x^2$, and so on. Substituting Eq. (4.14.4) in Eq. (4.14.1), we get

$$\frac{N_i}{N} = \frac{1}{q}\exp\left[-\left(\frac{1}{2m}\right)(p_x^2+p_y^2+p_z^2)/kT\right] \tag{4.14.5}$$

Probability Distribution Function of Momentum

Let $f_p(p_x, p_y, p_z)$ be the probability distribution function which identifies the probability of finding a molecule having the components of momentum p_x, p_y and p_z. Obviously, the function will be proportional to the fraction N_i/N given by Eq. (4.14.5). Hence, we can write

$$f_p(p_x, p_y, p_z) \propto \frac{N_i}{N}$$

i.e.

$$f_p(p_x, p_y, p_z) = \frac{c}{q}\exp\left[-\left(\frac{1}{2m}\right)(p_x^2+p_y^2+p_z^2)/kT\right] \tag{4.14.6}$$

The constant of proportionality c can be determined from the fact that the probability of a molecule having all possible momentum will be equal to unity. Hence, we can write

$$\iiint_{-\infty}^{+\infty} f_p(p_x, p_y, p_z)\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z = 1$$

i.e.

$$\frac{c}{q}\left[\int_{-\infty}^{-\infty} \mathrm{e}^{-(1/2mkT)p_x^2}\,\mathrm{d}p_x\right]\left[\int_{-\infty}^{+\infty} \mathrm{e}^{-(1/2mkT)p_y^2}\,\mathrm{d}p_y\right]\left[\int_{-\infty}^{+\infty} \mathrm{e}^{-(1/2mkT)p_z^2}\,\mathrm{d}p_z\right] = 1$$

or

$$\frac{c}{q}\,[(2\pi mkT)^{1/2}]\,[(2\pi mkT)^{1/2}]\,[(2\pi mkT)^{1/2}] = 1$$

or

$$\frac{c}{q} = \frac{1}{(2\pi mkT)^{3/2}} \tag{4.14.7}$$

Substituting Eq. (4.14.7) in Eq. (4.14.6), we get

$$f_p(p_x, p_y, p_z) = \frac{1}{(2\pi mkT)^{3/2}} \exp\left[-\left(\frac{1}{2m}\right)(p_x^2 + p_y^2 + p_z^2)/kT\right] \quad (4.14.8)$$

The probability of finding a molecule in the momentum components in the range p_x to $p_x + \mathrm{d}p_x$, p_y to $p_y + \mathrm{d}p_y$ and p_z to $p_z + \mathrm{d}p_z$ is given by

$$f_p(p_x, p_y, p_z)\, \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z = \frac{1}{(2\pi mkT)^{3/2}} \exp\left[-\left(\frac{1}{2mkT}\right)(p_x^2 + p_y^2 + p_z^2)\right] \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \quad (4.14.9)$$

Probability Distribution Function of Velocity

Since $p_x = m\upsilon_x$, the distribution function which identifies the probability of finding a molecule with velocity components in the range υ_x to $\upsilon_x + \mathrm{d}\upsilon_x$, υ_y to $\upsilon_y + \mathrm{d}\upsilon_y$ and υ_z to $\upsilon_z + \mathrm{d}\upsilon_z$ can be written as

$$f_\upsilon(\upsilon_x, \upsilon_y, \upsilon_z)\, \mathrm{d}\upsilon_x\, \mathrm{d}\upsilon_y\, \mathrm{d}\upsilon_z$$

$$= \frac{1}{(2\pi mkT)^{3/2}} \exp\left[-\left(\frac{m}{2kT}\right)(\upsilon_x^2 + \upsilon_y^2 + \upsilon_z^2)\right](m\,\mathrm{d}\upsilon_x)\,(m\,\mathrm{d}\upsilon_y)\,(m\,\mathrm{d}\upsilon_z)$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\left(\frac{m}{2kT}\right)(\upsilon_x^2 + \upsilon_y^2 + \upsilon_z^2)\right] \mathrm{d}\upsilon_x\, \mathrm{d}\upsilon_y\, \mathrm{d}\upsilon_z \quad (4.14.10)$$

The function f_υ is called the *velocity probability density function.*

Equation (4.14.10) can be written as

$$f_\upsilon(\upsilon_x, \upsilon_y, \upsilon_z)\, \mathrm{d}\upsilon_x\mathrm{d}\upsilon_y\mathrm{d}\upsilon_z = \left[\left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-m\upsilon_x^2/2kT}\mathrm{d}\upsilon_x\right]\left[\left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-m\upsilon_y^2/2kT}\mathrm{d}\upsilon_y\right]$$

$$\left[\left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-m\upsilon_z^2/2kT}\mathrm{d}\upsilon_z\right]$$

$$= [f(\upsilon_x)\, \mathrm{d}\upsilon_x]\; [f(\upsilon_y)\, \mathrm{d}\upsilon_y]\; [f(\upsilon_z)\, \mathrm{d}\upsilon_z]$$

$$= f(\upsilon_x)\, f(\upsilon_y)\, f(\upsilon_z)\, \mathrm{d}\upsilon_x\, \mathrm{d}\upsilon_y\, \mathrm{d}\upsilon_z \quad (4.14.11)$$

that is, the probability of a molecule having velocities in the range υ_x to $\upsilon_x + \mathrm{d}\upsilon_x$, υ_y to $\upsilon_y + \mathrm{d}\upsilon_y$ and υ_z to $\upsilon_z + \mathrm{d}\upsilon_z$ is equal to the product of individual probabilities of a molecule having component velocities in the range υ_x to $\upsilon_x + \mathrm{d}\upsilon_x$, υ_y to $\upsilon_y + \mathrm{d}\upsilon_y$ and υ_z to $\upsilon_z + \mathrm{d}\upsilon_z$, respectively.

The fact that

$$f(\upsilon_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-m\upsilon_x^2/2kT} \quad (4.14.12)$$

can also be established by finding the probability of a molecule having component velocity range from υ_x to $\upsilon_x + \mathrm{d}\upsilon_x$ with all possible velocity components υ_y and υ_z.

This probability is given by

$$f_v(v_x)\,\mathrm{d}v_x = \mathrm{d}v_x \iint\limits_{-\infty}^{+\infty} f(v_x, v_y, v_z)\,\mathrm{d}v_y\,\mathrm{d}v_z$$

$$= \mathrm{d}v_x \left(\frac{m}{2\pi kT}\right)^{3/2} \mathrm{e}^{-mv_x^2/2kT} \int\limits_{-\infty}^{+\infty} \mathrm{e}^{-mv_y^2/2kT}\,\mathrm{d}v_y \int\limits_{-\infty}^{+\infty} \mathrm{e}^{-mv_z^2/2kT}\,\mathrm{d}v_z$$

$$= \left[\mathrm{d}v_x \left(\frac{m}{2\pi kT}\right)^{3/2} \mathrm{e}^{-mv_x^2/2kT}\right] \left(\frac{2\pi kT}{m}\right)^{1/2} \left(\frac{2\pi kT}{m}\right)^{1/2}$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-mv_x^2/2kT}\,\mathrm{d}v_x \qquad (4.14.13)$$

Equation (4.14.13) gives

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-mv_x^2/2kT} \qquad \text{(Eq. 4.14.12)}$$

In terms of molar mass, we have

$$f(v_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} \mathrm{e}^{-Mv_x^2/2RT} \qquad (4.14.14)$$

The plot of $f(v_x)$ versus v_x for oxygen gas is shown in Fig. 4.13.1. The distribution is symmetrical.

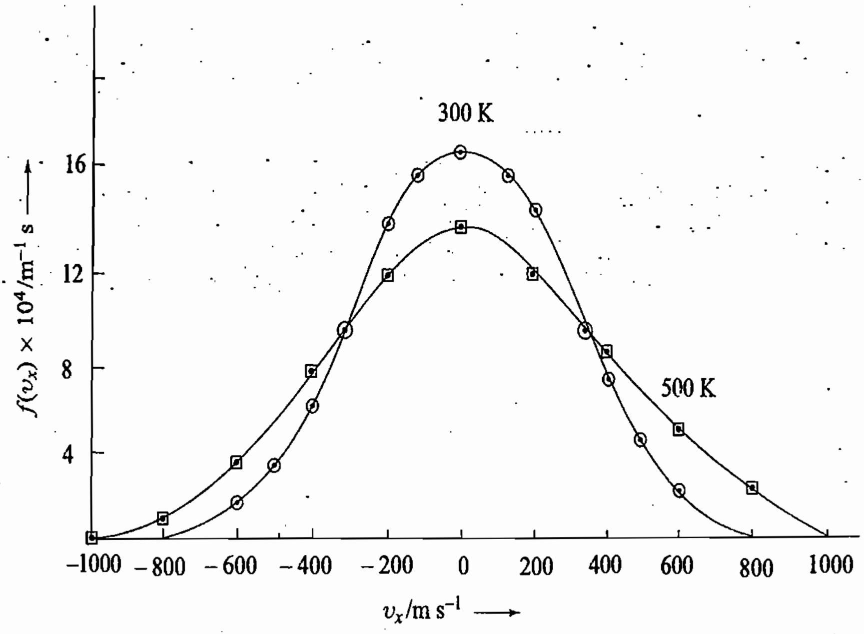


Fig. 4.14.1
Plot of $f(v_x)$ versus v_x

Average Value of v_x for a Gas at Rest

The average velocity in the x direction will be zero for a gas at rest. This follows from the fact that

$$\langle v_x\rangle = \int\limits_{-\infty}^{+\infty} v_x\,\mathrm{e}^{-mv_x^2/2kT}\,\mathrm{d}v_x = 0 \qquad (4.14.15)$$

Principle of Equipartition of Energy

The average kinetic energy in the x-direction is given by

$$(\overline{\mathrm{KE}})_x = \frac{1}{2} m \langle v_x^2 \rangle$$

The expression for $\langle v_x^2 \rangle$ is

$$\langle v_x^2 \rangle = \int_{-\infty}^{+\infty} v_x^2 f(v_x)\, \mathrm{d}v_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_{-\infty}^{+\infty} v_x^2\, \mathrm{e}^{-mv_x^2/2kT}\, \mathrm{d}v_x$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2} \left[\frac{1}{2}\left\{\frac{\pi}{(m/2kT)^3}\right\}^{1/2}\right]$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2} \left[\frac{1}{2\pi}\left\{\frac{2\pi kT}{m}\right\}^{3/2}\right]$$

$$= \frac{kT}{m} \tag{4.14.16}$$

Hence, $$(\overline{\mathrm{KE}})_x = \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} m \left(\frac{kT}{m}\right) = \frac{1}{2} kT \tag{4.14.17}$$

Similar expressions can be written for y- and z- components of kinetic energies. Equation (4.14.17) is, in fact, the proof of the classical principle of equipartition of energy which states that each quadratic term in component velocity or position coordinate contributes $(1/2)kT$ towards the average energy of a molecule.

MAXWELL DISTRIBUTION OF SPEEDS

The speed of a molecule is related to its component velocities by

$$v^2 = v_x^2 + v_y^2 + v_z^2 \tag{4.14.18}$$

The velocity components of a molecule can be represented by a point in velocity space as shown in Fig. 4.14.2.

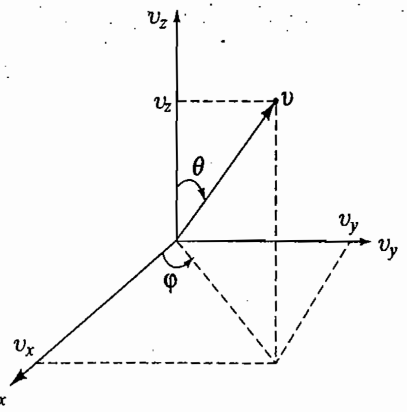


Fig. 4.14.2 Velocity space

The velocity of a molecule is represented by an arrow starting from the origin to the point representing the components v_x, v_y and v_z.

Probability Distribution Function of Speed

Since the speed of a molecule is represented by the magnitude of velocity vector without reference to its orientation, the probability of a molecule having speed in the range v to $v + \mathrm{d}v$ is represented by the number of points included in a spherical shell at a distance υ from the origin and having thickness of $\mathrm{d}\upsilon$. This probability function can be obtained by integrating Eq. (4.14.10), i.e.

$$F(\upsilon)\,\mathrm{d}\upsilon = \int f(\upsilon_x, \upsilon_y, \upsilon_z)\,\mathrm{d}\upsilon_x\,\mathrm{d}\upsilon_y\,\mathrm{d}\upsilon_z \qquad (4.14.19)$$

The above integration is conveniently carried out by converting the differential volume element $\mathrm{d}\upsilon_x\mathrm{d}\upsilon_y\mathrm{d}\upsilon_z$ in terms of spherical polar coordinates by using the expressions

$$\upsilon_z = \upsilon\cos\theta$$

$$\upsilon_x = \upsilon\sin\theta\cos\varphi$$

$$\upsilon_y = \upsilon\sin\theta\sin\varphi$$

and carrying out the integration over θ from 0 to π and over φ from 0 to 2π.

The differential volume element $\mathrm{d}\upsilon_x\,\mathrm{d}\upsilon_y\,\mathrm{d}\upsilon_z$ in the spherical polar coordinates is

$$\mathrm{d}\upsilon_x\mathrm{d}\upsilon_y\mathrm{d}\upsilon_z = \upsilon^2\,\mathrm{d}\upsilon\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi \qquad (4.14.20)$$

Substitution of Eq. (4.14.20) in Eq. (4.14.19) gives

$$F(\upsilon)\,\mathrm{d}\upsilon = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} f(\upsilon_x, \upsilon_y, \upsilon_z)\,\upsilon^2\,\mathrm{d}\upsilon\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

Substituting the expression of $f(\upsilon_x, \upsilon_y, \upsilon_z)$ from Eq. (4.14.10), we get

$$F(\upsilon)\,\mathrm{d}\upsilon = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left[-\left(\frac{m}{2kT}\right)(\upsilon_x^2+\upsilon_y^2+\upsilon_z^2)\right]\upsilon^2\,\mathrm{d}\upsilon\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

which on using Eq. (4.14.18) becomes

$$F(\upsilon)\,\mathrm{d}\upsilon = \left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m\upsilon^2}{2kT}\right)\upsilon^2\,\mathrm{d}\upsilon\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\varphi$$

$$= 4\pi\upsilon^2\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m\upsilon^2}{2kT}\right)\mathrm{d}\upsilon \qquad (4.14.21)$$

Hence, the function $F(\upsilon)$ which gives the probability of a molecule having the speed υ is given by

$$F(\upsilon) = 4\pi\upsilon^2\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m\upsilon^2}{2kT}\right) \qquad (4.14.22)$$

In terms of molar mass, the expression is

$$F(\upsilon) = 4\pi\upsilon^2\left(\frac{M}{2\pi RT}\right)^{3/2}\exp\left(-\frac{M\upsilon^2}{2RT}\right) \qquad (4.14.23)$$

The plot of $F(\upsilon)$ versus υ for oxygen is shown in Fig. 4.14.3.

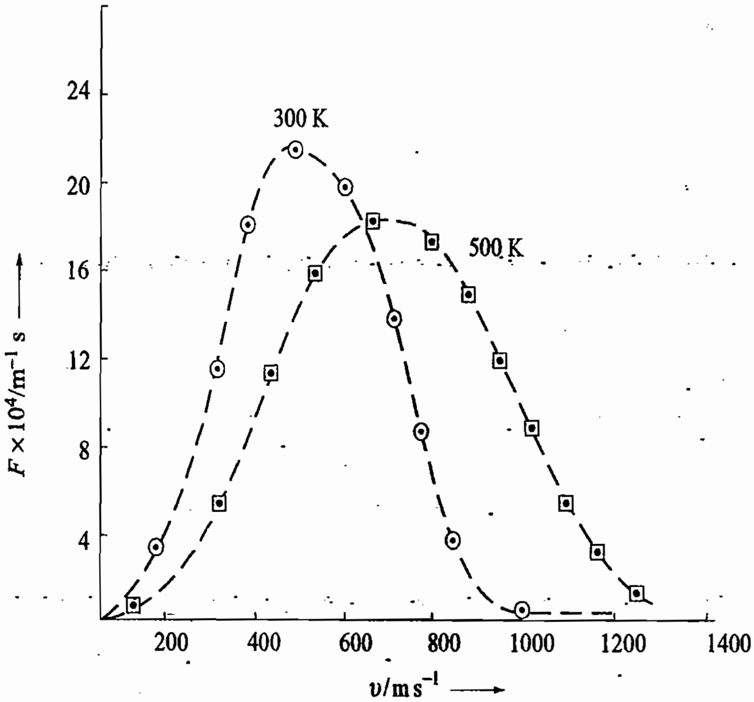


Fig. 4.14.3 Plot of $F(\upsilon)$ versus υ

Characteristics of Distribution of Speeds

The various characteristics of the plot shown in Fig. 4.14.3 are as follows.

- The function $F(\upsilon)$ is a product of two terms of opposite characteristics. The term υ^2 increases quadratically while the term $\exp(-M\upsilon^2/2RT)$ decreases exponentially with increase in the value of speed υ.
- In the lower range of speeds the change in the term υ^2 predominates over that of exponential term with the result that the function $F(\upsilon)$ increases with increase in the value of υ.
- In the high range of speeds, the change in the exponential term predominates over that of υ^2 with the result that the function $F(\upsilon)$ decreases with increase in the value of υ.
- As a consequence of the above two characteristics, the function $F(\upsilon)$ initially increases and after passing through a maximum, it starts decreasing with increase in the value of speed.
- The speed corresponding to the maximum value of $F(\upsilon)$ can be obtained mathematically by setting $\mathrm{d}F/\mathrm{d}\upsilon$ equal to zero. Hence, we have

$$\frac{\mathrm{d}F}{\mathrm{d}\upsilon} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left[2\upsilon\mathrm{e}^{-M\upsilon^2/2RT} + \upsilon^2\left(-\frac{2M\upsilon}{2RT}\right)\mathrm{e}^{-M\upsilon^2/2RT}\right]$$

Hence at υ_{mp} (most probable speed), we have

$$4\pi\upsilon_{\mathrm{mp}}\left(\frac{M}{2\pi RT}\right)^{3/2}\mathrm{e}^{-M\upsilon_{\mathrm{mp}}^2/2RT}\left[2-\frac{M\upsilon_{\mathrm{mp}}^2}{RT}\right] = 0$$

The expression υ_{mp} is obtained from the expression

$$2-\frac{M\upsilon_{\mathrm{mp}}^2}{RT} = 0 \quad \text{i.e.} \quad \upsilon_{\mathrm{mp}} = \sqrt{\frac{2RT}{M}} \tag{4.14.24}$$

- Since $\int_0^{\infty} F(v)\,\mathrm{d}v = 1$, the area under the plot is equal to one. In Fig. 4.11.3, two plots of $F(v)$ versus v at two temperatures (300 K and 500 K) are shown. The area under each of the two curves will be equal to one.
- The probability that a molecule has a speed between any two values is equal to the area under the plot between the two values of the speed.
- The function $F(v)$ decreases in the lower speed range with increase in temperature.
- The function $F(v)$ increases in the higher speed range with increase in temperature.
- The maximum of $F(v)$ moves to higher v with increase in temperature.
- The width of $F(v)$ at its maximum point becomes larger with increase in temperature. Also, its value decreases with increase in temperature.
- The probability distribution also depends on the mass of the molecule. At the same temperature, a heavy gas has a narrower distribution of speeds than a light gas. In general, the probability distribution depends upon the value of M/T. Thus, the distribution will be the same for a gas of molar mass $2M$ at temperature $2T$ since the ratio remains the same. For example, the distribution of O_2 molecules at temperature T will be the same as those of SO_2 molecules at temperature $2T$.

Average Speed of Molecules

The average speed of molecules is given by

$$\langle v\rangle = \int_0^{\infty} vF_v\,\mathrm{d}\tau = \int_0^{\infty} vF_v\,(v^2\mathrm{d}v) = \int_0^{\infty} v^3F_v\,\mathrm{d}v$$

$$= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^{\infty} v^3\,\mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v$$

$$= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left[\frac{1}{2(\pi M/2RT)^2}\right]$$

$$= \left(\frac{8RT}{\pi M}\right)^{1/2} \qquad (4.14.25)$$

Mean Square Speed of Molecules

The mean square speed of molecules is given by

$$\langle v^2\rangle = \int_0^{\infty} v^2\,F_v\,\mathrm{d}\tau = \int_0^{\infty} v^2F_v\,(v^2\,\mathrm{d}v) = \int_0^{\infty} v^4F_v\,\mathrm{d}v$$

$$= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^{\infty} v^4\,\mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v$$

$$= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left[\frac{3}{8}\left\{\frac{\pi}{(M/2RT)^5}\right\}^{1/2}\right] = \frac{3RT}{M} \qquad (4.14.26)$$

The expression of root mean square speed is

$$\langle v^2\rangle^{1/2} = \sqrt{\frac{3RT}{M}} \qquad (4.14.27)$$

Pressure of an Ideal Gas

The pressure of a gas is due to the molecular collisions with the sides of the vessel. We known that

$$p = \frac{F}{A} = \frac{ma}{A} = \frac{m}{A}\frac{dv}{dt} = \frac{1}{A}\frac{d(mv)}{dt} \tag{4.14.28}$$

that is, the pressure is equal to the rate of change of momentum per unit area of the wall.

Consider the wall of area A perpendicular to the x-direction (Fig. 4.14.3). If v_x is the velocity with which a molecule moves towards the wall, the change in magnitude of momentum of the molecule after it has undergone elastic collision with the wall is $| -mv_x - (mv_x) | = 2mv_x$.

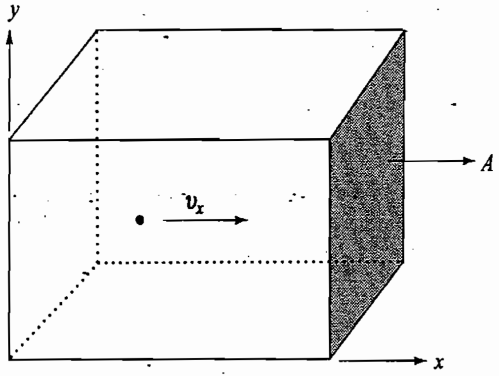


Fig. 4.14.3 Collision of a molecule having x-component of velocity v_x

The number of collisions per unit time made by the molecules with the side of area A will be equal to the number of molecules N' contained within the volume v_xA immediately in the vicinity of the wall. If N is the number of molecules in the volume V of the gas, then

$$N' = \frac{N}{V}(v_xA) \tag{4.14.29}$$

The rate of change in momentum (i.e. force exterted) due to these collisions will be

$$F = \frac{d(mv_x)}{dt} = N'(2mv_x) = \frac{N}{V}(2mA)\, v_x^2 \tag{4.14.30}$$

The probability of molecules moving with the velocity v_x is

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp(-mv_x^2/2kT)$$

Hence, the net rate of change of momentum will be given by

$$\frac{N}{V}(2mA)\, v_x^2 f(v_x) = \frac{N}{V}(2mA)\left(\frac{m}{2\pi kT}\right)^{1/2} v_x^2\, e^{-mv_x^2/2kT} \tag{4.14.31}$$

The pressure of the gas is obtained by integrating Eq. (4.14.31) over all possible positive v_x and dividing the resultant expression by the area of the wall, i.e.

$$P = \frac{F}{A} = \frac{N}{V}(2m)\left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^\infty v_x^2\, e^{-mv_x^2/2kT}\, dv_x$$

$$= \left(\frac{N}{V}\right)(2m)\left(\frac{m}{2\pi kT}\right)^{1/2}\left[\frac{1}{4}\left\{\frac{\pi}{(m/2kT)^3}\right\}^{1/2}\right] = \frac{NkT}{V} \tag{4.14.32}$$

Number of Molecules Striking a Wall

The number of molecules striking a wall of a container in a unit time is given by the expression

$$N' = \int_0^\infty N f(v_x) \mathrm{d}v_x$$

where N is the number of molecules contained within the volume $v_x A$ immediately in the vicinity of the wall of area A and $f(v_x)$ is the probability of the molecules moving with the velocity v_x. If N^* is the number of molecules per unit volume of the gas in the container then

$$N' = N^* (v_x A)$$

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-mv_x^2/2kT}$$

Hence $$N' = N^* A \left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^\infty v_x \, \mathrm{e}^{-mv_x^2/2kT} \, \mathrm{d}v_x$$

$$= N^* A \left(\frac{m}{2\pi kT}\right)^{1/2} \left(\frac{kT}{m}\right)$$

Thus $$\frac{N'}{A} = \frac{1}{4} N^* \left(\frac{8kT}{\pi m}\right)^{1/2} = \frac{1}{4} N^* \bar{u}$$

that is, the number of molecules per unit area of the wall is equal to (1/4) $N^* \bar{u}$.

REVISIONARY PROBLEMS

4.1 Show that the equilibrium distribution of particles following Boltzmann statistics is given by

$$N_i = N \frac{g_i \mathrm{e}^{-\beta\varepsilon_i}}{\sum_i g_i \mathrm{e}^{-\beta\varepsilon}} \quad \text{where } \beta = 1/kT$$

4.2 Show that the equilibrium distribution of particles following Bose-Einstein statistic is given by

$$N_i = \frac{g_i}{\mathrm{e}^{-\alpha} \mathrm{e}^{\beta\varepsilon_i} - 1}$$

where α and β are constants. Also show that for a system in which $g_i/N_i \gg 1$, the equilibrium distribution can be computed by using Boltzmann distribution law.

4.3 Show that the equilibrium distribution of particles following Fermi-Dirac statistics is given by

$$N_i = \frac{g_i}{\mathrm{e}^{-\alpha} \mathrm{e}^{\beta\varepsilon_i} + 1}$$

where α and β are constants. Also show that for a system in which $g_i/N_i \gg 1$, the equilibrium distribution can be computed by using Boltzmann distribution law.

4.4 How is molecular partition function defined? What is the physical significance of this quantity? What is the effect of temperature on the molecular partition function?

4.5 Show that the expression relating internal energy of a system to the molecular partition functions is given by

$$U = NkT^2 \left(\frac{\partial \ln q}{\partial T}\right)_V$$

4.6 Show that the differentials of heat (q') and work (w) are giving by

$$dq' = \sum_i \varepsilon_i dN_i \quad \text{and} \quad dw = \sum_i N_i d\varepsilon_i$$

4.7 Show that the pressure of a system is given by

$$p = NkT\left(\frac{\partial \ln q}{\partial V}\right)_T$$

4.8 Show that the entropy of a system is given by

$$S = k \ln W.$$

What is this equation known as?

4.9 Show that the entropy of a system involving distinguishable particles in terms of molecular partition function is given by

$$S = \frac{U}{T} + k\,N \ln q = Nk\left[T\left(\frac{\partial \ln q}{\partial T}\right)_V + \ln q\right]$$

4.10 Show that the entropy of a system involving indistinguishable particles is given by

$$S = Nk\left[\ln\left(\frac{q}{N}\right) + T\left(\frac{\partial \ln q}{\partial T}\right)_V + 1\right]$$

4.11 Derive the following thermodynamic relations in terms of molecular partition function.

$$H = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V + pV$$

$$C_V = Nk\left[\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln q}{\partial T}\right)_V\right]_V; \quad C_p = \left[\frac{\partial}{\partial T}\left\{NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V + pV\right\}\right]_p$$

$A = -NkT \ln q$ for distinguishable particles

$A = -NkT\left(\ln\frac{q}{N} + 1\right)$ for indistinguishable particles

$G = -NkT \ln q + pV$ for distinguishable particles

$G = -NkT \ln\left(\frac{q}{N}\right)$ for indistinguishable particles

4.12 Show that the molecular partition function of a diatomic molecule is given by $q = q_t q_r q_v q_e$, where the various subscripts have their usual meanings.

4.13 Show that for monatomic gases, the translational partition function is given by

$$q_t = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

4.14 What is thermal de Broglie wavelength? What is its unit?

4.15 Show that the internal energy of a monatomic gas is given by $U = (3/2)NkT$.

4.16 Show that the pressure of a monatomic gas is given by $p = NkT/V$.

4.17 Show that the entropy of a monatomic gas is given by

$$S_t = Nk\left[\ln\left\{\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}\right]$$

Show that the above expression can be written as

$$S^\circ_{\mathrm{m}} = R\left[-1.1541 + \frac{3}{2}\ln A_{\mathrm{r}} + \frac{5}{2}\ln\left(\frac{T}{\mathrm{K}}\right) - \ln\left(\frac{p}{p^\circ}\right)\right]$$

What is the above relation called?

4.18 Show that for a monatomic gas,

$$A = -NkT\left[\ln\left\{\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + 1\right];$$

$$G = -NkT\ln\left\{\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\}$$

4.19 Show that the electronic contributions towards the thermodynamic properties of a monatomic gas can be expressed as

$$U_{\mathrm{e}} = RT\left(\frac{q'_{\mathrm{e}}}{q_{\mathrm{e}}}\right); \qquad S_{\mathrm{e}} = R\left[\ln q_{\mathrm{e}} + \frac{q'_{\mathrm{e}}}{q_{\mathrm{e}}}\right]$$

$$A_{\mathrm{e}} = G_{\mathrm{e}} = -RT\ln q_{\mathrm{e}}; \qquad (C_p)_{\mathrm{e}} = (C_V)_{\mathrm{e}} = R\left[\frac{q'_{\mathrm{e}} + q''_{\mathrm{e}}}{q_{\mathrm{e}}} - \left(\frac{q'_{\mathrm{e}}}{q_{\mathrm{e}}}\right)^2\right]$$

where $q'_{\mathrm{e}} = T(\mathrm{d}q_{\mathrm{e}}/\mathrm{d}T)$ and $q''_{\mathrm{e}} = T(\mathrm{d}q'_{\mathrm{e}}/\mathrm{d}T)$.

4.20 Show that for an ideal diatomic gas,

$$q_{\mathrm{r}} = \left(\frac{8\pi^2 Ik}{\sigma h^2}\right)T = \frac{T}{\sigma\theta_{\mathrm{r}}}$$

$$U_{\mathrm{r}} = RT$$

$$S_{\mathrm{r}} = R\left[\ln\left(\frac{T}{\sigma\theta_{\mathrm{r}}}\right) + 1\right];$$

$$A_{\mathrm{r}} = G_{\mathrm{r}} = -RT\ln\left(\frac{T}{\sigma\theta_{\mathrm{r}}}\right)$$

$$q_{\mathrm{v}} = \frac{1}{1 - \mathrm{e}^{-\theta/T}} \quad \text{where } \theta = h\nu/k$$

$$U_{\mathrm{v}} = \frac{Nk\theta_{\mathrm{v}}}{\mathrm{e}^{\theta_{\mathrm{v}}/T} - 1}$$

$$S_{\mathrm{v}} = Nk\left[-\ln(1 - \mathrm{e}^{-\theta_{\mathrm{v}}/T}) + \frac{\theta_{\mathrm{v}}/T}{\mathrm{e}^{\theta_{\mathrm{v}}/T} - 1}\right]$$

$$A_{\mathrm{v}} - U_0 = G_{\mathrm{v}} - U_0 = NkT\ln(1 - \mathrm{e}^{-\theta_{\mathrm{v}}/T})$$

$$S_{\mathrm{e}} = R\ln g_0$$

$$A_{\mathrm{e}} = G_{\mathrm{e}} = -RT\ln g_0$$

$$q_{\mathrm{n}} = \Pi_i(2I_i + 1)$$

4.21 Show that the standard equilibrium constant of a reaction involving ideal diatomic gases can be expressed as

$$K^\circ = \left[\left(\frac{kT}{p^\circ}\right)^{\sum_i \nu_i}\right] \left[e^{-\Delta_r U^\circ/RT}\right] \left[\Pi_i \left(\frac{q_i}{V}\right)^{\nu_i}\right]$$

4.22 Derive the expression of rate constant in terms of partition function for the reaction

$$A + B \rightleftharpoons X^{\ddagger} \rightarrow \text{Products}$$

4.23 Show that for a monatomic solid, the heat capacity is given by

$$C_p = C_V = \frac{Nk(\theta_v/T)^2 e^{\theta_v/kT}}{(e^{\theta_v/T}-1)^2}$$

What are the limiting values of C_p when (a) $T \rightarrow 0$ and (b) $T \rightarrow \infty$?

4.24 Show that the temperature at which lead has the same heat capacity as that of diamond is smaller than the temperature of diamond.

4.25 Give a brief description of statistical treatment of the black-body radiation. Derive the Planck's distribution expression

$$\frac{\varepsilon_\nu dN_\nu}{V} = \frac{8\pi h}{c^3} \frac{\nu^3}{\exp(h\nu/kT)-1} d\nu$$

Derive the limiting cases of the above expression for (a) low frequency and (b) high frequency ranges.

4.26 Show that the probability function of gaseous molecules having the components p_x, p_y and p_z of momentum is given by

$$f_p(p_x, p_y, p_z) = \frac{1}{(2\pi mkT)^{3/2}} \exp[-(p_x^2 + p_y^2 + p_z^2)/2mkT]$$

4.27 Show that the probability function of gaseous molecules having the components v_x, v_y and v_z of velocity is given by

$$f_v(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp[-m(v_x^2 + v_y^2 + v_z^2)/2kT]$$

4.28 Show that

$$f_v(v_x, v_y, v_z) = f(v_x) f(v_y) f(v_z)$$

4.29 Show that for an ideal gas

$$\langle v_x^2 \rangle = kT/m$$

$$\overline{(\mathrm{KE})}_x = (1/2)kT$$

4.30 Show that the probability distribution function of speeds in an ideal gas is given by

$$F(v) = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp(-mv^2/2kT)$$

4.31 Show that for an ideal gas

$$\upsilon_{\mathrm{mp}} = \sqrt{2RT/M} \;;\qquad \langle \upsilon \rangle = \sqrt{8RT/\pi M} \;;\quad \langle \upsilon^2 \rangle = 3RT/M$$

$$p = NkT/V$$

NUMERICAL PROBLEMS

Boltzmann Distribution

4.1 Using Boltzmann probability distribution expression, calculate the possible ways of distributing 7 distinguishable particles among 4 energy levels with energies 0, ε, 2ε and 3ε, respectively. The total energy of the system remains constant at 3ε.

[**Ans.** $W(n_0 = 6, n_{3\varepsilon} = 1) = 7$, $W(n_0 = 5, n_\varepsilon = 1, n_{2\varepsilon} = 1) = 42$ and $W(n_0 = 4, n_\varepsilon = 3) = 35$]

Stirling Approximation

4.2 (a) Using Stirling approximation, calculate the value of ln 10!. If the correct value is 15.1044, what is the per cent error? [**Ans.** 13.0259, 13.76%]

(b) Repeat the calculations for ln 50!. If the correct value is 148.478, what is the per cent error? [**Ans.** 145.601, 1.94%]

4.3 Calculate the fraction of equilibrium population in the five energy levels with energies 0, ε, 2ε, 3ε and 4ε, where $\varepsilon = 1.106 \times 10^{-20}$ J at $T = 300$ K and $T = 500$ K.

[**Ans.** At 300 K, $p_0 = 0.930\,7$, $p_1 = 0.064\,5$, $p_2 = 0.004\,5$, $p_3 = 0.000\,3$ and $p_4 = 0$.
At 500 K, $p_0 = 0.798\,8$, $p_1 = 0.161\,0$, $p_2 = 0.032\,4$, $p_3 = 0.006\,6$ and $p_4 = 0.001\,3$]

Bose-Einstein Distribution

4.4 Using Bose-Einstein probability distribution expression, calculate the possible ways of distributing 5 bosons among 5 energy levels (each one is sixfold degenerate) with energies 0, ε, 2ε, 3ε and 4ε, respectively. The total energy of the system remains at 4ε.

[**Ans.** $W(n_0 = 4, n_4 = 1) = 756$ $\quad W(n_0 = 3, n_1 = 1, n_3 = 1) = 2\,016$
$W(n_0 = 3, n_2 = 2) = 1\,176$ $\quad W(n_0 = 2, n_1 = 2, n_2 = 1) = 2\,646$
$W(n_0 = 1, n_1 = 4) = 756$]

Fermi-Dirac Distribution

4.5 Using Fermi-Dirac probability distribution expression, calculate the possible ways of distributing 5 fermions among 5 energy levels (each one is sixfold degenerate) with energies 0, ε, 2ε, 3ε and 4ε such that the total energy of the system remains at 4ε.

[**Ans.** $W(n_0 = 4, n_4 = 1) = 90$ $\quad W(n_0 = 5, n_1 = 1, n_3 = 1) = 720$
$W(n_0 = 3, n_2 = 2) = 300$ $\quad W(n_0 = 2, n_1 = 2, n_2 = 1) = 1\,350$
$W(n_0 = 1, n_1 = 4) = 15$]

Translational Contribution

4.6 Evaluate the translational partition function for hydrogen atom at 300 K contained in a volume of 22.414 dm^3. [**Ans.** 2.18×10^{28}]

4.7 Calculate the translational contributions to U°_{m}, H°_{m}, S°_{m}, A°_{m} and G°_{m} for hydrogen atom at 300 K.

[**Ans.** 3 741.3 J mol^{-1}, 6 235.5 J mol^{-1}, 108.96 J K^{-1} mol^{-1}, – 28 946.7 J mol^{-1}, – 26 452.5 J mol^{-1}]

Rotational Contribution

4.8 Calculate the characteristic rotational constant for H_2 molecule. Given: The internuclear distance of H_2 is 74.17 pm. [**Ans.** 88.34]

4.9 Calculate the rotational contributions to internal energy, entropy and Gibbs free energy for diatomic chlorine at 500 K. Given: Internuclear distance of N_2 = 198.8 pm. [**Ans.** 4 157 J mol^{-1}, 63.04 J K^{-1} mol^{-1}, 27.36 kJ mol^{-1}]

4.10 Calculate the characteristic vibrational temperature of Cl_2 molecule. Given: $\widetilde{V}_e = 561.1$ cm^{-1} for Cl_2 molecule. [**Ans.** 808.2 K]

4.11 Calculate the vibrational contributions to internal energy, enthalpy, entropy and Gibbs free energy for 1 mole of diatomic fluorine at 298 K. Given: The vibrational frequency of F_2 corresponds to 923.1 cm^{-1}.
[**Ans.** 129.1 J mol^{-1}, 129.1 J mol^{-1}, 1.30 J K^{-1} mol^{-1}, − 28.76 J mol^{-1}]

Equilibrium Constant

4.12 Calculate the equilibrium constant of the reaction $(1/2)O_2 \rightleftharpoons O$ at 1000 K. Given: $D_0(O_2) = 491.888$ kJ mol^{-1}, θ_r of $O_2 = 2.079$ and θ_v of $O_2 = 2273.64$ K. g_0 for the ground electronic level of $O_2 = 3$ and that of O is 5.
[**Ans.** 1.75×10^{-10}]

4.13 Calculate the standard equilibrium constant K_c° for the reaction $H_2 \rightleftharpoons 2H$ at 3 000 K. Given: Ground state of H atom is $^2S_{1/2}$, H—H dissociation energy is 431.8 kJ mol^{-1}, H—H internuclear distance is 74 pm and $\theta_v(H_2) = 6\,210$ K.
[**Ans.** 1.14×10^{-4}]

Velocity Distribution

4.14 Calculate the values of x-component of velocity probability density, $f(\upsilon_x)$, for oxygen molecules at 300 K for the speeds from 0 to 1 000 m/s at the regular interval of 100 m/s. Plot the obtain data of $f(\upsilon_x)$ versus υ_x.
[**Ans.** The values of $f(\upsilon_x) \times 10^4/m^{-1}s$ are 14.29, 13.4, 11.06, 8.02, 5.12, 2.88, 1.42, 0.236 and 0.023 4]

4.15 Calculate the values of speed probability density, F, for oxygen molecules at 300 K for the speeds from 100 m/s to 1 200 m/s at the regular interval of 100 m/s. Plot the obtain data of F versus υ_x.
[**Ans.** The values of $F \times 10^4/m^{-1}s$ are 3.54, 11.35, 18.53, 21.0, 18.4, 13.1, 7.75, 3.87, 1.65, 0.6, 0.19 and 0.05]

4.16 Calculate the υ_{mp}, υ_{av} and υ_{rms} for oxygen molecules at 300 K.

4.17 Calculate the per cent composition of para and ortho dihydrogen at 20 K, 60 K, 100 K, 150 K, 200 K, 250 K, 300 K and 400 K. Draw a graph between per cent of ortho dihydrogen and temperature. Use $\theta_v = 86.5$ K.

4.18 The Euler-Maclaurin theorem is

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(n)\,dn = \frac{1}{2}f(0) - \frac{1}{12}\left(\frac{\partial f}{\partial n}\right)_{n=0} + \frac{1}{720}\left(\frac{\partial^3 f}{\partial n^3}\right)_{n=0} - \cdots$$

Show that this theorem when applied to the rotational partition function leads to Eq. (4.8.18).

4.19 Comment on the following statement.
The vibrational contribution towards molar heat capacity of a diatomic gas varies with temperature. It attains a maximum value of R at high temperature dependent on the characteristic temperature (θ_v) of the gas and approaches a zero value as temperature is lowered towards $T \rightarrow 0$.

4.20 For a homonuclear diatomic molecule having even number of protons and equal number of neutrons in the nuclei (e.g. $^{12}C_2$, $^4He_2$ and $^{16}O_2$), the contribution to the combined rotational-nuclear partition function from the odd rotational quantum numbers is zero. Explain. [**Hint.** $I = 0$ in Eq. (AII.2).]

4.21 Show that the limiting value of N_{ortho}/N_{para} for dideuterium is 2/3 at high temperature.

ANNEXURE I Alternative Method of Computing Translational Partition Function

The translational energy of a particle in a cubical box of edge-length l is given by

$$\varepsilon = \frac{h^2}{8ml^2}\left(n_x^2+n_y^2+n_z^2\right) = \frac{h^2}{8mV^{2/3}}\left(n_x^2+n_y^2+n_z^2\right) \tag{AI.1}$$

where n_x, n_y and n_z are the quantum numbers, each having integral values of 1, 2, 3, ...

A translational state may be represented by a point in a three-dimensional space of coordinates n_x, n_y and n_z, a two-dimensional cross-section of which is shown in Fig. AI.1.

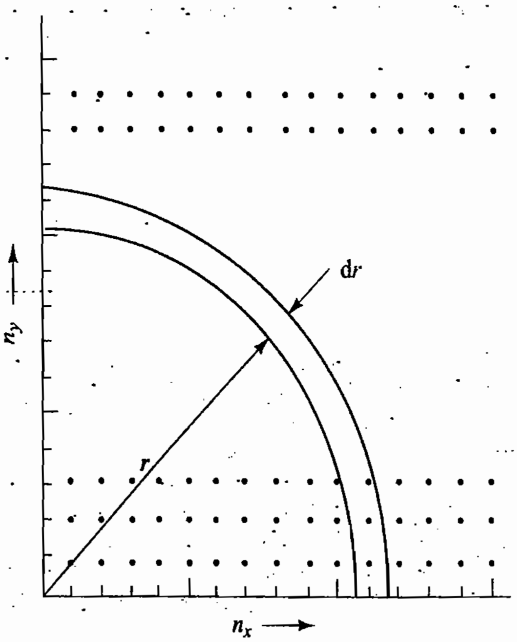


Fig. AI.1 Two-dimensional cross-section of three-dimensional space coordinates of n_x, n_y and n_z

The distance of a point in this space coordinates from the origin is given by

$$r^2 = n_x^2 + n_y^2 + n_z^2 \tag{AI.2}$$

With this, the expression of translational energy is given by

$$\varepsilon = \frac{h^2}{8mV^{2/3}}r^2 \tag{AI.3}$$

We consider the quantum states for which $r \gg 1$, so that r as well as ε may be considered to vary in a continuous manner.

The number of quantum states within the energy range ε to $\varepsilon + \mathrm{d}\varepsilon$ will be equal to the volume of the spherical shell from r to $r + \mathrm{d}r$ lying in the first quadrant of the space coordinates. The latter condition is due to the fact that the quantum numbers n_x, n_y and n_z have only positive values.

The volume of spherical shell from r to $r + \mathrm{d}r$ lying in the first quadrant will be 1/8 of the total volume of the shell which is $4\pi r^2 \mathrm{d}r$. Hence, the number of quantum states having energies in the range ε to $\varepsilon + \mathrm{d}\varepsilon$ is given by

$$g_{\mathrm{t}} = \frac{1}{8}\,(4\pi r^2 \mathrm{d}r) \tag{AI.4}$$

The differential of energy as given by Eq. (AI.3) is

$$\mathrm{d}\varepsilon = \frac{h^2}{8mV^{2/3}}\,(2r\mathrm{d}r) \qquad \text{i.e.} \qquad \mathrm{d}r = \frac{4mV^{2/3}}{h^2 r}\mathrm{d}\varepsilon$$

Hence,

$$r^2 \mathrm{d}r = \frac{4mV^{2/3}r}{h^2}\,\mathrm{d}\varepsilon \tag{AI.5}$$

Making use of Eq. (AI.3), we get

$$r^2\,\mathrm{d}r = \frac{4mV^{2/3}}{h^2}\left(\frac{8\pi V^{2/3}\varepsilon}{h^2}\right)^{1/2}\mathrm{d}\varepsilon = \frac{8mV}{h^3}\,(2m\varepsilon)^{1/2}\,\mathrm{d}\varepsilon \tag{AI.6}$$

Substituting Eq. (AI.6) in Eq. (AI.4), we get

$$g_{\mathrm{t}} = \frac{1}{2}\pi\left[\frac{8mV}{h^3}(2m\varepsilon)^{1/2}\mathrm{d}\varepsilon\right] = \frac{4\pi mV}{h^3}\,(2\,m\varepsilon)^{1/2}\,\mathrm{d}\varepsilon \tag{AI.7}$$

With the above expression of degeneracy of translational levels, the expression of translational partition function .

$$q_{\mathrm{t}} = \textstyle\sum_i g_i\, \mathrm{e}^{-\varepsilon_i/kT}$$

becomes

$$q_{\mathrm{t}} = \sum_i \left[\frac{4\pi mV}{h^3}(2m\varepsilon_i)^{1/2}\mathrm{d}\varepsilon_i\right]\mathrm{e}^{-\varepsilon_i/kT}$$

i.e.

$$q_{\mathrm{t}} = \frac{4\pi mV(2m)^{1/2}}{h^3}\int_0^\infty \varepsilon^{1/2}\,\mathrm{e}^{-\varepsilon/kT}\,\mathrm{d}\varepsilon$$

Let $x^2 = \varepsilon$, such that $2x\,\mathrm{d}x = \mathrm{d}\varepsilon$. With these, the above expression becomes

$$q_{\mathrm{t}} = \frac{4\pi mV(2m)^{1/2}}{h^3}\int_0^\infty 2\,x^2\,\mathrm{e}^{-x^2/kT}\,\mathrm{d}x$$

$$= \left[\frac{4\pi mV(2m)^{1/2}}{h^3}\right]\left[2\left\{\frac{1}{4}\left(\pi k^3T^3\right)^{1/2}\right\}\right]$$

$$= V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{AI.8}$$

ANNEXURE II Quantum Mechanical Explantion of Symmetry Number and Heat Capacity of Hydrogen Gas

Expression of Total Wave Function of a Molecule

The total wave function of a molecule is given by

$$\psi_{\text{total}} = \psi_t \, \psi_r \, \psi_v \, \psi_e \, \psi_n \tag{A.II.1}$$

where the subscripts t, r, v, e and n stand for translational, rotational, vibrational, electronic and nuclear, respectively.

Classification of Atoms into Bosons and Fermions

Two types of atoms may be distinguished based on the nuclear spin quantum number. These are

Bosons The nuclei of these atoms have integral spin quantum number. Examples include ^{2}H ($I = 1$), ^{14}N ($I = 1$) and ^{10}B ($I = 3$).

Fermions The nuclei of these atoms have half-integral spin quantum number. Examples include ^{1}H ($I = 1/2$), ^{15}N ($I = 1/2$), ^{17}O ($I = 5/2$) and ^{35}Cl ($I = 3/2$).

Nature of Wave Functions for Bosons and Fermions

We have the following requirements about the total wave function of bosons and fermions under the exchange of the two identical nuclei in a molecule.

For bosons the total wave function is symmetric.

For fermions, the total wave function is antisymmetric.

The above symmetry requirement has profound consequences on the thermodynamic properties of homonuclear diatomic molecules at low temperatures.

Symmetry Characteristics of Wave Functions

We have the following facts about the symmetry characteristics of the wave functions involved in the total wave function.

- Translational wave function depends only upon the coordinates of the centre of mass of the molecule, and thus this wave function is not affected by the exchange of two identical nuclei, i.e. the translational wave function is symmetric under the exchange of two identical nuclei.
- Vibrational wave function depends upon the magnitude of $r - r_{eq}$ and thus this wave function is also unaffected under the exchange of two identical nuclei, i.e. the vibration wave function is symmetric under the exchange of two identical nuclei.
- Most of molecules in the ground electronic state have the symmetric electronic wave function.
- The rotational wave functions have the same symmetry characteristics as those of the angular functions of the hydrogen atom.

ψ_r are symmetric for even values of rotational quantum number J

ψ_r are antisymmetric for odd values of rotational quantum number J.

- A nucleus with spin quantum number I has a total of $2I + 1$ spin states. These states are represented by the magnetic spin quantum number which can have values of

  $$+I, +(I-1), \ldots, -(I-1), -I$$

  For example, for a proton ($I = 1/2$) the two states are

  $m_I = +1/2$, known as α spin. Its wave function is represented by the symbol α.

  $m_I = -1/2$, known as β spin. Its wave function is represented by the symbol β.

  A diatomic molecule involving identical nuclei with spin quantum number I, has a total of $(2I+1)^2$ nuclear wave functions. Of these wave functions, we have

  $(2I+1)(2I)/2$, i.e. $I(2I+1)$ wave functions are antisymmetric

  and $(2I+1)^2 - I(2I+1)$, i.e. $(I+1)(2I+1)$ wave functions are symmetric.

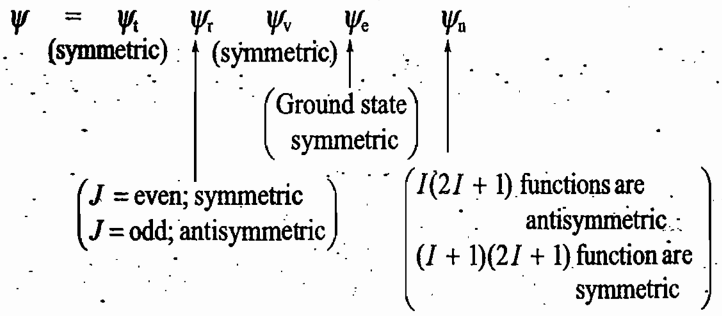
  From example, in hydrogen molecule we have

  Three symmetric nuclear spin wave functions. These are $\alpha\alpha$, $\beta\beta$ and $(1/\sqrt{2})(\alpha\beta + \beta\alpha)$.

  One antisymmetric nuclear spin wave function. This is $(1/\sqrt{2})(\alpha\beta - \beta\alpha)$.

Diagrammatic Display of Symmetries of Wave Functions

The above characteristics about the various wave functions may be depicted as follows.



Factor Deciding Symmetry of Total Wave Function

The symmetric/antisymmetric characteristic of the total wave function is decided by the proper coupling of rotational and nuclear wave function. We can have the following combinations.

1. For bosons, the total wave function has to be symmetric. This is possible when $I(2I + 1)$ antisymmetric nuclear spin functions couple with antisymmetric rotational wave functions for which rotational quantum number J has **odd** values. $(I + 1)(2I + 1)$ symmetric nuclear spin functions couple with symmetric rotational wave functions for which rotational quantum number J has **even** values.
2. For fermions, the total wave function has to be antisymmetric. This is possible only when $I(2I + 1)$ antisymmetric nuclear spin functions couple with symmetric rotational wave functions for which rotational quantum number J has **even** values. $(I + 1)(2I + 1)$ symmetric nuclear spin functions couple with antisymmetric rotational wave functions for which rotational quantum number J has **odd** values.

The above combinations are also applicable to linear polyatomic molecules such as CO_2 and C_2H_2.

Expressions of Partition Function

For bosons, we have

$$q_{\mathrm{r,\,n}} = (I+1)(2I+1) \sum_{\substack{J \\ \text{(even)}}} (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T} + I(2I+1) \sum_{\substack{J \\ \text{(odd)}}} (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T} \qquad \text{(AII.2)}$$

For fermions, we have

$$q_{\mathrm{r,\,n}} = (I+1)(2I+1) \sum_{\substack{J \\ \text{(odd)}}} (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T} + I(2I+1) \sum_{\substack{J \\ \text{(even)}}} (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T} \qquad \text{(AII.3)}$$

From the above expressions, it is obvious that the combined rotational and nuclear partition function cannot be factored into q_{r} and q_{n}. However, if $\theta_{\mathrm{r}}/T \leq 0.20$ for homonuclear diatomic molecules, this factorization is possible since

$$\sum_{\substack{J \\ \text{(even)}}} (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T} = \sum_{\substack{J \\ \text{(odd)}}} (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T}$$

$$= \frac{1}{2} \sum_{\substack{J \\ \text{(all)}}} (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T} = \frac{1}{2} \int_0^\infty (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T} = \frac{T}{2\theta_{\mathrm{r}}}$$

With this, Eqs (AII.2) and (AII.3) can be written as

$$q_{\mathrm{r,\,n}} = (2I+1)^2 \frac{T}{2\theta_{\mathrm{r}}} \qquad \text{(AII.4)}$$

in which $q_{\mathrm{n}} = (2I+1)^2$ and $q_{\mathrm{r}} = T/2\theta_{\mathrm{r}}$.

For heteronuclear diatomic molecules, $q_{\mathrm{r}} = T/\theta_{\mathrm{r}}$.

The factor 2 in the denominator of Eq. (AII.4) is known as **symmetry number**. This factor is due to the fact that for homonuclear diatomic molecules, the rotational partition function is given by Eq. (AII.2) or (AII.3). This is applicable only to the high-temperature limit such that $\theta_{\mathrm{r}}/T \leq 0.20$. For most of homonuclear diatomic molecules, the condition $\theta_{\mathrm{r}}/T \leq 0.20$ holds goods since their characteristic rotational temperatures have low values. Hydrogen is somewhat unusual in that its rotational constant is much greater than its boiling point.

COMMENT ON THE HEAT CAPACITY OF HYDROGEN GAS

Rotational Partition Function

For hydrogen atom, $I = 1/2$. Hence, from Eq. (AII.3) we can write

$$q_{\mathrm{r,\,n}} = (1) \sum_{\substack{J \\ \text{(even)}}} (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T} + (3) \sum_{\substack{J \\ \text{(odd)}}} (2J+1)\, \mathrm{e}^{-\theta_{\mathrm{r}} J(J+1)/T} \qquad \text{(AII.5)}$$

Ortho- and Para-Hydrogens

The hydrogen molecule with opposite nuclear spins (i.e. antisymmetric nuclear spin function) is called para-hydrogen. It is associated with rotational wave functions having only even values of rotational quantum numbers.

The hydrogen molecule with parallel (or same) nuclear spins (i.e. symmetric nuclear spin function) is called ortho-hydrogen. It is associated with rotational wave functions having only odd values of rotational quantum numbers.

The ratio of molecules of ortho and para dihydrogen is given by

$$\frac{N_{\text{ortho}}}{N_{\text{para}}} = \frac{(3)\sum\limits_{\text{odd }J}(2J+1)\mathrm{e}^{-\theta_\mathrm{r}J(J+1)/T}}{(1)\sum\limits_{\text{even }J}(2J+1)\mathrm{e}^{-\theta_\mathrm{r}J(J+1)/T}} \qquad \text{(AII.6)}$$

This ratio depends on the temperature of the system. The percentage of para dihydrogen is 100 at 0 K. It decreases with increase in temperature and attains a value of 25 per cent at high temperatures.

Example AII.1

Calculate the per cent equilibrium composition of para and ortho dihydrogens at its normal boiling point (20.4 K). Given: At low temperature condition, the value of $\theta_\mathrm{r} = 85.4$ K.

Solution

We have

$$\theta_\mathrm{r}/T = 85.4/20.4 = 4.186$$

Since

$$\frac{N_{\text{para}}}{N_{\text{ortho}}} = \frac{(1)\sum\limits_{\text{even }J}(2J+1)\mathrm{e}^{-\theta_\mathrm{r}J(J+1)/T}}{(3)\sum\limits_{\text{odd }J}(2J+1)\mathrm{e}^{-\theta_\mathrm{r}J(J+1)/T}}$$

we have

$$\frac{N_{\text{para}}}{N_{\text{ortho}}} = \frac{(1)\left[1+5\mathrm{e}^{-6\times4.186}+9\mathrm{e}^{-20\times4.186}+\cdots\right]}{(3)\left[3\mathrm{e}^{-2\times4.186}+7\mathrm{e}^{-12\times4.186}+\cdots\right]}$$

$$= \frac{(1)\left[1+5(1.237\times10^{-11})+9(4.374\times10^{-37})+\cdots\right]}{(3)\left[3(2.313\times10^{-4})+7(1.529\times10^{-22})+\cdots\right]}$$

$$= \frac{1}{2.082\times10^{-3}} = 480.4$$

Per cent of para H_2 = (480.4/481.4) x 100 = 99.79

Per cent of ortho H_2 = 0.21

Example AII.2

Calculate the per cent equilibrium composition of para and ortho dihydrogens at 300 K. Given: At high temperature condition, the value of $\theta_\mathrm{r} = 87.5$ K.

Solution

We have

$$\theta_\mathrm{r}/T = 87.5/300 = 0.292$$

Since

$$\frac{N_{\text{para}}}{N_{\text{ortho}}} = \frac{(1)\sum\limits_{\text{even } J} (2J+1)e^{-\theta_r J(J+1)/T}}{(3)\sum\limits_{\text{odd } J} (2J+1)e^{-\theta_r J(J+1)/T}}$$

we have

$$\frac{N_{\text{para}}}{N_{\text{ortho}}} = \frac{(1)\left[1+5e^{-6\times 0.292}+9e^{-20\times 0.292}+13e^{-42\times 0.292}+\cdots\right]}{(3)\left[3e^{-2\times 0.292}+7e^{-12\times 0.292}+11e^{-30\times 0.292}+\cdots\right]}$$

$$= \frac{(1)\left[1+5(0.173)+9(2.909\times 10^{-3})+13(4.718\times 10^{-6}+\cdots)\right]}{(3)\left[3(0.558)+7(0.030)+11(1.569\times 10^{-4}+\cdots)\right]}$$

$$= \frac{1.891}{5.657} = 0.334$$

$$\text{Per cent of para H}_2 = \frac{0.334}{1.334}\times 100 = 25.0$$

Per cent of ortho H_2 = 75.0

Comment on the Experimental and Calculated Values of Heat Capacities

The conversion of para into ortho as the temperature is increased (or the vice versa as the temperature is decreased) is extremely slow unless a catalyst (such as activated charcoal) is used. Without a catalyst, the experimental values of heat capacity of H_2 as its temperature is lowered from room temperature (where the ratio of ortho to para is 3 : 1) do not agree with those calculated by using the partition function given by Eq. (AII.5). This is due to the fact that the experimental values involve more or less 3 : 1 ratio of ortho : para dihydrogen while it changes in the calculated values. However, if experiments are carried out in the presence of activated charcoal, the disagreement between experimental and calculated values disappears. The use of activated charcoal ensures an equilibrium mixture of ortho and para dihydrogen at all temperatures.

ANNEXURE III The Concept of Ensemble

Introduction

For a system involving noninteracting particles, the partition function is called the molecular partition function because the energy levels in its expression refer to those of individual molecules. This is, however, not true for a system involving interacting particles and hence the expressions derived earlier for the thermodynamic properties in terms of molecular partition function are not applicable for such a system. To extend the statistical evaluation of thermodynamic properties of a system involving interacting particles as well, Gibbs invented the concept of ensemble which is a hypothetical collection of a large number of systems, each constructed to be a replica of the system under study. Each system of an ensemble has the same values of some of the macroscopic properties of the system under study. The various types of ensemble have been visualized. The commonly used ensembles are as follows.

Microcanonical Ensemble Each members of this ensemble has the same values of N, V and U. The expressions derived earlier for a system of noninteracting particles can be derived by using this ensemble.

Canonical Ensemble Each members of this ensemble has the same values of N, V and T. This type of ensemble finds more practical applications in statistical thermodynamics.

Grand Canonical Ensemble Each members of this ensemble has the same values of V, T and μ.

Isothermal-Isobaric Ensemble Each members of this ensemble has the same values of N, T and p.

Treatment of Canonical Ensemble

In this section, we deal with only canonical ensemble.

Some of the guidelines of computing thermodynamic properties of a system by using the concept of canonical ensemble are as follows.

- The diagrammatic representation of canonical ensemble is shown in Fig. AIII.1. Each system has the same values of N, V and T. The walls of each system is heat conducting. The entire ensemble is surrounded by thermal insulation, it is an isolated system with volume $\mathcal{A}V$, number of molecules $\mathcal{A}N$ and some total energy $\mathcal{E}$; where $\mathcal{A}$ is the number of systems in the ensemble.

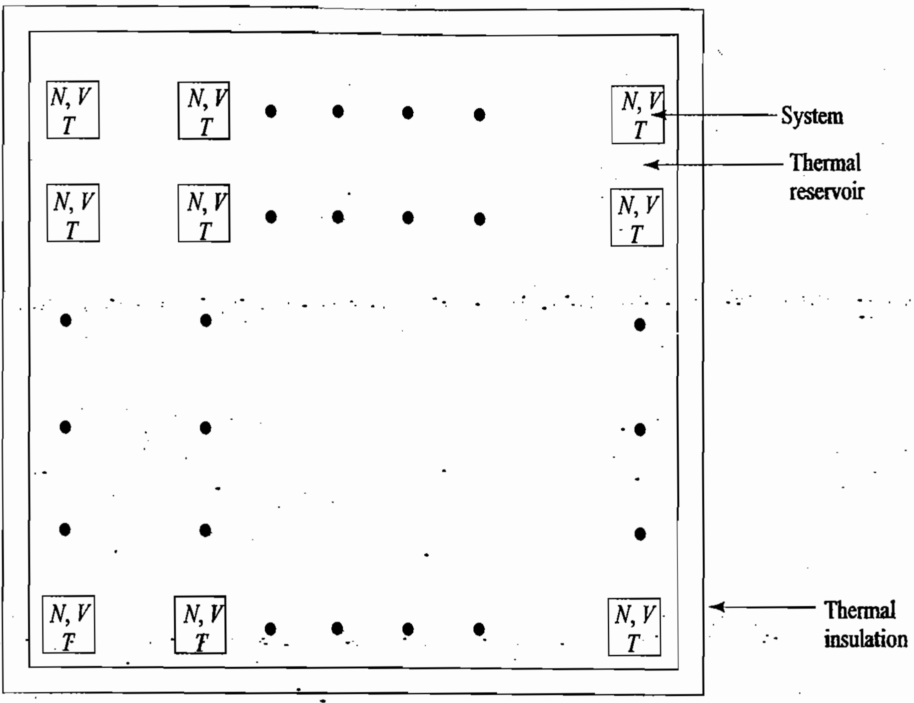


Fig. AIII.1 A diagrammatic representation of canonical ensemble

- The available energy states for a N-body system can, in principle, be obtained from the solution of Schrödinger equation

$$\mathcal{H}_{\text{op}}\,\psi_i = E_i\,\psi_i \qquad \text{where} \qquad i = 1, 2, 3, \ldots \tag{AIII.1}$$

- The principle of equal a priori probabilities is applicable, according to which, any particular system of the ensemble might be found in any of the available energy state.
- A state of the ensemble can be specified by stating the number of systems in each and every quantum states, say, for example,

$$\left.\begin{array}{llllll} \text{Energy of the state} & E_1 & E_2 & E_3 & \ldots & E_i \\ \text{Occupation number} & a_1 & a_2 & a_3 & \ldots & a_i \end{array}\right\} \tag{AIII.2}$$

The above distribution is subject to the following restrictions;

$$\text{Fixed number of systems in the ensemble:} \qquad \mathcal{A} = \textstyle\sum_i a_i \tag{AIII.3}$$

$$\text{Fixed energy of isolated ensemble:} \qquad \mathcal{E} = \textstyle\sum_i a_i E_i \tag{AIII.4}$$

- The number of ways of realizing a particular distribution of $\mathcal{A}$ distinguishable systems over the available energy states is given by

$$W = \frac{\mathcal{A}!}{\Pi_i\, a_i!} \tag{AIII.5}$$

One can obtain many distributions varying in the values of a_i in different energy states U_i subject to the two constraints as given by Eqs (AIII.3) and (AIII.4).

- For an ensemble involving a very large number of systems, the average value of any mechanical property (e.g. pressure, energy) is largely governed by the most probable distribution which has a maximum value of W for a particular set of a_is (denoted by a_i^*s). The average of value of mechanical property (say, energy) is given by

$$\bar{U} = \sum_i P_i U_i \tag{AIII.6}$$

where $P_i = \dfrac{a_i^*}{\mathcal{A}}$ (AIII.7)

This average value of energy corresponds to the thermodynamic energy of the system.

- The mathematical procedure to determine the most probable distribution is exactly the same as described earlier. We maximize ln W subject to the constraints of Eqs (AIII.3) and (AIII.4), i.e.

$$\mathrm{d}\ln W = \sum_i \frac{\partial \ln W}{\partial a_i}\mathrm{d}a_i = 0 \tag{AIII.8}$$

$$\mathrm{d}\mathcal{A} = \sum_i \mathrm{d}a_i = 0 \tag{AIII.9}$$

$$\mathrm{d}\mathcal{E} = \sum_i U_i \mathrm{d}a_i = 0 \tag{AIII.10}$$

Using the method of Lagrange multipliers, we get

$$\sum_i \left(\frac{\partial \ln W}{\partial a_i} + \alpha - \beta U_i\right)\mathrm{d}a_i = 0 \tag{AIII.11}$$

For the sum to be equal to zero, each of the coefficients of da_i is equated to zero, i.e.

$$\frac{\partial \ln W}{\partial a_i} + \alpha - \beta U_i = 0 \tag{AIII.12}$$

Now $\ln W = \ln \mathcal{A}! - \sum_i \ln a_i!$

Using Stirling's approximation, we get

$$\ln W = \mathcal{A}\ln\mathcal{A} - \mathcal{A} - \sum_i (a_i \ln a_i - a_i)$$

$$= \mathcal{A}\ln\mathcal{A} - \sum_i a_i \ln a_i$$

Hence, $\dfrac{\partial \ln W}{\partial a_i} = -\ln a_i - 1$

With this, Eq. (AIII.12) becomes

$$-\ln a_i^* - 1 + \alpha - \beta U_i = 0$$

or $a_i^* = \mathrm{e}^{\alpha'}\,\mathrm{e}^{-\beta U_i}$ (where $\alpha' = \alpha - 1$) (AIII.13)

Equation (AIII.13) gives the most probable distribution in terms of α and β.

Expression of α in Terms of β

Carrying out the summation over i on both sides of Eq. (AIII.13) gives

$$\sum_i a_i^* = e^{\alpha'} \sum_i e^{-\beta U_i}$$

or

$$e^{\alpha'} = \frac{\sum_i a_i^*}{\sum_i e^{-\beta U_i}} = \frac{\mathcal{A}}{\sum_i e^{-\beta U_i}} \tag{AIII.14}$$

Hence,

$$a_i^* = \frac{\mathcal{A} e^{-\beta U_i}}{\sum_i e^{-\beta U_i}} = \frac{\mathcal{A} e^{-\beta U_i}}{Q} \tag{AIII.15}$$

where Q is known as *canonical* (ensemble) *partition function.*

Expression of $\bar{U}$

By definition

$$\bar{U} = \sum_i P_i U_i = \frac{1}{\mathcal{A}} \sum_i a_i^* U_i$$

Using Eq. (AIII.15), this becomes

$$\bar{U} = \frac{1}{Q} \sum_i U_i e^{-\beta U_i}$$

Since $\left(\frac{\partial Q}{\partial \beta}\right)_{N,V} = \frac{\partial}{\partial \beta}\left(\sum_i e^{-\beta U_i}\right)_{N,V} = -\sum_i U_i e^{-\beta U_i}$, the above expression may be written as

$$\bar{U} = -\left(\frac{\partial Q/\partial \beta}{Q}\right)_{N,V} = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

Since $\beta = 1/kT$; this expression may be written as

$$\bar{U} = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \tag{AIII.16}$$

Expression of Pressure

From thermodynamics, the expression of pressure p_i is

$$p_i = -\left(\frac{\partial U_i}{\partial V}\right)_{N,T}$$

Hence, the canonical average of pressure is

$$\bar{p} = \sum_i p_i P_i = -\sum_i \left(\frac{\partial U_i}{\partial V}\right)_{N,T} \frac{a_i^*}{\mathcal{A}}$$

$$= -\sum_i \left(\frac{\partial U_i}{\partial V}\right)_{N,T} \frac{e^{-\beta U_i}}{Q} = \frac{\sum_i -\beta (e^{-\beta U_i})(\partial U/\partial V)_{N,T}}{\beta Q}$$

$$= \frac{\frac{\partial}{\partial V}\left(\sum_i e^{-\beta U_i}\right)_{N,T}}{\beta Q} = \frac{(\partial Q/\partial V)_{N,T}}{\beta Q} = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \tag{AIII.17}$$

Expression of Entropy

We will have

$$\bar{S} = \frac{S}{\mathcal{A}} = \frac{1}{\mathcal{A}}(k \ln W)$$

Substituting the expression of W from Eq. (AIII.5), we get

$$\bar{S} = \frac{1}{\mathcal{A}}\left[k\ln\left(\frac{\mathcal{A}!}{\Pi_i a_i^*!}\right)\right] = \frac{k}{\mathcal{A}}\,[\ln \mathcal{A}! - \Sigma_i \ln a_i^*!]$$

Invoking Stirling's approximation, we get

$$\bar{S} = \frac{k}{\mathcal{A}}\left[(\mathcal{A}\ln\mathcal{A} - \mathcal{A}) - (\Sigma_i a_i^* \ln a_i^* - a_i^*)\right]$$

$$= \frac{k}{\mathcal{A}}\left[-\Sigma_i a_i^* \ln\frac{a_i^*}{\mathcal{A}}\right]$$

Making use of Eq. (AII.15), this becomes

$$\bar{S} = \frac{k}{\mathcal{A}}\left[-\Sigma_i a_i^* \ln\frac{e^{-\beta U_i}}{Q}\right] = \frac{k}{\mathcal{A}}\left[\Sigma_i a_i^* \beta U_i + \Sigma a_i^* \ln Q\right]$$

$$= k\left[\beta\left(\Sigma_i \frac{a_i}{\mathcal{A}} U_i\right) + \ln Q\right] = k\,[\beta\,\bar{U} + \ln Q]$$

Substituting Eq. (AIII.16) in the above expression, we get

$$\bar{S} = k\left[\beta k T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + \ln Q\right] = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k \ln Q \qquad \text{(AIII.18)}$$

Expression of Helmholtz Free Energy

From thermodynamics, we have

$$\bar{A} = \bar{U} - T\,\bar{S}$$

Substituting the expressions of $\bar{U}$ and $\bar{S}$, we get

$$\bar{A} = -kT\ln Q \qquad \text{(AIII.19)}$$

It may be mentioned here that both A and Q have the same natural independent variables, i.e. N, V and T.

Expression of Enthalpy

Since $\bar{H} = \bar{U} + \bar{p}\,V$, we get

$$\bar{H} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + VkT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \qquad \text{(AIII.20)}$$

Expression of Gibbs Free Energy

Since $\bar{G} = \bar{A} + \bar{p}\,V$, we get

$$\bar{G} = -kT\ln Q + VkT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \qquad \text{(AIII.21)}$$

Canonical Partition Function for Distinguishable Noninteracting Particles

For distinguishable noninteracting particles, N-body Hamiltonian operator can be written as a sum of N individual terms, one for each particle. The number of quantum states available to N-body system will be equal to the product of number of quantum states available to individual particles. The expression of canonical partition function can be written as

$$Q_{N,V,T} = \sum_i e^{-U_i/kT} = \sum_i \sum_j \sum_{k'} \cdots e^{-(U_{i1} + U_{j2} + U_{k'3} + \cdots)/kT} \quad \text{(A.III.22)}$$

where numbers 1, 2, 3, ... refer to the particles. The above expression can be written as

$$Q_{N,V,T} = \left(\sum_i e^{-U_{i1}/kT}\right)\left(\sum_j e^{-U_{j2}/kT}\right)\left(\sum_{k'} e^{-U_{k'3}/kT}\right)\cdots$$

$$= q_1\, q_2\, q_3 \cdots \quad \text{(A.III.23)}$$

that is, the canonical partition function of a N-body system involving distinguishable noninteracting particles is equal to the product of individual molecular partition function.

If the energy states of all the particles are the same, then Eq. (AIII.22) becomes

$$Q_{N,V,T} = (q_{V,T})^N \qquad \text{(Distinguishable particles)} \qquad \text{(AIII.24)}$$

Canonical Partition Function for Indistinguishable Noninteracting Particles

If the particles are indistinguishable (i.e. the particles cannot be labelled as 1, 2, 3, ...), many of summation terms in Eq. (AIII.22) will represent one and the same case. It can be shown that the summation of Eq. (AIII.22) includes $N!$ identical terms. Hence, the canonical partition function in this case as given by Eq. (AIII.24) is divided by $N!$, i.e.

$$Q_{N,V,T} = \frac{(q_{N,V})^N}{N!} \qquad \text{(Indistinguishable particles)} \qquad \text{(AIII.25)}$$

Problem

Derive the expression of entropy of a system involving N indistinguishable noninteracting particles in terms of molecular partition function starting from the corresponding expression involving canonical partition function.

Solution

The expression of entropy in terms of canonical partition function is

$$\bar{S} = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k \ln Q$$

For indistinguishable noninteracting particles, we have

$$Q = \frac{q^N}{N!}$$

Hence $\quad \ln Q = N \ln q - \ln N!$

Invoking Stirling's approximation, we get

$$\ln Q = N \ln q - N \ln N + N$$

Hence, $\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = N\left(\frac{\partial \ln q}{\partial T}\right)_{N,V}$

The expression of entropy becomes

$$\bar{S} = kT\left[N\left(\frac{\partial \ln q}{\partial T}\right)_{N,V}\right] + k\,[N \ln q - N \ln N + N]$$

$$= NkT\left(\frac{\partial \ln q}{\partial T}\right)_{N,V} + Nk \ln\left(\frac{q}{N}\right) + kN$$

$$= Nk\left[T\left(\frac{\partial \ln q}{\partial T}\right)_{N,V} + \ln\left(\frac{q}{N}\right) + 1\right] \quad \text{(AIII.26)}$$

ANNEXURE IV Some Useful Data

III.26)

1. Data for a few Diatomic Molecules

Molecule	*Ground*	$\frac{r_{eq}}{\text{pm}}$	$\frac{\nu}{\text{Hz}}$	$\frac{D_0}{\text{kJ mol}^{-1}}$
H_2	$^1\Sigma$	74.17	1.32×10^{14}	431.44
F_2	$^1\Sigma$	140.9	2.77×10^{13}	153.42
Cl_2	$^1\Sigma$	198.8	1.68×10^{13}	238.32
Br_2	$^1\Sigma$	228.4	9.70×10^{12}	189.94
I_2	$^1\Sigma$	266.7	6.44×10^{12}	148.79
N_2	$^1\Sigma$	109.76	7.07×10^{13}	940.26
O_2	$^3\Sigma$	120.74	4.74×10^{13}	492.92
HF	$^1\Sigma$	91.68	1.24×10^{13}	563.18
HCl	$^1\Sigma$	127.46	8.97×10^{13}	426.53
HBr	$^1\Sigma$	141.4	7.95×10^{13}	361.76
HI	$^1\Sigma$	160.4	6.93×10^{13}	294.31
CO	$^1\Sigma$	112.81	6.51×10^{13}	1 068.63

2. Data for a few Triatomic Molecules

Molecule	*Bond Distance* r/pm	*Bond Angle*	$\frac{\tilde{\nu}}{\text{cm}^{-1}}$
CO_2	C—O; 192.6	180°	1 342.9, 667.3 (2), 2 349.3
CS_2	C—S; 155.3	180°	658, 396.8 (2), 1 532.5
N_2O	N—N; 112.82	180°	1 276.5, 589.2 (2), 2 223.7
	N—O; 118.42		
H_2O	O—H; 95.84	104.45°	3 657.1, 1 594.6 3 755.8
H_2S	S—H; 134.55	93.3°	2 614.6, 1 182.7, 2 627.5
NH_2	N—H; 102.5	103°	3 400, 1 550, 3 650
NO_2	N—O; 119.7	134.25°	1 357.8, 756.8, 1 665.5

3. Values of Some Standard Integrals

(i) $\int_0^\infty x^n e^{-ax^2} dx$

For				
	$n = 0$	$\frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$	$n = 3$	$\frac{1}{2a^2}$
	$n = 1$	$\frac{1}{2a}$	$n = 4$	$\frac{3}{8}\left(\frac{\pi}{a^5}\right)^{1/2}$
	$n = 2$	$\frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$	$n = 5$	$\frac{1}{a^3}$

(ii) $\int_{-\infty}^{+\infty} x^n e^{-ax^2} dx = 0$ when $n = 1, 3, 5, \ldots$

$$= 2\int_0^\infty x^n e^{-ax^2} dx \text{ when } n = 0, 2, 4, \ldots$$

5

Macromolecules

5.1 INTRODUCTION

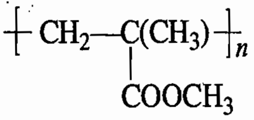
Macromolecules, also known as polymers, are formed by the covalent linkages between many repeating small molecules called monomers. The polymers may be classified into two categories, namely, synthetic polymers and biological polymers.

Synthetic polymers are man-made polymers. The starting materials are small number of identical repeating units, usually one or two. These polymers may be classified into two categories based on their methods of preparation.

Condensation (or Step Growth) Polymers The condensation polymers are formed by the reaction between two difunctional monomers with the elimination of a small molecule such as water. Examples include

Polyester	$\left[O—CO(CH_2)_4COOCH_2CH_2 \right]_n$
Polyurethane	$\left[O(CH_2)_6OCONH(CH_2)_6NHCO \right]_n$

Addition (or Chain Reaction) Polymers The addition polymers are formed in a chain reaction of monomers containing double bonds. Examples include

Polyethylene	$\left[CH_2—CH_2 \right]_n$
Polyvinyl chloride	$\left[CH_2—CHCl \right]_n$
Polystyrene	$\left[CH_2—CH(C_6H_5) \right]_n$
Poly(methylmethacrylate)	 $\left[CH_2—\underset{\displaystyle COOCH_3}{\underset{\mid}{C}}(CH_3) \right]_n$

In terms of repeating units, the polymers may be classified as *homopolymers* and *copolymers*. In homopolymers, there is only one monomer as repeating unit while in copolymer, there are two or more different monomers as repeating units.

Biological polymers include proteins and polysaccharides.

5.2 MOLAR MASS AVERAGES

In the preparation of a polymer from monomer molecules, the polymerization reactions proceed through different extent of reaction. This results into polydispersity with respect to molecular masses. To describe the distribution of molecular masses, the following averages are commonly used.

Number Average Molar Mass

The number average molar mass is obtained by carrying out the summation over the fraction of molecules multiplied by their corresponding molar mass, i.e.

$$\overline{M}_n = \sum_i f_i M_i \tag{5.2.1}$$

(The subscript 'n' stands for number and bar over the symbol M_n represents average.)

The fraction f_i is given by

$$f_i = \frac{N_i}{N_\text{total}} \tag{5.2.2}$$

where N_i is the number of molecules each having molar mass M_i and N_total is the total number of molecules which is given by

$$N_\text{total} = \sum_i N_i \tag{5.2.3}$$

Substituting Eq. (5.2.2) in Eq. (5.2.1), we get

$$\overline{M}_n = \sum_i \left(\frac{N_i}{N_\text{total}}\right) M_i = \frac{\sum_i N_i M_i}{N_\text{total}}$$

which in view of Eq. (5.2.3) becomes

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \tag{5.2.4}$$

Mass Average Molar Mass

The mass average molar mass is obtained by carrying out the summation over the mass fraction multiplied by their corresponding molar mass, i.e.

$$\overline{M}_m = \sum_i w_i M_i \tag{5.2.5}$$

(The subscript m stands for mass and bar over the symbol M_m stands for average.)

The mass fraction w_i is given by

$$w_i = \frac{m_i}{m_\text{total}} \tag{5.2.6}$$

where m_i is the mass of the polymer molecules, each having molar mass M_i and m_total is the total mass of the sample of the polymer which is given by

$$m_\text{total} = \sum_i m_i \tag{5.2.7}$$

Substituting Eq. (5.2.6) in Eq. (5.2.5), we get

$$\overline{M}_m = \sum_i \left(\frac{m_i}{m_\text{total}}\right) M_i = \frac{\sum_i m_i M_i}{m_\text{total}}$$

which in view of Eq. (5.2.7) becomes

$$\overline{M}_m = \frac{\sum_i m_i M_i}{\sum_i m_i} \tag{5.2.8}$$

Since $m_i = N_i\,(M_i/N_A)$, we get

$$\overline{M}_m = \frac{\sum_i [N_i(M_i/N_A)]M_i}{\sum_i N_i(M_i/N_A)} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \tag{5.2.9}$$

In terms of fraction of molecules, we have

$$\overline{M}_m = \frac{\sum_i f_i M_i^2}{\sum_i f_i M_i} \tag{5.2.10}$$

For all polydisperse system, $\overline{M}_m > \overline{M}_n$. This follows from the fact that the number average molar mass of a distribution counts the contribution of molecules in each class while the mass average molar mass is based on the mass contribution of each class. The molecules with higher molar mass contribute relatively more to the average when mass fraction rather than number fraction is used as the weighing factor.

The ratio $\overline{M}_m/\overline{M}_n$ is a measure of the polydispersity of a sample of a polymer.

z-Average Molar Mass

The *z*-average molar mass is defined as

$$\overline{M}_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} \tag{5.2.11}$$

Since the weighing factors in the *z*-average molar mass is $N_i M_i^2$, the molecules having higher molecular mass are weighed even more heavily resulting into

$$\overline{M}_z > \overline{M}_m > \overline{M}_n \tag{5.2.12}$$

Viscosity Average Molar Mass

The viscosity average molar mass is defined as

$$\overline{M}_v = \left(\frac{\sum_i N_i M_i^{a+1}}{\sum_i N_i M_i}\right)^{1/a} \tag{5.2.13}$$

where the variable a is characterized by the system under investigation and generally lies in the range $0.5 < a < 1.0$. Note that $\overline{M}_v = \overline{M}_m$ when $a = 1$. The constant a is known as Mark-Houwink exponent.

The viscosity average molar mass is not an absolute value, but a relative molar mass based on prior calibration with known molar mass for the same polymer-solvent-temperature conditions. The variable a depends on all these three conditions.

Table 5.2.1 lists the different molar masses described above along with the experimental methods to determine these averages.

Table 5.2.1 Description of Average Molar Masses

Average	*Definition*	*Methods*
$\overline{M}_n$	$\dfrac{\sum_i N_iM_i}{\sum_i N_i}$	Osmotic pressure and other colligative properties End group analysis
$\overline{M}_m$	$\dfrac{\sum_i N_iM_i^2}{\sum_i N_iM_i}$	Light scattering Sedimentation velocity
$\overline{M}_z$	$\dfrac{\sum_i N_iM_i^3}{\sum_i N_iM_i^2}$	Sedimentation equilibrium
$\overline{M}_v$	$\left(\dfrac{\sum_i N_iM_i^{1+a}}{\sum_i N_iM_i}\right)^{1/a}$	Intrinsic viscosity

Example 5.2.1 A solution contains equal number of particles with molar masses 10 000 g mol^{-1} and 20 000 g mol^{-1}, respectively. Calculate $\overline{M}_n$ and $\overline{M}_m$.

Solution By definition,

$$\overline{M}_n = \frac{N_1M_1+N_2M_2}{N_1+N_2}$$

Since $N_1 = N_2$, we have

$$\overline{M}_n = \frac{M_1+M_2}{2} = \frac{(10\,000+20\,000)\ \text{g mol}^{-1}}{2}$$

$$= 15\,000\ \text{g mol}^{-1}$$

By definition

$$\overline{M}_m = \frac{N_1M_1^2+N_2M_2^2}{N_1M_1+N_2M_2}$$

Since $N_1 = N_2$, we have

$$\overline{M}_m = \frac{M_1^2+M_2^2}{M_1+M_2} = \frac{[(10\,000)^2+(20\,000)^2]\ \text{g}^2\ \text{mol}^{-2}}{(10\,000+20\,000)\ \text{g mol}^{-1}}$$

$$= 16\,666.6\ \text{g mol}^{-1}$$

Example 5.2.2 A suspension contains equal masses of particles with molar masses 10 000 g mol^{-1} and 20 000 g mol^{-1}, respectively. Calculate $\overline{M}_n$ and $\overline{M}_m$.

Solution Since $m = nM = (N/N_A)M$, we have

$$N = (m/M)N_A$$

Hence, $$\overline{M}_n = \frac{N_1M_1 + N_2M_2}{N_1 + N_2} = \frac{\{(m_1/M_1)N_A\}M_1 + \{(m_2/M_2)N_A\}M_2}{(m_1/M_1)N_A + (m_2/M_2)N_A}$$

$$= \frac{m_1 + m_2}{(m_1/M_1) + (m_2/M_2)}$$

Since $m_1 = m_2$, we have

$$\overline{M}_n = \frac{1+1}{(1/M_1) + (1/M_2)} = \frac{2M_1M_2}{M_2 + M_1}$$

$$= \frac{2(10\,000\text{ g mol}^{-1})(20\,000\text{ g mol}^{-1})}{(20\,000 + 10\,000)\text{ g mol}^{-1}}$$

$$= 13\,333.3\text{ g mol}^{-1.}$$

$$\overline{M}_m = \frac{m_1M_1 + m_2M_2}{m_1 + m_2}$$

Since $m_1 = m_2$, we get

$$\overline{M}_m = \frac{M_1 + M_2}{2} = \frac{(10\,000 + 20\,000)\text{ g mol}^{-1}}{2}$$

$$= 15\,000\text{ g mol}^{-1}$$

Problem 5.2.1 Show that for a equimolar mixture of two substances

$$M_1 = \overline{M}_n + \left(\overline{M}_n\overline{M}_m - \overline{M}_n^2\right)^{1/2}$$

$$M_2 = \overline{M}_n - \left(\overline{M}_n\overline{M}_m - \overline{M}_n^2\right)^{1/2}$$

Solution We have

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2}{N_1 + N_2} = \frac{M_1 + M_2}{2}\,; \qquad (\text{since } N_1 = N_2)$$

$$\overline{M}_m = \frac{N_1M_1^2 + N_2M_2^2}{N_1M_1 + N_2M_2} = \frac{M_1^2 + M_2^2}{M_1 + M_2}\,; \qquad (\text{since } N_1 = N_2)$$

From these two expressions, we get

$$M_1 + M_2 = 2\,\overline{M}_n \tag{1}$$

$$M_1^2 + M_2^2 = \overline{M}_m\,(M_1 + M_2) = 2\,\overline{M}_n\overline{M}_m$$

Since $(M_1 + M_2)^2 = M_1^2 + M_2^2 + 2M_1M_2$, we have

$$2M_1M_2 = (M_1 + M_2)^2 - (M_1^2 + M_2^2)$$

$$= 4\,\overline{M}_n^2 - 2\,\overline{M}_n\overline{M}_m$$

Also $$(M_1 - M_2)^2 = (M_1 + M_2)^2 - 4M_1M_2$$

$$= 4\,\overline{M}_n^2 - 8\,\overline{M}_n^2 + 4\,\overline{M}_n\overline{M}_m$$

$$= 4\,\overline{M}_n\overline{M}_m - 4\,\overline{M}_n^2$$

This gives

$$M_1 - M_2 = 2\left(\overline{M}_n\overline{M}_m - \overline{M}_n^2\right)^{1/2} \qquad (2)$$

Solving M_1 and M_2 from Eqs (1) and (2), we get

$$M_1 = \overline{M}_n + \left(\overline{M}_n\overline{M}_m - \overline{M}_n^2\right)^{1/2}$$

$$M_2 = \overline{M}_n - \left(\overline{M}_n\overline{M}_m - \overline{M}_n^2\right)^{1/2}$$

Example 5.2.3 The Mark-Houwink exponent for poly(methylmethacrylate) has the value of 0.69 in acetone. Calculate the value of $\overline{M}_v$ that would be obtained with the following molar mass distribution if the sample was studied by the viscosity measurement.

$n_1 \times 10^3$/mol	1.2	2.7	4.9	3.1	0.9
$M_1 \times 10^{-5}$/g mol^{-1}	2.0	4.0	6.0	8.0	20.0

Solution Since

$$\overline{M}_v = \left(\frac{\sum_i N_i M_i^{1+a}}{\sum_i N_i M_i}\right)^{1/a} = \left(\frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i}\right)^{1/a}$$

we have

$$\begin{aligned}\sum_i n_i M_i^{1+a} &= [(1.2 \times 10^{-3})(2.0 \times 10^5)^{1.69} + (2.7 \times 10^{-3})(4.0 \times 10^5)^{1.69} \\ &\quad + (4.9 \times 10^{-3})(6.0 \times 10^5)^{1.69} + (3.1 \times 10^{-3})(8.0 \times 10^5)^{1.69} \\ &\quad + (0.9 \times 10^{-3})(20.0 \times 10^5)^{1.69}]\ \mathrm{g}^{1.69}\ \mathrm{mol}^{-0.69} \\ &= [1.091\,2 \times 10^6 + 7.922\,2 \times 10^6 + 2.852\,8 \times 10^7 + 2.934\,8 \times 10^7 \\ &\quad + 4.008\,5 \times 10^7]\ \mathrm{g}^{1.69}\ \mathrm{mol}^{-0.69} \\ &= 1.069\,7 \times 10^8\ \mathrm{g}^{1.69}\ \mathrm{mol}^{-0.69}\end{aligned}$$

$$\begin{aligned}\sum_i n_i M_i &= [(1.2 \times 10^{-3})(2.0 \times 10^5) + (2.7 \times 10^{-3})(4.0 \times 10^5) \\ &\quad + (4.9 \times 10^{-3})(6.0 \times 10^5) + (3.1 \times 10^{-3})(8.0 \times 10^5) \\ &\quad + (0.9 \times 10^{-3})(20.0 \times 10^5)]\ \mathrm{g} \\ &= [2.400\,0 \times 10^2 + 1.080\,0 \times 10^3 + 2.940\,0 \times 10^3 + 2.480\,0 \times 10^3 \\ &\quad + 1.800\,0 \times 10^3]\ \mathrm{g} \\ &= 8.540\,0 \times 10^3\ \mathrm{g}\end{aligned}$$

$$\overline{M}_v = \left(\frac{1.069\,7 \times 10^8\ \mathrm{g}^{1.69}\ \mathrm{mol}^{-0.69}}{8.5400 \times 10^3\ \mathrm{g}}\right)^{1/0.69} = (1.252\,5 \times 10^4)^{1.4493}\ \mathrm{g\ mol^{-1}}$$

$$= 8.68 \times 10^5\ \mathrm{g\ mol^{-1}}$$

5.3 DISTRIBUTION OF MOLECULAR SIZES IN STEP-GROWTH POLYMERIZATION

Consider the polymerization of molecules, each containing two active groups A and B (e.g. HO—$(CH_2)_n$—COOH) such that the end group A of a monomer gets attached to the end group B of another monomer in succession to form a polymer chain, represented as Ababab ... abaB. In this notations, the units a and b represent, respectively, the groups A and B which have undergone reactions to form ab linkages. For a chain containing k monomer molecules (known as $k$mer), there are $k-1$ number of units of a and one A group.

Let N_0 be the initial number of active groups A (which is also equal to the initial number of monomer molecules). At any extent of reaction, let N be the number of active groups A. It follows that

$$\text{Number of A groups undergone reactions} = N_0 - N$$

The fraction of groups A undergone reactions (known as *extent of polymerization*) is

$$p = \frac{N_0 - N}{N_0} = 1 - \frac{N}{N_0} \tag{5.3.1}$$

The fraction of groups A which remain unreacted is

$$1 - p = \frac{N}{N_0} \tag{5.3.2}$$

Probability of Forming $k$mer

The probability of each of the group A reacted to give a linkage ab in a polymer chain is taken to be equal to the fraction of groups A reacted, i.e. p. The probability of groups A remain unreacted will be equal to $1 - p$.

Since in a $k$mer, there are $k-1$ numbers of groups A reacted (to give $k-1$ number of ab linkages) and one group A unreacted, the probability of forming $k$mer is given by

$$P_k = p^{k-1}(1-p) \tag{5.3.3}$$

Identification of Probability with Number Fraction

Since the sum of probabilities (P_ks) and the number fractions (f_ks) of all possible $k$mer in solution are individually equal to one, i.e.

$$\textstyle\sum_k P_k = 1 \quad \text{and} \quad \sum_k f_k = 1 \tag{5.3.4}$$

we identify P_k equal to f_k. If N_k is the number of species that are k units long and N is the total number of species in the solution, then

$$P_k = f_k = \frac{N_k}{N} \tag{5.3.5}$$

Equating Eqs (5.3.3) and (5.3.5), we get

$$N_k = N p^{k-1}(1-p) \tag{5.3.6}$$

Average Value of k

The average value of k, known as *number average degree of polymerization*, is given by

$$k_{\text{av}} = \sum_{k=1}^{N_0} k P_k \tag{5.3.7}$$

where N_0 is the initial number of monomers. In Eq. (5.3.7), N_0 may be replaced by infinity as the value of P_k drops off rapidly with increasing value of k. Hence, we write Eq. (5.3.7) as

$$k_{\text{av}} = \sum_{k=1}^{\infty} k P_k \tag{5.3.8}$$

Making use of Eq. (5.3.5), the above expression becomes

$$k_{\text{av}} = \sum_{k=1}^{\infty} k\left(\frac{N_k}{N}\right) = \frac{1}{N} \sum_k kN_k \tag{5.3.9}$$

In terms of fraction p of molecules reacted (Eq. 5.3.3), the expression of k_{av} is

$$k_{\text{av}} = \sum_{k=1}^{\infty} kp^{k-1}(1-p) \tag{5.3.10}$$

$$= (1-p)\left(\sum_{k=1}^{\infty} kp^{k-1}\right) = (1-p)\left[\frac{1}{(1-p)^2}\right] \tag{5.3.11†}$$

$$= \frac{1}{1-p} \tag{5.3.12}$$

Total Number of Monomer Molecules

Since $k$mer contains k monomer molecules, the total number of monomer molecules to start with is given by

$$N_0 = \sum_{k=1}^{\infty} kN_k \tag{5.3.13}$$

Using Eq. (5.3.5), this becomes

$$N_0 = \sum_{k=1}^{\infty} k(NP_k) = N\sum_{k=1}^{\infty} kP_k. \tag{5.3.14}$$

which in view of Eq. (5.3.8) becomes

$$N_0 = Nk_{\text{av}} \tag{5.3.15}$$

Substituting k_{av} from Eq. (5.3.12), we get

$$N_0 = \frac{N}{1-p} \tag{5.3.16}$$

Number of $k$mer in Terms of Initial Number of Monomer Molecules

The number of $k$mer in terms of number N of species in the solution as given by Eq. (5.3.6) is

$$N_k = Np^{k-1}(1-p) \tag{5.3.17}$$

The number N in terms of N_0 is given by Eq. (5.3.16). Hence

$$N_k = N_0\, p^{k-1}(1-p)^2 \tag{5.3.18}$$

Number Average Molar Mass

If M_1 is the molar mass of repeating unit then the molar mass of $k$mer is given by

$$M_k = k\,M_1 + M_{\text{excess}} \tag{5.3.19}$$

where M_{excess} is the excess molar mass due to the presence of end groups.

[†] We know that $\sum_{k=0}^{\infty} p^k = 1 + p + p^2 + \cdots = \dfrac{1}{1-p}$

Differentiating both sides with respect to p, we get

$$\sum_{k=1}^{\infty} kp^{k-1} = \frac{1}{(1-p)^2}$$

The number average molar mass of the polymer is given by

$$\overline{M}_n = \frac{\sum_k N_k M_k}{\sum_k N_k}$$

Substituting M_k from Eq. (5.3.19), we get

$$\overline{M}_n = \frac{\sum_k N_k (kM_1 + M_{\text{excess}})}{\sum_k N_k}$$

$$= \frac{M_1 \sum_k N_k k + M_{\text{excess}} \sum_k N_k}{\sum_k N_k}$$

Since $\sum_k N_k = N$ and $\sum_k N_k k = N\,k_{\text{av}}$, we get

$$\overline{M}_n = M_1\,k_{\text{av}} + M_{\text{excess}} \qquad (5.3.20)$$

Substituting k_{av} from Eq. (5.3.12), we get

$$\overline{M}_n = \frac{M_1}{1-p} + M_{\text{excess}} \qquad (5.3.21)$$

Neglecting M_{excess} in comparison to $M_1/(1-p)$, we get

$$\overline{M}_n \doteq \frac{M_1}{1-p} \qquad (5.3.22)$$

Total Mass of the System

The total mass of the system is given by

$$m_{\text{total}} = \sum_{k=1}^{\infty} N_k \left(\frac{M_k}{N_{\text{A}}}\right); \qquad (N_{\text{A}} \text{ is Avogadro constant})$$

In terms of number average molar mass ($\overline{M}_n = \sum_k N_k M_k / N$), the above expression becomes

$$m_{\text{total}} = \frac{1}{N_{\text{A}}}(N\overline{M}_n)$$

Replacing N in terms of N_0 (Eq. 5.3.16), we get

$$m_{\text{total}} = \frac{1}{N_{\text{A}}}\,[N_0\,(1-p)]\,\overline{M}_n \qquad (5.3.23)$$

(Alternatively, $m_{\text{total}} = N_0\,(M_1/N_{\text{A}})$, which in view of Eq. (5.3.22) becomes $m_{\text{total}} = N_0\,(1-p)\,\overline{M}_n/N_{\text{A}}$.)

Mass Fraction of *k*mer

By definition

$$w_k = \frac{\text{Mass of } k\text{mer}}{\text{Total mass of the system}}$$

$$= \frac{N_k (M_k / N_{\text{A}})}{\sum_k N_k (M_k / N_{\text{A}})}$$

Using Eq. (5.3.18) for N_k, Eq. (5.3.19) for M_k and Eq. (5.3.23) for m_{total}, we get

$$w_k = \frac{[N_0 p^{k-1}(1-p)^2][(kM_1 + M_{\text{excess}})/N_A)}{N_0(1-p)\overline{M}_n/N_A}$$

$$= \frac{p^{k-1}(1-p)(kM_1 + M_{\text{excess}})}{\overline{M}_n} \qquad (5.3.24)$$

Substituting $\overline{M}_n$ from Eq. (5.3.21), we get

$$w_k = \frac{p^{k-1}(1-p)(kM_1 + M_{\text{excess}})}{M_1/(1-p) + M_{\text{excess}}} \qquad (5.3.25)$$

Neglecting M_{excess}, we get

$$w_k = k\,p^{k-1}(1-p)^2 \qquad (5.3.26)$$

Graphical display of w_k versus k

Figure 5.3.1 displays the plot of w_k versus k for the three larger values of p.

The main characteristics of Fig. 5.3.1 are as follows.

- The contributions from smaller and larger values of k are smaller than those of the intermediate values of k.
- The maximum in the plots is shifted to larger value of k with increasing value of p.

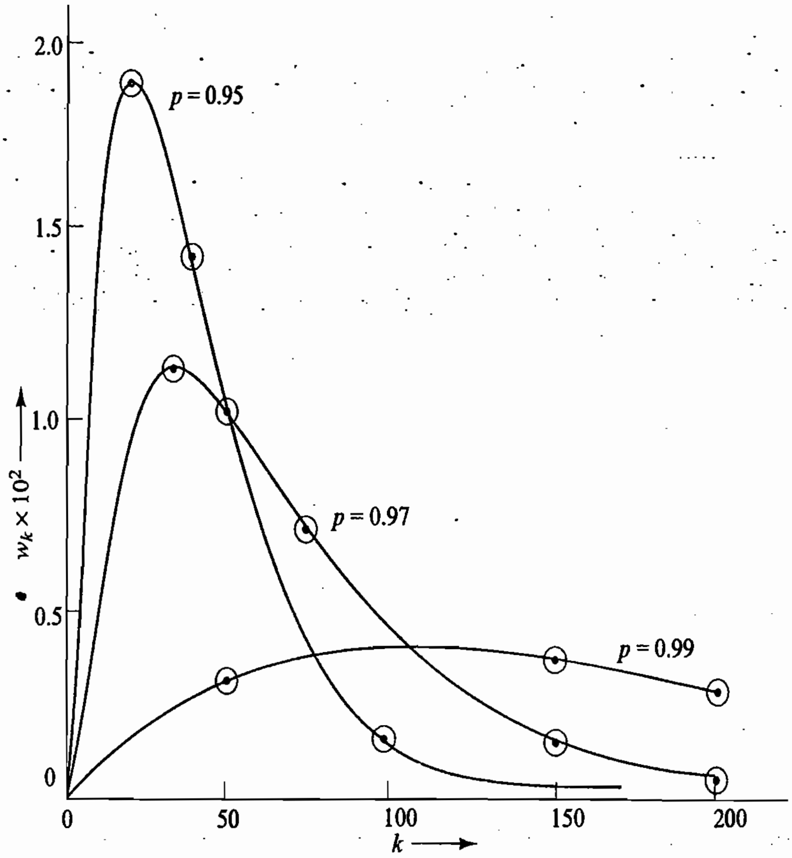


Fig. 5.3.1 Plot of w_k versus k

The value of k corresponding to $w_{\max}$ can be obtained by setting dw/dk equal to zero. Taking natural logarithm of Eq. (5.3.26), we get

$$\ln w_k = \ln k + (k-1)\ln p + 2\ln(1-p)$$

Differentiating this with respect to k keeping p constant, we get

$$\frac{1}{w_k}\left(\frac{\partial w_k}{\partial k}\right)_p = \frac{1}{k} + \ln p$$

This gives

$$\left(\frac{\partial w_k}{\partial k}\right)_p = w_k\left(\frac{1}{k} + \ln p\right) = [k\,p^{k-1}(1-p)^2]\left[\frac{1}{k} + \ln p\right]$$

Setting $\partial w_k/\partial k$ equal to zero, we get

$$k_{\max} = -\frac{1}{\ln p} \tag{5.3.27}$$

Hence for $p = 0.95$, 0.97 and 0.99, the values of $k_{\max}$ are 19.5, 32.8 and 99.5, respectively.

- The distribution becomes more broad with increasing value of p.

Mass Average Molar Mass

By definition

$$\bar{M}_m = \sum_k w_k M_k$$

Using Eq. (5.3.26) for w_k and Eq. (5.3.19) for M_k, we get

$$\bar{M}_m = \sum_k [kp^{k-1}(1-p)^2]\,[kM_1 + M_{\text{excess}}] \tag{5.3.28}$$

Ignoring M_{excess}, we get

$$\bar{M}_m = \left(\sum_k k^2 p^{k-1}\right)(1-p)^2 M_1 \tag{5.3.29†}$$

$$= \left[\frac{1+p}{(1-p)^3}\right](1-p)^2 M_1 = \frac{1+p}{1-p} M_1 \tag{5.3.30}$$

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† We have $\sum_k kp^{k-1} = 1/(1-p)^2$. Multiplying by p, we get

$$\sum_k kp^k = \frac{p}{(1-p)^2}$$

Differentiating both sides with respect to p, we get

$$\sum_k k^2 p^{k-1} = \frac{1}{(1-p)^2} + \frac{2p}{(1-p)^3} = \frac{1+p}{(1-p)^3}$$

Comparison between $\overline{M}_m$ and $\overline{M}_n$

From Eqs (5.3.22) and (5.3.30), we get

$$\frac{\overline{M}_m}{\overline{M}_n} = \frac{[(1+p)/(1-p)]M_1}{M_1/(1-p)} = 1 + p \tag{5.3.31}$$

For $p \simeq 1$, the value of $\overline{M}_m$ is twice that of $\overline{M}_n$.

Example 5.3.1

A hydroxyacid HO—$(CH_2)_5$ — COOH is polymerized and it is found that the product has a number average molar mass of 20 000 g mol^{-1}. (a) What is the extent of reaction p? (b) What is the degree of polymerization? (c) What is the mass average molar mass?

Solution

(a) From the expression $\overline{M}_n = M_1/(1-p)$, we get

$$p = 1 - M_1/\overline{M}_n = 1 - 132/20\,000 = 1 - 0.006\,6$$
$$= 0.993\,4$$

(b) $$k_{av} = 1/(1-p) = 1/(1 - 0.993\,4) = 151.5$$

(c) $$\overline{M}_m = \overline{M}_n(1+p)$$
$$= (20\,000 \text{ g mol}^{-1})\,(1 + 0.993\,4)$$
$$= 39\,868 \text{ g mol}^{-1}$$

5.4 END-TO-END DISTANCE IN A MACROMOLECULAR CHAIN

The statistical method has been used to describe the spatial configuration of macroscopic molecules. For a perfectly flexible one-dimensional chain of a macromolecule with negligible excluded volume of its repeat units (so that more than one repeat unit can be placed on the same site), the method adopted is known as *one-dimensional random walk.*

Description of One-Dimensional Random Walk

Let a chain involve n repeat linkages. It is built with the random placement of the successive repeat linkage in the increasing and decreasing directions of the chain. Let their respective numbers be n_1 and n_2, such that

$$n = n_1 + n_2 \tag{5.4.1}$$

The probability of occurrence of such a chain as given by Binomial distribution is given by

$$P = \left(\frac{n!}{n_1!n_2!}\right)\left(\frac{1}{2}\right)^{n_1}\left(\frac{1}{2}\right)^{n_2} \tag{5.4.2}$$

The first term in Eq. (5.4.2) gives the number of ways of selecting n_1 and n_2 out of the total of n repeat units and the factor 1/2 in the second and third terms is due to the fact that the placement of the successive repeat linkage in the increasing and decreasing directions of the chain is equally likely.

If l is the length of the repeat linkage, the displacement of the chain from the starting point (taken to be origin) is given by

$$x = (n_1 - n_2)\, l \qquad (5.4.3)$$

From Eqs (5.4.1) and (5.4.3), we get

$$n_1 = \frac{n + x/l}{2} \quad \text{and} \quad n_2 = \frac{n - x/l}{2}$$

Substituting these in Eq. (5.4.2), we get

$$P = \frac{n!}{\{(n + x/l)/2\}!\,\{(n - x/l)/2\}!}\left(\frac{1}{2}\right)^n \qquad (5.4.4)$$

Equation (5.4.4) is known as *Bernoulli's equation.*

For a polymer chain, n has a large value and thus Eq. (5.4.4) can be simplified by invoking Stirling approximation..

$$\ln y! = y \ln y - y \qquad (5.4.5)$$

Taking logarithm of Eq. (5.4.4) and using Stirling approximation, we get

$$\ln P = (n \ln n - n) - \left[\frac{n}{2}\left(1 + \frac{x}{nl}\right)\ln\left\{\frac{n}{2}\left(1 + \frac{x}{nl}\right)\right\} - \frac{n}{2}\left(1 + \frac{x}{nl}\right)\right]$$

$$- \left[\frac{n}{2}\left(1 - \frac{x}{nl}\right)\ln\left\{\frac{n}{2}\left(1 - \frac{x}{nl}\right)\right\} - \frac{n}{2}\left(1 - \frac{x}{nl}\right)\right] - n \ln 2$$

$$\doteq -\frac{n}{2}\left(1 + \frac{x}{nl}\right)\ln\left(1 + \frac{x}{nl}\right) - \frac{n}{2}\left(1 - \frac{x}{nl}\right)\ln\left(1 - \frac{x}{nl}\right) \qquad (5.4.6)$$

Since $x \ll nl$, we can approximate logarithm terms as

$$\ln\left(1 \pm \frac{x}{nl}\right) \simeq \pm\frac{x}{nl} - \frac{1}{2}\left(\frac{x}{nl}\right)^2$$

With this, Eq. (5.4.6) is reduced to

$$\ln P = -\frac{n}{2}\left(1 + \frac{x}{nl}\right)\left\{\frac{x}{nl} - \frac{1}{2}\left(\frac{x}{nl}\right)^2\right\} - \frac{n}{2}\left(1 - \frac{x}{nl}\right)\left\{-\frac{x}{nl} - \frac{1}{2}\left(\frac{x}{nl}\right)^2\right\}$$

which on simplification gives

$$\ln P = -\frac{x^2}{2nl^2} - \frac{n}{2}\left(\frac{x}{nl}\right)^3 \qquad (5.4.7)$$

Retaining only the first term, Eq. (5.4.7) may be written as

$$\ln P = -\frac{x^2}{2nl^2} + \text{constant} \qquad (5.4.8)$$

The expression of probability function may be written as

$$P = k \exp(-x^2/2nl^2) \qquad (5.4.9)$$

where k is a constant known as a normalization factor. Since x can have any value, the normalization factor is obtained from the expression

$$k \int_{-\infty}^{+\infty} \exp(-x^2/2nl^2)\, \mathrm{d}x = 1$$

This gives

$$k\,(2\pi n l^2)^{1/2} = 1 \qquad \text{i.e.} \qquad k = 1/(2\pi n l^2)^{1/2}$$

Hence, the probability function of locating the growing end of the chain at the distance x from the origin (i.e. the starting point) is given by

$$P = \frac{1}{(2\pi n l^2)^{1/2}} \exp\left(-\frac{x^2}{2nl^2}\right) \tag{5.4.10}$$

The probability that the growing end lies in between x and $x + \mathrm{d}x$ is

$$P\,\mathrm{d}x = \frac{1}{(2\pi n l^2)^{1/2}} \exp\left(-\frac{x^2}{2nl^2}\right) \mathrm{d}x \tag{5.4.11}$$

Computation of Mean Square End-to-End Distance

The mean square end-to-end distance of a one-dimensional flexible chain is given by

$$\overline{x^2} = \int_{-\infty}^{+\infty} P\,x^2\,\mathrm{d}x = \frac{1}{(2\pi n l^2)^{1/2}} \int_{-\infty}^{+\infty} x^2 \exp(-x^2/2nl^2)\,\mathrm{d}x$$

$$= \frac{1}{(2\pi n l^2)^{1/2}} \left[\frac{1}{2(1/2nl^2)}\left(\frac{\pi}{1/2nl^2}\right)^{1/2}\right]$$

$$= nl^2 \tag{5.4.12}$$

Extension to Three-Dimensional Chains

Since x, y, z-directions in a three-dimensional space are equally probable, a three-dimensional perfectly flexible chain consisting of n repeat linkages with zero excluded volume may be considered to contain $n/3$ repeat linkages growing in each of the three directions. If the chain is considered to start from the origin (0, 0, 0), the probability that the growing end of the chain lies within the infinitesimal volume $\mathrm{d}x\mathrm{d}y\mathrm{d}z$ situated at the point (x, y, z) will be equal to the product of probabilities of

(i) the growing end of the $n/3$ repeat linkages in the x-direction has the coordinates between x and $x + \mathrm{d}x$,

(ii) the growing end of the $n/3$ repeat linkages in the y-direction has the coordinates between y and $y + \mathrm{d}y$, and

(iii) the growing end of the $n/3$ repeat linkages in the z-direction has the coordinates between z and $z + \mathrm{d}z$.

Since Eq. (5.4.8) is applicable to each of the three directions, we have

$$P(x, y, z, n)\,\mathrm{d}x\mathrm{d}y\mathrm{d}z = \{P(x, n/3)\,\mathrm{d}x\}\;\{P(y, n/3)\,\mathrm{d}y\}\;\{P(z, n/3)\,\mathrm{d}z\}$$

$$= \left[\frac{1}{\{2\pi(n/3)l^2\}^{1/2}}\exp\left(-\frac{x^2}{2(n/3)l^2}\right)\mathrm{d}x\right]\left[\frac{1}{\{2\pi(n/3)l^2\}^{1/2}}\right.$$

$$\left.\times \exp\left(-\frac{y^2}{2(n/3)l^2}\right)\mathrm{d}y\right]\left[\frac{1}{\{2\pi(n/3)l^2\}^{1/2}}\exp\left(-\frac{z^2}{2(n/3)l^2}\right)\mathrm{d}z\right]$$

i.e. $$P\,\mathrm{d}x\mathrm{d}y\mathrm{d}z = \left(\frac{3}{2\pi nl^2}\right)^{3/2} \exp\left(-\frac{3(x^2+y^2+z^2)}{2nl^2}\right) \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$

In spherical polar coordinates, we have

$$P\,\mathrm{d}\tau = \left(\frac{3}{2\pi nl^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2nl^2}\right) r^2\,\mathrm{d}r \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

Since the growing end can lie anywhere all around the origin, we will have

$$P\,\mathrm{d}r = \left(\frac{3}{2\pi nl^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2nl^2}\right) r^2\,\mathrm{d}r \int_0^{\pi} \sin\theta\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\varphi$$

$$= \left(\frac{3}{2\pi nl^2}\right)^{3/2} 4\pi r^2 \exp\left(-\frac{3r^2}{2nl^2}\right) \mathrm{d}r \qquad (5.4.13)$$

The probability function for the end-to-end distance r is the product of two r–dependent terms, namely, r^2 and $\exp(-3r^2/2nl^2)$. For the lower values of r, the term r^2 predominates over the exponential term while for the larger value of r, the reverse is true. Consequently, the probability function initially increases and after passing through maximum, it starts decreasing with increasing value of r.

The mean square end-to-end distance is given by

$$\overline{r^2} = \int_0^{\infty} r^2\,(P\,\mathrm{d}r) = 4\pi \left(\frac{3}{2\pi nl^2}\right)^{3/2} \int_0^{\infty} r^4 \exp\left(-\frac{3r^2}{2nl^2}\right) \mathrm{d}r$$

$$= 4\pi \left(\frac{3}{2nl^2}\right)^{3/2} \left[\frac{n^2l^4}{6}\left(\frac{2\pi nl^2}{3}\right)^{1/2}\right]$$

$$= nl^2 \qquad (5.4.14)$$

Average End-to-End Distance for Polymethylene Chain with Free Rotation about the Bond

The expression of end-to-end distance for a polymethylene chain with free rotation about the C—C bond is given by

$$\overline{r^2} = Nl^2 \left(\frac{1+\cos\theta}{1-\cos\theta}\right) \qquad (5.4.15)^{\dagger}$$

where l is the length of C—C bond, N is the number of linkages and θ is the angle between the positive directions of successive bonds. It has a value of 180° – 109°28° = 70°32′.

Substituting cos 70°32′ = 0.333 in Eq. (5.4.15), we get

$$\overline{r^2} = 2\,Nl^2 \qquad (5.4.16)$$

which is twice that for an unrestricted polymer chain.

[†] See Annexure I at the end of the chapter for the derivation of Eq. (5.4.15).

If the rotation about C—C bond is also restricted within the angle φ, then Eq. (5.4.15) takes the form of

$$\overline{r^2} = N l^2 \left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\overline{\cos\varphi}}{1-\overline{\cos\varphi}}\right) \tag{5.4.17}$$

where $\overline{\cos\varphi}$ is the average value of $\cos\varphi$.

Example 5.4.1 Calculate the most probable end-to-end distance of a polymer chain $C_{20}H_{42}$, given that the C—C bond length is 154 pm and the bond angle is 109°28′. What would be the distance if the polymer chain is considered completely flexible?

Solution In $C_{20}H_{42}$ molecule, there will be 19 repeat linkages. Hence

$$\overline{r^2} = N l^2 \,\frac{1+\cos\theta}{1-\cos\theta}$$

$$= (19)\,(154\text{ pm})^2 \left[\frac{1+\cos(180°-109°28')}{1-\cos(180°-109°28')}\right]$$

$$= (19)\,(154\text{ pm})^2 \left(\frac{1+0.333}{1-0.333}\right)$$

$$= (19)\,(154\text{ pm})^2\,(2) = 901\,208\text{ pm}^2$$

Hence, $\sqrt{\overline{r^2}} = 949.3\text{ pm}$

For a completely flexible polymer chain

$$\overline{r^2} = N l^2 = 19\,(154\text{ pm})^2 = 450\,604\text{ pm}^2$$

Hence, $\sqrt{\overline{r^2}} = 671.3\text{ pm}$

5.5 OSMOTIC PRESSURE FOR THE MEASUREMENT OF MOLAR MASS

Expression of Osmotic Pressure for a Dilute Solution

Osmotic pressure is one of the four colligative properties which is used to determine the number average molar mass of a sample of polymer. The other three properties (namely, the relative lowering of vapour pressure, elevation of the boiling point and depression of the freezing point of a solvent) are not as sensitive as the osmotic pressure and hence are not used for this purpose.

The thermodynamic derivation of osmotic pressure of a solution results into the expression

$$\Pi\, V_{1,\mathrm{m}}^{*} = -RT \ln a_1 \tag{5.5.1}$$

where $V_{1,\mathrm{m}}^{*}$ is the molar volume of the solvent and a_1 is its activity in the solution.

For a dilute solution, Eq. (5.5.1) is simplified by using the following approximations.

1. The activity a_1 of the solvent is equal to its amount fraction, i.e. $a_1 \simeq x_1$, such that

$$\ln a_1 \simeq \ln x_1 \tag{5.5.2}$$[†]

[†] Throughout, the solvent is represented by the subscript 1 and solute by the subscript 2.

2. Since in a solution $x_1 + x_2 = 1$, we can write

$$\ln x_1 = \ln(1 - x_2)$$
$$= -\left(x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + \cdots\right) \qquad (5.5.3)$$

For a dilute solution, we retain only the first term on the right side. Hence

$$\ln x_1 \simeq -x_2 \qquad (5.5.4)$$

3. Since the solution is dilute, we will have $n_2 \ll n_1$. Hence, we write

$$x_2 = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1} \qquad (5.5.5)$$

4. For the dilute solution, we also have

$$V = n_1 V_{1,\,\mathrm{pm}} + n_2 V_{2,\,\mathrm{pm}} \simeq n_1 V_{1,\,\mathrm{pm}} \simeq n_1 V_{1,\mathrm{m}}^* \qquad (5.5.6)$$

where the subscript pm stands for partial molar and $V_{1,\mathrm{m}}^*$ is the molar volume of pure solvent.

With these approximations, Eq. (5.5.1) is modified to

$$\Pi\left(\frac{V}{n_1}\right) = -RT\left(-\frac{n_2}{n_1}\right)$$

i.e.
$$\Pi = \left(\frac{n_2}{V}\right) RT = c_2\, RT \qquad (5.5.7)$$

Expression of Osmotic Pressure for a Polymer Solution

A polymer solution does not behave as an ideal solution, probably due to the large difference in molecular volumes between polymeric solute and low molecular-mass solvent. This fact is taken into account by not truncating Eq. (5.5.3) to the first term, and thus Eq. (5.5.1) is expressed as

$$\Pi V_{1,\mathrm{m}}^* = RT\left(x_2 + \frac{1}{2}B'x_2^2 + \frac{1}{3}C'x_2^3 + \cdots\right) \qquad (5.5.8)$$

where B' and C' are respectively known as the second and third virial coefficients.

If the solution concentration is expressed as mass of solute per unit volume of solution, we will have

$$x_2 \simeq \frac{n_2}{n_1} \qquad \text{(Eq. 5.5.5)}$$

which on using the expressions $n_2 = m_2/M_2$ and $n_1 = V/V_{1,\mathrm{m}}^*$ (Eq. 5.5.6), becomes

$$x_2 = \frac{m_2/M_2}{V/V_{1,\mathrm{m}}^*} = \frac{(m_2/V)V_{1,\mathrm{m}}^*}{M_2} = \frac{c_2 V_{1,\mathrm{m}}^*}{M_2} \qquad (5.5.9)$$

Substituting Eq. (5.5.9) in Eq. (5.5.8), we get

$$\Pi V_{1,\mathrm{m}}^* = RT\left[\frac{c_2 V_{1,\mathrm{m}}^*}{M_2} + \frac{1}{2}B'\left(\frac{c_2 V_{1,\mathrm{m}}^*}{M_2}\right)^2 + \cdots\right]$$

or $$\frac{\Pi}{c_2RT} = \frac{1}{M_2} + \frac{1}{2}\left(\frac{B'V^*_{1,\mathrm{m}}}{M_2^2}\right)c_2 + \cdots$$

$$= \frac{1}{M_2} + B\,c_2 + \cdots \tag{5.5.10}$$

Retaining only the first two terms on right side as the higher terms are insignificant, we get

$$\frac{\Pi}{c_2RT} = \frac{1}{M_2} + Bc_2 \tag{5.5.11}$$

Equation (5.5.11) predicts that for a dilute nonideal solution, the graph between Π/c_2RT and c_2 is linear with slope equal to the second virial coefficient B and intercept equal to the inverse of molar mass M_2 of the solute.

Alternatively, one can plot Π/c_2 (known as reduced osmotic pressure) versus c_2. The slope and intercept of this plot is BRT and RT/M_2, respectively.

Nature of Molar Mass

For a polydisperse solute such as polymer, we will have

$$x_2 \approx \frac{\sum_i n_{2,i}}{n_1} = \frac{\sum_i n_{2,i}}{V/V^*_{1,m}} \tag{5.5.12}$$

The mass of polymer per unit volume of the solution is given by

$$c_2 = \sum_i c_{2,i} = \frac{\sum_i m_{2,i}}{V} = \frac{\sum_i n_{2,i}\,M_{2,i}}{V} \equiv \left(\frac{\sum_i n_{2,i}\,M_{2,i}}{\sum_i n_{2,i}}\right)\left(\frac{\sum_i n_{2,i}}{V}\right)$$

$$= \overline{M}_n\left(\frac{\sum_i n_{2,i}}{V}\right)$$

or $$\sum_i n_{2,i} = \frac{c_2V}{\overline{M}_n} \tag{5.5.13}$$

Substituting Eq. (5.5.13) in Eq. (5.5.12), we get

$$x_2 = \frac{c_2}{\overline{M}_n}V^*_{1,\mathrm{m}} \tag{5.5.14}$$

Substituting Eq. (5.5.14) in Eq. (5.5.8), we get

$$\Pi V^*_{1,\mathrm{m}} = RT\left[\frac{c_2V^*_{1,\mathrm{m}}}{\overline{M}_\mathrm{n}} + \frac{1}{2}B'\left(\frac{c_2V^*_{1,\mathrm{m}}}{\overline{M}_\mathrm{n}}\right)^2 + \cdots\right]$$

i.e. $$\frac{\Pi}{c_2RT} = \frac{1}{\overline{M}_n} + \frac{1}{2}\left(\frac{B'V^*_{1,\mathrm{m}}}{\overline{M}_\mathrm{n}^2}\right)c_2 + \cdots$$

$$= \frac{1}{\overline{M}_n} + B\,c_2 + \cdots \tag{5.5.15}$$

Retaining only the first two terms on right sight of Eq. (5.5.15), we get

$$\frac{\Pi}{c_2RT} = \frac{1}{\overline{M}_n} + Bc_2 \tag{5.5.16}$$

Hence, the graph between Π/c_2RT and c_2 provides the number average molar mass of the polysystem from the intercept which is equal to $1/\overline{M}_n$. The slope of the graph gives the value of second virial coefficient. It can be shown that the second virial coefficient is related to the excluded volume (symbol: u) of the solute through the expression

$$B = \frac{1}{2}\,\frac{N_A u}{M_2^2} \tag{5.5.17}$$

Example 5.5.1

The following data were obtained for the osmotic pressure of nitrocellulose in acetone at 20 °C.

$c/\mathrm{g\,L^{-1}}$	1.16	3.66	8.38	19.0
$\Pi/\mathrm{cmH_2O}$	0.69	2.56	7.52	25.4

Calculate the limiting value of Π/c and $\overline{M}_n$. Also calculate the value of second virial coefficient.

Solution

From the given data, we have

$10^3\,c/\mathrm{g\,cm^{-3}}$	1.16	3.66	8.38	19.0
$\Pi'(=\Pi\rho_{\mathrm{H_2O}}g)/\mathrm{dyn\,cm^{-2}}$	676.6	2 510	7 374	24 907
$10^{-3}\,(\Pi'/c)/\mathrm{erg\,g^{-1}}$	583	686	879	1311

The plot of Π'/c versus c is shown in Fig. 5.5.1. Its slope = 40.54 and intercept = 520. Thus, we have

$$\frac{\Delta(10^{-3}\Pi'/c)/\mathrm{erg\,g^{-1}}}{\Delta(10^3 c)/\mathrm{g\,cm^{-3}}} = 40.54 \quad\Rightarrow\quad \frac{\Delta(\Pi'/c)}{\Delta c} = 40.56\times10^6\ \mathrm{erg\,cm^3\,g^{-2}}$$

$$\text{Intercept} = 520\times10^3\ \mathrm{erg\,g^{-1}}$$

$$\text{Hence,}\quad \overline{M}_n = \frac{RT}{\text{Intercept}} = \frac{(8.314\times10^7\ \mathrm{erg\,K^{-1}\,mol^{-1}})(293\ \mathrm{K})}{520\times10^3\ \mathrm{erg\,g^{-1}}}$$

$$= 46\,846\ \mathrm{g\,mol^{-1}} \simeq 47\,000\ \mathrm{g\,mol^{-1}}$$

The value of second virial coefficient is

$$B = \text{slope} = 40.54\times10^6\ \mathrm{erg\,cm^3\,g^{-2}}$$

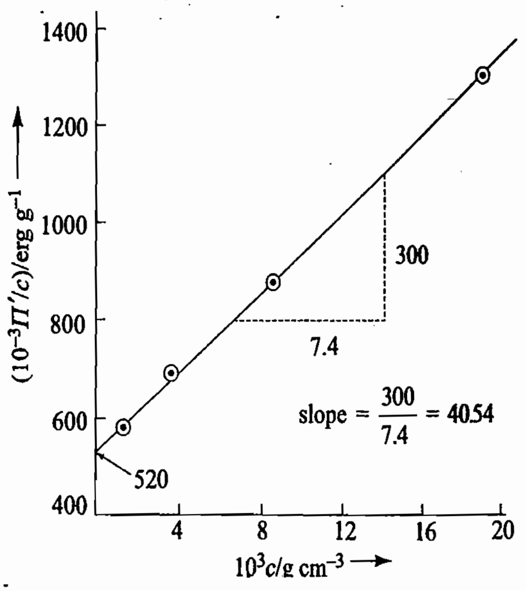


Fig. 5.5.1

5.6 VISCOSITY FOR THE MEASUREMENT OF MOLAR MASS

Definition of Viscosity

Suppose a fluid capable of flowing in a set of infinitesimal thin layers be placed between two rigid parallel plates of area A. Let a shear force F_s be applied at the top of the surface as shown in Fig. 5.6.1. When the system acquires stationary state, there exists a velocity gradient ($= \Delta v/\Delta y$, also known as shear strain) between the layers of the fluid. The lowest layer in touch with the plate remains stationary (see Fig. 5.6.1).

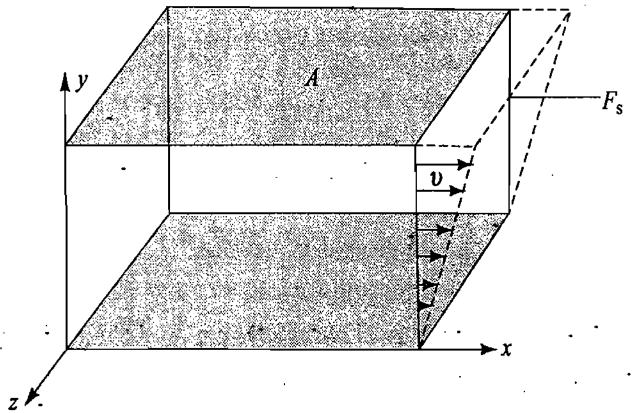


Fig. 5.6.1 Shear force F_s applied to a fluid

By definition, the viscosity of the fluid is defined as

$$\eta = \frac{\text{shear stress}}{\text{shear strain}}$$

$$= \frac{F_s/A}{\Delta v/\Delta y} \tag{5.6.1}$$

Equation (5.6.1) is known as Newton's law of viscosity.

Unit of Viscosity

In CGS system, we have

$$\text{unit of viscosity} = \frac{\text{dyn/cm}^2}{(\text{cm s}^{-1})/\text{cm}} = \text{dyn cm}^{-2}\,\text{s}$$

Since 1 dyn = 1 g cm s^{-2}, we have

$$\text{unit of viscosity} = (\text{g cm s}^{-2})\,(\text{cm}^{-2}\,\text{s}) = \text{g cm}^{-1}\,\text{s}^{-1}$$

The unit 1 g cm^{-1} s^{-1} is known as 1 poise (= 1 P).

In SI units,

$$\text{unit of viscosity} = \frac{\text{N/m}^2}{(\text{m s}^{-1})/\text{m}} = \text{N m}^{-2}\,\text{s}$$

Obviously,

$$1\ \text{N m}^{-2}\,\text{s} \equiv 1\ (\text{kg m s}^{-2})\,(\text{m}^{-2}\,\text{s}) = 1\ \text{kg m}^{-1}\,\text{s}^{-1}$$

Also $\quad 1\ \text{kg m}^{-1}\,\text{s}^{-1} \equiv 1\ (10^3\ \text{g})\,(10^2\ \text{cm})^{-1}\,\text{s}^{-1} = 10\ \text{g cm}^{-1}\,\text{s}^{-1} = 10\ \text{P}$

Definition of Viscosity in Terms of Energy Dissipation

The deforming force which induces flow in liquid is not recovered when the force is removed. The force imparts kinetic energy to the fluid, an energy which is dissipated within the fluid. The viscosity represents an internal friction which resists the flow of the fluid. This friction is due to molecular interactions during the flow of the fluid.

The viscosity may be expressed in terms of the rate of shear energy dissipated per unit volume of the fluid. This follows from the following identity.

$$\frac{F}{A}\frac{\Delta v}{\Delta y} \equiv \frac{F}{A}\frac{(\Delta x/\Delta t)}{\Delta y} \equiv \frac{(F\Delta x)/\Delta t}{(A\Delta y)} \equiv \frac{(\Delta U/\Delta t)}{\Delta V}$$

$$\equiv \frac{(\Delta U/\Delta V)}{\Delta t} \equiv \frac{\Delta W}{\Delta t} \tag{5.6.2}$$

where ΔW is the energy dissipated per unit volume. We can write Eq. (5.6.1) as

$$\frac{F}{A} = \eta\,\frac{\Delta v}{\Delta y}.$$

Multiplying both sides by $\Delta v/\Delta y$, we get

$$\frac{F}{A}\,\frac{\Delta v}{\Delta y} = \eta\left(\frac{\Delta v}{\Delta y}\right)^2$$

which on using Eq. (5.6.2) becomes

$$\frac{\Delta W}{\Delta t} = \eta\left(\frac{\Delta v}{\Delta y}\right)^2 \tag{5.6.3}$$

Equations (5.6.1) and (5.6.3) require that the velocity gradient is uniform throughout the fluid. Since this may not be the case over macroscopic distances, we write Eqs (5.6.1) and (5.6.3) for infinitesimal distances as

$$\eta = \frac{F_s/A}{\mathrm{d}v/\mathrm{d}y} \quad \text{and} \quad \eta = \frac{\mathrm{d}W/\mathrm{d}t}{(\mathrm{d}v/\mathrm{d}y)^2} \tag{5.6.4}$$

Viscosity of a Dilute Solution Involving Spherical Solute

For a dilute solution involving spherical solute, the shear force required to impart the potential gradient identical to that for pure solvent is found to be greater than that required for the pure solvent and is given by the expression

$$F_{\text{solution}} = \frac{F_{\text{solvent}}}{1-\phi} \tag{5.6.5}$$

where ϕ is the volume fraction of solute particles in the solution. For a solution, we have

$$\eta_{\text{solution}} = \frac{F_{\text{solution}}/A}{\mathrm{d}v/\mathrm{d}y} = \frac{1}{1-\phi}\,\frac{F_{\text{solvent}}/A}{\mathrm{d}v/\mathrm{d}y} = \frac{1}{1-\phi}\,\eta_{\text{solvent}} \tag{5.6.6}$$

Since $\phi < 1$, $\eta_{\text{solution}} > \eta_{\text{solvent}}$.

The more involved consideration of individual spherical particles of solute requires the addition of one more term in Eq. (5.6.6). The modified expression is

$$\eta_{\text{solution}} = \frac{\eta_{\text{solvent}}}{1-\phi} + \frac{1.5\phi\,\eta_{\text{solvent}}}{(1-\phi)^2}$$

$$= \frac{1+0.5\phi}{(1-\phi)^2}\,\eta_{\text{solvent}} \qquad (5.6.7)$$

The alternative form of Eq. (5.6.7) is obtained by the following replacement.

$$\frac{1}{(1-\phi)^2} = (1-\phi)^{-2} = (1+\phi+\phi^2+\cdots)^2$$

Hence, $\eta_{\text{solution}} = (1+0.5\phi)(1+\phi+\phi^2+\cdots)^2\,\eta_{\text{solvent}}$

$$= (1+2.5\phi+4\phi^2+\cdots)\,\eta_{\text{solvent}} \qquad (5.6.8)$$

Equation (5.6.8) is known as *Einstein's equation* for the viscosity of a solution.

Viscosity of a Polymer Solution

While dealing with a polymer solution, the solute concentration is usually expressed in terms of mass per unit volume. We can express volume fraction of solute in terms mass per unit volume of solution as follows.

We have

$$\phi = \frac{n_2V_{2,\text{pm}}}{n_1V_{1,\text{pm}} + n_2V_{2,\text{pm}}} \qquad (5.6.9)$$

For a dilute solution, this is simplified as

$$\phi \simeq \frac{n_2V_{2,\text{pm}}}{n_1V_{1,\text{pm}}} \simeq \frac{(m_2/M_2)V_{2,\text{pm}}}{V} \qquad (V \text{ is the volume of solution})$$

$$= \left(\frac{m_2}{V}\right)\left(\frac{V_{2,\text{pm}}}{M_2}\right) = c_2\left(\frac{V_{2,\text{pm}}}{M_2}\right) \qquad (5.6.10)$$

Substituting Eq. (5.6.10) in Eq. (5.6.8), we get

$$\eta_{\text{solution}} = \left[1 + 2.5c_2\left(\frac{V_{2,\text{pm}}}{M_2}\right) + 4c_2^2\left(\frac{V_{2,\text{pm}}}{M_2}\right)^2 + \cdots\right]\eta_{\text{solvent}} \qquad (5.6.11)$$

The above expression is a special case of the expression

$$\eta = \eta_0 + B\,c_2 + C\,c_2^2 + \cdots \qquad (5.6.12)$$

where the constants B, C, ... are determined by fitting the experimental data on the variation of viscosity with concentration of the solution and η_0 is the viscosity of the pure solvent.

Definitions of a few Terms

While dealing with the data on viscosity, the following terms are often used.

Relative Viscosity This is defined as

$$\eta_r = \frac{\eta}{\eta_0} \tag{5.6.13}$$

From Eq. (5.6.12), we get

$$\eta_r = 1 + B'c_2 + C'c_2^2 + \cdots \tag{5.6.14}$$

The IUPAC name of η_r is the *viscosity ratio*.

Specific Viscosity This is defined as

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 \tag{5.6.15}$$

From Eq. (5.6.14), we get

$$\eta_{sp} = B'c_2 + C'c_2^2 + \cdots \tag{5.6.16}$$

Reduced Viscosity This is defined as

$$\eta_{red} = \frac{1}{c_2}\left(\frac{\eta}{\eta_0} - 1\right) = \frac{\eta_{sp}}{c_2} \tag{5.6.17}$$

From Eq. (5.6.16), we get

$$\eta_{red} = B' + C'c_2 + \cdots \tag{5.6.18}$$

The IUPAC name of η_{red} is the *viscosity number*.

Intrinsic Viscoisity This is defined as

$$[\eta] = \lim_{c_2 \to 0} \eta_{red} \tag{5.6.19}$$

From Eq. (5.6.18), we find that

$$[\eta] = B' \tag{5.6.20}$$

The value of intrinsic viscosity is obtained by determining the value of intercept of the graph of η_{red} versus c_2. The intrinsic viscosity is often used as its value directly reflects the molecular properties of the solute. The IUPAC name of $[\eta]$ is the *limiting viscosity number*.

According to Eq. (5.6.11), the intrinsic viscosity is given by

$$[\eta] = \lim_{c_2 \to 0} \frac{1}{c_2}\left(\frac{\eta}{\eta_0} - 1\right) = 2.5\,\frac{V_{2,\mathrm{pm}}}{M_2} \tag{5.6.21}$$

where η and η_0 are viscosities of solution and solvent, respectively.

Assuming the macromolecule to be globular, its radius of gyration can be computed from the expression

$$[\eta] = \frac{2.5N_A}{M_2}\left(\frac{4}{3}\pi \overline{r_g^2}\right)^{3/2} \tag{5.6.22}$$

Inherent Viscosity This is defined as

$$\eta_{\text{inh}} = \frac{1}{c_2} \ln \left(\frac{\eta}{\eta_0} \right) \tag{5.6.23}$$

From Eq. (5.6.14), we get

$$\eta_{\text{inh}} = \frac{1}{c_2} \ln (1 + B' c_2 + C' c_2^2 + \cdots) \tag{5.6.24}$$

A graph between η_{inh} and c_2 also provides the intrinsic viscosity when extrapolated to $c_2 \rightarrow 0$. The IUPAC name of η_{inh} is the *logarithmic viscosity number*.

The Mark-Houwink Equation The intrinsic viscosity of a polymer solution is found to increase with increase in the average molar mass of the polymer. This dependence is expressed as

$$[\eta] = k\overline{M}^a \tag{5.6.25}$$

Equation (5.6.25) is known as the Mark-Houwink equation. The constants k and a are known as the Mark-Houwink constants for a system. The values of k and a depend on the (i) nature of polymer, (ii) nature of the solvent, and (iii) temperature. In Eq. (5.6.25), both $[\eta]$ and k are expressed in the same unit (say, $\text{cm}^3\ \text{g}^{-1}$; dL g^{-1}). The molar mass $\overline{M}$ carries the unit of mass used in the concentration term appeared in the quantity $[\eta]$.

The extensive tabulations of k and a are available in the literature.

The average molar mass referred to in Eq. (5.6.25) is the viscosity average defined earlier in Eq. (5.2.13). This follows from the following analysis.

Since $[\eta]$ is a limiting value as $c_2 \rightarrow 0$, the concentration effect it contains can be written as

$$[\eta] = \frac{\eta_{\text{sp}}}{c_2} \tag{5.6.26}$$

For a polydisperse system, we also have

$$\eta_{\text{sp}} = \sum_i \eta_{\text{sp},i} = \sum_i c_i[\eta]_i = \sum_i c_i\, (kM_i^a)$$

$$c_2 = \sum_i c_i$$

Hence, $$[\eta] = \frac{\sum_i c_i(kM_i^a)}{\sum_i c_i} \tag{5.6.27}$$

But $[\eta] = k\overline{M}^a$. Hence

$$\overline{M}^a = \frac{\sum_i c_i M_i^a}{\sum_i c_i} \tag{5.6.28}$$

Since c_i's are mass per unit volume, the above expression can be written as

$$\overline{M}^a = \frac{\sum_i m_i M_i^a}{\sum_i m_i} \tag{5.6.29}$$

where m_i is the mass of the ith category of the polymer having molar mass M_i. Since $m_i = (N_i/N_A)\, M_i$, we get

$$\overline{M}_{\mathrm{v}} = \left(\frac{\sum_i N_i M_i^{1+a}}{\sum_i N_i M_i} \right)^{1/a} \qquad (5.6.30)$$

In general $\overline{M}_n > \overline{M}_{\mathrm{v}} > \overline{M}_m$. For $a = 1$, $\overline{M}_{\mathrm{v}} = \overline{M}_m$. For most polymer system, the value a lies in the range 0.5–1.0.

Example 5.6.1 The relative viscosities of solutions of a sample of polystyrene in toluene were determined with an Ostwald viscometer at 25 °C.

$c/10^{-2}$ g cm^{-3}	0.249	0.499	0.999	1.998
η/η_0	1.355	1.782	2.879	6.090

If the values of the Mark-Houwink constants are $k = 3.7 \times 10^{-2}\ \mathrm{g}^{-(1+a)}\ \mathrm{cm}^3\ \mathrm{mol}^a$ and $a = 0.62$ for this polymer, when the concentrations are expressed in g cm^{-3}, calculate the molar mass.

Solution From the given values, we calculate the values of η_{sp}/c and then plot η_{sp}/c versus c to get the intercept at $c \to 0$. The obtained values η_{sp}/c are as follows.

$c/10^{-2}$ g cm^{-3}	0.249	0.499	0.999	1.998
η/η_0	1.335	1.782	2.879	6.90
η_{sp}	0.335	0.782	1.879	5.90
$\eta_{\mathrm{sp}}/(c/\mathrm{g\ cm^{-3}})$	1.35×10^2	1.57×10^2	1.88×10^2	2.55×10^2

The graph between η_{sp}/c and c is shown in Fig. 5.6.2. The intercept of the graph is 1.225. Hence, $[\eta]_{c\,=\,0} = 1.225 \times 10^2\ \mathrm{g}^{-1}\ \mathrm{cm}^3$.

$$\overline{M}_{\mathrm{v}}/\mathrm{g\ mol^{-1}} = \left(\frac{[\eta]}{k} \right)^{1/a} = \left(\frac{1.225 \times 10^2}{3.7 \times 10^{-2}} \right)^{1/0.62}$$

$$\overline{M}_{\mathrm{v}} = 4.8 \times 10^5\ \mathrm{g\ mol^{-1}}$$

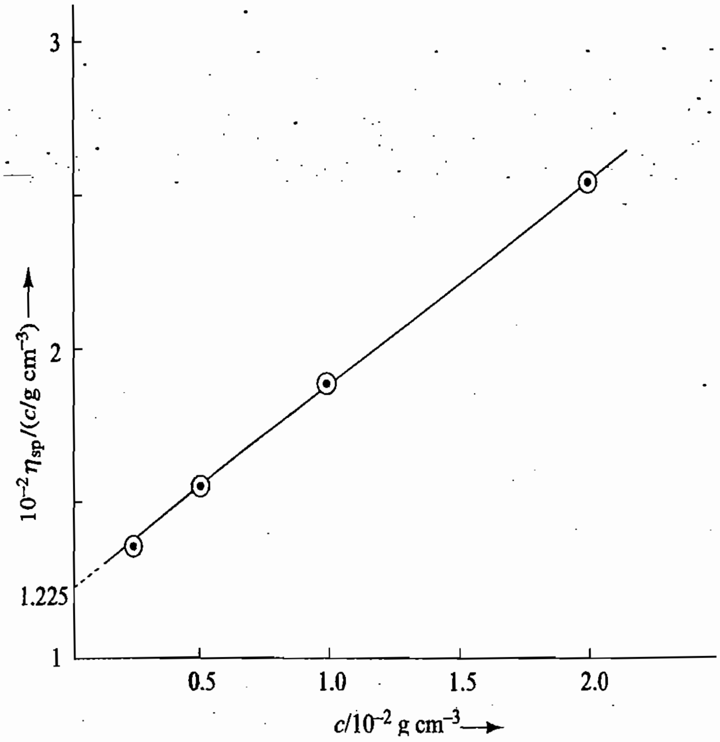


Fig. 5.6.2

5.7 ULTRACENTRIFUGE SEDIMENTATION FOR THE MEASUREMENT OF MOLAR MASS

The phenomenon of ultracentrifuge sedimentation involves the migration of macromolecules from the bulk of the solution towards the bottom of a cell under the influence of a centrifugal force which is about 10^5 times greater than the gravitational force. The solution of the sample of macromolecules is taken in a transparent cell and is placed in the cavity of a rotor operating at very high speed (say, 60 000 rotations per minute) in an instrument which allows vibration-free, constant temperature operation. The movement of molecules in the sample solution is monitored by the optical systems.

Stationary-State Velocity of a Macromolecule

In the sample solution, a molecule of mass m at a distance r from the axis of rotation is under the influence of the following forces.

- The centrifugal force due to the rotation of molecule. This imparts radial acceleration $\omega^2 r$ to the molecule, where ω is the angular velocity (expressed in radians per second). The expression of centrifugal force is

$$F_c = m\,(\omega^2 r) = (M/N_A)\,(\omega^2 r) \tag{5.7.1}$$

- The buoyant force due to the replacement of volume V of solution equivalent to that of the molecule. This is given by

$$F_b = V_2\,\rho\omega^2 r = \left(\frac{M}{N_A\rho_2}\right)\rho\omega^2 r \tag{5.7.2}$$

- The viscous force as given by Stokes law is

$$F_f = f\,v_s \tag{5.7.3}$$

  where f is the frictional coefficient (for spherical molecule it is equal to $6\pi\eta R$) and v_s the stationary-state velocity of the macromolecule.

The molecule attains v_s when

$$F_c = F_b + F_f$$

i.e.

$$\frac{M}{N_A}\,\omega^2 r = \left(\frac{M}{N_A\rho_2}\right)\rho\,\omega^2 r + f\,v_s \tag{5.7.4}$$

This gives

$$v_s = \frac{1}{f}\,\frac{M}{N_A}\left(1-\frac{\rho}{\rho_2}\right)\omega^2 r$$

$$= s\,\omega^2 r \tag{5.7.5}$$

where

$$s = \frac{1}{f}\,\frac{M}{N_A}\left(1-\frac{\rho}{\rho_2}\right) \tag{5.7.6}$$

and is known as *sedimentation coefficient* which is equal to the stationary-state velocity per unit acceleration. The values of sedimentation coefficient are characteristic of the settling molecules. The unit of s is second. A unit of 10^{-13}s is known as svedberg (symbol: S) after the name of Svedberg – a pioneer worker in the field of ultracentrifuge sedimentation.

Radial Location of Molecule with Time

Since $v_s = \mathrm{d}r/\mathrm{d}t$, Eq. (5.7.5) can be written as

$$\frac{\mathrm{d}r}{\mathrm{d}t} = s\omega^2 r \tag{5.7.7}$$

This gives

$$\frac{\mathrm{d}r}{r} = s\omega^2\,\mathrm{d}t$$

which on integration gives

$$\ln (r/r^\circ) = s\omega^2 t + \text{constant} \tag{5.7.8}$$

where r° is the unit value of r.

Thus, $\ln (r/r^\circ)$ of the molecule varies linearly with t with slope equal to $s\omega^2$, from which the value of s can be calculated.

Example 5.7.1

About how long will it take the boundary of a polymer sample to move 1 mm in a centrifuge operating at 50 000 rotations per minute if the initial distance of the sample boundary from the centre of rotation is 6.0 cm? The sedimentation coefficient for the sample is 2.20×10^{-13} s at 20 °C.

Solution

Equation (5.7.8) for the two sets of data is given by

$$\ln\left(\frac{r_2}{r_1}\right) = s\omega^2(\Delta t)$$

Since $\omega = 2\pi\nu$, we have

$$\omega = \frac{50000 \times 2 \times 3.14}{60}\ \text{rad/s} = 5.233 \times 10^3\ \text{rad/s}$$

$$\text{Hence,}\quad \Delta t = \frac{\ln (r_2/r_1)}{s\omega^2} = \frac{\ln (6.1/6.0)}{(2.20 \times 10^{-13}\,\text{s})(5.233 \times 10^3\ \text{s}^{-1})^2}$$

$$= 2.744 \times 10^3\ \text{s} = 45.73\ \text{min}$$

Comments on Sedimentation Coefficient

The sedimentation coefficients are frequently corrected for concentration dependence and reduced to standard conditions.

- To eliminate concentration dependence, the values of s are determined at different concentrations and then extrapolated to zero concentration. This limiting value is represented by s°.
- The sedimentation coefficient are reduced to standard conditions by using the expression

$$\frac{s_s^\circ}{s_{\text{exp}}^\circ} = \frac{(1-\rho/\rho_2)_s}{(1-\rho/\rho_2)_{\text{exp}}}\ \frac{\eta_{0,\text{exp}}}{\eta_{0,s}} \tag{5.7.9}$$

Use of Sedimentation Coefficient

The sedimentation coefficient can be used in the following ways.

- Assuming the macromolecule to be spherical of radius R, we will have

$$m = \frac{M}{N_A} = \left(\frac{4}{3}\pi R^3\right)\rho_2 \tag{5.7.10}$$

$$f = 6\,\pi\,\eta_0 R \tag{5.7.11}$$

Substituting these expressions in Eq. (5.7.6), we get

$$s = \left(\frac{1}{6\pi\eta_0 R}\right)\left(\frac{4}{3}\pi R^3 \rho_2\right)\left(1-\frac{\rho}{\rho_2}\right)$$

$$= \frac{2R^2(\rho_2-\rho)}{9\eta_0} \qquad (5.7.12)$$

Knowing the values of ρ_2, ρ (from separate experiments) and η_0, the above expression can be used to determine R from the experimentally determined value of s, which, in turn, can be used to compute M from Eq. (5.7.6). This value of M corresponds to a hypothetical spherical particle which settles at the same rate as the actual molecule.

- It can shown that the frictional coefficient is given by

$$f = \frac{kT}{D} \qquad (5.7.13)$$

where D, the diffusion coefficient, is defined as the rate at which material diffuses per unit area, perpendicular to the concentration gradient of unity.[†] The value of D can be determined experimentally and hence the value of frictional coefficient can be estimated. Substituting this value in Eq. (5.7.6) helps determining the value of molar mass. The resultant expression is

$$s = \frac{D}{kT}\frac{M}{N_A}\left(1-\frac{\rho}{\rho_2}\right) = \frac{D}{kT}\frac{M}{N_A}(1-\bar{\upsilon}\rho) \qquad (5.7.14)$$

where $\bar{\upsilon}$ is the specific volume of solute.

- For polydisperse systems, the value of M calculated by the above method corresponds to mass average molar mass. To avoid concentration dependence, the value of s/D extrapolated to $c = 0$ may be used.

Example 5.7.2

A sample of γ globulin gives the following experimental results at 20 °C: Specific volume of solute 0.718 mL g^{-1}, density of solvent 1.00 g mL^{-1}, sedimentation coefficient 7.12 × 10^{-13} s, diffusion coefficient 4.0 × 10^{-11} m^2 s^{-1}. Calculate the molar mass of γ globulin.

Solution

From Eq. (5.7.14) we get

$$M = \frac{s kT N_A}{D(1-\bar{\upsilon}\rho)} = \frac{sRT}{D(1-\bar{\upsilon}\rho)}$$

$$= \frac{(7.12\times10^{-13}\,\text{s})(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})(293\,\text{K})}{(4.0\times10^{-11}\,\text{m}^2\,\text{s}^{-1})\{1-(0.718\,\text{mL g}^{-1})(1.00\,\text{g mL}^{-1})\}}$$

$$= 153.76\ \text{kg mol}^{-1}$$

[†] By definition, the rate at which material diffuses per unit area perpendicular to the concentration gradient is given by Fick's first law, expressed as $J = -D\,(dc/dx)$. See also Annuxure II at the end of the chapter.

5.8 SEDIMENTATION EQUILIBRIUM FOR THE MEASUREMENT OF MOLAR MASS

If a sedimentation experiment is carried out over a long period, a state of equilibrium is reached where the rate of sedimentation (due to the centrifugal field) becomes equal to the rate of diffusion (due to the concentration gradient) which operates in the opposite direction of sedimentation.

We have

- The rate of sedimentation is the given by

$$J_{\text{sed}} = c v_{\text{s}}$$

which in view of Eq. (5.7.7) becomes

$$J_{\text{sed}} = c\,(s\omega^2 r) \tag{5.8.1}$$

- The rate of diffusion as given by Fick's first law is given by

$$J_{\text{diff}} = -D\,\frac{\mathrm{d}c}{\mathrm{d}r} \tag{5.8.2}$$

Hence, at sedimentation equilibrium

$$D\,\frac{\mathrm{d}c}{\mathrm{d}r} = c\,s\omega^2 r \tag{5.8.3}$$

Separating the variables followed by integration, we get

$$\int \frac{\mathrm{d}c}{c} = \frac{s\omega^2}{D} \int r\,\mathrm{d}r$$

i.e.

$$\ln\left(\frac{c}{c^\circ}\right) = \frac{s\omega^2}{2D}\,r^2 + \text{constant} \tag{5.8.4}$$

Substituting the expressions of s from Eq. (5.7.6) and D from Eq. (5.7.13), we get

$$\ln\left(\frac{c}{c^\circ}\right) = \frac{\{(1/f)(M/N_{\mathrm{A}})(1-\rho/\rho_2)\}\omega^2}{2(kT/f)}\,r^2 + \text{constant}$$

$$= \frac{M(1-\rho/\rho_2)}{2N_{\mathrm{A}}kT}\,\omega^2 r^2 + \text{constant} \qquad (5.8.5)^{\dagger}$$

Thus, a plot of $\ln(c/c^\circ)$ versus r^2 is linear with slope equal to $M(1-\rho/\rho_2)\,\omega^2/2N_{\mathrm{A}}kT$. Knowing ρ and ρ_2 in separate experiments, the slope can be used to determine the molar mass.

- For a polydisperse sample with a continuous distribution of molar masses, several kinds of average molar masses can be obtained by using the technique of sedimentation equilibrium. If a polymer consists of molecules involving discrete molar masses (such as protein sample) rather than a broad distribution of molar masses, it is possible to resolve the data so as yield the molar masses of individual components.

[†] $1/\rho_2$ in Eq. (5.8.5) may be written as specific volume $\overline{v}$ of the solute.

Example 5.8.1 For the following data on sedimentation equilibrium at 25 °C, calculate the molar mass. Initial concentration = 0.10 g L^{-1}, rotation speed 299.6 rps, ρ_2 = 1.67 g cm^{-3} and ρ = 1.0 g cm^{-3}. At r_2 = 5.75 cm, c_2 = 42.18 (arbitrary units) and at r_1 = 5.72 cm, c_1 = 39.76 (arbitrary units).

Solution Equation (5.8.5) for the two data set is given by

$$\ln\frac{c_2}{c_1} = \frac{M(1-\rho/\rho_2)}{2N_A kT}\,\omega^2(r_2^2 - r_1^2)$$

Hence, $M = \dfrac{2RT}{(1-\rho/\rho_2)}\,\dfrac{1}{\omega^2(r_2^2-r_1^2)}\,\ln\dfrac{c_2}{c_1}$

Now $\omega = 2\pi\nu = 2(3.14)(299.6)\ \text{rad/s} = 1\,881.5\ \text{rad/s}$

$$1 - \rho/\rho_2 = 1 - 1.0/1.67 = 0.40$$

$$r_2^2 - r_1^2 = (5.75^2 - 5.72^2)\ \text{cm}^2 = 0.344\ \text{cm}^2 = 0.344 \times 10^{-4}\ \text{m}^2$$

Thus. $M = \dfrac{2(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})(298\,\text{K})}{(0.40)(1\,881.5\,\text{s}^{-1})^2(0.344\times10^{-4}\,\text{m}^2)}\ \ln\left(\dfrac{42.18}{39.76}\right)$

$$= (101.73\ \text{kg mol}^{-1})\ (0.0591)$$

$$= 6.01\ \text{kg mol}^{-1}$$

5.9 LIGHT SCATTERING FOR THE MEASUREMENT OF MOLAR MASS

Definition of Turbidity If a non-absorbing light is passed through a substance, nearly all of it is transmitted and a very small fraction of it is scattered in all directions (Fig. 5.9.1).

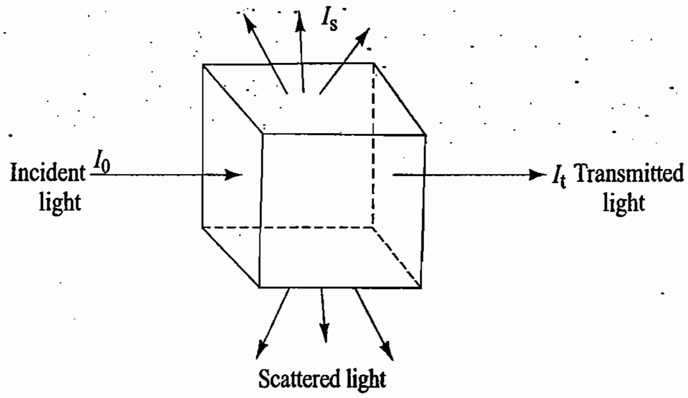


Fig. 5.9.1 Scattering of light by a sample

The scattering (known as Rayleigh scattering) of light is due to the interaction of oscillating electric field of the incident light with the particles of the medium. This interaction induces oscillating dipole in the particle, which is responsible for emitting scattered light. The frequency of the scattered light is identical to that of the incident light. The intensity of scattered light is given by

$$I_s = I_0 - I_t \qquad (5.9.1)$$

For a system exhibiting only scattering, the intensity of the transmitted light is related to that of incident light by the expression

$$\ln \frac{I_\mathrm{t}}{I_0} = -\tau x \tag{5.9.2}$$

where x is the path over which light passes and τ is known as the *turbidity* of the system.

Since $\quad \ln \frac{I_\mathrm{t}}{I_0} = \ln \frac{(I_0 - I_\mathrm{s})}{I_0} = \ln\left(1 - \frac{I_\mathrm{s}}{I_0}\right) \simeq -\frac{I_\mathrm{s}}{I_0}$

we write Eq. (5.9.2) as

$$\tau = \frac{1}{x}\,\frac{I_\mathrm{s}}{I_0} \tag{5.9.3}$$

The derivation of expressions of turbidity of a system in terms of molecular parameters is quite involved, we describe only the derived expressions which are useful in determining the mass average molar mass of the particles of the system.

Turbidity of a Gaseous System

For a gaseous system involving particles of dimensions smaller than the wavelength of the incident light, the expression of turbidity is given by

$$\tau = \frac{8\pi^3\alpha^2}{3\varepsilon_0^2\lambda_0^4}\left(\frac{\rho N_\mathrm{A}}{M}\right) \tag{5.9.4}$$

where α is the polarizability of the particle, ε_0 is the permittivity of vacuum. λ_0 is the wavelength of incident light, ρ is the density of the medium, N_A is Avogadro constant, and M is the molar mass of particles of the sample.

In many cases, turbidity τ is expressed in terms of the quantity known as optical-molecular factor R_θ. These two are related through the expression

$$\tau = R_\theta \int_0^\pi (1 + \cos^2\theta)\sin\theta\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\varphi = R_\theta\left(\frac{16\pi}{3}\right)$$

Thus $\quad R_\theta = \left(\frac{3}{16\pi}\right)\tau = \left(\frac{3}{16\pi}\right)\left(\frac{8\pi^3\alpha^2}{3\varepsilon_0^2\lambda_0^4}\,\frac{\rho N_\mathrm{A}}{M}\right) = \frac{1}{2}\,\frac{\pi^2\alpha^2\rho N_\mathrm{A}}{\varepsilon_0^2\lambda_0^4 M} \quad (5.9.5)$

The polarizability in Eq. (5.9.4) can be replaced in terms of index of refraction (*n*) of the medium through the Lorentz-Lorenz equation

$$\frac{n^2-1}{n^2+2}\,\frac{M}{\rho} = \frac{N_\mathrm{A}}{3\varepsilon_0}\,\alpha \tag{5.9.6}$$

For the gaseous system $n \simeq 1$, we can write

$$\frac{n^2-1}{n^2+2} = \frac{(n+1)(n-1)}{n^2+2} \simeq \frac{2}{3}\,(n-1) \tag{5.9.7}$$

Hence, $\quad \alpha = \left[\frac{2}{3}(n-1)\right]\left(\frac{M}{\rho}\right)\left(\frac{3\varepsilon_0}{N_\mathrm{A}}\right) = \frac{2\varepsilon_0}{\rho}\,\frac{M}{N_\mathrm{A}}\,(n-1) \quad (5.9.8)$

With this, Eq. (5.9.4) becomes

$$\tau = \left(\frac{8\pi^3}{3\varepsilon_0^2\lambda_0^4}\frac{\rho N_A}{M}\right)\left[\frac{2\varepsilon_0}{\rho}\frac{M}{N_A}(n-1)\right]^2$$

$$= \frac{32\pi^3}{3\lambda_0^4}\left(\frac{M}{\rho N_A}\right)(n-1)^2 \qquad (5.9.9)$$

Equation (5.9.9) is a useful expression as it can be used to determine the value of Avogadro constant.

Turbidity of a Liquid System

The scattering of liquids involving low molar-mass molecules is due to the fluctuations of concentrations in the small domains with reference to the bulk concentration. The size of domains is considered to be smaller than the wavelength of visible light used for the scattering experiment.

When Eq. (5.9.4) is applied to fluctuation of concentrations in the small domains of a liquid system, it is given by

$$\tau = \frac{8\pi^3}{3\varepsilon_0^2\lambda^4}\left(\frac{\rho N_A}{M}\right)\overline{\delta\alpha^2} = \frac{8\pi^3}{3\varepsilon_0^2\lambda^4}N^*\,\overline{\delta\alpha^2} \qquad (5.9.10)$$

where λ is the wavelength of the incident light in the liquid medium, N^* is the number of molecules per unit volume in the fluctuation domain and $\overline{\delta\alpha^2}$ is the mean square fluctuation in the polarizability of the domain with reference to the macroscopic average value of the liquid.

The fluctuation in the polarizability is expressed in terms of the variation in the refractive index of the liquid with the change in concentration of molecules in the fluctuation domain through the use of Clausius-Mosottii equation. Equation (5.9.10) is modified to

$$\tau = \frac{8\pi^3}{3\{\lambda^4(\varepsilon/\varepsilon_0)^2\}}\left(2n\frac{dn}{d\rho}\right)^2\frac{1}{N^*}\,\overline{\delta\rho^2}$$

$$= \frac{8\pi^3}{3\lambda_0^4}\left(2n\frac{dn}{d\rho}\right)^2\frac{1}{N^*}\,\overline{\delta\rho^2} \qquad (5.9.11)$$

where λ_0 is the wavelength of light in air (or vacuum),
$dn/d\rho$ is the change in refractive index of the domain with change in its density,

and $\overline{\delta\rho^2}$ is the mean square fluctuation in the density of the domain.

The density fluctuation in a domain is associated with change in Gibbs free energy, which is given by

$$\overline{\delta\rho^2} = \frac{kT}{(\partial^2 G/\partial\rho^2)_0}$$

where the subscript zero stands for the quantity at the equilibrium state of the system.

With this, Eq. (5.9.11) is modified to

$$\tau = \frac{32\pi^3}{3\lambda_0^4}\frac{1}{N^*}\left(n\frac{\mathrm{d}n}{\mathrm{d}\rho}\right)^2 \frac{kT}{(\partial^2 G/\partial \rho^2)_0} \tag{5.9.12}$$

If the concentration of solution is expressed in mass/volume, Eq. (5.9.12) is given by

$$\tau = \frac{32\pi^3}{3\lambda_0^4}\frac{1}{N^*}\left(n\frac{\mathrm{d}n}{\mathrm{d}c_2}\right)^2 \frac{kT}{(\partial^2 G/\partial c_2^2)_0} \tag{5.9.13}$$

Turbidity of a Solution

While dealing with the solutions, the term $(\partial^2 G/\partial c_2^2)_0$ is expressed in terms of measurable property of the system. The convenient property chosen is the change in osmotic pressure of the solution with concentration c_2. With this, Eq. (5.9.13) is modified to

$$\tau = \frac{32\pi^3}{3\lambda_0^4}\left(n\frac{\mathrm{d}n}{\mathrm{d}c_2}\right)^2 \frac{kT\,c_2}{(\partial \Pi/\partial c_2)_0} \tag{5.9.14}$$

where $(\partial \Pi/\partial c_2)_0$ stands for the concentration dependence of the equilibrium osmotic pressure.

The expression of the equilibrium osmotic pressure as a function of concentration is

$$\Pi = RT\left(\frac{c_2}{M} + Bc_2^2 + \cdots\right)$$

Hence, $$\left(\frac{\partial \Pi}{\partial c_2}\right)_0 = RT\left(\frac{1}{M} + 2Bc_2 + \cdots\right) \tag{5.9.15}$$

With the retention of the first two terms, Eq. (5.9.14) modifies to

$$\tau = \frac{32\pi^3}{3\lambda_0^4}\left(n\frac{\mathrm{d}n}{\mathrm{d}c_2}\right)^2 \frac{1}{N_\mathrm{A}}\,\frac{c_2}{\{(1/M) + 2Bc_2\}} \tag{5.9.16}$$

Inverting Eq. (5.9.16), we get

$$\frac{1}{\tau} = \frac{1}{Hc_2}\left(\frac{1}{M} + 2Bc_2\right) \tag{5.9.17}$$

where $$H = \frac{32\pi^3 (n\,\mathrm{d}n/\mathrm{d}c_2)^2}{3\lambda_0^4 N_\mathrm{A}} \tag{5.9.18}$$

and is known as *Debye factor*. Equation (5.9.17) is usually written as

$$\frac{Hc_2}{\tau} = \frac{1}{M} + 2Bc_2 \tag{5.9.19}$$

Thus, a plot of Hc_2/τ versus c_2 is a straight line with slope equal to $2B$ and intercept equal to $1/M$.

Nature of Obtained Molar Mass

For a polydisperse system, the molar mass obtained is the mass average molar mass. This follows from the following analysis.

For a polydisperse system

$$c_2 = \sum_i c_{2,i} \quad \text{and} \quad \tau = \sum_i \tau_i$$

Thus $$M = \frac{\tau}{Hc_2} = \frac{\sum_i \tau_i}{H\sum_i c_i}$$

For each component $Hc_i/\tau_i = 1/M_i$. Hence

$$M = \frac{\sum_i \tau_i}{H\sum_i c_i} = \frac{\sum_i Hc_iM_i}{H\sum_i c_i} = \frac{\sum_i c_iM_i}{\sum_i c_i} = \frac{\sum_i m_iM_i}{\sum_i m_i} = \frac{\sum_i N_iM_i^2}{\sum_i N_iM_i} \tag{5.9.20}$$

which is the definition of mass average molar mass.

Condition for the Applicability of Eq. (5.9.20)

Equation (5.9.14) is applicable provided no interference between the scattered radiations from different scattering domains in the solution takes place. This is found to be applicable provided

$$\left(\frac{4\pi R}{\lambda}\right)\left(\frac{n_2}{n_1}-1\right) \ll 1 \tag{5.9.21}$$

where R is the radius of the overall molecule and n_1 and n_2 are the indices of refraction of the solvent and solute, respectively.

Example 5.9.1

Light scattering measurement were carried out for bovine serum albumin in 0.1 M KI solution at isoelectric point (pH = 5.7). The wavelength was set at 546 nm. The following turbidity data were obtained.

$10^3c_2/\text{g cm}^{-3}$	0.936	1.902	2.801	3.701	5.590
$10^4\tau/\text{cm}^{-1}$	2.88	5.75	8.18	10.59	15.37

The value of the refractive index of solvent was 1.334 2 and $\mathrm{d}n/\mathrm{d}c_2$ was found to be 0.168 $\text{g}^{-1}\,\text{cm}^3$. Plot Hc_2/τ versus c_2 to determine the molar mass and the second virial coefficient.

Solution

The value of Debye factor H is

$$H = \frac{32\pi^3(n\mathrm{d}n/\mathrm{d}c)^2}{3\lambda_0^4N_\mathrm{A}}$$

$$= \frac{(32)(3.14)^3\{(1.334\,2)(0.168\ \text{g}^{-1}\,\text{cm}^3)\}^2}{3(546\times10^{-7}\ \text{cm})^4(6.022\times10^{23}\ \text{mol}^{-1})}$$

$$= 3.099\,5\times10^{-6}\ \text{g}^{-2}\,\text{cm}^2\,\text{mol}$$

The values of Hc_2/τ are as follows.

$10^3c_2/\text{g cm}^{-3}$	0.936	1.902	2.801	3.701	5.590
$(10^5\,Hc_2/\tau)/\text{g}^{-1}\,\text{mol}$	1.007	1.025	1.061	1.083	1.127

The plot of Hc_2/τ versus c_2 is shown in Fig. 5.9.1.

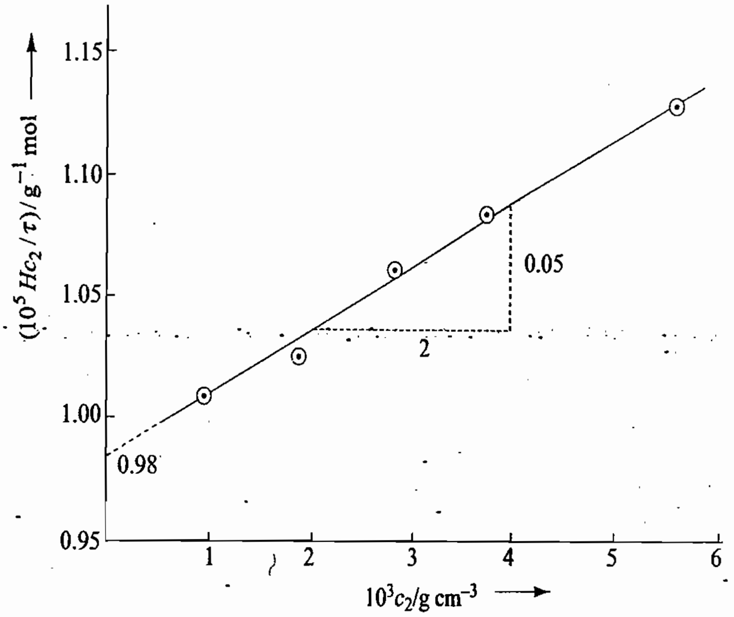


Fig. 5.9.1

The intercept of the plot shown in Fig. 5.9.1 is 0.98×10^{-5} g^{-1} mol. Hence, the molar mass is

$$M = \frac{1}{\text{intercept}} = \frac{1}{0.98 \times 10^{-5}\ \text{g}^{-1}\ \text{mol}} = 1.02 \times 10^5\ \text{g mol}^{-1}$$

The slope of the plot is

$$\text{slope} = \frac{0.05 \times 10^{-5}\ \text{g}^{-1}\ \text{mol}}{2 \times 10^{-3}\ \text{g cm}^{-3}} = 2.5 \times 10^{-4}\ \text{g}^{-2}\ \text{cm}^3\ \text{mol}$$

The value of second virial coefficient is

$$B = \frac{\text{slope}}{2} = 1.25 \times 10^{-4}\ \text{g}^{-2}\ \text{cm}^3\ \text{mol}$$

Modification of Eq. (5.9.20) for a Polymer Solution

Equation (5.9.19) expressed in terms of optical-molecular factor (Eq. 5.9.5) takes the form of

$$\frac{Hc_2}{(16\pi/3)\,R_\theta} = \frac{1}{M} + 2Bc_2$$

i.e.

$$\frac{Kc_2}{R_\theta} = \frac{1}{M} + 2Bc_2 \tag{5.9.22}$$

where K, known as scattering constant, is given by

$$K = \frac{3}{16\pi}\,H = \frac{2\pi^3 (n\,\mathrm{d}n/\mathrm{d}c)^2}{\lambda_0^4 N_\mathrm{A}} \tag{5.9.23}$$

For a solution containing macromolecules, the interference between the scattering light from different sites of the same macromolecule cannot be excluded. If this interference is taken into account, Eq. (5.9.22) is modified to

$$\frac{Kc_2}{R_\theta} = \frac{1}{P_\theta} \cdot \left(\frac{1}{M} + 2Bc_2\right) \tag{5.9.24}$$

where P_θ is given by the expression

$$P_\theta = 1 - \frac{s^2}{3}\,\overline{r_g^2} \tag{5.9.25}$$

The expression of s in Eq. (5.9.25) is

$$s = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \tag{5.9.26}$$

where θ is the angle between the scattered light and the transmitted light (Fig. 5.9.2). The symbol $\overline{r_g^2}$ in Eq. (5.9.25) represents the radius of gyration[†] of the molecule.

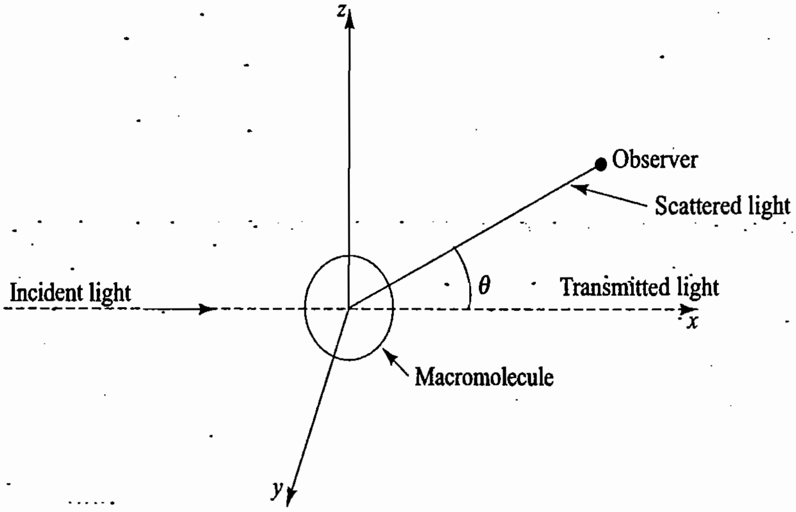


Fig. 5.9.2 The scattering of light

Substitution of Eq. (5.9.25) in Eq. (5.9.24), we get

$$\frac{Kc_2}{R_\theta} = \left(\frac{1}{1-\overline{r_g^2}\,s^2/3}\right)\left(\frac{1}{M}+2Bc_2\right)$$

$$\simeq \left(1+\frac{s^2}{3}\overline{r_g^2}\right)\left(\frac{1}{M}+2Bc_2\right)$$

Using Eq. (5.9.26), this becomes

$$\frac{Kc_2}{R_\theta} = \left[1+\frac{1}{3}\overline{r_g^2}\left(\frac{4\pi}{\lambda}\sin\frac{\theta}{2}\right)^2\right]\left(\frac{1}{M}+2Bc_2\right)$$

$$= \left(1+\frac{16\pi^2}{3\lambda^2}\overline{r_g^2}\sin^2\frac{\theta}{2}\right)\left(\frac{1}{M}+2Bc_2\right) \tag{5.9.27}$$

[†] By definition, the radius of gyration is the radial distance from the axis of rotation at which all of the mass could be concentrated to produce the same amount of moment of inertia that the actual distribution of mass possesses. By using Eq. (5.4.13), it can be shown that for a three-dimensional flexible polymer chain,

$$\sqrt{\overline{r_g^2}} = n\,l^2/6$$

Determination of Molar Mass and Radius of Gyration

In the limit of $c_2 \to 0$, Eq. (5.9.27) is reduced to

$$\left(\frac{Kc_2}{R_\theta}\right)_{c_2\to 0} = \left(1+\frac{16\pi^2}{3\lambda^2}\overline{r_g^2}\sin^2\frac{\theta}{2}\right)\frac{1}{M} \qquad (5.8.28)$$

Thus, a plot of $(Kc_2/R_\theta)_{c_2\to 0}$ versus $\sin^2\theta/2$ would yield a straight line with

$$\text{slope} = \frac{16\pi^2}{3\lambda^2 M}\,\overline{r_g^2} \qquad (5.9.29)$$

$$\text{intercept} = \frac{1}{M} \qquad (5.9.30)$$

Eliminating M in the above two expressions give

$$\overline{r_g^2} = \frac{3\lambda^2}{16\pi^2}\left(\frac{\text{slope}}{\text{intercept}}\right)_{c_2\to 0} \qquad (5.9.31)$$

Zimm Plot

Zimm Plot is the representation of light-scattering data which can be used to conduct the following extrapolations of Eq. (5.9.27) on a single graph.

- In the limit $c_2 = 0$ and $\theta = 0°$, $(Kc_2/R_\theta)_{c_2=0,\theta=0} = \dfrac{1}{M_m}$ (5.9.32)
- In the limit $\theta = 0°$, $(Kc_2/R_\theta)_{\theta=0} = (1/\overline{M}_m) + 2Bc_2$ (5.9.33)
- In the limit $c_2 = 0$, $(Kc_2/R_\theta)_{c_2=0} = (1/\overline{M}_m)\,[1 + (16\pi^2\cdot\overline{r_g^2}/3\lambda^2)\sin^2\theta/2]$ (5.9.34)

The extrapolated data can be used to compute $\overline{M}_m$, B and $\overline{r_g^2}$. The procedure of Zimm plot is exemplified by the Example 5.9.2.

Example 5.9.2

For polystyrene in butanone at 67 °C the following values of $(Kc_2/R_\theta) \times 10^6$ were reported in literature at the indicated concentrations and angles. Construct a Zimm plot and evaluate $\overline{M}_m$, B and $\left(\overline{r^2}\right)^{1/2}$. The values of λ_0 = 546 nm and n = 1.359 for butanone.

θ	c_2/g cm^{-3}	
	1.9×10^{-3}	3.8×10^{-4}
36.9°	1.84	1.50
53.0°	1.93	1.58
66.4°	1.98	1.62
90.0°	2.10	1.74
113.6°	2.23	1.87
143.1°	2.34	1.98

Solution

(i) In Zimm plot, the values of Kc_2/R_θ are plotted against $\sin^2(\theta/2) + kc_2$, where k, a constant, is chosen so as to give a good display of data points on the graph. Let we use k = 100 cm^3 g^{-1}.

(ii) The values of $\sin^2(\theta/2) + kc_2$ at the indicated values of θ and c_2 are tabulated in the following.

θ	$c_2/\mathrm{g\ cm^{-3}}$	
	1.9×10^{-3}	3.8×10^{-4}
36.9°	0.29	0.14
53.0°	0.39	0.24
66.4°	0.49	0.34
90.0°	0.69	0.54
113.6°	0.89	0.74
143.1°	1.09	0.94

(iii) The data points representing Kc_2/R_θ versus $\sin^2(\theta/2) + kc_2$ are shown in Fig. 5.9.2

(iv) The line joining data points for each of the constant concentrations is drawn. On this line, the point having the abscissa kc (i.e. the value of $\sin^2\theta/2 + kc$ for $\theta = 0°$) is marked. These are shown by the points enclosed in square symbols. A line joining these points is drawn and extrapolated for zero value of abscissa.

$$\text{Slope of } \theta = 0° \text{ line} = \frac{0.362\,5 \times 10^{-6}\ \mathrm{g^{-1}\ mol}}{0.001\,52\ \mathrm{g\ cm^{-3}}} = 2.38 \times 10^{-4}\ \mathrm{cm^3\ mol\ g^{-2}}$$

From Eq. (5.9.27) or Eq. (5.9.33), we get

$$B = \frac{\text{slope}}{2} = \frac{2.38 \times 10^{-4}\ \mathrm{cm^3\ mol\ g^{-2}}}{2} = 1.19 \times 10^{-4}\ \mathrm{cm^3\ mol\ g^{-2}}$$

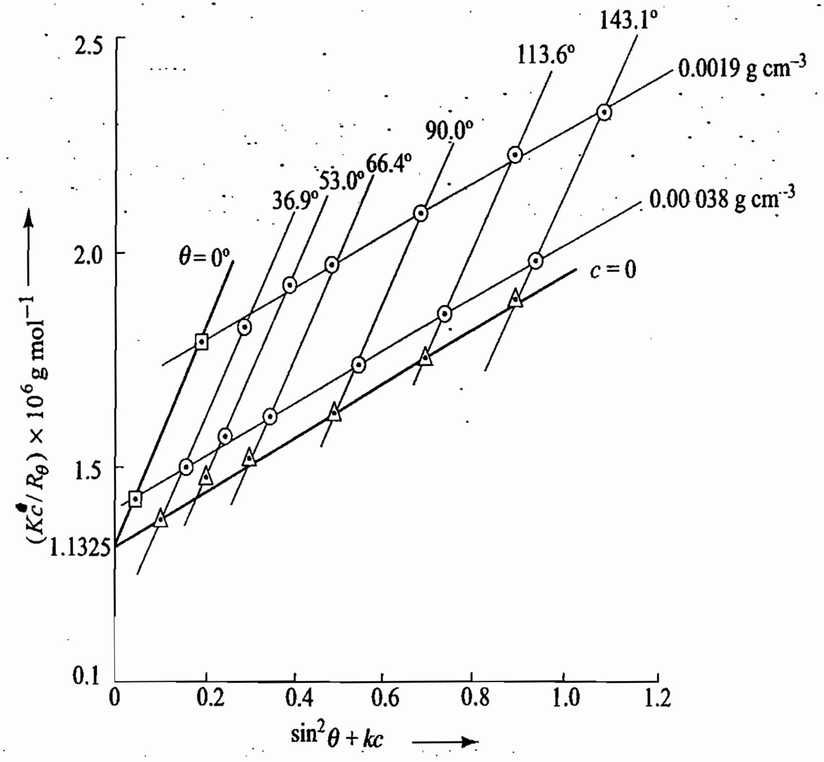


Fig. 5.9.2

(v) The line joining data points for each of the constant angles is drawn. On this line, the point having the abscissa $\sin^2\theta/2$ (i.e. the value of $\sin^2\theta/2 + kc$ for $c = 0$) is marked. These are shown by the points enclosed in triangle symbols. A line joining these points is drawn and extrapolated to zero value of abscissa.

Both the lines meet at a common point for which $c_2 = 0$ and $\theta = 0°$. This point corresponds to $1/\overline{M}_m$ as given by Eq. (5.9.27) or Eq. (5.9.32). Hence

$$\overline{M}_m = 1/\text{Intercept} = 1/(1.13\times10^{-6}\ \text{g}^{-1}\ \text{mol}) = 8.85\times10^{5}\ \text{g mol}^{-1}$$

$$\text{Slope of } c_2 = 0 \text{ line} = \frac{0.25\times10^{-6}\ \text{g}^{-1}\ \text{mol}}{0.4} = 6.25\times10^{-7}\ \text{g}^{-1}\ \text{mol}$$

From Eq. (5.9.31), we find

$$\overline{r_g^2} = \frac{3\lambda^2}{16\pi^2}\left(\frac{\text{slope}}{\text{intercept}}\right)_{c=0}$$

Hence,

$$\overline{r_g^2} = \frac{3(546\ \text{nm})^2}{16(3.14)^2}\left(\frac{6.25\times10^{-7}\ \text{g}^{-1}\ \text{mol}}{1.13\times10^{-6}\ \text{g}^{-1}\ \text{mol}}\right)$$

$$= 3\,135.66\ \text{nm}^2$$

$$\left(\overline{r_g^2}\right)^{1/2} = 56\ \text{nm}$$

5.10 SIZE-EXCLUSION CHROMATOGRAPHY

Introduction

The size-exclusion chromatography (SEC) is based on the different rates of permeation of molecules of different sizes through the porous material of the stationary phase. The largest molecules are excluded from the pores to the greatest extent and thus are emerged first through the chromatographic column followed by the progressive collection of smaller molecules. Thus, the size-exclusion chromatography functions as a reverse sieving operations at the molecular level. Through the use of caliberation curves, it is possible to characterise quantitatively the different fractions of the eluted material.

Different Names of SEC

The self-exclusion chromatography is known by different names in different field of chemistry.

- In the polymer literature, SEC is known by gel permeation chromatography (GPC). The mobile phase in this chromatography is an organic solvent. This analytical technique is used in determining the molar mass and molar mass distribution of a synthetic polymer sample.

In the biochemical literature, SEC is known by gel filtration chromatography (GFC). The mobile phase in this chromatography is an aqueous phase. This technique is mainly used to separate and characterise biological polymers such as proteins.

Determination of Molar Mass

Through the use of caliberation curve between log M (or $[\eta]$ M, where $[\eta]$ is the intrinsic viscosity) and retention volume V_R, it is possible to analyse a chromatograph to determine the number average and mass average molar masses of a sample of polymer. The given chromatograph is sliced into small segments (Fig. 5.10.1). For the indicated retention volumes, the corresponding molar mass is determined through the use of caliberation curves. The height h_i at a given V_R within the chromatograph is proportional to the mass of that component of material of molar mass M_i. Guided by this fact, one can determine molar masses by using the following expressions.

$$\overline{M}_n = \frac{\sum_i n_i M_i}{\sum_i n_i} = \frac{\sum_i (h_i/M_i)M_i}{\sum_i (h_i/M_i)} = \frac{\sum_i h_i}{\sum_i (h_i/M_i)}$$

$$\overline{M}_m = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i h_i M_i}{\sum_i h_i}$$

Instead of h_i, one can also use A_i, the area of the ith slice (Fig. 5.10.1)

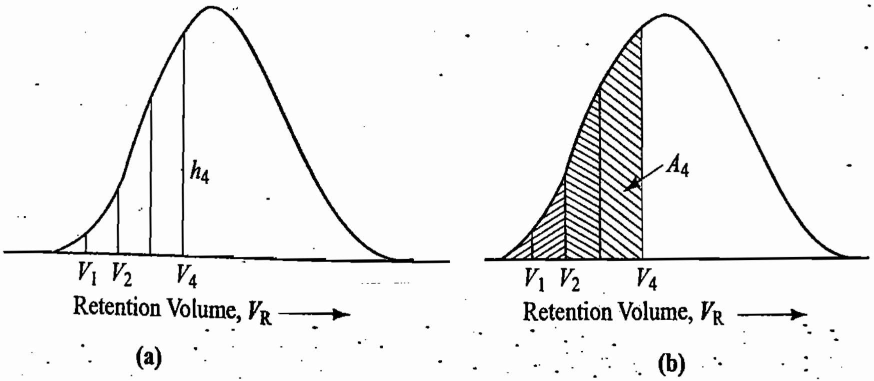


Fig. 5.10.1 Analysis of the chromatograph, (a) h_i versus $V_{R,i}$, and (b) A_i versus $V_{R,i}$

REVISIONARY PROBLEMS

Types of Polymer

5.1 Distinguish between condensation and addition polymers. Give two examples of each.

5.2 Distinguish between homopolymer and copolymer. Give two examples of each.

Average Molar Masses

5.3 Define number average molar mass.

5.4 Define mass average molar mass.

5.5 For a sample of polymer which one has a larger value—number average or mass average molar mass?

5.6 Define *z*-average molar mass. Is it greater or smaller than mass average molar mass for a polydisperse system?

5.7 Define viscosity average molar mass.

5.8 Define extent of a polymerization reaction.

5.9 Show that the fraction of *k*mer in a sample of polymer is given by

$$N_k = N p^{k-1} (1-p)$$

where the various symbols have their usual meanings.

5.10 Show that the average value of polymerization in a polymerization reaction is equal to $1/(1-p)$.

5.11 Show that the number of *k*mer in terms of initial number of monomer molecules is given by

$$N_k = N_0 p^{k-1} (1-p)^2$$

where the various symbols have their usual meanings.

5.12 Show that the number average molar mass is given by $\overline{M}_n = M_1/(1-p)$, where the various symbols have their usual meanings.

5.13 Show that the mass average molar mass is given by

$$\overline{M}_m = \frac{1+p}{1-p} M_1$$

where the various symbols have their usual meanings.

End-to-End Distance

5.14 Using the method of one-dimensional random walk, show that the probability of locating the growing end of the chain at distances *x* and *x* + d*x* from the starting point is given by

$$P\,\mathrm{d}x = \frac{1}{(2\pi n l^2)^{1/2}} \exp(-x^2/2nl^2)\,\mathrm{d}x$$

5.15 Show that the most probable end-to-end distance of a one-dimensional polymer chain is given by

$$\sqrt{\overline{x^2}} = \sqrt{n}\,l$$

where *n* is the number of repeat linkages in the polymer.

5.16 Show that the probability of locating the growing chain at distance *r* and *r* + d*r* from the starting point is given by

$$P'\mathrm{d}r = \left(\frac{3}{2\pi n l^2}\right)^{3/2} 4\pi r^2 \exp\left(-\frac{3r^2}{2nl^2}\right)\mathrm{d}r$$

5.17 Show that the most probable end-to-end distance of a three-dimensional polymer chain is given by

$$\sqrt{\overline{x^2}} = \sqrt{n}\, l$$

where n is the repeat linkages in the polymer.

Osmotic Pressure

5.18 Discuss in brief the theory underlying the determination of molar mass of a sample of polymer by the measurement of osmotic pressure. What type of average molar mass is determined by this method?

Viscosity

5.19 Define coefficient of viscosity? What are its CGS and SI units and how are these inter-related with each other?

5.20 Write down the Einstein's equation for the viscosity of a solution. Show that for a polymer solution, it is expressed as

$$\eta = \eta_0 + B\, c_2 + C\, c_2^2 + \cdots$$

where c_2 is expressed as mass per unit volume of the solution.

5.21 Define the following terms.

Relative viscosity, specific viscosity, reduced viscosity, intrinsic viscosity and inherent viscosity.

5.22 Write down the Mark-Houwink equation for the intrinsic viscosity of a solution. What type of average molar mass is determined from the measurement of viscosity of a polymer solution?

Sedimentation

5.23 Show that the sedimentation coefficient is given by

$$s = \frac{1}{f}\,\frac{M}{N_A}\left(1 - \frac{\rho}{\rho_2}\right)$$

where the various symbols have their usual meanings.

5.24 Show that the location of a macromolecule with time in a sedimentation experiment is given by

$$\ln (r/r^\circ) = s\, \omega^2 t + \text{constant}$$

5.25 How is the molar mass of a polymer sample determined by using the technique of ultracentrifuge sedimentation?

5.26 What do you understand by sedimentation equilibrium?

5.27 Show that in a sedimentation equilibrium, the plot of $\ln (c/c^\circ)$ versus r^2 is linear. What is its slope? How does this help determining the molar mass of a sample of polymer?

Light Scattering

5.28 Describe in brief the determination of molar mass of a sample of polymer by light-scattering method? What type of average molar mass is determined by this method?

5.29 Describe Zimm plot. How does this help determining the molar mass, second virial coefficient and radius of gyration of molecules of a sample of polymer.

Size Exclusion Chromatograph

5.30 Describe in brief the technique of size-exclusion chromatography in determining the molar mass of a sample of polymer.

NUMERICAL PROBLEMS

Average Molar Masses

5.1 A solution contains 1 : 2 ratio of number of particles of two substances with molar masses 10 000 g mol^{-1} and 20 000 g mol^{-1}, respectively. Calculate the values of number average and mass average molar masses.

[**Ans.** 16 667 g mol^{-1}, 18 000 g mol^{-1}]

5.2 A solution contains 1 : 2 ratio of masses of particles of two substances with molar masses 10 kg mol^{-1} and 20 kg mol^{-1}, respectively. Determine the number average and mass average molar masses.

[**Ans.** 15 kg mol^{-1}, 16.67 kg mol^{-1}]

5.3 A equimolar mixture of two substances has $\overline{M}_n$ = 10 kg mol^{-1} and $\overline{M}_m$ = 15 kg mol^{-1}. Calculate the respective molar masses.

[**Ans.** 17.07 kg mol^{-1}, 2.93 kg mol^{-1}]

5.4 A hydroxyacid HO—(CH$_2$)$_5$—COOH is polymerized and it is found that the product has a number average molar mass of 22000 g mol^{-1}. (a) What is the extent of reaction, *p*? (b) What is the degree of polymerization? (c) What is the mass average molar mass?

[**Ans.** 0.994, 166.67, 39880 g mol^{-1}]

5.5 A hydroxyacid HO—(CH$_2$)$_5$—COOH is polymerized and it is found that the product has a mass average molar mass of 35640 g mol^{-1}. (a) What is the extent of reaction, *p*? (b) What is the degree of polymerization? (c) What is the number average molar mass?

[**Ans.** 0.9926, 135, 17 886 g mol^{-1}]

End-to-End Distance

5.6 Calculate the most probable end-to-end distance of a polymer chain C$_{25}$H$_{52}$, given that the C—C bond length is 154 pm and the bond angle 109°28′. What would be the distance if the polymer chain is considered completely flexible?

[**Ans.** 1 067 pm, 754.4 pm]

5.7 Given that the most probable end-to-end distance of a polyethene chain is 7.5 nm. Calculate the molar mass of polyethene. Given: *r*(C—C) = 154 pm.

[**Ans.** 33.205 kg mol^{-1}]

Viscosity

5.8 At 25 °C, the Mark-Houwink exponent for poly(methylmethacylate) has the value of 0.83 in chloroform. Calculate the value of $\overline{M}_v$ that would be obtained for a sample with the following molar mass distribution if the sample was studied by viscometry.

$n_i \times 10^3$/mol	1.2	2.7	4.9	3.1	0.9
$M_i \times 10^{-5}$/g mol^{-1}	2.0	4.0	6.0	8.0	10.0

[**Ans.** 6.65 × 10^5 g mol^{-1}]

5.9 The intrinsic viscosity of polystyrene in benzene at 25 °C is 5.27 dL/g, and in 27.2% methanol –72.8% toluene it is 1.39 dL/g. Calculate the molar mass of polystyrene. Take $k/k° = 9.71 \times 10^{-5}$ and $a = 0.74$ for benzene, and $k/k° = 8.81 \times 10^{-4}$ and $a = 0.5$ for 27.2% methanal –72.8% toluene where $k° = 1$ g$^{-(1+a)}$ cm^3 mol^a.

Osmotic Pressure

5.10 The following osmotic pressures for polyisobutene in benzere are available. Find the molar mass of the sample.

c/g mL^{-1}	0.0200	0.0150	0.0100	0.0075	0.0050	0.0025
Π/bar	0.0118	0.0067	0.0030	0.00175	0.00091	0.00035

[**Ans.** 253 00 g mol^{-1}]

5.11 A plot of Π/c_2 versus c_2 for a series of polymer solution gave a value of second virial coefficient equal to 1.25 × 10^{-4} m^2 kg^{-2} mol. If molar mass is 25 kg mol^{-1}, determine the value of excluded volume.

[**Ans.** 2.59 × 10^{-25} m^3]

Sedimentation

5.12 The sedimentation of an enzyme in an aqueous buffer at pH = 7.0 was carried out at 20 °C in an ultracentrifuge at 56 000 rotations per minutes. The position of boundary changed with time as follows.

t/min	0	20	40	60	80
r/cm	5.91	6.022	6.114	6.207	6.304

Determine the value of sedimentation coefficient of the enzyme.

[**Ans.** 9.53×10^{-13} min^{-1}]

5.13 Sedimentation-velocity studies of human haemoglobin in water at 20 °C yield a sedimentation coefficient of 4.46×10^{-13}s. The specific volume of haemoglobin is estimated to be 0.75 cm^3 g^{-1}, and the density ρ of the solvent is 1 g cm^{-3}. The diffusion coefficient for haemoglobin under the same conditions is 6.9×10^{-11} m^2 s^{-1}. Estimate the molar mass of haemoglobin. [**Ans.** 62.983 kg mol^{-1}]

5.14 About how long will it take the boundary of a myoglobin sample to move 2 mm in a centrifuge operating at 60 000 rotations per minute if the initial distance of the sample boundary from the centre of rotation is 5 cm? The sedimentation constant reported for myoglobin is 2.04×10^{-13} s at 20 °C [**Ans.** 81.25 min]

5.15 In a study of the sedimentation of bovine serum albumin in water, sedimentation coefficient s was determined at a number of concentrations. When corrected to 25 °C the following data were obtained

c_0	0.29	0.59	0.87	1.17	1.76
$s \times 10^{13}$/s	4.927	4.839	4.772	4.663	4.475

(a) From these data determine the value of s at $c_2 = 0$.

(b) Using D_0 at 25 °C (= 6.97×10^{-7} cm^2/s) and $\bar{v}$ (= 0.734 cm^3/g), calculate the molar mass. [**Ans.** 65.93 kg mol^{-1}]

5.16 The following data are obtained in the sedimentation equilibrium study for a sample at 12.4 °C. Deduce the value of molar mass.

r/cm	6.827	6.917	6.979	7.026	7.093
c/arbitrary units	3.52	5.52	7.52	9.52	11.52

Given: rotor speed = 15 000 rotations/minute, $\rho/\rho_2 = 0.723$.

[**Ans.** 22.28 kg mol^{-1}]

5.17 A pure sample of a protein in water is centrifuged to equilibrium at 25 °C and at 15 000 revolutions per minute. The top of the centrifuge tube is 6.77 cm from the axis of revolution, and the concentrations at distances 0.450 cm and 1.25 cm from the top of the tube are measured to be 3.16 g cm^{-3} and 17.84 g cm^{-3}, respectively. The density of water at 25 °C is 0.997 g cm^{-3} and the specific volume of the protein $\bar{v}_2$ is 0.750 cm^3 g^{-1}. Calculate molar mass of protein. [**Ans.** 11 300 g mol^{-1}]

Light Scattering

5.18 The light scattering of an unknown sample of polymer solution gives the following data.

c/kg m^{-3}	1.30	2.01	3.01	5.49	6.62
$10^3 R_\theta$/m^{-1}	3.83	5.88	7.67	11.80	13.25

The wavelength of light is 435.8 nm. The values n and dn/dc were found to be 1.513 and 1.11×10^{-4} m^3 kg^{-1}. Calculate the molar mass of the polymer sample. [**Ans.** 130.2 kg mol^{-1}]

ANNEXURE I Average End-to-End Distance for the Polymethylene Chain

Figure AI.1 displays a schematic sketch of section of a polymethylene chain. In this chain, all bond vectors have the same length and the angle between the positive directions of successive bond vectors is 70°32′ (= 180° – 109°28′).

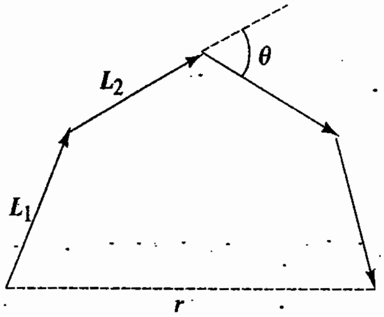


Fig. AI.1 A schematic sketch of polymethylene chain

The average end-to-end distance between the hydrocarbon chain of $N+1$ carbon atoms involving N bonds (represented by the vectors $L_1, L_2, \ldots, L_N$) is given by

$$\overline{r^2} = \overline{\boldsymbol{r}\cdot\boldsymbol{r}} = \overline{\left(\sum_{i=1}^{N} \boldsymbol{L}_i\right)\cdot\left(\sum_{j=1}^{N} \boldsymbol{L}_j\right)} \qquad \text{(AI.1)}$$

The summation in Eq. (AI.1) involves the terms of the type $\boldsymbol{L}_i \cdot \boldsymbol{L}_i$, $\boldsymbol{L}_i \cdot \boldsymbol{L}_{i+1}$, $\boldsymbol{L}_i \cdot \boldsymbol{L}_{i+2}$, and so on. Figure AI.2 displays the three successive bond vectors $\boldsymbol{L}_i$, $\boldsymbol{L}_{i+1}$ and $\boldsymbol{L}_{i+2}$ with a constant angle θ. The vectors $\boldsymbol{L}_i$ and $\boldsymbol{L}_{i+1}$ lie on the same plane. The tip of the vector $\boldsymbol{L}_{i+2}$ can lie any where on the circle as the rotation of $\boldsymbol{L}_{i+2}$ vector around the vector $\boldsymbol{L}_{i+1}$ is unrestricted, i.e. the angle φ can have any value from 0° to 360°.

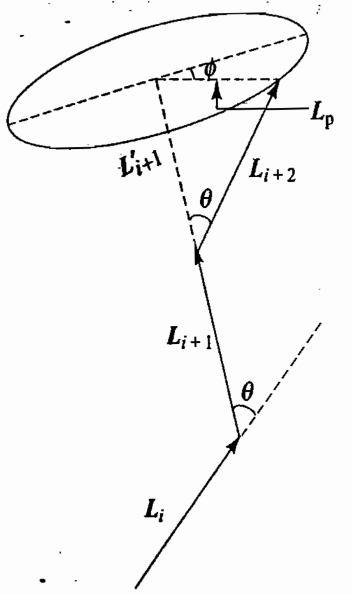


Fig. AI.2 A display of three successive bond vectors

We now proceed to derive the expressions of $\overline{L_i \bullet L_i}$, $\overline{L_i \bullet L_{i+1}}$, $\overline{L_i \bullet L_{i+2}}$, and so on.

Expression of $\overline{L_i \bullet L_i}$

Number of terms for i equal to $j = N$ (AI.2)

The expression of $L_i \bullet L_i$ is

$$\overline{L_i \bullet L_i} = L^2 \cos\theta = L^2 \cos 0^\circ = L^2 \tag{AI.3}$$

Expression of $\overline{L_i \bullet L_{i+1}}$

There are $2(N-1)$ such terms as shown in the following.

$$\begin{array}{ccccccc} i & 1 & 2 & 3 & \bullet\quad\bullet\quad\bullet & N-1 & N \\ j & 2 & 1,3 & 2,4 & & N-2,N & N-1 \end{array}$$

a total of $2(N-2)$ terms

$$\text{Total number of terms} = 1 + 2(N-2) + 1 = 2(N-1) \tag{AI.4}$$

From Fig. AI.2, it follows that

$$\overline{L_i \bullet L_{i+1}} = L^2 \cos\theta \tag{AI.5}$$

Expression of $\overline{L_i \bullet L_{i+2}}$

There are $2(N-2)$ such terms as shown in the following.

$$\begin{array}{ccccccccc} i & 1 & 2 & 3 & 4 & \bullet\quad\bullet\quad\bullet & N-2 & N-1 & N \\ j & 3 & 4 & 1,5 & 2,6 & & N-4,N & N-3 & N-2 \end{array}$$

a total of $2(N-4)$ terms

$$\text{Total number of terms} = 1 + 1 + 2(N-4) + 1 + 1 = 2(N-2) \tag{AI.6}$$

The vector L_{i+2} can be resolved into two components L'_{i+1} and L_p acting along and perpendicular to the vector L_{i+1}, respectively. The length of these vectors are

$$L'_{i+1} = L_{i+2} \cos\theta \qquad \text{and} \qquad L_p = L_{i+2} \sin\theta$$

Now $\overline{L_i \bullet L_{i+2}} = \overline{L_i \bullet (L'_{i+1} + L_p)} = \overline{L_i \bullet L'_{i+1}} + \overline{L_i \bullet L_p}$

The expression of $\overline{L_i \bullet L'_{i+1}}$ is

$$\overline{L_i \bullet L'_{i+1}} = L_i L'_{i+1} \cos\theta = L\,(L\cos\theta)\cos\theta = L^2 \cos^2\theta$$

The expression of $\overline{L_i \bullet L_p}$ is

$$\overline{L_i \bullet L_p} = L_i L_p \cos\alpha = L\,(L\sin\theta)\cos\alpha = L^2 \sin\theta \cos\alpha$$

where α is the angle between the vectors L_i and L_p.

Since the angle φ can have all possible values, there will exist an equally probable configuration with angle $180^\circ - \alpha$ corresponding to the configuration with angle α. The value of $L_i \bullet L_p$ for the former will be $-L^2 \sin\theta \cos\alpha$. Consequently, the average value of $\overline{L_i \bullet L_p}$ will be zero. Hence, we have

$$\overline{L_i \bullet L_{i+2}} = \overline{L_i \bullet L'_{i+1}} = L^2 \cos^2\theta \tag{AI.7}$$

Expression of $\overline{L_i \bullet L_{i+3}}$

There are 2(*N* – 3) such terms as shown in the following.

i	1	2	3	4	• • •	$N-3$	$N-2$	$N-1$	N
j	4	5	6	1, 7		$N-6, N$	$N-5$	$N-4$	$N-3$

a total of 2(*N* – 6) terms

$$\text{Total number of terms} = 3 + 2(N-6) + 3 = 2(N-3)\,. \tag{AI.8}$$

The vactor $\boldsymbol{L}_{i+3}$ may be resolved into two components $\boldsymbol{L}'_{i+2}$ and $\boldsymbol{L}_\text{p}$ acting along and perpendicular to the vector $\boldsymbol{L}_{i+2}$; respectively. The lengths of these vectors are

$$L'_{i+2} = L_{i+3}\cos\theta \qquad \text{and} \qquad L_\text{p} = L_{i+3}\sin\theta$$

$$\text{Now}\quad \overline{\boldsymbol{L}_i \bullet \boldsymbol{L}_{i+3}} = \overline{\boldsymbol{L}_i \bullet (\boldsymbol{L}'_{i+2} + \boldsymbol{L}_\text{p})} = \overline{\boldsymbol{L}_i \bullet \boldsymbol{L}'_{i+2}} + \overline{\boldsymbol{L}_i \bullet \boldsymbol{L}_\text{p}}$$

The average scalar product $\overline{\boldsymbol{L}_i \bullet \boldsymbol{L}_\text{p}}$ will be zero due to the free rotation of the vector $\boldsymbol{L}_{i+3}$ around the vector $\boldsymbol{L}_{i+2}$. Hence, we are left with

$$\overline{\boldsymbol{L}_i \bullet \boldsymbol{L}_{i+3}} = \overline{\boldsymbol{L}_i \bullet \boldsymbol{L}'_{i+2}}$$

The vector $\boldsymbol{L}'_{i+2}$, in turn, can be resolved into two components, $\boldsymbol{L}'_{i+1}$ parallel to $\boldsymbol{L}_{i+1}$ and $\boldsymbol{L}'_\text{p}$ perpendicular to $\boldsymbol{L}_{i+1}$. The lengths of these vectors are

$$L'_{i+1} = L'_{i+2}\cos\theta = (L_{i+3}\cos\theta)\cos\theta = L\cos^2\theta$$

$$L'_\text{p} = L'_{i+2}\sin\theta = (L_{i+3}\cos\theta)\sin\theta = L\cos\theta\sin\theta.$$

$$\text{Hence,}\quad \overline{\boldsymbol{L}_i \bullet \boldsymbol{L}'_{i+2}} = \overline{\boldsymbol{L}_i \bullet (\boldsymbol{L}'_{i+1} + \boldsymbol{L}'_\text{p})} = \overline{\boldsymbol{L}_i \bullet \boldsymbol{L}'_{i+1}} + \overline{\boldsymbol{L}_i \bullet \boldsymbol{L}'_\text{p}}$$

The average value of $\boldsymbol{L}_i \bullet \boldsymbol{L}'_\text{p}$ will be zero due to the free rotation of $\boldsymbol{L}'_{i+2}$ around $\boldsymbol{L}_{i+1}$. Hence,

$$\overline{\boldsymbol{L}_i \bullet \boldsymbol{L}'_{i+2}} = \overline{\boldsymbol{L}_i \bullet \boldsymbol{L}'_{i+1}} = L_i L'_{i+1}\cos\theta$$

$$= L\,(L\cos^2\theta)\cos\theta = L^2\cos^3\theta \tag{AI.9}$$

Generalization for $\overline{L_i \bullet L_{i+k}}$

From Eqs (AI.4), (AI.6) and (AI.8), we conclude that

$$\text{Number of terms} = 2(N-k) \tag{AI.10}$$

$$\text{Expression of } \overline{\boldsymbol{L}_i \bullet \boldsymbol{L}_{i+k}} = L^2\cos^k\theta \tag{AI.11}$$

Expression for Eq. (AI.1)

We have

$$\overline{r^2} = \overline{\left(\sum_{i=1}^{N}\boldsymbol{L}_i\right)\bullet\left(\sum_{j=1}^{N}\boldsymbol{L}_j\right)} = \sum_{i=1}^{N}\sum_{j=1}^{N}\overline{\boldsymbol{L}_i \bullet \boldsymbol{L}_j}$$

$$= N\overline{\boldsymbol{L}_i \bullet \boldsymbol{L}_i} + \sum_{k=1}^{N-1} 2(N-k)\,\overline{\boldsymbol{L}_i \bullet \boldsymbol{L}_{i+k}}$$

$$= NL^2 + 2(N-1)L^2\cos\theta + 2(N-2)L^2\cos^2\theta + \cdots + 2L^2\cos^{N-1}\theta$$

$$= L^2\,[N + 2(N-1)\cos\theta + 2(N-2)\cos^2\theta + \cdots] \tag{AI.12}$$

The value of successive term decreases as both the terms $N-k$ and $\cos^k\theta$ decrease with increase in the value of k. Only the first few terms will have significant values. Since for a polymer chain, N has a large value, Eq. (AI.12) may be written as

$$\overline{r^2} = L^2\,(N + 2N\cos\theta + 2N\cos^2\theta + \cdots)$$

$$= NL^2\,(1 + 2\cos\theta + 2\cos^2\theta + \cdots)$$

Since $\cos\theta < 1$, the above expression may be written as

$$\overline{r^2} = NL^2\left(\frac{1+\cos\theta}{1-\cos\theta}\right) \qquad \text{(AI.13)}$$

Equation (AI.13) is applicable provided $N \geq 100$.

For a polymer chain with restricted rotation around C—C bond, Eq. (AI.13) is modified to

$$\overline{r^2} = NL^2\left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}\right)$$

where $\overline{\cos\phi}$ is the average value of $\cos\phi$.

ANNEXURE II The Phenomenon of Diffusion

Definition of Flux

The phenomenon of diffusion involves the migration of solute molecules from the more concentrated region of a solution to the less concentrated region until the solution acquires uniform concentration. The rate of diffusion of matter across a unit area of cross-section perpendicular to the concentration gradient is known as flux (symbol: J). It is expressed as

$$J = \frac{1}{A}\frac{\mathrm{d}Q}{\mathrm{d}t} \quad \text{where } c = Q/V \tag{AII.1}$$

Fick's First Law of Diffusion

According to Fick's first law, the flux J is directly proportional to the concentration gradient, i.e.

$$J \propto \frac{\mathrm{d}c}{\mathrm{d}x}$$

or

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}x} \tag{AII.2}$$

where D is known as diffusion coefficient. The minus sign in Eq. (AII.2) is due to the fact that the matter flows in the direction of decreasing concentration.

Combining Eq. (AII.1) and (AII.2), we get

$$\frac{1}{A}\frac{\mathrm{d}Q}{\mathrm{d}t} = -D\frac{\mathrm{d}c}{\mathrm{d}x}$$

Since $c = Q/V$, we get

$$\frac{1}{A}\frac{\mathrm{d}Q}{\mathrm{d}t} = -D\frac{\mathrm{d}(Q/V)}{\mathrm{d}x} = -\frac{D}{V}\frac{\mathrm{d}Q}{\mathrm{d}x} \tag{AII.3}$$

Fick's Second Law of Diffusion

Consider an infinitesimal small volume element of area of cross-section A and thickness dx through which the material diffuses perpendicular to the area A from the more concentrated region to the less concentrated region (Fig. AII.1).

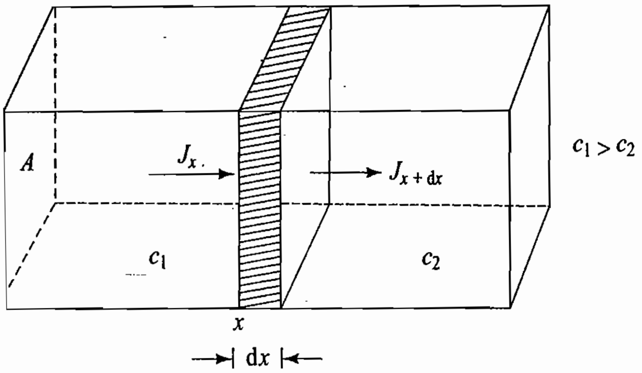


Fig. AII.1 Flow of the material from the more concentrated region to the less concentrated region

We have

Matter entering the volume element at x in time $\mathrm{d}t$ is

$$Q_x = J_x A\,\mathrm{d}t \tag{AII.4}$$

Matter leaving the volume element at $x + \mathrm{d}x$ in time $\mathrm{d}t$ is

$$Q_{x+\mathrm{d}x} = -J_{x+\mathrm{d}x} A\,\mathrm{d}t \tag{AII.5}$$

The net change of matter in the volume element is

$$\mathrm{d}Q = (J_x - J_{x+\mathrm{d}x}) A\,\mathrm{d}t \tag{AII.6}$$

Since $c = Q/V$, we have

$$\mathrm{d}Q = V\,\mathrm{d}c = (A\,\mathrm{d}x)\,\mathrm{d}c$$

With this, Eq. (AII.6) becomes

$$(A\,\mathrm{d}x)\,\mathrm{d}c = (J_x - J_{x+\mathrm{d}x})A\,\mathrm{d}t$$

or $$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{1}{\mathrm{d}x}(J_x - J_{x+\mathrm{d}x}) \tag{AII.7}$$

Using Eq. (AII.2), we get

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{1}{\mathrm{d}x}\left[-D\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)_x + D\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)_{x+\mathrm{d}x}\right]$$

$$= D\left[\frac{1}{\mathrm{d}x}\left\{\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)_{x+\mathrm{d}x} - \left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)_x\right\}\right]$$

$$= D\,\frac{\mathrm{d}^2c}{\mathrm{d}x^2} \tag{AII.8}$$

Equation (AII.8) is known as Fick's second law of diffusion.

Diffusion Coefficient and Frictional Factor

The driving force for the diffusion is due to the difference in the chemical potential of the solute in two regions. For the distance $\mathrm{d}x$, we can write

$$\frac{\mathrm{d}\mu}{\mathrm{d}x} = \frac{\mathrm{d}(\mu_2^\circ + RT\ln c_2)}{\mathrm{d}x} = \frac{RT}{c_2}\,\frac{\mathrm{d}c_2}{\mathrm{d}x}$$

For a single particle, the above expression is given by

$$F = \frac{1}{N_\mathrm{A}}\,\frac{\mathrm{d}\mu}{\mathrm{d}x_2} = \frac{kT}{c_2}\,\frac{\mathrm{d}c_2}{\mathrm{d}x} \tag{AII.9}$$

Under the stationary-state flow condition, the driving force is counter balanced by the force of viscous resistance, which is equal to $f\upsilon_\mathrm{s}$, where υ_s is the stationary velocity. Hence, we have

$$\frac{kT}{c_2}\,\frac{\mathrm{d}c_2}{\mathrm{d}x} = -f\upsilon_\mathrm{s}$$

Using Eq. (AII.2), we get

$$\frac{kT}{c_2}\left(-\frac{J}{D}\right) = -f\upsilon_s.$$

or

$$D = \frac{kT}{f}\left(\frac{J}{c_2\upsilon_s}\right) \tag{AII.10}$$

It can be shown that $J = c_2\upsilon_s$:

$$c_2\upsilon_s = \left(\frac{\mathrm{d}Q}{\mathrm{d}V}\right)\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) = \left(\frac{\mathrm{d}Q}{A\mathrm{d}x}\right)\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) = \frac{1}{A}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right) = J \tag{AII.11}$$

With this, Eq. (AII.10) is reduced to

$$D = \frac{kT}{f} \tag{AII.12}$$

Solution of Eq. (AII.8)

Equation (AII.8) is

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

Its solution is given by

$$c = \frac{l^\circ c_0}{2\left(\sqrt{\pi D t}\right)}\exp(-x^2/4Dt) \tag{AII.13}$$

where l° is the standard unit length. Given the initial concentration of a solute set at $x = 0$, it is possible to calculate the concentration at any position at a latter time, provided the value of diffusion coefficient is available. Figure AII.2 displays the shapes of plots of c versus x at two time intervals.

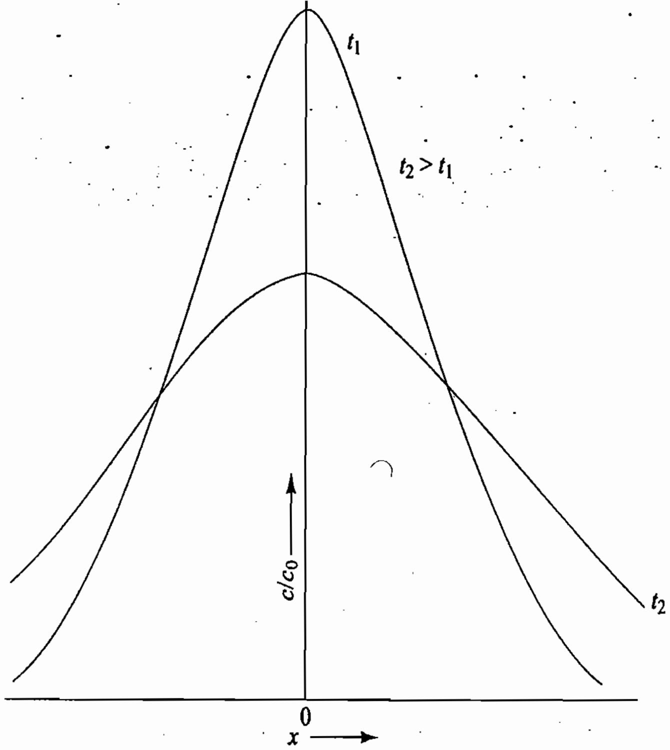


Fig. AII.2 Concentration profile at two different time intervals

If the concentration profiles at different times are available, it is possible to determine the diffusion coefficient by the graphical method. We have

Area under the curve obtained on integrating Eq. (AII.13) = $l^{\circ}c_0$

Also $$\text{Height (at } x = 0) = \frac{l^{\circ}c_0}{2\sqrt{\pi Dt}}$$

Hence, $$\frac{\text{Area}}{\text{Height}} = 2\sqrt{\pi Dt} \qquad \text{(AII.14)}$$

Thus, if a plot between (area/height)^2 and t is plotted, one gets a straight line with slope equal to $4\pi D$ (Fig. AII.3). From this, the value of D can be computed.

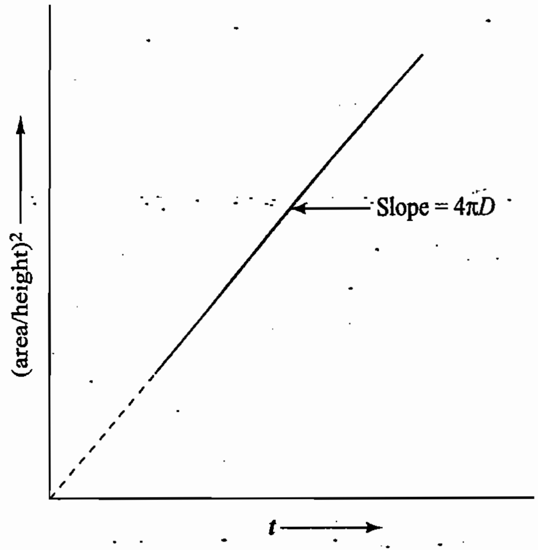


Fig. AII.3 Determination of the diffusion coefficient from the area/height plot

Diffusion and Random-Walk Statistics

The diffusing particle undergoes random motion due to its collisions with solvent molecules, each occurring after every average distance equal to its mean free path. Hence, the displacement of the particle in one direction, say x-direction, may be described by the random-walk statistics described in section 5.4.

According to the random-walk statistics, the probability function of locating the particle at the displacement x from the starting point is given by

$$P(x) = \frac{1}{(2\pi n l^2)^{1/2}} \exp(-x^2/2nl^2) \qquad \text{(AII.15)}$$

where n is the number of steps, each of length l, which the particle moves in arriving at the displacement x from the starting point.

In the diffusion process,

l^2 is replaced by $\overline{\lambda^2}$, where λ is the mean free path

n is interpreted as the number of successive collisions made by the solute particle.

This may be taken proportional to time, i.e. $n = At$, where A is constant of proportionality.

With these, Eq. (AII.15) modifies to

$$P(x, t) = \frac{1}{(2\pi At\overline{\lambda^2})^{1/2}} \exp(-x^2/2At\ \overline{\lambda^2}) \qquad \text{(AII.16)}$$

The probability function $P(x, t)$ may be identified as

$$P(x, t) = \frac{1}{l^\circ}\left(\frac{c_{x,t}}{c_0}\right) \qquad \text{(AII.17)}$$

where $c(x, t)$ is the concentration of solute at a distance x after time t from the start of diffusion at which concentration of solute was c_0 and l° is the standard unit length.

Substituting Eq. (AII.17) in Eq. (AII.16), we get

$$c_{x,t} = \frac{l^\circ c_0}{\left(2\pi At\overline{\lambda^2}\right)^{1/2}} \exp\left(-x^2/2At\overline{\lambda^2}\right) \qquad \text{(AII.18)}$$

The expression of A may be derived by using Fick's second law of diffusion (Eq. AII.8). From Eq. (AII.18), we get

$$\left(\frac{\partial c}{\partial t}\right)_x = \left[\frac{l^\circ c_0}{\left(2\pi A\overline{\lambda^2}\right)^{1/2}}\left(-\frac{1}{2t^{3/2}}\right) + \frac{l^\circ c_0}{\left(2\pi At\overline{\lambda^2}\right)^{1/2}}\left(\frac{x^2}{2At^2\overline{\lambda^2}}\right)\right]\exp(-x^2/2At\overline{\lambda^2})$$

$$= \frac{l^\circ c_0}{(2\pi At\overline{\lambda^2})^{1/2}}\left[-\frac{1}{2t} + \frac{x^2}{2At^2\overline{\lambda^2}}\right]\exp(-x^2/2At\ \overline{\lambda^2}) \qquad \text{(AII.19)}$$

Also $$\left(\frac{\partial c}{\partial x}\right)_t = \frac{l^\circ c_0}{(2\pi At\overline{\lambda^2})^{1/2}}\left(-\frac{x}{At\overline{\lambda^2}}\right)\exp(-x^2/2At\overline{\lambda^2})$$

$$\left(\frac{\partial^2 c}{\partial x^2}\right)_t = \frac{l^\circ c_0}{\left(2\pi At\overline{\lambda^2}\right)^{1/2}}\left[-\frac{1}{At\overline{\lambda^2}} + \frac{x^2}{\left(At\overline{\lambda^2}\right)^2}\right]\exp(-x^2/2At\ \overline{\lambda^2}) \qquad \text{(AII.20)}$$

Substituting Eqs (AII.19) and (AII.20) in Eq. (AII.8), and cancelling the common terms, we get

$$-\frac{1}{2t} + \frac{x^2}{2At^2\overline{\lambda^2}} = D\left[-\frac{1}{At\overline{\lambda^2}} + \frac{x^2}{\left(At\overline{\lambda^2}\right)^2}\right]$$

i.e. $$\frac{-At\overline{\lambda^2} + x^2}{2At^2\overline{\lambda^2}} = D\left(\frac{-At\overline{\lambda^2} + x^2}{\left(At\overline{\lambda^2}\right)^2}\right)$$

or $$D = \frac{\left(At\overline{\lambda^2}\right)^2}{2At^2\overline{\lambda^2}} = \frac{1}{2}A\overline{\lambda^2}$$

Hence, $A = 2D/\overline{\lambda^2}$

With this, Eq. (AII.18) becomes

$$c_{x,t} = \frac{l^\circ c_0}{(4\pi Dt)^{1/2}} \exp(-x^2/4Dt) \qquad \text{(AII.21)}$$

which is identical with Eq. (AII.13)

6 Introduction to Irreversible Processes

6.1 ENTROPY PRODUCTION IN IRREVERSIBLE PROCESSES

Clausius Inequality

According to Clausius inequality, a real transformation (which is also an irreversible process) satisfies the expression

$$\Delta S > \int_A^B \frac{dq_{irr}}{T} \tag{6.1.1}$$

For an isolated system, $dq_{irr} = 0$. Hence

$$\Delta S > 0 \tag{6.1.2}$$

that is, a real transformation occurring in an isolated system is accompanied with an increase in its entropy.

Internal and External Changes in Entropy

Equation (6.1.1) may be written as

$$\Delta S = \int_A^B \frac{dq_{irr}}{T} + \Delta_i S \tag{6.1.3}$$

where $\Delta_i S$, which has a positive value, is known as internal change in entropy or entropy production in the system as a result of spontaneous process occurring in the system.

For an infinitesimal change, Eq. (6.1.3) is written as

$$dS = \frac{dq_{irr}}{T} + d_i S \tag{6.1.4}$$

The first term on the right side is written as

$$d_e S = \frac{dq_{irr}}{T} \tag{6.1.5}$$

which represents the entropy exchanged between the system and surrounding. The subscipt e stands for external.

Uncompensated Heat

De donder defined $d_i S$ in terms of uncompensated heat by the expression

$$d_i S = \frac{dq'}{T} \tag{6.1.6}$$

With this, Eq. (6.1.4) becomes

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{irr}}}{T} + \frac{\mathrm{d}q'}{T} \tag{6.1.7}$$

Since $\mathrm{d_i}S > 0$, it follows that $\mathrm{d}q' > 0$.

Power of Irreversibility

De donder also defined the term power of irreversibility by the expression

$$P = \frac{\mathrm{d}q'}{\mathrm{d}t} = T\frac{\mathrm{d_i}S}{\mathrm{d}t} \tag{6.1.8}$$

In a system, both $\mathrm{d}q'$ and P are positive so long irreversible process is occurring in a closed system. When the system achieves the equilibtium state, both $\mathrm{d}q'$ and P become zero.

Examples of Entropy Production in Irreversible Processes

Heat Transfer Between Two Solids

Suppose two solids of identical composition but at different temperatures are brought in contact with each other. Because of inequality of temperature, heat flows from a body at higher temperature to a body at lower temperature. For an infinitesimal heat transfer, we will have

$$\mathrm{d}S_{\mathrm{h}} = -\frac{\mathrm{d}q}{T_{\mathrm{h}}} \quad \text{and} \quad \mathrm{d}S_{\mathrm{c}} = \frac{\mathrm{d}q}{T_{\mathrm{c}}} \qquad ;\ (\mathrm{d}q \text{ has a positive value})$$

The total change in entropy is

$$\mathrm{d}S = \mathrm{d}S_{\mathrm{h}} + \mathrm{d}S_{\mathrm{c}} = \mathrm{d}q\left(\frac{1}{T_{\mathrm{c}}} - \frac{1}{T_{\mathrm{h}}}\right)$$

Since $T_{\mathrm{h}} > T_{\mathrm{c}}$, it follows that $\mathrm{d}S > 0$, that is, an infinitesimal heat transfer (assuming no change in temperature of the bodies) is accompanied with increase in entropy of the system.

Isothermal Change in Volume of an Ideal Gas

Suppose an ideal gas is partitioned in two chambers by a movable piston as shown in Fig. 6.1.1. The gases in two chambers are maintained at constant temperature but at different pressures p_1 and p_2 with $p_1 > p_2$. The piston may be held at its position with a set of stops.

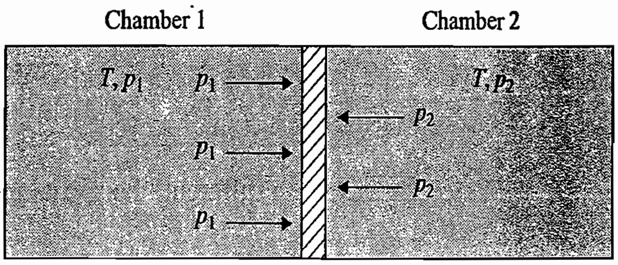


Fig. 6.1.1 An ideal gas in two chambers at the same temperature but at different pressures

Because of the pressure difference, the gas in Chamber 1 has a tendency to push the piston to the right. Consequently the gas in the Chamber 1 undergoes expansion while that in the Chamber 2 undergoes compression. This process is continued till the pressures on either sider of the piston have identical values. Considering the infiniitesimal change, we have

$$\mathrm{d}V_1 = \mathrm{d}V \quad \text{and} \quad \mathrm{d}V_2 = -\,\mathrm{d}V \qquad (\mathrm{d}V \text{ has a positive value})$$

Since the temperatures of the gases are held constant, we will have

$$\mathrm{d}U_1 = 0; \qquad \mathrm{d}q_1 = -\,\mathrm{d}w_1 = -\,(-p_2\,\mathrm{d}V_1) = p_2\,\mathrm{d}V$$

$$\mathrm{d}U_2 = 0; \qquad \mathrm{d}q_2 = -\,\mathrm{d}w_2 = -\,(-p_1\,\mathrm{d}V_2) = -\,p_1\,\mathrm{d}V$$

$$\mathrm{d}q_{\mathrm{irr}} = \mathrm{d}q_1 + \mathrm{d}q_2 = (p_2 - p_1)\,\mathrm{d}V$$

If the above process is to be carried reversibly, we will have

$$\mathrm{d}U_1 = 0; \qquad \mathrm{d}q_1' = -\,\mathrm{d}w_1' = -\,(-p_1\,\mathrm{d}V_1) = p_1\,\mathrm{d}V$$

$$\mathrm{d}U_2 = 0; \qquad \mathrm{d}q_2' = -\,\mathrm{d}w_2' = -\,(-p_2\,\mathrm{d}V_2) = -\,p_2\,\mathrm{d}V$$

$$\mathrm{d}q_{\mathrm{rev}} = \mathrm{d}q_1' + \mathrm{d}q_2' = (p_1 - p_2)\,\mathrm{d}V$$

The entropy change of the system is given by

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \left(\frac{p_1 - p_2}{T}\right)\mathrm{d}V$$

Since for an irreversible process

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{irr}}}{T} + \mathrm{d_i}S$$

we have

$$\left(\frac{p_1 - p_2}{T}\right)\mathrm{d}V = \left(\frac{p_2 - p_1}{T}\right)\mathrm{d}V + \mathrm{d_i}S$$

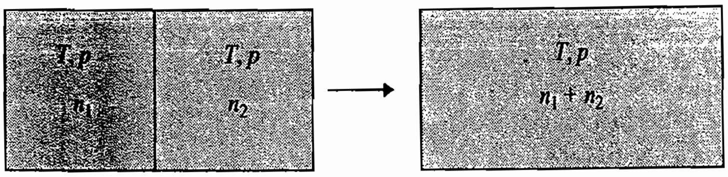
Thus $\quad \mathrm{d_i}S = 2\left(\dfrac{p_1 - p_2}{T}\right)\mathrm{d}V \qquad (6.1.11)$

Since $p_1 > p_2$, it follows that $\mathrm{d_i}S > 0$.

Mixing of Ideal Gases

Consider the mixing of two different ideal gases at the same temperature and pressure as shown in Fig. 6.1.2.

Fig. 6.1.2 Mixing of two different ideal gases at the same *T* and *p*.



Since the gases are different, the partial pressures of the gases after mixing are

$$p_1 = x_1\,p \quad \text{and} \quad p_2 = x_2\,p$$

The entropy changes of the two gases will be due to change in pressures. Hence

$$\Delta S_1 = n_1 RT \ln \frac{p}{p_1} \quad \text{and} \quad \Delta S_2 = n_2 RT \ln \frac{p}{p_2}$$

The total change in entropy is

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= RT\left[n_1 \ln \frac{p}{p_1} + n_2 \ln \frac{p}{p_2}\right] \tag{6.1.12}$$

Since $p > p_1$ and $p > p_2$, ΔS has a positive value.

Chemical Reaction

For a reaction undergoing completion from reactants to products at constant temperature and pressure, we will have

$$q_{T,p} = \Delta_r H$$

Also $\Delta_r S = \dfrac{q_{T,p}}{T} + \Delta_i S$

On rearranging this expression, we get

$$-T\,\Delta_i S = q_{T,p} - T\,\Delta_r S$$

$$= \Delta_r H - T\,\Delta_r S = \Delta_r G$$

Since for spontaneous reaction, $\Delta_r G < 0$, we will have

$$\Delta_i S = -\frac{\Delta_r G}{T} > 0 \tag{6.1.13}$$

In terms of affinity A $(= -\Delta_r G)$ of the reaction, we have

$$\Delta_i S = \frac{A}{T} > 0 \tag{6.1.14}$$

Entropy Production During the Progress of a Chemical Reaction

Taking $U = f(S, V, n_i)$, we have

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} \mathrm{d}V + \sum_{i=1}^{n}\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j\,(j\neq i)} \mathrm{d}n_i$$

$$= T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_{i=1}^{n} \mu_i\,\mathrm{d}n_i$$

or $$\mathrm{d}S = \frac{\mathrm{d}U + p\,\mathrm{d}V}{T} - \frac{1}{T}\sum_{i=1}^{n} \mu_i\,\mathrm{d}n_i$$

$$= \mathrm{d_e}S + \mathrm{d_i}S \tag{6.1.15}$$

Hence $$\mathrm{d_i}S = -\frac{1}{T}\sum_{i=1}^{n} \mu_i\,\mathrm{d}n_i \tag{6.1.16}$$

With the progress of a reaction, $\mathrm{d}n_i$ is given by

$$\mathrm{d}n_i = \nu_i\,\mathrm{d}\xi \tag{6.1.17}$$

where ν_i is the stoichiometric number of ith constituent of the reaction (ν_i is positive for a product and is negative for a reactant) and $\mathrm{d}\xi$ is the extent of reaction.

Substituting Eq. (6.1.17) in Eq. (6.1.16), we get

$$\mathrm{d_i}S = \frac{1}{T}\left(\sum_{i=1}^{n}(-\mu_i \nu_i)\right)\mathrm{d}\xi = \frac{A}{T}\,\mathrm{d}\xi \qquad (6.1.18)$$

where A is the affinity of the chemical reaction. The rate at which entropy is produced is given by

$$\frac{\mathrm{d_i}S}{\mathrm{d}t} = \frac{A}{T}\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad (6.1.19)$$

Various Criteria of Irreversible Processes

The criteria $\mathrm{d}U_{S,\,V} < 0$, $\mathrm{d}H_{S,\,p} < 0$, $\mathrm{d}A_{A,\,V} < 0$ and $\mathrm{d}G_{T,\,p} < 0$ for the spontaneous processes can be conveniently derived in terms of $\mathrm{d_i}S$ as shown in the following.

Criterion of $\mathrm{d}U_{S,\,V} < 0$

From the first law of thermodynamics, we have

$$\begin{aligned}\mathrm{d}U &= \mathrm{d}q + \mathrm{d}w\\ &= T\,\mathrm{d_e}S - p\,\mathrm{d}V = T(\mathrm{d}S - \mathrm{d_i}S) - p\,\mathrm{d}V\\ &= T\,\mathrm{d}S - T\,\mathrm{d_i}S - p\,\mathrm{d}V\end{aligned}$$

Hence $\mathrm{d}U_{S,\,V} = -T\,\mathrm{d_i}S$

Since $\mathrm{d_i}S > 0$ for the irreversible processes, it follows that

$$\mathrm{d}U_{S,\,V} < 0$$

Criterion of $\mathrm{d}H_{S,\,p} < 0$

Since $H = U + pV$, we have

$$\begin{aligned}\mathrm{d}H &= \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p\\ &= (T\,\mathrm{d}S - T\,\mathrm{d_i}S - p\,\mathrm{d}V) + p\,\mathrm{d}V + V\,\mathrm{d}p\\ &= T\,\mathrm{d}S - T\,\mathrm{d_i}S + V\,\mathrm{d}p\end{aligned}$$

Hence $\mathrm{d}H_{S,\,p} = -T\,\mathrm{d_i}S < 0$ (as $\mathrm{d_i}S > 0$)

Criterion of $\mathrm{d}A_{T,\,V} < 0$

Since $A = U - TS$, we have

$$\begin{aligned}\mathrm{d}A &= \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T\\ &= (T\,\mathrm{d}S - T\,\mathrm{d_i}S - p\,\mathrm{d}V) - T\,\mathrm{d}S - S\,\mathrm{d}T\\ &= -\,T\,\mathrm{d_i}S - p\,\mathrm{d}V - S\,\mathrm{d}T\end{aligned}$$

Hence $\mathrm{d}A_{T,\,V} = -T\,\mathrm{d_i}S < 0$ (as $\mathrm{d_i}S > 0$)

Criterion of $\mathrm{d}G_{T,\,p} < 0$

Since $G = H - TS$, we have

$$\begin{aligned}\mathrm{d}G &= \mathrm{d}H - T\,\mathrm{d}S - S\,\mathrm{d}T\\ &= (T\,\mathrm{d}S - T\,\mathrm{d_i}S + V\,\mathrm{d}p) - T\,\mathrm{d}S - S\,\mathrm{d}T\\ &= -\,T\,\mathrm{d_i}S + V\,\mathrm{d}p - S\,\mathrm{d}T\end{aligned}$$

Hence $\mathrm{d}G_{T,\,p} = -T\,\mathrm{d_i}S < 0$ (as $\mathrm{d_i}S > 0$)

6.2 THERMODYNAMIC PROOF OF $\Delta_\mathrm{i}S$ ASSOCIATED WITH A CHEMICAL REACTION

The state of a closed system involving a chemical reaction may be defined by the three variables, namely, T, p and ξ (extent of reaction). For example, the enthalpy of the system may be written as

$$H = f(T, p, \xi)$$

Hence $$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_{p,\xi}\mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\xi}\mathrm{d}p + \left(\frac{\partial H}{\partial \xi}\right)_{T,p}\mathrm{d}\xi \tag{6.2.1}$$

Since $H = U + pV$, we will have

$$\begin{aligned} \mathrm{d}H &= \mathrm{d}U + p\,\mathrm{d}V + V\mathrm{d}p \\ &= (\mathrm{d}q + \mathrm{d}w) + p\,\mathrm{d}V + V\mathrm{d}p \qquad \text{(First law of thermodynamics)} \\ &= (\mathrm{d}q - p\,\mathrm{d}V) + p\,\mathrm{d}V + V\mathrm{d}p \\ &= \mathrm{d}q + V\mathrm{d}p \end{aligned} \tag{6.2.2}$$

Comparing Eqs (6.2.1) and (6.2.2), we get

$$\mathrm{d}q = \left(\frac{\partial H}{\partial T}\right)_{p,\xi}\mathrm{d}T + \left[\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right]\mathrm{d}p + \left(\frac{\partial H}{\partial \xi}\right)_{T,p}\mathrm{d}\xi$$

Dividing throughout by T, we get

$$\frac{\mathrm{d}q}{T} = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,\xi}\mathrm{d}T + \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right]\mathrm{d}p + \frac{1}{T}\left(\frac{\partial H}{\partial \xi}\right)_{T,p}\mathrm{d}\xi \tag{6.2.3}$$

Let us assume that $\mathrm{d}q/T$ (= $\mathrm{d}S$) is an axact differential, for which, the following Euler's reciprocity relations must hold good.

$$\frac{\partial}{\partial p}\left[\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,\xi}\right]_{T,\xi} = \frac{\partial}{\partial T}\left[\frac{1}{T}\left\{\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right\}\right]_{p,\xi} \tag{6.2.4}$$

$$\frac{\partial}{\partial \xi}\left[\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,\xi}\right]_{T,p} = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial H}{\partial \xi}\right)_{T,p}\right]_{p,\xi} \tag{6.2.5}$$

and $$\frac{\partial}{\partial \xi}\left[\frac{1}{T}\left\{\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right\}\right]_{T,p} = \frac{\partial}{\partial p}\left[\frac{1}{T}\left(\frac{\partial H}{\partial \xi}\right)_{T,p}\right]_{T,\xi} \tag{6.2.6}$$

Result of Eq. (6.2.4) Carrying out the differentiation in Eq. (6.2.4), we get

$$\frac{1}{T}\frac{\partial^2 H}{\partial p\,\partial T} = -\frac{1}{T^2}\left\{\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right\} + \frac{1}{T}\left[\frac{\partial^2 H}{\partial T\,\partial p} - \left(\frac{\partial V}{\partial T}\right)_{p,\xi}\right]$$

Since $\partial^2 H/\partial T\,\partial p = \partial^2 H/\partial p\,\partial T$, we get

$$\frac{1}{T^2}\left\{\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right\} = -\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_{p,\xi}$$

or $$\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V = -T\left(\frac{\partial V}{\partial T}\right)_{p,\xi} \tag{6.2.7}$$

Equation (6.2.7) is the expression of thermodynamic equation of state, which we know holds good for all substances.

Result of Eq. (6.2.5) Carrying out the differentiation in Eq. (6.2.5), we get

$$\frac{1}{T}\frac{\partial^2 H}{\partial \xi \partial T} = -\frac{1}{T^2}\left(\frac{\partial H}{\partial \xi}\right)_{T,p} + \frac{1}{T}\frac{\partial^2 H}{\partial T \partial \xi}$$

Since $\partial^2 H/\partial\xi\,\partial T = \partial^2 H/\partial T\,\partial\xi$, we get

$$\Delta_\mathrm{r} H = \left(\frac{\partial H}{\partial \xi}\right)_{T,p} = 0 \tag{6.2.8}$$

that is, the enthalpy of reaction must be equal to zero.

Result of Eq. (6.2.6) Carrying out the differentiation in Eq. (6.2.6), we get

$$\frac{1}{T}\left[\frac{\partial^2 H}{\partial \xi \partial p} - \left(\frac{\partial V}{\partial \xi}\right)_{T,p}\right] = \frac{1}{T}\frac{\partial^2 H}{\partial p \partial \xi}$$

Since $\partial^2 H/\partial\xi\,\partial p = \partial^2 H/\partial p\,\partial\xi$, we get

$$\Delta_\mathrm{r} V = \left(\frac{\partial V}{\partial \xi}\right)_{T,p} = 0 \tag{6.2.9}$$

that is, the change in volume involved in a chemical reaction must be equal to zero.

Comment on Eqs (6.2.8) and (6.2.9) In general, Eqs (6.2.8) and (6.2.9) may not be satisfied for a chemical reaction. This is due to the fact that the term $\mathrm{d}q/T$ in Eq. (6.2.3), which is assumed to be exact differential, is not valid because of irreversible nature of the chemical reaction.

Introducing Entropy Production in Eq. (6.2.3) There is a need of introducting the term $\mathrm{d_i}S$ (entropy production) in the expression of $\mathrm{d}q/T$ (= $\mathrm{d}S$). Thus; we must have

$$\mathrm{d}S = \frac{\mathrm{d}q}{T} + \mathrm{d_i}S \tag{6.2.10}$$

Introducing Eq. (6.2.3) in the above expression, we get

$$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,\xi}\mathrm{d}T + \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right]\mathrm{d}p + \frac{1}{T}\left(\frac{\partial H}{\partial \xi}\right)_{T,p}\mathrm{d}\xi + \mathrm{d_i}S$$

which in view of Eq. (6.2.7) and the fact that $(\partial H/\partial T)_{p,\xi} = C_{p,\xi}$ and $(\partial H/\partial \xi)_{T,p} = \Delta_\mathrm{r} H$, we get

$$\mathrm{d}S = \left(\frac{C_{p,\xi}}{T}\right)\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_{p,\xi}\mathrm{d}p + \frac{\Delta_\mathrm{r} H}{T}\mathrm{d}\xi + \mathrm{d_i}S \tag{6.2.11}$$

In order that the expressions $(\partial S/\partial T)_p = C_p/T$ and $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$ remain unaffected and the application of Euler's reciprocity relations do not lead to

Eqs (6.2.8) and (6.2.9), it is required that the term $\mathrm{d_i}S$ should depend only on $\mathrm{d}\xi$. In fact, the expression as guided by Eq. (6.1.18) is

$$\mathrm{d_i}S = \frac{A}{T}\mathrm{d}\xi \tag{6.2.12}$$

where A, known as affinity of a chemical reaction, is given by

$$A = -\Delta_\mathrm{r}G = -\Sigma_i\, \nu_i\, \mu_i \tag{6.2.13}$$

where ν_i is the stoichimetric number (negative for reactants and positive for products) and μ_i is the chemical potential of ith species involved in the balanced chemical equation of the reaction.

Introducing Eq. (6.2.12) in Eq. (6.2.11), we get

$$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,\xi}\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_{p,\xi}\mathrm{d}p + \frac{\Delta_\mathrm{r}H + A}{T}\mathrm{d}\xi \tag{6.2.14}$$

Verification of d*S* as Exact Differential

For dS in Eq. (6.2.14) to be an exact differential, we will have to verify the following cross derivatives.

$$\frac{\partial}{\partial\xi}\left[\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,\xi}\right]_{T,p} = \frac{\partial}{\partial T}\left[\frac{\Delta_\mathrm{r}H + A}{T}\right]_{p,\xi} \tag{6.2.15}$$

and

$$\frac{\partial}{\partial\xi}\left[-\left(\frac{\partial V}{\partial T}\right)_{p,\xi}\right]_{T,p} = \frac{\partial}{\partial p}\left[\frac{\Delta_\mathrm{r}H + A}{T}\right]_{T,\xi} \tag{6.2.16}$$

Verification of Eq. (6.2.15) The left side of Eq. (6.2.15) gives

$$\frac{\partial}{\partial\xi}\left[\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,\xi}\right]_{T,p} = \frac{1}{T}\frac{\partial^2 H}{\partial\xi\,\partial T}$$

The right side of Eq. (6.2.15) gives

$$\frac{\partial}{\partial T}\left[\frac{\Delta_\mathrm{r}H + A}{T}\right]_{p,\xi} = \frac{\partial}{\partial T}\left[\frac{1}{T}\left\{\left(\frac{\partial H}{\partial\xi}\right)_{T,p} - \sum_i \nu_i\,\mu_i\right\}\right]_{p,\xi}$$

$$= -\frac{1}{T^2}\left[\left(\frac{\partial H}{\partial\xi}\right)_{T,p} - \sum_i \nu_i\,\mu_i\right] + \frac{1}{T}\left[\frac{\partial^2 H}{\partial T\,\partial\xi} - \sum_i \nu_i\left(\frac{\partial\mu_i}{\partial T}\right)_{p,\xi}\right]$$

Since $(\partial\mu_i/\partial T)_{p,\xi} = -S_i$, we get

$$\frac{\partial}{\partial T}\left[\frac{\Delta_\mathrm{r}H + A}{T}\right]_{p,\xi} = -\frac{1}{T^2}\left[\left(\frac{\partial H}{\partial\xi}\right)_{T,p} - \sum_i \nu_i\mu_i\right] + \frac{1}{T}\left[\frac{\partial^2 H}{\partial T\,\partial\xi} + \sum_i \nu_i S_i\right]$$

$$= -\frac{\Delta_\mathrm{r}H}{T^2} + \frac{1}{T^2}\left[\sum_i \nu_i\mu_i + T\sum_i \nu_i S_i\right] + \frac{1}{T}\frac{\partial^2 H}{\partial T\,\partial\xi}$$

$$= -\frac{\Delta_r H}{T^2} + \frac{1}{T^2}[\Delta_r G + T\,\Delta_r S] + \frac{1}{T}\frac{\partial^2 H}{\partial T\,\partial \xi}$$

$$= -\frac{\Delta_r H}{T^2} + \frac{\Delta_r H}{T^2} + \frac{1}{T}\frac{\partial^2 H}{\partial T\,\partial \xi}$$

$$= \frac{1}{T}\frac{\partial^2 H}{\partial T\,\partial \xi}$$

Since $\partial^2 H/\partial\xi\partial T = \partial^2 H/\partial T\partial\xi$, both sides of Eq. (6.2.15) are identical. Hence, Euler's reciprocity relation is satisfied.

Verification of Eq. (6.2.16) The left side of Eq. (6.2.16) gives

$$\frac{\partial}{\partial \xi}\left[-\left(\frac{\partial V}{\partial T}\right)_{p,\xi}\right]_{T,p} = \frac{\partial}{\partial \xi}\left[\frac{1}{T}\left\{\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right\}\right]_{T,p} \qquad \text{(Eq. 6.2.7)}$$

$$= \frac{1}{T}\left[\frac{\partial^2 H}{\partial \xi\,\partial p} - \left(\frac{\partial V}{\partial \xi}\right)_{T,p}\right]$$

$$= \frac{1}{T}\left[\frac{\partial^2 H}{\partial \xi\,\partial p} - \Delta_r V\right]$$

The right side of Eq. (6.2.16) gives

$$\frac{\partial}{\partial p}\left[\frac{\Delta_r H + A}{T}\right]_{T,\xi} = \frac{\partial}{\partial p}\left[\frac{1}{T}\left\{\left(\frac{\partial H}{\partial \xi}\right)_{T,p} - \sum_i \nu_i \mu_i\right\}\right]_{T,\xi}$$

$$= \frac{1}{T}\frac{\partial^2 H}{\partial p\,\partial \xi} - \frac{1}{T}\sum_i \nu_i \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\xi}$$

Since $(\partial\mu_i/\partial p)_{T,\xi} = V_i$, we get

$$\frac{\partial}{\partial p}\left[\frac{\Delta_r H + A}{T}\right]_{T,\xi} = \frac{1}{T}\frac{\partial^2 H}{\partial p\,\partial \xi} - \frac{1}{T}\sum_i \nu_i V_i$$

$$= \frac{1}{T}\left[\frac{\partial^2 H}{\partial p\,\partial \xi} - \Delta_r V\right]$$

Since $\partial^2 H/\partial\xi\partial p = \partial^2 H/\partial p\partial\xi$, both sides of Eq. (6.2.16) are identical. Hence, Euler's reciprocity relation is satisfied.

6.3 ALTERNATIVE EXPRESSIONS OF AFFINITY OF A CHEMICAL REACTION

For an irreversible process, the second law of thermodynamics gives

$$\mathrm{d}S = \mathrm{d_e}S + \mathrm{d_i}S = \frac{\mathrm{d}q}{T} + \mathrm{d_i}S \qquad (6.3.1)$$

Expression Involving Internal Energy

From the first law of thermodynamics, we have

$$dq = dU - dw = dU + p\,dV$$

Hence
$$dS = \frac{dU + p\,dV}{T} + d_i S \tag{6.3.2}$$

For a chemical reaction

$$d_i S = \frac{A}{T}\,d\xi$$

Hence
$$dS = \frac{dU + p\,dV}{T} + \frac{A}{T}\,d\xi$$

or
$$dU = T\,dS - p\,dV - A\,d\xi \tag{6.3.3}$$

From this, it follows that

$$A = -\left(\frac{\partial U}{\partial \xi}\right)_{S,V} \tag{6.3.4}$$

Expression Involving Enthalpy

Since $H = U + pV$, we get

$$dH = dU + p\,dV + V\,dp$$

Substituting dU from Eq. (6.3.3) in the above expression, we get

$$\begin{aligned} dH &= (T\,dS - p\,dV - A\,d\xi) + p\,dV + V\,dp \\ &= T\,dS + V\,dp - A\,d\xi \end{aligned} \tag{6.3.5}$$

From Eq. (6.3.5), it follows that

$$A = -\left(\frac{\partial H}{\partial \xi}\right)_{S,p} \tag{6.3.6}$$

Expression Involving Helmholtz Function

We use the symbol F for the Helmholtz function in order to distinguish it from the symbel A used for affinity of a chemical reaction.

Since $F = U - TS$, we get

$$dF = dU - T\,dS - S\,dT$$

Substituting dU from Eq. (6.3.3) in the above expression, we get

$$\begin{aligned} dF &= (T\,dS - p\,dV - A\,d\xi) - T\,dS - S\,dT \\ &= -S\,dT - p\,dV - A\,d\xi \end{aligned} \tag{6.3.7}$$

From Eq. (6.3.7), it follows that

$$A = -\left(\frac{\partial F}{\partial \xi}\right)_{T,V} \tag{6.3.8}$$

Expression Involving Free Energy

Since $G = H - TS$, we have

$$dG = dH - T\,dS - S\,dT$$

Substituting dH from Eq. (6.3.5), we get

$$\begin{aligned} dG &= (T\,dS + V\,dp - A\,d\xi) - T\,dS - S\,dT \\ &= -S\,dT + V\,dp - A\,d\xi \end{aligned} \tag{6.3.9}$$

From Eq. (6.3.9), it follows that

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p} \tag{6.3.10}$$

This, we have

$$A = -\left(\frac{\partial U}{\partial \xi}\right)_{S,V} = -\left(\frac{\partial H}{\partial \xi}\right)_{S,p} = -\left(\frac{\partial F}{\partial \xi}\right)_{T,V} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p}$$

(*Note:* The variables kept constant in each derivative are the corresponding natural independent variables.)

Problem 6.3.1 Starting from $U = f(T, V, \xi)$ and $H = f(T, p, \xi)$, prove that

(i) $$A = T\left(\frac{\partial S}{\partial \xi}\right)_{T,V} - \left(\frac{\partial U}{\partial \xi}\right)_{T,V}$$

(ii) $$A = T\left(\frac{\partial S}{\partial \xi}\right)_{T,p} - \left(\frac{\partial H}{\partial \xi}\right)_{T,p}$$

Solution (i) Taking $U = f(T, V, \xi)$, we write

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_{V,\xi} \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_{T,\xi} \mathrm{d}V + \left(\frac{\partial U}{\partial \xi}\right)_{T,V} \mathrm{d}\xi$$

Also $\mathrm{d}U = \mathrm{d}q - p\,\mathrm{d}V = T(\mathrm{d}S - \mathrm{d_i}S) - p\,\mathrm{d}V$

$$= T\,\mathrm{d}S - p\,\mathrm{d}V - T\,\mathrm{d_i}S = T\mathrm{d}S - p\,\mathrm{d}V - A\,\mathrm{d}\xi$$

Equating the two expression of dU, we get

$$T\,\mathrm{d}S - p\,\mathrm{d}V - A\,\mathrm{d}\xi = \left(\frac{\partial U}{\partial T}\right)_{V,\xi} \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_{T,\xi} \mathrm{d}V + \left(\frac{\partial U}{\partial \xi}\right)_{T,V} \mathrm{d}\xi$$

or $$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,\xi} \mathrm{d}T + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{T,\xi} + p\right]\mathrm{d}V + \frac{1}{T}\left[\left(\frac{\partial U}{\partial \xi}\right)_{T,V} + A\right]\mathrm{d}\xi \quad (1)$$

Since dS is an exact differential, the cross derivatives of the first two terms gives

$$\frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,\xi}\right]_{T,\xi} = \frac{\partial}{\partial T}\left[\frac{1}{T}\left\{\left(\frac{\partial U}{\partial V}\right)_{T,\xi} + p\right\}\right]_{V,\xi}$$

i.e. $$\frac{1}{T}\frac{\partial^2 U}{\partial V\,\partial T} = -\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_{T,\xi} + p\right] + \frac{1}{T}\left[\left(\frac{\partial^2 U}{\partial T\,\partial V}\right) + \left(\frac{\partial p}{\partial T}\right)_{V,\xi}\right]$$

Since $\partial^2 U/\partial V\,\partial T = \partial^2 U/\partial T\,\partial V$, we get

$$\left(\frac{\partial U}{\partial V}\right)_{T,\xi} + p = T\left(\frac{\partial p}{\partial T}\right)_{V,\xi}$$

With this, Eq. (1) becomes

$$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,\xi} \mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_{V,\xi} \mathrm{d}V + \frac{1}{T}\left[\left(\frac{\partial U}{\partial \xi}\right)_{T,V} + A\right]\mathrm{d}\xi$$

From this expression, we get

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,V} = \frac{1}{T}\left[\left(\frac{\partial U}{\partial \xi}\right)_{T,V} + A\right] \quad \text{or} \quad A = T\left(\frac{\partial S}{\partial \xi}\right)_{T,V} - \left(\frac{\partial U}{\partial \xi}\right)_{T,V}$$

(ii) Taking $H = f(T, p, \xi)$, we write

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\xi} \mathrm{d}p + \left(\frac{\partial H}{\partial \xi}\right)_{T,p} \mathrm{d}\xi$$

Also $\mathrm{d}H = \mathrm{d}\,(U + pV) = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p$

$$= (\mathrm{d}q - p\,\mathrm{d}V) + p\,\mathrm{d}V + V\,\mathrm{d}p = \mathrm{d}q + V\,\mathrm{d}q$$

$$= T\,(\mathrm{d}S - \mathrm{d_i}S) + V\,\mathrm{d}p = T\,\mathrm{d}S + V\,\mathrm{d}p - T\,\mathrm{d_i}S$$

$$= T\,\mathrm{d}S + V\,\mathrm{d}S - A\,\mathrm{d}\xi$$

Equating the two expressions of dH, we get

$$T\,\mathrm{d}S + V\,\mathrm{d}p - A\,\mathrm{d}\xi = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\xi} \mathrm{d}p + \left(\frac{\partial H}{\partial \xi}\right)_{T,p} \mathrm{d}\xi$$

or

$$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{T,\xi} \mathrm{d}T + \frac{1}{T}\left\{\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right\}\mathrm{d}p + \frac{1}{T}\left[\left(\frac{\partial H}{\partial \xi}\right)_{T,p} + A\right]_{T,p} \mathrm{d}\xi \quad (2)$$

The cross derivatives of the first two terms, we get

$$\frac{\partial}{\partial p}\left[\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,\xi}\right]_{T,\xi} = \frac{\partial}{\partial T}\left[\frac{1}{T}\left\{\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right\}\right]_{p,\xi}$$

i.e.

$$\frac{1}{T}\frac{\partial^2 H}{\partial p\,\partial T} = -\frac{1}{T^2}\left\{\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V\right\} + \frac{1}{T}\left[\left(\frac{\partial^2 H}{\partial T\,\partial p}\right) - \left(\frac{\partial V}{\partial T}\right)_{p,\xi}\right]$$

Since $\partial^2 H/\partial p\,\partial T = \partial^2 H/\partial T\,\partial p$, we get

$$\left(\frac{\partial H}{\partial p}\right)_{T,\xi} - V = -T\left(\frac{\partial V}{\partial T}\right)_{p,\xi}$$

With this, Eq. (2) becomes

$$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial H}{\partial p}\right)_{T,\xi} \mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_{p,\xi} \mathrm{d}p + \frac{1}{T}\left[\left(\frac{\partial H}{\partial \xi}\right)_{T,p} + A\right]\mathrm{d}\xi$$

From this expression, it is obvious that

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,p} = \frac{1}{T}\left[\left(\frac{\partial H}{\partial \xi}\right)_{T,p} + A\right]$$

or $$A = T\left(\frac{\partial S}{\partial \xi}\right)_{T,p} - \left(\frac{\partial H}{\partial \xi}\right)_{T,p}$$

(*Note:* This derivation also follows from the definition of A as shown in the following.)

$$A = -\Delta_r G = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = -\left[\frac{\partial (H-TS)}{\partial \xi}\right]_{T,p} = -\left(\frac{\partial H}{\partial \xi}\right)_{T,p} + T\left(\frac{\partial S}{\partial \xi}\right)_{T,p}$$

6.4 THERMODYNAMIC TREATMENT OF IRREVERSIBLE PROCESSES

System at Local Equilibrium

A system involving an irreversible process does not have uniform value of any of the intensive variable within the system. The total value of its thermodynamic function, such as U, H, S, A and G, cannot be defined in terms of its independent variables (e.g., $U = f(S, V)$, $H = f(S, p)$, $A = f(T, V)$ and $G = f(T, p)$). However, such a system can be treated thermodynamically by considering it to be in local equilibrium[†] which involves the following characteristics.

- The system is treated as a large number of elemental cells of small volume, each in equilibrium, exchanging energy and matter with the neighbouring cells.
- Though the volume of elemental cell is small, yet it is large enough to ignore the influence of fluctuations on the physical properties of the subsystem.[‡]
- The intensive variables have well defined values in each cell and may vary from cell to cell. These are considered as the point functions which depend on position x and time t, i.e.

$$T = f(x, t); \qquad p = f(x, t); \qquad \mu = f(x, t); \cdots \qquad (6.4.1)$$

- Since intensive variables have well defined values in an elemental cell, these form the basis of defining extensive variables. The expression of these variables are exactly the same as those applicable to a thermodynamic system at equilibrium. Representing extensive variables in a cell by the lower case letters, we will have $h = u + pv$; $g = h - Ts$ and so on.

[†] See Annexure I at the and of this chapter for the concept of local equilibrium

[‡] See Annexure II at the end of this chapter for the theory of fluctuations. See Eq. (AII.34c) which states that the relative fluctuation of number of particles in a small volume depends inverseley upon the square root of average number of particles.

For example, the expression

$$U = TS - pV + \textstyle\sum_i n_i \mu_i \tag{6.4.2}$$

which is applicable to a system and can be derived by using Euler's theorem for homogeneous function, will take the following form for an elemental cell of the system

$$u = Ts - pv + \textstyle\sum_i n_i \mu_i \tag{6.4.3†}$$

- In local equilibrium, the extensive variables are replaced by their densities, i.e. extensive variable per unit volume of the elemental cell. These densities are represented as u_v, s_v, c_i,... such that .

  $$u_v = \frac{u}{v}; \quad s_v = \frac{s}{v}; \quad c_i = \frac{n_i}{v}, \cdots$$

  In terms of local quantities, Eq. (6.4.3) becomes

  $$u_v v = T(s_v v) - pv + \textstyle\sum_i (c_i v)\, \mu_i$$

  Canelling v, we get

  $$u_v = T\, s_v - p + \textstyle\sum_i c_i\, \mu_i \tag{6.4.4}$$

- The changes in thermodynamic variables are also given by expressions similar to those of a system at equilibrium. For example, if s, u and n_i are the entropy, intrinsic energy and amount of ith component, respectively, in an elemental cell of volume v, then the change in intrinsic energy at constant T and p is given by

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[†] **Derivation of Eq. (6.4.3) by using Euler's theorem** For a homogeneous function $\Phi(x, y, z, ...)$ of order n, Euler's theorem is

$$n\,\Phi = x\left(\frac{\partial \Phi}{\partial x}\right)_{y,z} + y\left(\frac{\partial \Phi}{\partial y}\right)_{x,z} + z\left(\frac{\partial \Phi}{\partial z}\right)_{x,y} + \cdots$$

The extensive property of a thermodynamic system is a homogeneous function of first order. Hence, the property $u(s, v, n_i)$ is given by

$$u = s\left(\frac{\partial u}{\partial s}\right)_{v,n_i} + v\left(\frac{\partial u}{\partial v}\right)_{s,n_i} + \sum_i n_i\left(\frac{\partial u}{\partial n_i}\right)_{s,v}$$

Also from thermodynamics,

$$\left(\frac{\partial u}{\partial s}\right)_{v,n_i} = T; \quad \left(\frac{\partial u}{\partial v}\right)_{s,n_i} = -p \text{ and } \left(\frac{\partial u}{\partial n_i}\right)_{s,v} = \mu_i$$

Hence $\quad u = Ts - pv + \sum_i n_i \mu_i$

$$\mathrm{d}u = T\,\mathrm{d}s - p\,\mathrm{d}v + \Sigma_i\,\mu_i \mathrm{d}n_i + \Sigma_i (z_i F\phi)\,\mathrm{d}n_i \qquad (6.4.5)$$

where

$T\,\mathrm{d}s$ corresponds to heat exchange

$-p\,\mathrm{d}v$ corresponds to mechanical work

$\mu_i\,\mathrm{d}n_i$ corresponds to change in the amount $\mathrm{d}n_i$ of ith species

and $(z_i F\phi)\,\mathrm{d}n_i$ is the electrical work ($\mathrm{d}w_{\mathrm{el}}$) associated with the amount $\mathrm{d}n_i$ of ith species carrying the charge z_i (may be positive or negative) under the influence of potential difference ϕ at the point under study. For an uncharged species, $z_i = 0$ and thus $\mathrm{d}w_{\mathrm{el}} = 0$.

Equation (6.4.5) may be written as

$$\mathrm{d}u = T\,\mathrm{d}s - p\,\mathrm{d}v + \Sigma_i\,\tilde{\mu}_i\,\mathrm{d}n_i \qquad (6.4.6)$$

where $\tilde{\mu}_i = \mu_i + z_i F\phi$, and is known as electrochemical potential. For an uncharged species $\tilde{\mu}_i = \mu_i$.

Expressing Eq. (6.4.6) in Terms of Local Quantities Substituting $u = u_v v$, $s = s_v v$ and $n_i = c_i v$ in Eq. (6.4.6), we get

$$\mathrm{d}(u_v v) = T\,\mathrm{d}(s_v v) - p\,\mathrm{d}v + \Sigma_i\,\tilde{\mu}_i\;\mathrm{d}(c_i v)$$

This gives

$$u_v\,\mathrm{d}v + v\,\mathrm{d}u_v = T\,(s_v\,\mathrm{d}v + v\,\mathrm{d}s_v) - p\,\mathrm{d}v + \Sigma_i\,\tilde{\mu}_i\,(c_i\,\mathrm{d}v + v\mathrm{d}c_i)$$

i.e. $$v\left(\mathrm{d}u_v - T\,\mathrm{d}s_v - \Sigma_i\,\tilde{\mu}_i\,\mathrm{d}c_i\right) + \overline{\mathrm{d}v}\left(u_v - Ts_v + p - \Sigma_i\,\tilde{\mu}_i\,c_i\right) = 0$$

which is view of Eq. (6.4.4) becomes

$$v\left(\mathrm{d}u_v - T\,\mathrm{d}s_v - \Sigma_i\,\tilde{\mu}_i\,\mathrm{d}c_i\right) = 0$$

Since v is not zero, we get

$$\mathrm{d}u_v - T\,\mathrm{d}s_v - \Sigma_i\,\tilde{\mu}_i\,\mathrm{d}c_i = 0 \qquad (6.4.7)$$

- The system is not far away from the equilibrium so as to have very small gradients in the intensive quantities within the system. This ensures constant values of intensive variables within the small volume of the elemental cell of the system. A system far away from equilibrium leads to large gradients in the intensive variables and the assumption of constant values of intensive variables within the small volume v may not be applicable.

6.5 FIRST LAW OF THERMODYNAMICS FOR AN OPEN SYSTEM

In an open system, the matter can be exchanged between the system and surroundings. If the exchange of pure heat is represented by $\mathrm{d}q'$ and that due to the exchange of matter by $\Sigma_i\,h_{i,\mathrm{pm}}\,\mathrm{d}n_i$, (where $h_{i,\mathrm{pm}}$ is the partial molar enthalpy of ith constituent), then the first law of thermodynamics ($\mathrm{d}u = \mathrm{d}q - p\,\mathrm{d}v$) may be written as

$$\mathrm{d}u = \mathrm{d}q + \mathrm{d}w$$

$$= \left(\mathrm{d}q' + \Sigma_i h_{i,\mathrm{pm}} \mathrm{d}n_i\right) - p\,\mathrm{d}v \qquad (6.5.1)^{\dagger}$$

(*Note:* For an open system $\mathrm{d}q = \mathrm{d}q' + \Sigma_i h_{i,\mathrm{pm}} \mathrm{d}n_i$ while for a closed system $\mathrm{d}q = \mathrm{d}q'$ as $\mathrm{d}n_i = 0$.)

Eq. (6.5.1) in Local Quantities

We write

$$u = u_v v\,; \quad n_i = c_i v \quad \text{and} \quad \mathrm{d}q' = \mathrm{d}q'_v v$$

where $\mathrm{d}q'_v$ the heat exchanged per unit volume of the system. Substituting these expressions in Eq. (6.5.1), we get

$$\mathrm{d}(u_v v) = v\,\mathrm{d}q'_v + \Sigma_i h_{i,\mathrm{pm}}\,\mathrm{d}(c_i v) - p\,\mathrm{d}v$$

This gives

$$u_v\,\mathrm{d}v + v\,\mathrm{d}u_v = v\,\mathrm{d}q'_v + \Sigma_i h_{i,\mathrm{pm}}\,(c_i\,\mathrm{d}v + v\,\mathrm{d}c_i) - p\,\mathrm{d}v$$

i.e.
$$v\left(\mathrm{d}u_v - \mathrm{d}q'_v - \Sigma_i h_{i,\mathrm{pm}}\,\mathrm{d}c_i\right) + \mathrm{d}v\left(u_v - \Sigma_i h_{i,\mathrm{pm}}\,c_i + p\right) = 0 \qquad (6.5.2)$$

Since $h = u + pv$, we get

$$h_v v = u_v v + p\,v \quad \text{i.e.} \quad h_v = u_v + p$$

Also
$$\Sigma_i h_{i,\mathrm{pm}}\,c_i = \sum\nolimits_i h_{i,\mathrm{pm}}\left(\frac{n_i}{v}\right) = \frac{\Sigma_i h_{i,\mathrm{pm}}\,n_i}{v} = \frac{h}{v} = h_v$$

With these, Eq. (6.5.2) becomes

$$v\left(\mathrm{d}u_v - \mathrm{d}q'_v - \Sigma_i h_{i,\mathrm{pm}}\,\mathrm{d}c_i\right) = 0$$

Since v is not zero, we must have

$$\mathrm{d}u_v - \mathrm{d}q' - \Sigma_i h_{i,\mathrm{pm}}\,\mathrm{d}c_i = 0$$

i.e.
$$\mathrm{d}u_v - \mathrm{d}q_v = 0 \quad \text{or} \quad \mathrm{d}u_v = \mathrm{d}q_v \qquad (6.5.3)$$

(*Note:* For a closed system $\mathrm{d}c_i = 0$ and hence $\mathrm{d}u_v = \mathrm{d}q'_v$ and also $\mathrm{d}q'_v = \mathrm{d}q_v$).

[†] Let the two compartments containing a fluid be separated from each other by a rigid membrane through which the fluid can be made to pass through from one compartment to the other. Let U_m and V_m be the molar energy and molar volume, respectively, of the fluid. If the amount dn of the fluid is transferred from one compartment to the other, then the energy associated with this are as follows.

- The energy $U_\mathrm{m}\,\mathrm{d}n$ associated with the amount dn of the fluid.
- In pushing fluid from one compartment to the other, the work equal to $p\,(V_\mathrm{m}\,\mathrm{d}n)$ is involved where p is the pressure offered by the fluid in the compartment receiving the fluid.

Hence, the total energy involved with the transfer of the amount dn of the fluid is

$$U_\mathrm{m}\,\mathrm{d}n + p\,(V_\mathrm{m}\,\mathrm{d}n) = (U_\mathrm{m} + pV_\mathrm{m})\,\mathrm{d}n = H_\mathrm{m}\,\mathrm{d}n$$

where H_m is the molar enthalpy of the fluid. If, besides flow of matter, there is a flow of heat also, then the total energy involved is given by

$$\mathrm{d}U = \mathrm{d}q' + H_\mathrm{m}\,\mathrm{d}n\cdot$$

6.6 EXPRESSION OF ENTROPY PRODUCTION AND DISSIPATION FUNCTION

Rate of Change of Local Quantities

Equation (6.4.7) is

$$\mathrm{d}u_v - T\,\mathrm{d}s_v - \Sigma_i \tilde{\mu}_i\ \mathrm{d}c_i = 0$$

Since $\mathrm{d}u_v = \mathrm{d}q_v$ (Eq. 6.5.3), we get

$$T\,\mathrm{d}s_v = \mathrm{d}q_v - \Sigma_i \tilde{\mu}_i\ \mathrm{d}c_i \qquad (6.6.1)$$

Dividing Eq. (6.6.1) by $\mathrm{d}t$ and keeping in mind that the space coordinates are constant, we get

$$T\frac{\partial s_v}{\partial t} = \frac{\partial q_v}{\partial t} - \sum_i \tilde{\mu}_i \frac{\partial c_i}{\partial t} \qquad (6.6.2)$$

Equation (6.6.2) is used to determine the local rate of entropy production in a continuous system.

Equation (6.6.2) Expressed in Divergence

According to the laws of conservation and continuity, we have

$$\frac{\partial s_i}{\partial t} = -\,\mathrm{div}\, \boldsymbol{J}_s + \sigma \qquad \text{(Eq. AI. 20)}$$

$$\frac{\partial c_i}{\partial t} = -\,\mathrm{div}\,(c_i V) + \nu_i J_\mathrm{r} = -\,\mathrm{div}\, \boldsymbol{J}_i + \nu_i J_\mathrm{r} \qquad \text{(Eq. AI. 19)}$$

The expression of $\partial q_v / \partial t$ may be written as

$$\frac{\partial q_v}{\partial t} = -\,\mathrm{div}\, \boldsymbol{J}_q$$

where $\boldsymbol{J}_q$ is the total heat flow across the boundary of the volume v of the elemental cell. Introducing the above expressions in Eq. (6.6.2), we get

$$T(-\,\mathrm{div}\, \boldsymbol{J}_s + \sigma) = -\,\mathrm{div}\, \boldsymbol{J}_q - \Sigma_i \tilde{\mu}_i(-\,\mathrm{div}\, \boldsymbol{J}_i + \nu_i J_\mathrm{r})$$

i.e.

$$-\,\mathrm{div}\, \boldsymbol{J}_s + \sigma = -\frac{1}{T}\mathrm{div}\, \boldsymbol{J}_q + \sum_i \frac{\tilde{\mu}_i}{T}\,\mathrm{div}\, \boldsymbol{J}_i + \frac{\Sigma_i(-\nu_i \tilde{\mu}_i)}{T} J_\mathrm{r}$$

$$= -\frac{1}{T}\mathrm{div}\, \boldsymbol{J}_q + \sum_i \frac{\tilde{\mu}_i}{T}\,\mathrm{div}\, \boldsymbol{J}_i + \frac{\tilde{A}}{T} J_\mathrm{r} \qquad (6.6.3)$$

where $\tilde{A}(= -\Sigma_i \nu_i \tilde{\mu}_i)$ represents the affinity of chemical reaction involving both charged and uncharged species. Expressing it explicitly, we have

$$\tilde{A} = -\Sigma_i \nu_i \tilde{\mu}_i = -\Sigma_i \nu_i(\mu_i + z_i F\varphi)$$

$$= A - (\Sigma_i \nu_i z_i)\ F\varphi \qquad (6.6.4)$$

Expression of Local Entropy Production

Since

$$\operatorname{div} a\boldsymbol{b} = a \operatorname{div} \boldsymbol{b} + \boldsymbol{b} \bullet \operatorname{grad} a \tag{6.6.5†}$$

we can write

$$a \operatorname{div} \boldsymbol{b} = \operatorname{div} a\boldsymbol{b} - \boldsymbol{b} \bullet \operatorname{grad} a$$

Using this expression in the first two terms on the right side of Eq. (6.6.3), we get

$$\frac{1}{T}\operatorname{div} \boldsymbol{J}_q = \operatorname{div}\left(\frac{\boldsymbol{J}_q}{T}\right) - \boldsymbol{J}_q \bullet \operatorname{grad}\left(\frac{1}{T}\right)$$

$$\frac{\tilde{\mu}_i}{T}\operatorname{div} \boldsymbol{J}_i = \operatorname{div}\left(\frac{\tilde{\mu}_i \boldsymbol{J}_i}{T}\right) - \boldsymbol{J}_i \bullet \operatorname{grad}\left(\frac{\tilde{\mu}_i}{T}\right)$$

With these, Eq. (6.3.3) becomes

$$\begin{aligned} -\operatorname{div} \boldsymbol{J}_s + \sigma &= -\left[\operatorname{div}\left(\frac{\boldsymbol{J}_q}{T}\right) - \boldsymbol{J}_q \bullet \operatorname{grad}\left(\frac{1}{T}\right)\right] \\ &\quad + \sum\nolimits_i \operatorname{div}\left[\left(\frac{\tilde{\mu}_i \boldsymbol{J}_i}{T}\right) - \boldsymbol{J}_i \bullet \operatorname{grad}\left(\frac{\tilde{\mu}_i}{T}\right)\right] + \frac{\tilde{A}}{T} J_{\mathrm{r}} \qquad (6.6.6) \\ &= -\operatorname{div}\left(\frac{\boldsymbol{J}_q}{T} - \sum\nolimits_i \frac{\tilde{\mu}_i \boldsymbol{J}_i}{T}\right) + \boldsymbol{J}_q \bullet \operatorname{grad}\left(\frac{1}{T}\right) + \sum\nolimits_i \boldsymbol{J}_i \bullet \operatorname{grad}\left(-\frac{\tilde{\mu}_i}{T}\right) + \frac{\tilde{A}}{T} J_{\mathrm{r}} \end{aligned}$$

Comparing the left and right sides of the above expression, we get

$$\boldsymbol{J}_s = \frac{\boldsymbol{J}_q - \sum_i \tilde{\mu}_i \boldsymbol{J}_i}{T} \tag{6.6.7}$$

and

$$\sigma = \boldsymbol{J}_q \bullet \operatorname{grad}\left(\frac{1}{T}\right) + \sum\nolimits_i \boldsymbol{J}_i \bullet \operatorname{grad}\left(-\frac{\tilde{\mu}_i}{T}\right) + \frac{\tilde{A}}{T} J_{\mathrm{r}} \tag{6.6.8}$$

Equation (6.6.7) gives the external flow of entropy across the boundary of the elemental cell and Eq. (6.6.8) gives the production of local entropy within the elemental cell. The production of entropy is expressed as the sum of products of flow with the corresponding conjugate force. There is one term for each process (i.e. energy transfer, material transfer or diffusion and chemical reaction). Each of these terms vanishes when the corresponding process is no more operative. Equation (6.6.8) is usually expressed as

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[†] $\operatorname{div}(a\boldsymbol{b}) = \nabla \bullet a\boldsymbol{b}$

$$= \left(\frac{\partial}{\partial x}\hat{\boldsymbol{i}} + \frac{\partial}{\partial y}\hat{\boldsymbol{j}} + \frac{\partial}{\partial z}\hat{\boldsymbol{k}}\right) \bullet \left(ab_x\,\hat{\boldsymbol{i}} + ab_y\,\hat{\boldsymbol{j}} + ab_z\,\hat{\boldsymbol{k}}\right) = \frac{\partial}{\partial x}(ab_x) + \frac{\partial}{\partial y}(ab_y) + \frac{\partial}{\partial z}(ab_z)$$

$$= a\left(\frac{\partial b_x}{\partial x} + \frac{\partial b_y}{\partial y} + \frac{\partial b_z}{\partial z}\right) + \left(b_x\frac{\partial a}{\partial x} + b_y\frac{\partial a}{\partial y} + b_z\frac{\partial a}{\partial z}\right)$$

$$= a \operatorname{div} \boldsymbol{b} + \boldsymbol{b} \bullet \operatorname{grad} a$$

$$\sigma = \sum_i J_i \bullet X_i \qquad (6.6.9)^{\dagger}$$

where X_i is the force conjugate to the flow J_i. In Eq. (6.6.8), we have

- Flow of heat J_q and the conjugate force X_q is grad $(1/T)$
- Flow of matter J_i and the conjugate force X_i is grad $(-\tilde{\mu}_i/T)$
- Occurring of a chemical reaction J_r and the conjugate force is $\tilde{A}/T$.

The product of each of the flow and the corresponding conjugate force has the dimension of entropy production.

Alternative Expression of Local Entropy Production

Since
$$\operatorname{grad}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\operatorname{grad} T$$

and
$$\operatorname{grad}\left(\frac{\tilde{\mu}_i}{T}\right) = \frac{1}{T}\operatorname{grad}\tilde{\mu}_i - \frac{\tilde{\mu}_i}{T^2}\operatorname{grad} T$$

we can write Eq. (6.6.8) as

$$\begin{aligned}
\sigma &= J_q \bullet \left(-\frac{1}{T^2}\operatorname{grad} T\right) + \Sigma_i J_i \bullet \left(-\frac{1}{T}\operatorname{grad}\tilde{\mu}_i + \frac{\tilde{\mu}_i}{T^2}\operatorname{grad} T\right) + J_r\frac{\tilde{A}}{T} \\
&= \frac{1}{T^2}J_q \bullet \operatorname{grad}(-T) + \sum_i \frac{J_i}{T} \bullet \operatorname{grad}(-\tilde{\mu}_i) - \frac{\Sigma_i \tilde{\mu}_i J_i}{T^2} \bullet \operatorname{grad}(-T) + J_r\frac{\tilde{A}}{T} \\
&= \frac{J_q - \Sigma_i \tilde{\mu}_i J_i}{T^2} \bullet \operatorname{grad}(-T) + \sum_i \frac{J_i}{T} \bullet \operatorname{grad}(-\tilde{\mu}_i) + J_r\frac{\tilde{A}}{T}
\end{aligned}$$

[†] The form of Eq. (6.6.9) can be derived on the basis of fluctuation theory of Einstein (see, Annexure AII). It can be shown that

$$\Delta S = -\frac{1}{2}\sum_{i,j=i}^{n} g_{ij}\alpha_i\alpha_j \qquad \text{(Eq. AII.21)}$$

where α represents fluctuation of a parameter from its equilibrium value and g_{ij} is given by

$$g_{ij} = -\left(\frac{\partial^2 S}{\partial \xi_i\, \partial \xi_j}\right) \qquad \text{(Eq. AII.22)}$$

The thermodynamic force is defined by

$$X_i = \frac{\partial(\Delta S)}{\partial \alpha_i} = -\sum_{j=1}^{n} g_{ij}\,\alpha_j \qquad \text{(Eq. AII.52)}$$

The expression of entropy production is

$$\frac{\partial(\Delta S)}{\partial t} = \sum_{i=1}^{n}\left(\frac{\partial \alpha_i}{\partial t}\right)\sum_{j=1}^{n}\left(-g_{ij}\,\alpha_j\right) = \sum_{i=1}^{n} J_i\, X_i$$

where the flux J_i is $\partial\alpha_i/\partial t$ and the force is X_i

which in view of Eq. (6.6.7) becomes

$$\sigma = \frac{J_s}{T} \bullet \text{grad}\,(-T) + \sum_i \frac{J_i}{T} \bullet \text{grad}\,(-\tilde{\mu}_i) + J_r \frac{\tilde{A}}{T} \qquad (6.6.10)$$

Equation (6.6.10) is also made up of different terms, each one is a product of a flow and the corresponding force and thus it is in the same form as given by Eq. (6.6.9), that is, $\sigma = \Sigma_i \, J_i \bullet X_i$ (6.6.11)

In the above expression, we find that

- Conjugate force for the flow of entropy (J_s) is grad$(-T)$ $/T$
- Conjugate force for the flow of meterial (J_i) is grad$(-\tilde{\mu}_i)/T$
- Conjugate force for the chemical reaction (flow is J_r) is $\tilde{A}/T$.

Each of the term in Eq. (6.6.10) has a dimension of entropy production. Equation (6.6.10) is a transformed expression of Eq. (6.6.8) and such a transformation has on effect on the production of entropy in a system.

Dissipation Function Lord Rayleigh defined a function which has a dimension of free energy instead of entropy. This function, known as dissipation function, is given by the expression

$$\Phi = T\sigma \qquad (6.6.12)$$

Equation (6.6.12) gives the rate of local dissipation of free energy per unit time as a result of irreversible process occurring in the elemental cell of a system. From Eq. (6.6.10), we find that

$$\Phi = J_s \bullet \text{grad}\,(-T) + \Sigma_i J_i \bullet \text{grad}\,(-\tilde{\mu}_i) + J_r \tilde{A} \qquad (6.6.13)$$

Equation (6.6.13), like Eq. (6.6.11), is the sum of different terms involving the product of a flow and its conjugate force, i.e.

$$\Phi = \Sigma_i J_i \bullet (TX_i) = \Sigma_i J_i \bullet X_i' \qquad (6.6.14)^\dagger$$

Examples of Entropy Production as a Product of Flow and Force

Electrical Conduction in a Wire Consider a wire of uniform cross-sectional area A at a constant uniform temperature. Let a steady current (due to the movement of electrons) flow in the wire under the influence of a potential gradient (from less potential to the more potential) along the wire. Consider an infinitesimal section of the wire of lenght dx as shown in Fig. 6.6.1

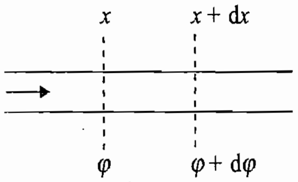

Fig. 6.6.1 Flow of charge in a wire

The system shown in Fig. 6.6.1 is in a steady state with the characteristics of

$$dU = 0 \quad \text{and} \quad dS = 0$$

Since $dS = d_eS + d_iS = dq/T + d_iS$, we will have

$$0 = dq/T + d_iS \quad \text{i.e.} \quad d_iS = -\,dq/T \qquad (6.6.15)$$

---

† For scalar quantities, only product is involved. Also for one-dimensional system, the vectors J_i and X_i may be treated as scalar quantities.

From the first law of thermodynamics, we have

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \quad \text{i.e.} \quad 0 = \mathrm{d}q + \mathrm{d}w$$

Hence $\mathrm{d}q = -\mathrm{d}w$

Work done by the electrostatic force in moving the charge $\mathrm{d}Q$ (which has a negative value) from x to $x + \mathrm{d}x$ is

$$\mathrm{d}w = -\,\mathrm{d}Q\,[(\varphi + \mathrm{d}\varphi) - \varphi] = -\,\mathrm{d}Q\,\mathrm{d}\varphi$$

With this, the expression of $\mathrm{d}q$ becomes

$$\mathrm{d}q = -(-\,\mathrm{d}Q\,\mathrm{d}\varphi) = \mathrm{d}Q\,\mathrm{d}\varphi$$

Hence, Eq. (6.6.15) gives

$$\mathrm{d_i}S = -\,\frac{\mathrm{d}Q\,\mathrm{d}\varphi}{T} \tag{6.6.16}$$

Since $\mathrm{d}Q = -\mathrm{ve}$, it follows that $\mathrm{d_i}S = +\mathrm{ve}$, i.e. the production of entropy is positive. The rate of production of entropy per unit volume ($= A\,\mathrm{d}x$) of the wire is

$$\sigma = \frac{1}{V}\frac{\mathrm{d_i}S}{\mathrm{d}t} = \frac{1}{A\,\mathrm{d}x}\,\frac{(-\mathrm{d}Q\,\mathrm{d}\phi/T)}{\mathrm{d}t} = \left[\frac{1}{A}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)\right]\left(-\frac{\mathrm{d}\varphi/T}{\mathrm{d}x}\right) \tag{6.6.17}$$

$$= I\ \mathrm{grad}\,(-\,\varphi/T)$$

Thus, σ is the product of flow (of electric current per unit area) and the conjugate force (which is grad $(-\,\varphi/T)$).

The expression of dissipation function is

$$T\sigma = \left[\frac{1}{A}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)\right]\left(-\frac{\mathrm{d}\varphi}{\mathrm{d}x}\right)_T$$

$$= J_\mathrm{i}\,X_\mathrm{i} \tag{6.6.18}$$

where $J_\mathrm{i} = \dfrac{1}{A}\left(\dfrac{\mathrm{d}Q}{\mathrm{d}t}\right)$, rate of flow of charge per unit area

and $X_i = -\,(\mathrm{d}\varphi/\partial x)_T$, force due to which charge flows in the wire

Heat Condution in a Bar

Consider a bar of uniform cross section A whose ends are maintained at different temperatures. Let the surface of the bar is insulated so that the heat flows entirely in the bar. Consider a small section of the bar of thickness $\mathrm{d}x$ as shown in Fig. 6.7.2.

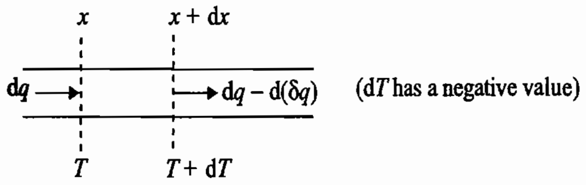

Fig. 6.6.2 Heat Conduction in a bar with $\mathrm{d}T < 0$

Let the heat $\mathrm{d}q$ enters at x where temperature is T and the heat $\mathrm{d}q - \mathrm{d}(\delta q)$ leaves at $x + \mathrm{d}x$ where temperature is $T + \mathrm{d}T$ in the time interval $\mathrm{d}t$. Thus,

Heat retained by the small section of the bar $= \mathrm{d}(\delta q)$

Assuming the above heat is absorbed by the small section of the bar at temperature T (as $\mathrm{d}T$ may be considered to have a small value in comparison to T), the change in entropy of this section of bar is

$$\mathrm{d}S = \frac{\mathrm{d}(\delta q)}{T} \tag{6.6.19}$$

The expression of $\mathrm{d_e}S$ is

$$\mathrm{d_e}S = \frac{\mathrm{d}q}{T} - \frac{\mathrm{d}q - \mathrm{d}(\delta q)}{T + \mathrm{d}T}$$

$$= \frac{T\,\mathrm{d}q + \mathrm{d}q\,\mathrm{d}T - T\,\mathrm{d}q + T\,\mathrm{d}(\delta q)}{T\,(T + \mathrm{d}T)}$$

Assuming $\mathrm{d}T$ to be negligible in comparison to T, we get

$$\mathrm{d_e}S = \frac{\mathrm{d}q\,\mathrm{d}T}{T^2} + \frac{\mathrm{d}(\delta q)}{T}$$

which in view of Eq. (6.6.19) becomes

$$\mathrm{d_e}S = \frac{\mathrm{d}q\,\mathrm{d}T}{T^2} + \mathrm{d}S$$

or $$\mathrm{d}S = \mathrm{d_e}S - \frac{\mathrm{d}q\,\mathrm{d}T}{T^2} = \mathrm{d_e}S + \mathrm{d_i}S$$

where $$\mathrm{d_i}S = (\mathrm{d}q)\left(-\frac{\mathrm{d}T}{T^2}\right) \tag{6.6.20}$$

Since $\mathrm{d}q > 0$ and $\mathrm{d}T < 0$, it follow that $\mathrm{d_i}S > 0$. The rate of production of entropy per unit volume is

$$\sigma = \frac{1}{V}\frac{\mathrm{d_i}S}{\mathrm{d}t} = \frac{1}{A\,\mathrm{d}x}\left(\frac{\mathrm{d}q}{\mathrm{d}t}\right)\left(-\frac{\mathrm{d}T}{T^2}\right)$$

$$= \left[\frac{1}{A}\left(\frac{\mathrm{d}q}{\mathrm{d}t}\right)\right]\left(-\frac{1}{T^2}\frac{\mathrm{d}T}{\mathrm{d}x}\right)$$

$$= J_q X_q \tag{6.6.21}$$ [†]

where J_q is the rate of heat flow per unit area and X_q is the corresponding force (= grad (1 / T))

The dissipation function is

$$T\sigma = \left[\frac{1}{A}\left(\frac{\mathrm{d}q}{\mathrm{d}t}\right)\right]\left(-\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}x}\right)$$

$$= J_q \bullet \frac{\mathrm{grad}\,(-T)}{T} \tag{6.6.22}$$

6.7 DEPENDENCE OF FLOW ON ITS CONJUGATE FORCE

Many examples are known in which flow of a quantity depends directly on its conjugate force. A few examples are listed in the following

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[†] Both J_q and X_q may be treated as scalar quantities as these act in x-direction

Fourier Law The flow of heat is linearly dependent on the negative gradient of its temperature, i.e.

$$J_q = -\lambda \text{ grad } T \tag{6.7.1}$$

where λ is known as thermal conductivity of the system.

Ohm's Law The flow of electricity is linearly dependent on the electromotive force, i.e.

$$J_e = -\gamma \text{ grad } \phi \tag{6.7.2}$$

where γ is known as electrical conductivity.

Fick's Law The rate of diffusion (i.e. flow of a material) is linearly dependent on the negative gradient of concentration; i.e.

$$J_i = -D \text{ grad } c_i \tag{6.7.3}$$

where D is known as diffusion coefficient.

Comments on the Laws The constants λ, γ and D are all positive quantities. These are not function of space and time. Fourier's law is applicable to an isotropic material and Ohm's law is applicable to a metallic conductor. The validity of the above mentioned laws is limited to a single flow and their applications require small gradients of forces.

Problem 6.7.1 The entropy production due to flow of heat is given by $\sigma = J_q \cdot \text{grad}\,(1/T)$. Using the fact that $\sigma > 0$. show that the thermal conductivity has a positive value.

Solution We have $\sigma = J_q \bullet \text{grad}\,(1/T) = -\dfrac{J_q}{T^2} \bullet \text{grad } T$

Introducing $J_q = -\lambda \text{ grad } T$ (Fourier law), we get

$$\sigma = \frac{(\lambda \text{ grad } T)}{T^2} \bullet \text{grad } T = \lambda \frac{(\text{grad } T)^2}{T^2}$$

Since $(\text{grad } T)^2$ and T^2 are always positive, and the fact that $\sigma > 0$ for an irreversible process, it follows that λ has a positive value.

Phenomenological Equation In the thermodynamic of irreversible processes, the dependence of flow (J) on its, conjugate force (X) such as involved in Eq. (6.6.11) is expressed as

$$J = LX \tag{6.7.4}$$[†]

where L is known as the phenomenological coefficient. It is a function of defining parameters of the volume element. It does not depend on the gradients of these parameters which define the appropriate force and also on the resultant flow.

6.8 COUPLING PHENOMENON

Many examples are known in which flow of a quantity, besides depending on its conjugate force, is also linearly dependent on a nonconjugative force. Similarly, a force, besides causing the flow of its conjugate quantity, also causes the flow of a nonconjugative quantity. This type of example is known as coupling phenomenon.

Example of Coupling Phenomenon One of the examples of a coupling phenomenon is described in the following.

Seeback Effect A gradient in temperature in a bimetallic system causes the generation of a gradient in electric potential.

[†] For dissipation function such as given by Eq. (6.6.14), the dependence of flow (J) on the conjugate force (X') is expressed as $J = L\,X' = L\,(XT) = (LT)\,X = L'\,X$

Peltier Effect Passage of electric current through a bimetallic circuit due to a potential difference causes absorption of heat at one junction and liberation of heat at the other junction.

From the above two effects, it may be concluded that the flow of heat is dependent upon the gradient of electrtic potential as well as upon the gradient of temperature. Also, the flow of electricity is a function of not only on the potential gradient but also on the temperature gradient.

Coupling Equations As proved earlier, the forces corresponding to flow of electricity and heat are given by the expressions

$$X_e = -\text{grad}\,(\phi / T) \tag{6.8.1}$$

$$X_q = \text{grad}\,(1 / T) \tag{6.8.2}$$

Due to coupling phenomenon, it is expected that the fluxes J_e and J_q depend both on the forces X_e and X_q. The fluxes J_e and J_q may be expanded in a Taylor series about the points $X_q = 0$ and $X_e = 0$. The zero order terms $J_e(0, 0)$ and $J_q(0, 0)$ are zero as the flows of electricity and heat vanish when the forces are zero, i.e. the gradients in the expressions of these are zero. The expressions in Taylor series are:

$$J_e(X_e, X_q) = X_e\left(\frac{\partial J_e}{\partial X_e}\right)_{X_e=0,\,X_q=0} + X_q\left(\frac{\partial J_e}{\partial X_q}\right)_{X_e=0,\,X_q=0} + \text{higher differential terms} \tag{6.8.3}$$

$$J_q(X_e, X_q) = X_e\left(\frac{\partial J_q}{\partial X_e}\right)_{X_e=0,\,X_q=0} + X_q\left(\frac{\partial J_q}{\partial X_q}\right)_{X_e=0,\,X_q=0} + \text{higher differential terms} \tag{6.8.4}$$

If the gradients X_e and X_q are very small in comparison to unity, the higher differential terms may be ignored relative to the respective first order terms. The resultant expressions may be represented as

$$J_e = L_{ee}X_e + L_{eq}X_q \tag{6.8.5}$$†

$$J_q = L_{qe}X_e + L_{qq}X_q \tag{6.8.6}$$

where $L_{ee} = \left(\frac{\partial J_e}{\partial X_e}\right)_{X_e=0,\,X_q=0}$; $L_{eq} = \left(\frac{\partial J_e}{\partial X_q}\right)_{X_e=0,\,X_q=0}$

$L_{qe} = \left(\frac{\partial J_q}{\partial X_e}\right)_{X_e=0,\,X_q=0}$; $L_{qq} = \left(\frac{\partial J_q}{\partial X_q}\right)_{X_e=0,\,X_q=0}$

Equations (6.8.5) and (6.8.6) are known as the phenomenological equations and the terms L_{ee}, L_{eq}, L_{qe} and L_{qq}, known as phenomenological coefficients, provide the weighing factors to the forces in the phenomenological equations. The terms L_{eq} and L_{qe} are indicative of coupling effects between electrical and thermal effects in the thermoelectric phenomenon.

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† In Eq. (6.8.5) and (6.8.6), the vectorial notation is not used since all forces and flows need not be vector quantities

Comparison with Ohm's Law

For an isothemal condition,

$$X_q = \text{grad}\,(1/T) = -\frac{1}{T^2}\,\text{grad}\,T = 0$$

With this, Eq. (6.8.5) gives

$$J_e = L_{ee}\,X_e$$

$$= L_{ee}\,\{-\text{grad}\,(\phi/T)\} = -\frac{L_{ee}}{T}\,\text{grad}\,\phi \qquad (6.8.7)$$

Comparing Eq. (6.8.7) with Ohm's law (Eq. 6.8.2), we get

$$\gamma = \frac{L_{ee}}{T} \qquad (6.8.8)$$

Comparison with Fourier's Law

Under the condition of $J_e = 0$, Eq. (6.8.5) becomes

$$0 = L_{ee}X_e + L_{eq}X_q$$

i.e.
$$X_e = -\frac{L_{eq}}{L_{ee}}\,X_q \qquad (6.8.9)$$

Substituting Eq. (6.8.9) in Eq. (6.8.6), we get

$$J_q = L_{qe}\left(-\frac{L_{eq}}{L_{ee}}\,X_q\right) + L_{qq}\,X_q = \left(L_{qq} - \frac{L_{qe}\,L_{eq}}{L_{ee}}\right)X_q$$

Substituting X_q from Eq. (6.8.2); we get

$$J_q = \left(L_{qq} - \frac{L_{qe}L_{eq}}{L_{ee}}\right)\text{grad}\,(1/T)$$

$$= \left(\frac{L_{qq}\,L_{ee} - L_{qe}\,L_{eq}}{L_{ee}}\right)\left(-\frac{1}{T^2}\right)\text{grad}\,T \qquad (6.8.10)$$

Comparing Eq. (6.8.10) with Fourier Law (Eq. 6.7.1), we get

$$\lambda = \left(\frac{L_{qq}\,L_{ee} - L_{qe}\,L_{eq}}{L_{ee}\,T^2}\right) \qquad (6.8.11)$$

6.9 GENERAL TREATMENT OF THE PHENOMENOLOGICAL EQUATIONS

Generalized Equations

The linear dependence of various flows in a system on the conjugate and nonconjugate forces as suggested by Onsager in 1931 are as follows.

$$J_1 = L_{11}X_1 + L_{12}X_2 + \cdots + L_{1n}X_n$$
$$J_2 = L_{21}X_1 + L_{22}X_2 + \cdots + L_{2n}X_n$$
$$\vdots$$
$$J_n = L_{n1}X_1 + L_{n2}X_2 + \cdots + L_{nn}X_n \qquad (6.9.1)^*$$

where $J_1, J_2, \ldots, J_n$ are the flows and $X_1, X_2, \ldots, X_n$ are the corresponding conjugate forces.

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*The explanation of double subscripts is as follows.
The first subscript refers to the component moving (and is thus the same as the subscript on the correspsonding J) and the second subscript refers to the component whose gradient is being taken into account.

The above expression may be written as

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \qquad (i = 1, 2, \dots n) \tag{6.9.2}$$

where $$L_{ij} = \left(\frac{\partial J_i}{\partial X_j} \right)_{k(k \neq j)} \tag{6.9.3}$$

Applicability of Eq. (6.9.3)

The partial derivatives in Eq. (6.9.3) are evaluated at the points $X_k = 0$ except $X_j = 0$. The terms appeared in Eq. (6.9.2) are the first-order contribution in a Taylor expansion of J_i as a function of X_j (see, Eq. 6.8.4). Thus, these equations are applicable only when the higher-order differentials are smaller than the first-order differentials. This holds good only when the forces are small and the system is close to equilibrium conditions.

The choices of flows and conjugate forces are such that the product $J_i X_i$ has the dimension of entropy production.

The coefficients $L_{11}, L_{22}, \dots, L_{nn}$ are known as **straight coefficients** indicating the proportionality of flows on their conjugate forces. The coefficients L_{12}, L_{13}, ..., etc. are known as **coupling** or **mutual influence cross coefficients** indicating the proportionality of flows on the nonconjugate forces.

Equation (6.9.1) Expressed in Vector Form

In the vector notations Eq. (6.9.1) is written as

$$\underbrace{\begin{bmatrix} J_1 \\ J_2 \\ \vdots \\ J_n \end{bmatrix}}_{\text{Vector of flows}} = \underbrace{\begin{bmatrix} L_{11} & L_{12} & \cdots & L_{1n} \\ L_{21} & L_{22} & \cdots & L_{2n} \\ \cdots & & & \\ L_{n1} & L_{n2} & \cdots & L_{nn} \end{bmatrix}}_{\text{Matrix of phenomeno-logical coefficients}} \underbrace{\begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_n \end{bmatrix}}_{\text{Vectors of flows}} \tag{6.9.4}$$

The equations representing forces in terms of flows may be worked out through the following manipulation.

$$\begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_n \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} & \cdots & L_{1n} \\ L_{21} & L_{22} & \cdots & L_{2n} \\ \cdots & & & \\ L_{n1} & L_{n2} & \cdots & L_{nn} \end{bmatrix}^{-1} \begin{bmatrix} J_1 \\ J_2 \\ \vdots \\ J_n \end{bmatrix} \tag{6.9.5}$$

The Curie-Prigogine Principle

A flow and its conjugative force may be either scalar quantities or vector quantities. The example of scalar quantities is chemical reaction and its associated affinity. The transfer of heat or matter and its associated force is an example of vector quantities.

Statement of Principle The Curie-Prigogine principle states that there exists no coupling between scalar flow and vectorial force or vice versa for an isotropic system (a system in which the properties are identical in all directions). For such a system, the phenomenological equations split into two sets of equations representing the coupling between the same types of flows and forces. These may be expressed as

$J_n = L_{sn} X_n$; where n goes over scalar quantities

$J'_n = L_{vn} X'_n$; where n goes over vector quantities

Illustration Let a system involve simultaneous occurrence of a chemical reaction and flow of heat. If there exists coupling between them, we would have

$$J_q = L_{qq} X_q + L_{qr} X_r$$
$$v = L_{rq} X_q + L_{rr} X_r$$

where $X_q = \text{grad}\,(1/T)$ and $X_r = A/T$.

In an isothermal condition, $X_q = 0$. Hence, we would have

$$J_q = L_{qr} X_r$$

Unless $L_{qr} = 0$, the above expression implies that a scalar force X_r produces a vectorial flow, which is not in agreement with the Curie-Prigogine principle. Hence, L_{qr} must be equal to zero.

Onsager Symmetry Rule

If the flows and forces in the phenomenological equations are properly selected so as to satisfy the expression

$$\sigma = \Sigma_i J_i X_i$$

then, the matrix of phenomenological coefficients is symmetric, that is, the coefficients satisfy the expression

$$L_{ij} = L_{ji} \qquad ; (i \neq j) \tag{6.9.6}$$

Expressed in words this implies that the coefficient which expresses the influence of the force j on the flux of i is the same as the coefficient which expresses the effect of the force i on the flux of j.

Equation (6.9.6) is known as Onsager symmetry rule. It holds good for irreversible processes close to equilibrium. This law may be considered as an axiom supplementary to classical thermodynamics.

Equation (6.9.6) implies that

$$\left(\frac{\partial J_i}{\partial X_j}\right)_{X_{k;(k\neq j)}} = \left(\frac{\partial J_j}{\partial X_i}\right)_{X_{k;(k\neq i)}} \tag{6.9.7}$$

that is, the change in the flux J_i caused by unit change in the force X_j keeping all other forces constant is equal to the change in the flux J_j caused by unit change in the force X_i keeping all other forces constant.

Restriction on Phenomenological Coefficients

Though the phenomenological coefficients involved in Eq. (6.9.1) are independent of each other, yet the absolute magnitude of the coupling coefficients is restricted by the magnitude of the straight coefficients because of the positive-definite value of the entropy production. This restriction may be illustrated by taking an example involving two flows and two forces. The entropy production is given by

$$\sigma = J_1 X_1 + J_2 X_2 \tag{6.9.8}$$

where $J_1 = L_{11}X_1 + L_{12} X_2$ (6.9.9)

and $J_2 = L_{21} X_1 + L_{22} X_2$ (6.9.10)

Substituting Eqs (6.9.9) and (6.9.10) in Eq. (6.9.8), we get

$$\begin{aligned}\sigma &= (L_{11} X_1 + L_{12} X_2)X_1 + (L_{21} X_1 + L_{22} X_2)X_2 \\ &= L_{11} X_1^2 + (L_{12} + L_{21})X_1 X_2 + L_{22} X_2^2 \end{aligned} \tag{6.9.11}$$

Since $L_{12} = L_{21}$ (Onsager law) and $\sigma > 0$, we must have

$$L_{11} X_1^2 + 2 L_{12} X_1 X_2 + L_{22} X_2^2 > 0 \tag{6.9.12}$$

Since either X_1 or X_2 may be made to vanish, we must have the requirements of

$$L_{11} X_1^2 \ge 0 \quad \text{and} \quad L_{22} X_2^2 \ge 0 \tag{6.9.13}$$

This leads to the conclusion that both straight coefficients L_{11} and L_{22} must be positive. Equation (6.9.13) may be written as

$$\left(\sqrt{L_{11}}X_1 + \sqrt{L_{22}}X_2\right)^2 - 2\sqrt{L_{11}L_{22}}X_1X_2 + 2L_{12}X_1X_2 \ge 0$$

or $$\left(\sqrt{L_{11}}X_1 + \sqrt{L_{22}}X_2\right)^2 \ge 2\left(\sqrt{L_{11}L_{22}} - L_{12}\right)X_1X_2 \tag{6.9.14}$$

In order that the right side of this expression is to be zero or positive, we must have

$$\sqrt{L_{11}L_{22}} - L_{12} \ge 0 \quad \text{or} \quad \sqrt{L_{11}L_{22}} \ge L_{12} \quad \text{or} \quad L_{11}L_{22} \ge L_{12}^2 \qquad (6.9.15)^{\dagger}$$

Generalization of Eq. (6.9.15)

In general, the two conditions, involving any number of flows and forces are as follows.

$$L_{ii} > 0 \tag{6.9.16}$$

and $$\begin{vmatrix} L_{11} & L_{12} & \cdots & L_{1n} \\ L_{21} & L_{22} & \cdots & L_{2n} \\ \vdots & & & \\ L_{n1} & L_{n2} & \cdots & L_{nn} \end{vmatrix} \ge 0 \tag{6.9.17}$$

6.10 COMMENT ON THE CHOICE OF FLUXES AND FORCES

The entropy production in an irreversible process is given by the expression

$$\sigma = \sum_{i=1}^{n} J_i X_i \tag{6.10.1}$$

[†] Alternatively, this expression may be derived by using the matrix notation for Eq. (6.9.12). We have

$$[X_1\, X_2]\begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix}\begin{bmatrix} X_1 \\ X_2 \end{bmatrix} \ge 0$$

The satisfaction of this expression requires that

$$\begin{vmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{vmatrix} \ge 0 \quad \text{i.e.} \quad L_{11}L_{22} - L_{12}L_{21} \ge 0$$

which, in view of Onsager law, leads to $L_{11}L_{22} \ge L_{12}^2$

The phenomenological relations are

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \qquad (i = 1, 2, \ldots, n) \tag{6.10.2}$$

with $\quad L_{ij} = L_{ji} \qquad$ (Onsager reciprocal relation) $\qquad$ (6.10.3)

Though the entropy production in an irreversible process is unique, yet the choices of J_i and X_i are not unique, the only condition to be satisfied is given by Eq. (6.10.1). It can be shown that the Onsager reciprocal relation holds good even when a set of linearly transformed fluxes and forces are used in Eq. (6.10.1).

Expression of Transformed Fluxes

Let the transformed fluxes be given as

$$J_i' = \sum_{j=1}^{n} \beta_{ij} J_j \qquad (i = 1, 2, \ldots, n) \tag{6.10.4}$$

Expression of Original Forces in Terms of Transformed Forces

The expression of original force X_j in terms of transformed forces may be worked out as follows. The entropy production in terms of transformed fluxes and forces is

$$\sigma = \sum_{i=1}^{n} J_i' X_i' \tag{6.10.5}$$

Replacing J_i' by using Eq. (6.10.4), we get

$$\sigma = \sum_{i=1}^{n} \left(\sum_{j=1}^{n} \beta_{ij} J_j \right) X_i' = \sum_{j=1}^{n} J_j \left(\sum_{i=1}^{n} \beta_{ij} X_i' \right)$$

From this, it follows that

$$X_j = \sum_{i=1}^{n} \beta_{ij} X_i' \tag{6.10.6}$$

Transformed Phenomenological Equations

The phenomenological relation involving transformed flexes and forces are

$$J_i' = \sum_{j=1}^{n} L_{ij}' X_j' \qquad (\text{with } L_{ij}' = L_{ji}') \tag{6.10.7}$$

This expression $L_{ij}' = L_{ji}'$ may be generated as follows. Equation (6.10.4) is

$$J_i' = \sum_{j=1}^{n} \beta_{ij} J_j$$

Replacing J_j by using Eq. (6.10.2), we get

$$J_i' = \sum_{j=1}^{n} \beta_{ij} \left[\sum_{k=1}^{n} L_{jk} X_k \right]$$

Now replacing X_k by using Eq. (6.10.6), we get

$$J_i' = \sum_{j=1}^{n} \beta_{ij} \left[\sum_{k=1}^{n} L_{jk} \left(\sum_{m=1}^{n} \beta_{mk} X_m' \right) \right]$$

This may be written as

$$J'_i = \sum_{m=1}^{n} \left[\sum_{j=1}^{n} \sum_{k=1}^{n} \beta_{ij} L_{jk} \beta_{mk} \right] X'_m = \sum_{m=1}^{n} \left[\sum_{j=1}^{n} \sum_{k=1}^{n} \beta_{ij} L_{jk} \beta^{\dagger}_{km} \right] X'_{\mathrm{m}}$$

Comparing this, with Eq. (6.10.7), we get

$$L'_{im} = \sum_{j=1}^{n} \sum_{k=1}^{n} \left(\beta_{ij} L_{jk} \beta^{\dagger}_{km} \right)$$

Validity of Onsager Reciprocal Relations

Now since

$$\beta_{ij} = \beta^{\dagger}_{ji}; \qquad L_{jk} = L_{kj}; \qquad \beta^{\dagger}_{km} = \beta_{mk}$$

the above expression may be written as

$$L'_{im} = \sum_{j=1}^{n} \sum_{k=1}^{n} \left(\beta^{\dagger}_{ji} L_{kj} \beta_{mk} \right) \equiv \sum_{j=1}^{n} \sum_{k=1}^{n} \left(\beta_{mk} L_{kj} \beta^{\dagger}_{ji} \right)$$

$$= L'_{mi} \tag{6.10.8}$$

6.11 AN EXAMPLE ILLUSTRATING PHENOMENOLOGICAL EQUATION

One of the examples illustrating phenomenological equation is a chemical reaction near to its equilibrium position.

General Expression of a Chemical Reaction

In general, a chemical reaction may be depicted as

$$0 = \Sigma_{\mathrm{B}} \nu_{\mathrm{B}} \mathrm{B} \tag{6.11.1}$$

where ν_{B} is the stoichiometric numbers of the species B in the chemical equation of the reaction. It has a negative value for a reactant and a positive value for a product.

Progress of a Chemical Reaction

The progress of a chemical reaction is depicted by the physical quantity known as extent of reaction. If the reaction has proceeded to the extent ξ, then the concentration of the species B in the reaction is given by

$$[\mathrm{B}] = [\mathrm{B}]_0 + \nu_{\mathrm{B}} \xi \tag{6.11.2}$$

where $[\mathrm{B}]_0$ is the inital concentration of B in the reaction where $\xi = 0$.

- If ξ_{eq} is the extent of reaction at equilibtium, then

$$[\mathrm{B}]_{\mathrm{eq}} = [\mathrm{B}]_0 + \nu_{\mathrm{B}} \xi_{\mathrm{eq}} \tag{6.11.3}$$

Let the extent of reaction near to the equilibrium be represented as

$$\xi = \xi_{\mathrm{eq}} (1 + x) \tag{6.11.4}$$

where $| x | << 1$. It has a negative value just before the equilibrium and has a positive value just after the equilibrium position of the reaction. In terms of x, Eq. (6.11.2) becomes

$$\begin{aligned}[\mathrm{B}] &= [\mathrm{B}]_0 + \nu_\mathrm{B}[\xi_\mathrm{eq}(1 + x)] \\ &= ([\mathrm{B}]_0 + \nu_\mathrm{B}\,\xi_\mathrm{eq}) + \nu_\mathrm{B}\,\xi_\mathrm{eq}\,x \\ &= [\mathrm{B}]_\mathrm{eq} + \nu_\mathrm{B}\,\xi_\mathrm{eq}\,x \qquad (6.11.5)\end{aligned}$$

Affinity of a Reaction

By definition, the affinity of a chemical reaction is

$$A = -\textstyle\sum_\mathrm{B} \nu_\mathrm{B}\,\mu_\mathrm{B} \qquad (6.11.6)$$

where the chemical potential, μ_B, is given by

$$\mu_\mathrm{B} = \mu_\mathrm{B}^\circ + RT\ln\left(\frac{[\mathrm{B}]}{c^\circ}\right) \qquad (6.11.7)$$

where μ_B° is the standard chemical potential of B where $[\mathrm{B}] = c^\circ$ (=1 mol dm^{-3}). Substitution of Eq. (6.11.7) in Eq. (6.11.6) gives

$$\begin{aligned}A &= -\sum\nolimits_\mathrm{B}\nu_\mathrm{B}\left[\mu_\mathrm{B}^\circ + RT\ln\left(\frac{[\mathrm{B}]}{c^\circ}\right)\right] \\ &= A^\circ - \sum\nolimits_\mathrm{B}\nu_\mathrm{B}\left[RT\ln\left(\frac{[\mathrm{B}]}{c^\circ}\right)\right] \qquad (6.11.8a)\end{aligned}$$

Affinity of a Reaction Near to Equilibrium Position

Substitution of Eq. (6.11.2) in Eq. (6.11.7) gives

$$A = A^\circ - \sum\nolimits_\mathrm{B}\nu_\mathrm{B}\left[RT\ln\left(\frac{[\mathrm{B}]_0 + \nu_\mathrm{B}\xi}{c^\circ}\right)\right]$$

which in view of Eq. (6.11.4) becomes

$$\begin{aligned}A &= A^\circ - \sum\nolimits_\mathrm{B}\nu_\mathrm{B}\left[RT\ln\left(\frac{[\mathrm{B}]_0 + \nu_\mathrm{B}\xi_\mathrm{eq}(1+x)}{c^\circ}\right)\right] \\ &= A^\circ - \sum\nolimits_\mathrm{B}\nu_\mathrm{B}\left[RT\ln\left(\frac{[\mathrm{B}]_\mathrm{eq} + \nu_\mathrm{B}\xi_\mathrm{eq}\,x}{c^\circ}\right)\right] \qquad (6.11.8b)\end{aligned}$$

where Eq. (6.11.3) has been used to replace $[\mathrm{B}]_0$ by $[\mathrm{B}]_\mathrm{eq}$. Equation (6.11.8) may be written as

$$A = A^\circ - \sum\nolimits_\mathrm{B}\nu_\mathrm{B}\,RT\ln\left(\frac{[\mathrm{B}]_\mathrm{eq}}{c^\circ}\right) - \sum\nolimits_\mathrm{B}\nu_\mathrm{B}\,RT\ln\left(1 + \frac{\nu_\mathrm{B}\xi_\mathrm{eq}x}{[\mathrm{B}]_\mathrm{eq}}\right) \qquad (6.11.9)$$

At the equillibrium position $A = 0$ and $x = 0$. With these, Eq. (6.11.9) reduces to

$$A^\circ - \sum\nolimits_\mathrm{B}\nu_\mathrm{B}\,RT\ln\left(\frac{[\mathrm{B}]_\mathrm{eq}}{c^\circ}\right) = 0$$

With this, Eq. (6.11.9) reduces to

$$A = -\sum_{\mathrm{B}} \nu_{\mathrm{B}}\, RT \ln\left(1 + \frac{\nu_{\mathrm{B}}\xi_{\mathrm{eq}}x}{[\mathrm{B}]_{\mathrm{eq}}}\right)$$

Since $\nu_{\mathrm{B}}\xi_{\mathrm{eq}}\, x \,/\, [\mathrm{B}]_{\mathrm{eq}} < 1$, we approximate the above expression as

$$A = -\sum_{\mathrm{B}} \nu_{\mathrm{B}}\, RT\left(\frac{\nu_{\mathrm{B}}\xi_{\mathrm{eq}}x}{[\mathrm{B}]_{\mathrm{eq}}}\right) \tag{6.11.10}$$

Rate of Forward Reaction Near the Equilibrium

The rate of forward reaction is

$$r_{\mathrm{f}} = k_{\mathrm{f}} \prod_{\mathrm{R}}\left([\mathrm{R}]^{|\nu_{\mathrm{R}}|}\right)$$

where R stands for reactants. Using Eq. (6.11.5), we write the above expression as

$$r_{\mathrm{f}} = k_{\mathrm{f}} \prod_{\mathrm{R}}\left[[\mathrm{R}]_{\mathrm{eq}} + \nu_{\mathrm{R}}\xi_{\mathrm{eq}}x\right]^{|\nu_{\mathrm{R}}|}$$

$$= k_{\mathrm{f}} \prod_{\mathrm{R}}\left[[\mathrm{R}]_{\mathrm{eq}}\left(1 + \frac{\nu_{\mathrm{R}}\xi_{\mathrm{eq}}x}{[\mathrm{R}]_{\mathrm{eq}}}\right)\right]^{|\nu_{\mathrm{R}}|} = \left(k_{\mathrm{f}} \prod_{\mathrm{R}}[\mathrm{R}]_{\mathrm{eq}}^{|\nu_{\mathrm{R}}|}\right)\left[\prod_{\mathrm{R}}\left(1 + \frac{\nu_{\mathrm{R}}\xi_{\mathrm{eq}}x}{[\mathrm{R}]_{\mathrm{eq}}}\right)\right]^{|\nu_{\mathrm{R}}|}$$

$$= r_{\mathrm{f,\,eq}}\left[\prod_{\mathrm{R}}\left(1 + \frac{\nu_{\mathrm{R}}\xi_{\mathrm{eq}}x}{[\mathrm{R}]_{\mathrm{eq}}}\right)^{|\nu_{\mathrm{R}}|}\right]$$

Since $\nu_{\mathrm{R}}\xi_{\mathrm{eq}}\, x \,/\, [\mathrm{R}]_{\mathrm{eq}} \ll 1$, the above expression may be approximated as

$$r_{\mathrm{f}} = r_{\mathrm{f,\,eq}}\left[1 + \sum_{\mathrm{R}} |\nu_{\mathrm{R}}| \frac{\nu_{\mathrm{R}}\xi_{\mathrm{eq}}x}{[\mathrm{R}]_{\mathrm{eq}}}\right] \tag{6.11.11}$$

Rate of Backward Reaction Near the Equilibrium

The Rate of backward reaction is

$$r_{\mathrm{b}} = k_{\mathrm{b}} \prod_{\mathrm{P}}\left([\mathrm{P}]^{\nu_{\mathrm{P}}}\right)$$

where P stands for products. Proceeding similarly as in the case of forward reaction, we have

$$r_{\mathrm{b}} = k_{\mathrm{b}} \prod_{\mathrm{P}}\left([\mathrm{P}]^{\nu_{\mathrm{P}}}\right) = k_{\mathrm{b}} \prod_{\mathrm{P}}\left([\mathrm{P}]_0 + \nu_{\mathrm{P}}\xi\right)^{\nu_{\mathrm{P}}}$$

$$= k_{\mathrm{b}} \prod_{\mathrm{P}}\left[[\mathrm{P}]_0 + \nu_{\mathrm{P}}\xi_{\mathrm{eq}}(1+x)\right]^{\nu_{\mathrm{P}}} = k_{\mathrm{b}} \prod_{\mathrm{P}}\left([\mathrm{P}]_{\mathrm{eq}} + \nu_{\mathrm{P}}\xi_{\mathrm{eq}}x\right)^{\nu_{\mathrm{P}}}$$

$$= k_{\mathrm{b}} \prod_{\mathrm{P}}\left[[\mathrm{P}]_{\mathrm{eq}}\left(1 + \frac{\nu_{\mathrm{P}}\xi_{\mathrm{eq}}x}{[\mathrm{P}]_{\mathrm{eq}}}\right)\right]^{\nu_{\mathrm{P}}}$$

$$= \left(k_b \prod_P [\mathrm{P}]_{eq}^{\nu_P}\right)\left[\prod_P \left(1 + \frac{\nu_P \xi_{eq} x}{[\mathrm{P}]_{eq}}\right)\right]^{\nu_P}$$

$$= r_{b,\,eq}\left[\prod_P \left(1 + \frac{\nu_P \xi_{eq} x}{[\mathrm{P}]_{eq}}\right)\right]^{\nu_P}$$

Since $\nu_P\, \xi_{eq}\, x\, /\, [\mathrm{P}]_{eq} \ll 1$, the above expression may be approximated as

$$r_b = r_{b,\,eq}\left[1 + \sum\nolimits_P \nu_P \frac{\nu_P \xi_{eq} x}{[\mathrm{P}]_{eq}}\right] \tag{6.11.12}$$

Net Rate of Reaction The net rate of reaction is given by

$$r = r_f - r_b$$

$$= r_{f,\,eq}\left[1 + \sum\nolimits_R |\nu_R| \frac{\nu_R \xi_{eq} x}{[\mathrm{R}]_{eq}}\right] - r_{b,\,eq}\left[1 + \sum\nolimits_P \nu_P \frac{\nu_P \xi_{eq} x}{[\mathrm{P}]_{eq}}\right]$$

Since at equilibrium, $r_{f,\,eq} = r_{b,\,eq}$, we write the above expression as

$$r = r_{f,\,eq}\left[\sum\nolimits_R |\nu_R| \frac{\nu_R \xi_{eq} x}{[\mathrm{R}]_{eq}} - \sum\nolimits_P \nu_P \frac{\nu_P \xi_{eq} x}{[\mathrm{P}]_{eq}}\right]$$

Since $|\nu_R| = -\nu_R$, we get

$$r = -\,r_{f,\,eq}\left[\sum\nolimits_R \nu_R \frac{\nu_R \xi_{eq} x}{[\mathrm{R}]_{eq}} + \sum\nolimits_P \nu_P \frac{-\nu_P \xi_{eq} x}{[\mathrm{P}]_{eq}}\right]$$

$$= -\,r_{f,\,eq}\left[\sum\nolimits_B \nu_B \frac{\nu_B \xi_{eq} x}{[\mathrm{B}]_{eq}}\right] \tag{6.11.13}$$

which in view of Eq. (6.11.10) becomes

$$r = r_{f,\,eq}\left(\frac{A}{RT}\right) \tag{6.11.14}$$

Form of Phenomenological Equation Writing flow and force of a chemical reaction as

$$J_r = r \quad \text{and} \quad X_r = \frac{A}{T} \tag{6.11.15}$$

and substituting these in Eq. (6.11.14), we get

$$J_r = \frac{r_{f,\,eq}}{R}\, X_r = L X_r \tag{6.11.16}$$

where L, the phenomenological coefficient, is

$$L = r_{f,\,eq}\, /\, R \tag{6.11.17}$$

The phenomenological coefficient is not a constant, it is a function of the characteristic parameters, $r_{f,\,eq}$, of the reaction. It may be emphasised here that

Eq. (6.11.16) holds good only when the reaction is close to its equilibrium position where the reaction is expected to proceed with slow speed.

Expression of Entropy Production

The expression of entropy production is

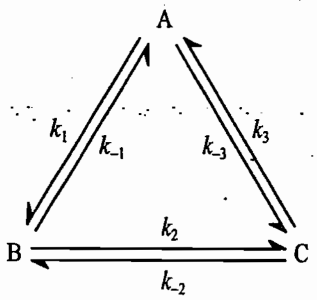
$$\sigma = (\text{Flow})\ (\text{Force})$$

$$= (r)\left(\frac{A}{T}\right) = \left[r_{\mathrm{f,eq}}\left(\frac{A}{RT}\right)\right]\left(\frac{A}{T}\right)$$

$$= \frac{r_{\mathrm{f,eq}}}{R}\left(\frac{A}{T}\right)^2 = L\left(\frac{A}{T}\right)^2 = \frac{1}{L}\left(L\frac{A}{T}\right)^2 = \frac{1}{L}r^2 \qquad (6.11.18)$$

6.12 AN EXAMPLE ILLUSTRATING ONSAGER PRINCIPLE

One of the examples illustrating Onsager principle of symmetry of phenomenological coefficient is provided by the cyclic reactions depicted in the following.



Rates and Affinities of Reactions

The affinities and rates of the three reactions are

$$A_1 = \mu_{\mathrm{A}} - \mu_{\mathrm{B}}; \quad J_1 = k_1\,[\mathrm{A}] - k_{-1}[\mathrm{B}] \qquad (6.12.1a)$$

$$A_2 = \mu_{\mathrm{B}} - \mu_{\mathrm{C}}; \quad J_2 = k_2[\mathrm{B}] - k_{-2}[\mathrm{C}] \qquad (6.12.1b)$$

$$A_3 = \mu_{\mathrm{C}} - \mu_{\mathrm{A}}; \quad J_3 = k_3\,[\mathrm{C}] - k_{-3}\,[\mathrm{A}] \qquad (6.12.1c)$$

The affinity A_3 may be considered as dependent on A_1 and A_2, since

$$A_3 = -(A_1 + A_2) \qquad (6.12.2)$$

The thermodynamic criterion of equilibrium for the reactions are

$$(\mu_{\mathrm{A}})_{\mathrm{eq}} = (\mu_{\mathrm{B}})_{\mathrm{eq}} = (\mu_{\mathrm{C}})_{\mathrm{eq}}$$

With this, we have

$$(A_1)_{\mathrm{eq}} = (A_2)_{\mathrm{eq}} = (A_3)_{\mathrm{eq}} = 0$$

Also, the principle of microscopic reversibility requires that a molecular process and its reverse process on an average with the same speed at equilibrium. Hence, we will have

$$k_1[\mathrm{A}]_{\mathrm{eq}} = k_{-1}[\mathrm{B}]_{\mathrm{eq}}; \quad (J_1)_{\mathrm{eq}} = 0 \qquad (6.12.3a)$$

$$k_2[\mathrm{B}]_{\mathrm{eq}} = k_{-2}[\mathrm{C}]_{\mathrm{eq}}; \quad (J_2)_{\mathrm{eq}} = 0 \qquad (6.12.3b)$$

$$k_3[\mathrm{C}]_{\mathrm{eq}} = k_{-3}[\mathrm{A}]_{\mathrm{eq}}; \quad (J_3)_{\mathrm{eq}} = 0 \qquad (6.12.3c)$$

Expressions of Rates and Affinities Near the Equilibrium

Consider each of the three reactions near to equilibrium, We may write

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} + \epsilon_{\mathrm{A}} \qquad (6.12.4a)$$

$$[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq}} + \epsilon_{\mathrm{B}} \qquad (6.12.4b)$$

$$[\mathrm{C}] = [\mathrm{C}]_{\mathrm{eq}} + \epsilon_{\mathrm{C}} \qquad (6.12.4c)$$

With these, Eq. (6.12.1a) becomes

$$\begin{aligned} J_1 &= k_1([\mathrm{A}]_{\mathrm{eq}} + \epsilon_{\mathrm{A}}) - k_{-1}([\mathrm{B}]_{\mathrm{eq}} + \epsilon_{\mathrm{B}}) \\ &= (k_1[\mathrm{A}]_{\mathrm{eq}} - k_{-1}[\mathrm{B}]_{\mathrm{eq}}) + (k_1 \epsilon_{\mathrm{A}} - k_{-1} \epsilon_{\mathrm{B}}) \\ &= k_1 \epsilon_{\mathrm{A}} - k_{-1} \epsilon_{\mathrm{B}}; \qquad \text{(using Eq. 6.12.3a)} \qquad (6.12.5\mathrm{a}) \end{aligned}$$

Similarly,

$$J_2 = k_2 \epsilon_{\mathrm{B}} - k_{-2} \epsilon_{\mathrm{C}} \qquad (6.12.5\mathrm{b})$$

$$J_3 = k_3 \epsilon_{\mathrm{C}} - k_{-3} \epsilon_{\mathrm{A}} \qquad (6.12.5\mathrm{c})$$

The affinity A_1, is

$$\begin{aligned} A_1 &= \mu_{\mathrm{A}} - \mu_{\mathrm{B}} \\ &= \left(\mu_{\mathrm{A}}^{\circ} + RT \ln \frac{[\mathrm{A}]}{c^{\circ}}\right) - \left(\mu_{\mathrm{B}}^{\circ} + RT \ln \frac{[\mathrm{B}]}{c^{\circ}}\right) \\ &= \left[\mu_{\mathrm{A}}^{\circ} + RT \ln \left(\frac{[\mathrm{A}]_{\mathrm{eq}} + \epsilon_{\mathrm{A}}}{c^{\circ}}\right)\right] - \left[\mu_{\mathrm{B}}^{\circ} + RT \ln \left(\frac{[\mathrm{B}]_{\mathrm{eq}} + \epsilon_{\mathrm{B}}}{c^{\circ}}\right)\right] \\ &= \left[\mu_{\mathrm{A}}^{\circ} + RT \ln \left\{\frac{[\mathrm{A}]_{\mathrm{eq}}}{c^{\circ}}\left(1 + \frac{\epsilon_{\mathrm{A}}}{[\mathrm{A}]_{\mathrm{eq}}}\right)\right\}\right] - \left[\mu_{\mathrm{B}}^{\circ} + RT \ln \left\{\frac{[\mathrm{B}]_{\mathrm{eq}}}{c^{\circ}}\left(1 + \frac{\epsilon_{\mathrm{B}}}{[\mathrm{B}]_{\mathrm{eq}}}\right)\right\}\right] \\ &= \left[A_1^{\circ} - RT \ln \left(\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}}\right)\right] + RT \ln \left(1 + \frac{\epsilon_{\mathrm{A}}}{[\mathrm{A}]_{\mathrm{eq}}}\right) - RT \ln \left(1 + \frac{\epsilon_{\mathrm{B}}}{[\mathrm{B}]_{\mathrm{eq}}}\right) \qquad (6.12.6) \end{aligned}$$

where $A_1^{\circ} = \mu_{\mathrm{A}}^{\circ} - \mu_{\mathrm{B}}^{\circ}$

For the reaction $\mathrm{A} \rightleftharpoons \mathrm{B}$ at equilibrium, we substitute $A_1 = 0$, $\epsilon_{\mathrm{A}} = 0$ and $\epsilon_{\mathrm{B}} = 0$ in Eq. (6.12.6) and get

$$A_1^{\circ} - RT \ln \left(\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}}\right) = 0$$

With this, Eq. (6.12.6) becomes

$$A_1 = RT \ln \left(1 + \frac{\epsilon_{\mathrm{A}}}{[\mathrm{A}]_{\mathrm{eq}}}\right) - RT \ln \left(1 + \frac{\epsilon_{\mathrm{B}}}{[\mathrm{B}]_{\mathrm{eq}}}\right)$$

Since $\epsilon_{\mathrm{A}}/[\mathrm{A}]_{\mathrm{eq}} << 1$ and $\epsilon_{\mathrm{B}}/[\mathrm{B}]_{\mathrm{eq}} << 1$, the above expression may be approximated as

$$A_1 = RT \left(\frac{\epsilon_{\mathrm{A}}}{[\mathrm{A}]_{\mathrm{eq}}} - \frac{\epsilon_{\mathrm{B}}}{[\mathrm{B}]_{\mathrm{eq}}}\right)$$

which in view of Eq. (6.12.3a), becomes

$$A_1 = \frac{RT}{k_1[\mathrm{A}]_{\mathrm{eq}}}(k_1 \epsilon_{\mathrm{A}} - k_{-1} \epsilon_{\mathrm{B}})$$

Using Eq. (6.12.5a), this becomes

$$A_1 = \frac{RT}{k_1[\mathrm{A}]_{\mathrm{eq}}} J_1 \quad \text{or} \quad J_1 = \frac{k_1[\mathrm{A}]_{\mathrm{eq}}}{RT} A_1 \tag{6.12.6a}$$

Similarly,

$$A_2 = \frac{RT}{k_2[\mathrm{B}]_{\mathrm{eq}}} J_2 \quad \text{or} \quad J_2 = \frac{k_2[\mathrm{B}]_{\mathrm{eq}}}{RT} A_2 \tag{6.12.6b}$$

and

$$A_3 = \frac{RT}{k_3[\mathrm{C}]_{\mathrm{eq}}} J_3 \quad \text{or} \quad J_3 = \frac{k_3[\mathrm{C}]_{\mathrm{eq}}}{RT} A_3 \tag{6.12.6c}$$

In view of Eq. (6.12.2), we can write Eq. (6.12.6c) as

$$J_3 = -\frac{k_3[\mathrm{C}]_{\mathrm{eq}}}{RT}(A_1 + A_2) \tag{6.12.6d}$$

Expression of Entropy Production

The entropy production is given by

$$\begin{aligned} \sigma &= J_1 (A_1/T) + J_2 (A_2/T) + J_3 (A_3/T) \\ &= J_1 (A_1/T) + J_2 (A_2/T) - J_3 (A_1 + A_2)/T \\ &= (J_1 - J_3)(A_1/T) + (J_2 - J_3)(A_2/T) \end{aligned} \tag{6.12.7}$$

where the flows $J_1 - J_3$ and $J_2 - J_3$ as given by Eqs. (6.12.6a) – (6.12.6d) are as follows.

$$\begin{aligned} J_1 - J_3 &= \left(\frac{k_1[\mathrm{A}]_{\mathrm{eq}}}{RT}\right) A_1 + \left(\frac{k_3[\mathrm{C}]_{\mathrm{eq}}}{RT}\right)(A_1 + A_2) \\ &= \left(\frac{k_1[\mathrm{A}]_{\mathrm{eq}} + k_3[\mathrm{C}]_{\mathrm{eq}}}{RT}\right) A_1 + \left(\frac{k_3[\mathrm{C}]_{\mathrm{eq}}}{RT}\right) A_2 \end{aligned} \tag{6.12.8a}$$

$$\begin{aligned} J_2 - J_3 &= \left(\frac{k_2[\mathrm{B}]_{\mathrm{eq}}}{RT}\right) A_2 + \left(\frac{k_3[\mathrm{C}]_{\mathrm{eq}}}{RT}\right)(A_1 + A_2) \\ &= \left(\frac{k_3[\mathrm{C}]_{\mathrm{eq}}}{RT}\right) A_1 + \left(\frac{k_2[\mathrm{B}]_{\mathrm{eq}} + k_3[\mathrm{C}]_{\mathrm{eq}}}{RT}\right) A_2 \end{aligned} \tag{6.12.8b}$$

Expression of Phenomenological Coefficients

The phenomenological equations correponding to Eq. (6.12.7) are

$$J_1 - J_3 = L_{11}(A_1/T) + L_{12}(A_2/T) \tag{6.12.9a}$$

$$J_2 - J_3 = L_{21}(A_1/T) + L_{22}(A_2/T) \tag{6.12.9b}$$

Comparing Eqs. (6.12.8) and (6.12.9), we get

$$L_{11} = \frac{k_1[\mathrm{A}]_{\mathrm{eq}} + k_3[\mathrm{C}]_{\mathrm{eq}}}{R} \tag{6.12.10a}$$

$$L_{12} = L_{21} = \frac{k_3[\mathrm{C}]_{\mathrm{eq}}}{R} \tag{6.12.10b}$$

$$L_{22} = \frac{k_2[\mathrm{B}]_{\mathrm{eq}} + k_3[\mathrm{C}]_{\mathrm{eq}}}{R} \tag{6.12.10c}$$

Equation (6.12.10b) establishes the Onsager principle of symmetry of phenomenological coefficients.

6.13 ELECTROKINETIC EFFECTS

Phenomenon of Electro-Osmosis

Consider a system of two compartments separated by a porous diaphragm. The two compartments are occupied by a fluid of uniform composition inclusive of ionic species at a constant temperature. A potential difference across the diaphragm is applied by inserting electrodes in the fluid on either side of the diaphragm (Fig. 6.13.1).

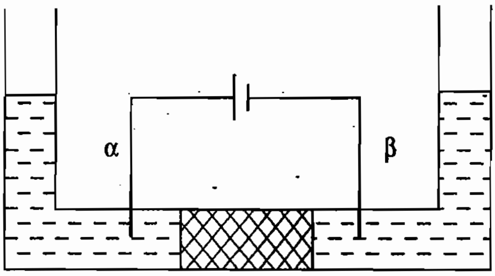


Fig. 6.13.1 Illustration of electrokinetic effect

Because of the applied potential, a current *I* flows and due to this, the fluid flows through the diaphragm. Eventually, a stage is reached where the pressure difference, Δp, developed across the diaphragm just balances the effect of applied potential. This causes the stoppage of flow of the fluid. The observed value of Δp is found to be dependent on both the fluid and the nature of the diaphragm. Its value is proportional to the applied potential. The flow of fluid under the influence of applied potential is known as electro-osmosis.

Expression of Entropy Production

The entropy production due to transfer of fluid from the phase α to the phase β is given by the expression

$$d_iS = \frac{1}{T}\left[\sum\nolimits_i (\tilde{\mu}_i(\beta)\ dn_i - \tilde{\mu}_i(\alpha)\, dn_i)\right] \tag{6.13.1}$$

where $\tilde{\mu}_i$, the electrochemical potential of the *i*th species, is related to its chemical potential by the expression

$$\tilde{\mu}_i = \mu_i + z_i F\varphi \tag{6.13.2}$$

where z_i is the charge number of the *i*th species and φ is the potential of the electrode dipped in the solution.

Substituting Eq. (6.13.2) in Eq. (6.13.1), we get

$$\begin{aligned} d_iS &= -\frac{1}{T}\left[\sum\nolimits_i \left\{\left(\mu_{i\,(\beta)} + z_iF\varphi_\beta\right) - \left(\mu_{i(\alpha)} + z_iF\varphi_\alpha\right)\right\} dn_i\right] \\ &= -\frac{1}{T}\left[\sum\nolimits_i \left\{\left(\mu_{i\,(\beta)} - \mu_{i(\alpha)}\right) + z_iF\left(\varphi_\beta - \varphi_\alpha\right)\right\} dn_i\right] \\ &= -\frac{1}{T}\left[\sum\nolimits_i (\Delta\mu_i + z_iF\Delta\varphi)\, dn_i\right] \end{aligned} \tag{6.13.3}$$

The expression of $\Delta\mu_i$ as a result of pressure difference at constant temperature is

$$\Delta\mu_i = \left(\frac{\partial\mu_i}{\partial p}\right)_T \Delta p = V_{i,\,\mathrm{pm}}\,\Delta p$$

With this, Eq. (6.13.3) becomes

$$T\,\mathrm{d}_iS = \sum_i (V_{i,\mathrm{pm}}\,\mathrm{d}n_i)(-\Delta p) + \sum_i (z_iF\mathrm{d}n_i)(-\Delta\varphi) \tag{6.13.4}$$

The rate of production of entropy is given by the expression

$$\frac{\mathrm{d_i}S}{\mathrm{d}t} = \sum_i \left(V_{i,\mathrm{pm}}\frac{\mathrm{d}n_i}{\mathrm{d}t}\right)\left(-\frac{\Delta p}{T}\right) + \sum_i\left(z_iF\frac{\mathrm{d}n_i}{\mathrm{d}t}\right)\left(-\frac{\Delta\varphi}{T}\right)$$

$$= J_\mathrm{m}X_\mathrm{m} + I X_I \tag{6.13.5}$$

Phenomenological Equations

The phenomenological equations corresponding to entropy production as given by Eq. (6.13.5) are

$$J_\mathrm{m} = L_{11}\left(-\frac{\Delta p}{T}\right) + L_{12}\left(-\frac{\Delta\varphi}{T}\right) \tag{6.13.6a}$$

$$J_I = L_{21}\left(-\frac{\Delta p}{T}\right) + L_{22}\left(-\frac{\Delta\varphi}{T}\right) \qquad ; (J_I = I) \tag{6.13.6b}$$

Applications of Eqs. (6.13.6a) and (6.13.6b)

Streaming Potential The value of $\Delta\varphi$ for a given value of Δp at which $I = 0$ is known as streaming potential. From Eq. (6.13.6b), we can write

$$0 = L_{21}\left(-\frac{\Delta p}{T}\right)_{I=0} + L_{22}\left(-\frac{\Delta\varphi}{T}\right)_{I=0}$$

or $$(\Delta\varphi)_{I=0} = -\frac{L_{21}}{L_{22}}(\Delta p)_{I=0} \tag{6.13.7}$$

Steaming Current The streaming current is defined as

$$I_\mathrm{sc} = \left(\frac{I}{J_\mathrm{m}}\right)_{\Delta\varphi=0} \tag{6.13.8a}$$

Suppose the electrodes are short-circuited in order to have $\Delta\varphi = 0$. The fluid is forced to passed through the diaphragm under the influence of pressure difference, Δp. The current flowing in the wires of the short-circuited electrodes is known as streaming current. This may be measured with the help of ammeter. From Eqs. (6.13.6a) and (6.13.6b), we find that

$$(J_\mathrm{m})_{\Delta\varphi=0} = L_{11}\left(-\frac{\Delta p}{T}\right)_{\Delta\varphi=0} \quad \text{and} \quad (I)_{\Delta\varphi=0} = L_{21}\left(-\frac{\Delta p}{T}\right)_{\Delta\varphi=0}$$

Hence, $$I_\mathrm{sc} = \left(\frac{I}{J_\mathrm{m}}\right)_{\Delta\varphi=0} = \frac{L_{21}}{L_{11}} \tag{6.13.8b}$$

Electro-Osmotic Pressure The value of Δp at which $J_{\bar{\mathrm{m}}} = 0$ for the given value of $\Delta\varphi$ is known as electro-osmotic pressure. From Eq. (6.13.6a), we get

$$0 = L_{11}\left(-\frac{\Delta p}{T}\right)_{J_\mathrm{m}=0} + L_{12}\left(-\frac{\Delta\varphi}{T}\right)_{J_\mathrm{m}=0}$$

Hence $$(\Delta p)_{J_m=0} = -\frac{L_{12}}{L_{11}}(\Delta\varphi)_{J_m=0} \tag{6.13.9}$$

Electro-Osmosis Effect The electro-osmosis effect is the flow of fluid under the influence of $\Delta\varphi$ keeping $\Delta p = 0$. From Eqs. (6.13.6a) and (6.13.6b), we get

$$(J_m)_{\Delta p=0} = L_{12}\left(-\frac{\Delta\varphi}{T}\right)_{\Delta p=0} \quad \text{and} \quad (I)_{\Delta p=0} = L_{22}\left(-\frac{\Delta\varphi}{T}\right)_{\Delta p=0}$$

Hence $$\left(\frac{J_m}{I}\right)_{\Delta p=0} = \frac{L_{12}}{L_{22}} \tag{6.13.10}$$

Saxen's Relations

- From Eqs. (6.13.7) and (6.13.10), we have

$$\left(\frac{\Delta\varphi}{\Delta p}\right)_{I=0} = -\frac{L_{21}}{L_{22}} \quad \text{and} \quad \left(\frac{J_m}{I}\right)_{\Delta p=0} = \frac{L_{12}}{L_{22}}$$

Since $L_{12} = L_{21}$ (Onsager principle), we have

$$\left(\frac{\Delta\varphi}{\Delta p}\right)_{I=0} = -\left(\frac{J_m}{I}\right)_{\Delta p=0} \tag{6.13.11}$$

- From Eqs. (6.13.8b) and (6.13.9), we have

$$\left(\frac{I}{J_m}\right)_{\Delta\varphi=0} = \frac{L_{21}}{L_{11}} \quad \text{and} \quad \left(\frac{\Delta p}{\Delta\varphi}\right)_{J_m=0} = -\frac{L_{12}}{L_{11}}$$

Since $L_{12} = L_{21}$, we have

$$\left(\frac{I}{J_m}\right)_{\Delta\varphi=0} = -\left(\frac{\Delta p}{\Delta\varphi}\right)_{J_m=0} \tag{6.13.12}$$

Equations (6.13.11) and (6.13.12) are known as reciprocity relations.

6.14 THERMOELECTRICITY

The themoelectric phenomena were the first coupled processes for which a detailed study has been carried out.

Consider a thermocouple consisting of two metals A and B whose junctions in electrical contact are at temperatures T and $T + \Delta T$ as shown in Fig. 6.14.1.

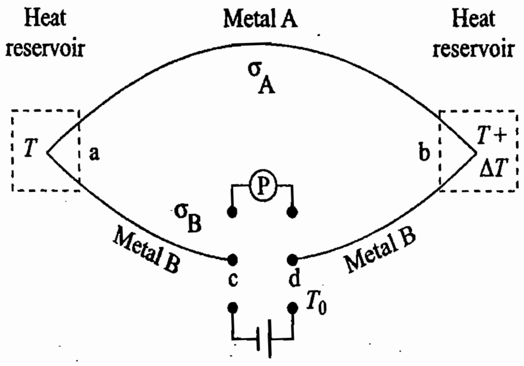


Fig. 6.14.1 Schematic set up of thermocouple

As a result of the temperature difference, thermal and potential gradients will be set up in the thermocouple and thus flow of both heat and electricity take place in a thermocouple.

Three observations with reference to the thermocouple shown in Fig. 6.14.1 are described here.

Seebeck Effect

In Seebeck effect, the points c and d in the metal B are held at the same temperature across which emf generated in the circuit is determined with a potentiometer ensuring no current flow in the circuit.

The relative thermoelectric power of the metal B against the metal A is defined as

$$\varepsilon_r = \frac{d(\Delta\phi_{cd})_{I=0}}{dT} \qquad (6.14.1)$$

where $\Delta\phi_{cd}$ is the potential devolved across cd in Fig. 6.14.1.

Peltier Effect

In the Peltier effect, the two junctions are kept at the same temperature, but a current is passed through the wires. A quantity of heat J_q is absorbed at one junction and equal quantity of heat is released at the other junction. On reversing the direction of current, heat liberated and absorbed at the two junctions are also reversed.

The rate at which heat must be supplied to or removed from the junctions to maintain temperature constant for unit current is known as Peltier heat (symbol: Π). It is expressed as

$$\Pi = \left(\frac{dq/dt}{I}\right)_{\Delta T=0} \qquad (6.14.2)$$

The unit of Peltier heat is J A^{-1} s^{-1} ($\equiv$ J C^{-1})

Thomson Effect

Thomson observation is based on the following experiment.

Consider a homogeneous metallic conductor as shown in Fig. 6.14.2.

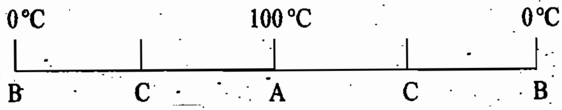


Fig. 6.14.2 Illsutration of Thomson effect

Let the metallic conductor be maintained at 100 °C at some point (say, A) as shown in Fig. 6.14.2. At the two neighbouring points (say, B) on either sides of the point A, let the temperature of 0 °C be maintained. It is found that at the two points equidistant from hot and cold points (shown by the points C) the temperatures were found to be identical. However, when a current is passed through the conductor, the temperature at the points C were found to be different. The passage of current disturbs the temperature gradient, and thus the original gradient can be maintained only be addition or removal of heat from the appropriate region of the metallic conductor.

Thomson heat is defined as the rate at which heat is added or removed for unit current to maintain a unit temperature gradient in the metallic conductor. Mathematically, Thomson heat is defined as

$$\sigma = \frac{(dq/dt)}{I(dT)} \qquad (6.14.3)$$

The unit of Thomson heat is $J\,K^{-1}\,A^{-1}\,s^{-1}$ ($\equiv J\,K^{-1}\,C^{-1}$) Thomson heat is a function of the nature of the metallic conductor and its temperature.

The above three effects, namely, Seebeck, Peltier and Thomson, indicate the coupling between thermal and electrical phenomena does exist.

Theoretical Treatment of Thermoelectricity

Entropy Production The entropy production due to thermal flow and the flow of electrons at any point in the themocouple as given by Eq. (6.6.8) is

$$\sigma = J_q \operatorname{grad}\left(\frac{1}{T}\right) + J_e \operatorname{grad}\left(-\frac{\tilde{\mu}_e}{T}\right) \tag{6.14.4}$$

Now $\tilde{\mu}_e = \mu_e - F\varphi = -F\varphi$; (since $\mu_e = 0$)

Moreover, the potential is measured across the points at the same temperature, we can write

$$J_e \operatorname{grad}\left(-\frac{\tilde{\mu}_e}{T}\right) = (-FJ_e)\frac{\operatorname{grad}(-\varphi)}{T} = I\frac{\operatorname{grad}(-\varphi)}{T}$$

With this, Eq. (6.14.4) becomes

$$\sigma = J_q \operatorname{grad}\left(\frac{1}{T}\right) + I\frac{\operatorname{grad}(-\varphi)}{T} \tag{6.14.5}$$

Phenomenological Equations The phenomenological equations may be written

$$J_q = L_{11} \operatorname{grad}\left(\frac{1}{T}\right) + L_{12}\left(\frac{\operatorname{grad}(-\varphi)}{T}\right) \tag{6.14.6}$$

$$I = L_{21} \operatorname{grad}\left(\frac{1}{T}\right) + L_{22}\left(\frac{\operatorname{grad}(-\varphi)}{T}\right) \tag{6.14.7}$$

Explanation of Seebeck Effect In the experiment of Seebeck effect two junctions a and b of the bimetallic couple shown in Fig. 6.14.1 are held at different temperatures, but the points c and d across which potential is determined with the help of a potentiometer (ensuring no-flow of electrons) are held at the same temperature. For this condition, we set $I = 0$ in Eq. (6.14.7).

Hence

$$0 = L_{21} \operatorname{grad}\left(\frac{1}{T}\right) + L_{22}\left(\frac{\operatorname{grad}(-\varphi)}{T}\right)$$

$$= -\frac{L_{21}}{T^2}\operatorname{grad} T - \frac{L_{22}}{T}\operatorname{grad}\varphi$$

Thus $$-\left(\frac{\operatorname{grad}\varphi}{\operatorname{grad}T}\right)_{I=0} = \frac{1}{T}\frac{L_{21}}{L_{22}}$$

i.e. $$-\left(\frac{d\varphi}{dT}\right)_{I=0} = \frac{1}{T}\frac{L_{21}}{L_{22}} \tag{6.14.8}$$

Since the emf ε is negative of φ, we have

$$\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}\right)_{I=0}=\frac{1}{T}\frac{L_{21}}{L_{22}} \tag{6.14.9}$$

Equation (6.14.8) implies that in the absence of electric current but in the presence of temperature gradient, a potential difference appears in the circuit. This is, in fact, Seebeck effect.

Explanationn of Peltier Effect

In the Peltier effect, the two junctions are kept at the same temperature and a current is passed through the circuit. In this case, we set $\Delta T = 0$, i.e. grad $(1/T) = 0$ in Eqs (6.14.6) and (6.14.7) and thus get

$$(J_q)_{\Delta T=0}=L_{12}\,\frac{\text{grad}(-\varphi)}{T} \quad \text{and} \quad (I_i)_{\Delta T=0}=L_{22}\,\frac{\text{grad}(-\varphi)}{T}$$

Hence

$$\left(\frac{J_q}{I}\right)_{\Delta T=0}=\frac{L_{12}}{L_{22}} \tag{6.14.10}$$

Combining Eqs (6.14.9) and (6.14.10), we get the expression of Peltier heat

$$\Pi=\left(\frac{\mathrm{d}q/\mathrm{d}t}{I}\right)_{\Delta T=0}=\left(\frac{J_q}{I}\right)_{\Delta T=0}=T\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}\right)_{I=0} \tag{6.14.11}$$

where $L_{12} = L_{21}$ has been used. Equation (6.14.11) is known as Kelvin's relation. Experimentally, this relation holds good for a large number of thermocouples indicating the validity of Onsager symmetry principle.

Heat of Transfer of Electrons

By definition, heat of transfer of electrons in the metallic strip of a thermocouple is given by the expression

$$q^*=\left(\frac{J_q}{J_\mathrm{e}}\right)_{\Delta T=0} \tag{6.14.12}$$

From Eq. (6.14.10), it follows that

$$\left(\frac{J_q}{I}\right)_{\Delta T=0}=\left(\frac{J_q}{-FJ_\mathrm{e}}\right)_{\Delta T=0}=\frac{L_{12}}{L_{22}}$$

or

$$q^*=\left(\frac{J_q}{J_\mathrm{e}}\right)_{\Delta T=0}=-F\frac{L_{21}}{L_{22}} \tag{6.14.13}$$

Also, from Eq. (6.14.8), we have

$$\left(\frac{\mathrm{d}\varphi}{\mathrm{d}T}\right)_{I=0}=\left(\frac{\mathrm{d}\varphi}{\mathrm{d}T}\right)_{J_\mathrm{e}=0}=-\frac{1}{T}\frac{L_{21}}{L_{22}} \tag{6.14.14}$$

From Eqs (6.14.13) and (6.14.14), it follows that

$$\left(\frac{\mathrm{d}\varphi}{\mathrm{d}T}\right)_{J_\mathrm{e}=0}=\frac{q^*}{F\,T} \qquad (\text{since } L_{12}=L_{21}) \tag{6.14.15}$$

Expression of Relative Thermoelectric Power

As defined in Eq. (6.14.1), the relative thermoelectric power of the metal B against the metal A is defined as

$$\varepsilon_{\mathrm{T}} = \frac{\mathrm{d}\,(\Delta\phi_{\mathrm{cd}})_{I=0}}{\mathrm{d}T} \qquad \text{(Eq. 6.14.1)}$$

where $\Delta\phi_{\mathrm{cd}}$ is the potential across cd in Fig. 6.14.1.

From Fig. 6.14.1, we will have

$$(\Delta\phi_{\mathrm{cd}})_{J_{\mathrm{e}}=0} = (\phi_{\mathrm{a}} - \phi_{\mathrm{c}})_{J_{\mathrm{e}}=0} + (\phi_{\mathrm{b}} - \phi_{\mathrm{a}})_{J_{\mathrm{e}}=0} + (\phi_{\mathrm{d}} - \phi_{\mathrm{b}})_{J_{\mathrm{e}}=0}$$

$$= \int_{T_0}^{T} \left(\frac{\mathrm{d}\varphi}{\mathrm{d}T}\right)_{\mathrm{B}} \mathrm{d}T + \int_{T}^{T+\Delta T} \left(\frac{\mathrm{d}\varphi}{\mathrm{d}T}\right)_{\mathrm{A}} \mathrm{d}T + \int_{T+\Delta T}^{T_0} \left(\frac{\mathrm{d}\varphi}{\mathrm{d}T}\right)_{\mathrm{B}} \mathrm{d}T$$

$$= \int_{T}^{T+\Delta t} \left(\frac{\mathrm{d}\varphi}{\mathrm{d}T}\right)_{\mathrm{A}} \mathrm{d}T - \int_{T}^{T+\Delta t} \left(\frac{\mathrm{d}\varphi}{\mathrm{d}T}\right)_{\mathrm{B}} \mathrm{d}T$$

Making use of Eq. (6.14.15), we get

$$(\Delta\phi_{\mathrm{cd}})_{J_{\mathrm{e}}=0} = \frac{q_{\mathrm{A}}^*}{F} \int_{T}^{T+\Delta t} \frac{\mathrm{d}T}{T} - \frac{q_{\mathrm{B}}^*}{F} \int_{T}^{T+\Delta t} \frac{\mathrm{d}T}{T}$$

$$= \frac{q_{\mathrm{A}}^*}{F} \ln\left(\frac{T+\Delta T}{T}\right) - \frac{q_{\mathrm{B}}^*}{F} \ln\left(\frac{T+\Delta T}{T}\right)$$

$$= \left(\frac{q_{\mathrm{A}}^* - q_{\mathrm{B}}^*}{F}\right) \ln\left(\frac{T+\Delta T}{T}\right) = \left(\frac{q_{\mathrm{A}}^* - q_{\mathrm{B}}^*}{F}\right) \ln\left(1+\frac{\Delta T}{T}\right)$$

$$= \left(\frac{q_{\mathrm{A}}^* - q_{\mathrm{B}}^*}{F}\right)\left(\frac{\Delta T}{T}\right)$$

Hence

$$\left(\frac{\Delta\phi_{\mathrm{cd}}}{\Delta T}\right)_{J_{\mathrm{e}}=0} = \frac{q_{\mathrm{A}}^* - q_{\mathrm{B}}^*}{FT} \qquad (6.14.16)$$

Thus, the relative thermoelectric power of the metal B against A depends on the heats of transfer of electrons of metals B and A. Since the heat of transfer depends on the cross phenomenological coefficient (Eq. 6.14.13), Eq. (6.14.16) is one of the expressions indicating the coupling between the electrical and thermal phenomena.

First Equation of Thomson

The first relation of Thomson for thermoelectricity is obtained by writing the energy balance for the circuit shown in Fig. 6.14.1. The involved energies in the circuit are as follows,

(i) Let the amount $\mathrm{d}n_{\mathrm{e}}$ of electrons enter at the point c and leave from the point d of the circuit due to the potential difference $\Delta\phi$ ($\phi_{\mathrm{d}} - \phi_{\mathrm{c}}$). The electrical energy received by the circuit is

$$E_1 = F\,(\Delta\varphi)\,\mathrm{d}n_{\mathrm{e}}$$

(ii) The electrons move from c to a with the change in temperature from T_0 to T. The energy received by the circuit from the surroundings is

$$E_2 = F\,\sigma_B\,\mathrm{d}n_e\,(T - T_0) \qquad \text{(Eq. 6.14.3)}$$

(iii) At the junction a, the electrons enters from the metal B to the metal A at temperature T. The circuit absorbs Petlier heat from the surroundings. This energy is

$$E_3 = F\Pi\,\mathrm{d}n_e \qquad \text{(Eq. 6.14.2)}$$

(iv) The electrons move from the point a to the point b with the change in temperature from T to $T + \Delta$T. The energy received from the surroundings is

$$E_4 = F\,\sigma_A\,\mathrm{d}n_e\,\{(T - \Delta T) - T\}$$

$$= F\,\sigma_A\,\mathrm{d}n_e\,\Delta T$$

(v) At the junction b, the electrons enters from the metal A to the metal B at temperature $T + \Delta T$. The circuit leaves Petlier heat to the surroundings. This energy is

$$E_5 = -F\left(\Pi + \frac{\mathrm{d}\Pi}{\mathrm{d}T}\Delta T\right)\mathrm{d}n_e$$

(vi) The electrons move from b to d with the change in temperature from $T + \Delta T$ to T_0. The energy received from the surroundings is

$$E_6 = F\,\sigma_B\,\mathrm{d}n_e\,\{(T_0 - (T + \Delta T)\}$$

Since the .energy of the entire circuit remains unchanged, we must have

$$E_1 + (E_2 + E_6) + E_3 + E_4 + E_5 = 0$$

i.e.

$$\left[\Delta\varphi + \sigma_B\,\{(T - T_0) + (T_0 - T - \Delta T)\} + \Pi + \sigma_A\,\Delta T - \{\Pi + \left(\frac{\mathrm{d}\Pi}{\mathrm{d}T}\right)\Delta T\}\right]F\,\mathrm{d}n_e = 0$$

or $$\frac{\Delta\varphi}{\Delta T} - \sigma_B + \sigma_A - \frac{\mathrm{d}\Pi}{\mathrm{d}T} = 0$$

or $$\sigma_B - \sigma_A = \frac{\Delta\varphi}{\Delta T} - \frac{\mathrm{d}\Pi}{\mathrm{d}T} \qquad (6.14.17)$$

Equation (6.14.17) is known as first equation of Thomson.

It will shown that

$$\Pi = T\left(\frac{\Delta\varphi}{\Delta T}\right)_{J_e = 0} \qquad \text{(Eq. 6.14.22)}$$

Hence $$\frac{\mathrm{d}\Pi}{\mathrm{d}T} = \left(\frac{\Delta\varphi}{\Delta T}\right) + T\,\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\Delta\varphi}{\Delta T}\right)$$

With this, Eq. (6.14.17) becomes

$$\sigma_A - \sigma_B = T\,\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\Delta\varphi}{\Delta T}\right) = T\,\frac{\partial^2\varphi}{\partial T^2} \qquad (6.14.17b)$$

Second Equation of Thomson

The second equation of Thomson for thermoelectricity can be derived by considering the processes occurring at the junction of two metals A and B during a steady current flow under the condition of constant temperature.

Under the condition of constant temperature, the phenomenological equations (Eqs. 6.14.6 and 6.14.7) give

$$I = -L_{22}^{(A)}\frac{\text{grad}\,\varphi_A}{T} = -L_{22}^{(B)}\frac{\text{grad}\,\varphi_B}{T} \tag{6.14.18}$$

$$J_q^{(A)} = -L_{12}^{(A)}\frac{\text{grad}\,\varphi_A}{T}; \qquad J_q^{(B)} = -L_{12}^{(B)}\frac{\text{grad}\,\varphi_B}{T} \tag{6.14.19}$$

The quantities $J_q^{(A)}$ and $J_q^{(B)}$ will not be equal since Peltier heat Π (Eq. 6.14.2) is either absorbed or released at the junction to maintain its temperature constant. If more heat flows in the conductor B (i.e. $J_q^{(B)} > J_q^{(A)}$) then it leads to cooling at the junction a and heating at the junction b. For this situation, we write

$$J_q^{(A)} = J_q^{(B)} - I\,\Pi$$

or

$$\Pi = \frac{J_q^{(B)} - J_q^{(A)}}{I}$$

Substituting $J_q^{(A)}$ and $J_q^{(B)}$ from Eq. (6.14.19), we get

$$\Pi = \frac{1}{I}\left(-L_{12}^{(B)}\frac{\text{grad}\,\varphi_B}{T} + L_{12}^{(A)}\frac{\text{grad}\,\varphi_A}{T}\right)$$

which in view of Eq. (6.14.18) becomes

$$\Pi = \left(\frac{L_{12}^{(B)}}{L_{22}^{(B)}} - \frac{L_{12}^{(A)}}{L_{22}^{(A)}}\right) \tag{6.14.20}$$

Since $q^*/F = -L_{12}/L_{22}$ (Eq. 6.14.13), we write the above expression as

$$\Pi = \frac{q_A^* - q_B^*}{F} \tag{6.14.21}$$

which on making use of Eq. (6.14.16) can be written as

$$\Pi = T\left(\frac{\Delta\phi_{cd}}{\Delta T}\right)_{J_e=0} \tag{6.14.22}$$

Equation (6.14.22) is known as second equation of Thomson.

6.15 ISOTHERMAL DIFFUSION IN A CONTINUOUS SYSTEM

Thermodynamic Background

The chemical potential of *i*th constituent in a solution depends on temperature, pressure and amounts of other constituents present in the solution. We can write

$$\mathrm{d}\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{p,\,n_i} \mathrm{d}T + \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\,n_i} \mathrm{d}p + \sum_{j=1}^{n}\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,\,p\;n_{k\neq j}} \mathrm{d}n_j$$

$$= -S_{i,\,\mathrm{pm}}\,\mathrm{d}T + V_{i,\,\mathrm{pm}}\,\mathrm{d}p + \sum_{j=1}^{n}\mu_{ij}\,\mathrm{d}n_j \qquad (6.15.1)$$

where $\mu_{ij} = (\partial\mu_i / \partial n_j)_{T,\,p\;n_{k\neq j}}$. For a case in which μ_i does not depend upon the amounts of other components, we will have

$$\mu_{ij} = 0 \quad \text{for} \quad i \neq j \qquad (6.15.2)$$

In this case, Eq. (6.15.1) becomes

$$\mathrm{d}\mu_i = -S_{i,\,\mathrm{pm}}\,\mathrm{d}T + V_{i,\,\mathrm{pm}}\,\mathrm{d}p + \mu_{ii}\,\mathrm{d}n_i \qquad (6.15.3)$$

Since μ_i depends on the concentration of ith species (for example, for an ideal solution, $\mu_i = \mu_i^\circ + RT\ln(c/c^\circ)$, we can write μ_{ii} as

$$\mu_{ii} = \frac{\partial \mu_i}{\partial n_i} = \frac{\partial \mu_i^{(c)}}{\partial n_i}$$

where $\mu_i^{(c)}$ is the concentration-dependent term of the chemical potential μ_i. With this, Eq. (6.15.3) becomes

$$\mathrm{d}\mu_i = -S_{i,\,\mathrm{pm}}\,\mathrm{d}T + V_{i,\,\mathrm{pm}}\,\mathrm{d}p + \mathrm{d}\mu_i^{(c)} \qquad (6.15.4)$$

In terms of gradients, Eq. (6.15.4) is given by

$$\mathrm{grad}\,(-\mu_i) = S_{i,\,\mathrm{pm}}\,\mathrm{grad}\,(T) + V_{i,\,\mathrm{pm}}\,\mathrm{grad}\,(-p) + \mathrm{grad}\,(-\mu_i^{(c)}) \qquad (6.15.5)$$

For an isothermal-isobaric diffusional flow, Eq. (6.15.5) may be written as

$$\mathrm{grad}\,(-\mu_i) = \mathrm{grad}\,(-\mu_i^{(c)}) \qquad (6.15.6)$$

Entropy Production

Assuming isothermal diffusion to take place in one direction, the entropy production in this process is given by

$$T\sigma = \sum_{i=1}^{n} J_i\,\mathrm{grad}\,(-\mu_i)$$

which in view of Eq. (6.15.6) becomes

$$T\sigma = \sum_{i=1}^{n} J_i\,\mathrm{grad}\,(-\mu_i^{(c)}) \qquad (6.15.7)$$

Diffusion of Solutes Relative to Solvent

Equation (6.15.7) includes the flows of both solvent and solutes. Representing solvent by the subscript 1 and solutes by 2, 3,..., etc., we may write Eq. (6.15.7) as

$$T\sigma = J_1\,\mathrm{grad}\left(-\mu_1^{(c)}\right) + \sum_{i=2}^{n} J_i\,\mathrm{grad}\left(-\mu_i^{(c)}\right) \qquad (6.15.8)$$

The flows and forces mentioned in Eq. (6.15.8) are not independent. These are related to each other as mentioned in the following.

- The various forces are related through Gibbs-Duhem equation

$$\sum_{i=1}^{n} c_i\,\mathrm{grad}\left(-\mu_i^{(c)}\right) = 0 \qquad (6.15.9)$$

- The various flows are related through the expression based on the fact that there occurs no flow of volume of the solution. The volume of the solution is

$$V = \sum_{i=1}^{n} n_i V_{i,\mathrm{pm}}$$

where $V_{i,\,\mathrm{pm}}$ is the partial molar volume of the ith constituent in the solution. Assuming these to remain constants, the rate of flow of volume of the solution is

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \sum_{i=1}^{n}\left(\frac{\mathrm{d}n_i}{\mathrm{d}t}\right) V_{i,\mathrm{pm}} = \sum_{i=1}^{n} J_i V_{i,\mathrm{pm}}$$

Since $\mathrm{d}V/\mathrm{d}t = 0$ (the condition of no flow of volume of the solution), we have

$$\sum_{i=1}^{n} J_i V_{i,\mathrm{pm}} = 0 \tag{6.15.10}$$

Using Eqs. (6.15.9) and (6.15.10), one can eliminate the dependent solvent term in Eq. (6.15.8). We will have

$$\mathrm{grad}\cdot\left(-\mu_1^{(c)}\right) = -\sum_{i=2}^{n}\left(\frac{c_i}{c_1}\right)\mathrm{grad}\left(-\mu_i^{(c)}\right) \tag{6.15.11}$$

$$J_1 = -\sum_{j=2}^{n} J_j \left(\frac{V_{j,\mathrm{pm}}}{V_{1,\mathrm{pm}}}\right) \tag{6.15.12}$$

Substituting these in Eq. (6.15.8), we get

$$\begin{aligned} T\sigma &= \left[\sum_{j=2}^{n} J_j \left(\frac{V_{j,\mathrm{pm}}}{V_{1,\mathrm{pm}}}\right)\right]\left[\sum_{i=2}^{n}\left(\frac{c_i}{c_1}\right)\mathrm{grad}\left(-\mu_i^{(c)}\right)\right] + \left[\sum_{i=2}^{n} J_i\,\mathrm{grad}\left(-\mu_i^{(c)}\right)\right] \\ &= \sum_{j=2}^{n} J_j \left\{\sum_{i=2}^{n}\frac{c_i}{c_1}\frac{V_{j,\mathrm{pm}}}{V_{1,\mathrm{pm}}}\,\mathrm{grad}\left(-\mu_i^{(c)}\right)\right\} + \sum_{i=2}^{n} J_i\,\mathrm{grad}\left(-\mu_i^{(c)}\right) \\ &= \sum_{j=2}^{n} J_j \left\{\sum_{i=2}^{n}\left(\delta_{ij} + \frac{c_i}{c_1}\frac{V_{j,\mathrm{pm}}}{V_{1,\mathrm{pm}}}\right)\mathrm{grad}\left(-\mu_i^{(c)}\right)\right\} \end{aligned} \tag{6.15.13}$$

where δ_{ij} is Kronecker delta (it is equal to 1 for $i = j$ and is zero for $i \neq j$). Equation (6.15.13) can be written as

$$T\sigma = \sum_{j=2}^{n} J_j Y_j \tag{6.15.14}$$

where $$Y_j = \sum_{i=2}^{n}\left(\delta_{ij} + \frac{c_i}{c_1}\frac{V_{j,\mathrm{pm}}}{V_{1,\mathrm{pm}}}\right)\mathrm{grad}\left(-\mu_i^{(c)}\right) \tag{6.15.15}$$

Isothermal Diffusion in a Binary Solution

Fick's Law of Diffusion

A binary solution involves a solute dissolved in a solvent. In this solution, the velocity of diffusion may be assumed to depend linearly on the driving force of diffusion (which is $-\mathrm{grad}\,\mu$). Hence, we may write

$$V = -\,\omega\,\text{grad}\,\mu \tag{6.15.16}$$

where ω, the proportionality constant, is the velocity per unit force. For dilute solution,

$$\text{grad}\,\mu = \frac{RT}{c}\,\text{grad}\,c \tag{6.15.17}$$

and
$$\begin{aligned} J = cV &= -\,\omega\,RT\,\text{grad}\,c \\ &= D'\,\text{grad}\,c \end{aligned} \tag{6.15.18}$$

where D' is known as diffusion constant. Equation (6.15.18) is known as Fick's law of diffusion. The expression

$$D' = \omega\,RT \tag{6.15.19}$$

is known as Planck-Einstein relation.

Phenomenological Equation

The phenomenological expression corresponding to Eq. (6.15.14) is

$$\begin{aligned} J_2 &= L_2\,Y_2 \\ &= L_2\left(1+\frac{c_2V_{2,\text{pm}}}{c_1V_{1,\text{pm}}}\right)\text{grad}\left(-\mu_2^{(c)}\right) \\ &= L_2\left(\frac{c_1V_{1,\text{pm}}+c_2V_{2,\text{pm}}}{c_1\,V_{1,\text{pm}}}\right)\text{grad}\left(-\mu_2^{(c)}\right) = L_2\left(\frac{1}{c_1\,V_{1,\text{pm}}}\right)\text{grad}\left(-\mu_2^{(c)}\right) \\ &= \left(\frac{L_2}{\phi_1}\right)\text{grad}\left(-\mu_2^{(c)}\right) \qquad \text{where } \phi_1 = c_1V_{1,\text{pm}}. \end{aligned} \tag{6.15.20†}$$

Since the concentration of solute is a function of its position in the solution, we write the concentration-dependent portion of chemical potential as

$$\text{grad}\,\mu_2^{(c)} = \frac{\partial\mu_2^{(c)}}{\partial c_2}\,\text{grad}\,c_2$$

For a dilute solution, $\mu_2^{(c)} = RT\ln c_2$. Hence

$$\frac{\partial\mu_2^{(c)}}{\partial c_2} = \frac{RT}{c_2}$$

Also $\phi_1 = c_1V_{1,\text{pm}} = (n_1/V)\,V_{1,\text{pm}} = n_1V_{1,\text{pm}}/V \approx 1$

With these, Eq. (6.15.20) becomes

$$J_2 = L_2\,\frac{RT}{c_2}\,\text{grad}\,c_2 \tag{6.15.21}$$

Comparing Eqs. (6.15.18) and (6.15.21), we get

$$D' = \frac{L_2RT}{c_2} \tag{6.15.22}$$

Isothermal Diffusion in a Ternary Solution

A ternary solution involves two solutes and one solvent. Representing the two solutes by the subscripts 2 and 3, we may write the expression of entropy production as

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[†] $c_1V_{1,\text{pm}} + c_2V_{2,\text{pm}} = (n_1/V)\,V_{1,\text{pm}} + (n_2/V)\,V_{2,\text{pm}} = (n_1V_{1,\text{pm}} + n_2V_{2,\text{pm}})/V = V/V = 1.$

$$T\sigma = J_2 Y_2 + J_3 Y_3 \qquad \text{(Eq. 6.15.14)}$$

where $$Y_j = \sum_{i=2}^{3}\left(\delta_{ij} + \frac{c_i V_{j,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\text{grad}\left(-\mu_i^{(c)}\right) \qquad (j = 2, 3)$$

The phenomenological equations are

$$J_2 = L_{22} Y_2 + L_{23} Y_3 \qquad (6.15.23)$$

$$J_3 = L_{32} Y_2 + L_{33} Y_3 \qquad (6.15.24)$$

where $$Y_2 = -\left(1 + \frac{c_2 V_{2,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\text{grad}\,\mu_2^{(c)} - \left(\frac{c_3 V_{2,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\text{grad}\,\mu_3^{(c)} \qquad (6.15.25)$$

$$Y_3 = -\left(\frac{c_2 V_{3,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\text{grad}\,\mu_2^{(c)} - \left(1 + \frac{c_3 V_{3,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\text{grad}\,\mu_3^{(c)} \qquad (6.15.26)$$

The dependence of chemical potential on position is due to the local changes in the solute concentrations c_2 and c_3 and may be expressed as

$$\text{grad}\,\mu_2^{(c)} = \frac{\partial \mu_2^{(c)}}{\partial c_2}\text{grad}\,c_2 + \frac{\partial \mu_2^{(c)}}{\partial c_3}\text{grad}\,c_3 \qquad (6.15.27)$$

$$\text{grad}\,\mu_3^{(c)} = \frac{\partial \mu_3^{(c)}}{\partial c_2}\text{grad}\,c_2 + \frac{\partial \mu_3^{(c)}}{\partial c_3}\text{grad}\,c_3 \qquad (6.15.28)$$

Writing $\partial\mu_i^{(c)}/\partial c_j$ as μ_{ij}, the above expressions become

$$\text{grad}\,\mu_2^{(c)} = \mu_{22}\,\text{grad}\,c_2 + \mu_{23}\,\text{grad}\,c_3 \qquad (6.15.29)$$

$$\text{grad}\,\mu_3^{(c)} = \mu_{32}\,\text{grad}\,c_2 + \mu_{33}\,\text{grad}\,c_3 \qquad (6.15.30)$$

With these, the expression of Y_2 becomes

$$Y_2 = -\left(1 + \frac{c_2 V_{2,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)(\mu_{22}\,\text{grad}\,c_2 + \mu_{23}\,\text{grad}\,c_3)$$

$$- \left(\frac{c_3 V_{2,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)(\mu_{32}\,\text{grad}\,c_2 + \mu_{33}\,\text{grad}\,c_3)$$

$$= -\left[\left(1 + \frac{c_2 V_{2,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\mu_{22} + \frac{c_3 V_{2,\text{pm}}}{c_1 V_{1,\text{pm}}}\mu_{32}\right]\text{grad}\,c_2$$

$$- \left[\left(1 + \frac{c_2 V_{2,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\mu_{23} + \left(\frac{c_3 V_{2,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\mu_{33}\right]\text{grad}\,c_3 \qquad (6.15.31)$$

$$= -a'\,\text{grad}\,c_2 - b'\,\text{grad}\,c_3$$

Working similarly of Y_3, we get

$$Y_3 = -\left(\frac{c_2 V_{3,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)(\mu_{22}\text{ grad } c_2 + \mu_{23}\text{ grad } c_3)$$

$$-\left(1+\frac{c_3 V_{3,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)(\mu_{32}\text{ grad } c_2 + \mu_{33}\text{ grad } c_3)$$

$$= -\left[\left(1+\frac{c_3 V_{3,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\mu_{32} + \left(\frac{c_2 V_{3,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\mu_{22}\right]\text{grad } c_2$$

$$-\left[\left(1+\frac{c_3 V_{3,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\mu_{33} + \left(\frac{c_2 V_{3,\text{pm}}}{c_1 V_{1,\text{pm}}}\right)\mu_{23}\right]\text{grad } c_3$$

$$= -c'\text{ grad } c_2 - d'\text{ grad } c_3 \tag{6.15.32}$$

The explicit expressions of J_2 and J_3 become

$$J_2 = -L_{22}\,(a'\text{ grad } c_2 + b'\text{ grad } c_3) - L_{23}\,(c'\text{ grad } c_2 + d'\text{ grad } c_3)$$

$$= -(a' L_{22} + c' L_{23})\text{ grad } c_2 - (b' L_{22} + d' L_{23})\text{ grad } c_3 \tag{6.15.33}$$

$$J_3 = -L_{32}\,(a'\text{ grad } c_2 + b'\text{ grad } c_3) - L_{33}\,(c'\text{ grad } c_2 + d'\text{ grad } c_3)$$

$$= -(a' L_{32} + c' L_{33})\text{ grad } c_2 - (b' L_{32} + d' L_{33})\text{ grad } c_3 \tag{6.15.34}$$

Comparison with Fick's Law

According to Fick's law, the diffusion flows are given by the expressions

$$J_2 = -D_{22}\text{ grad } c_2 - D_{23}\text{ grad } c_3 \tag{6.15.35}$$

$$J_3 = -D_{32}\text{ grad } c_2 - D_{33}\text{ grad } c_3 \tag{6.15.36}$$

where D_{22} and D_{33} are the principal or main coefficients, and D_{23} and D_{32} are the interaction or cross coefficients.

Comparing phenomenological equations with the corresponding expressions of Fick's law, we get

$$D_{22} = a' L_{22} + c' L_{23} \tag{6.15.37a}$$

$$D_{23} = b' L_{22} + d' L_{23} \tag{6.15.37b}$$

$$D_{32} = a' L_{32} + c' L_{33} \tag{6.15.37c}$$

$$D_{33} = b' L_{32} + d' L_{33} \tag{6.15.37d}$$

In the matrix form these can be represented as

$$\begin{bmatrix} D_{22} & D_{23} \\ D_{32} & D_{33} \end{bmatrix} = \begin{bmatrix} L_{22} & L_{23} \\ L_{32} & L_{33} \end{bmatrix}\begin{bmatrix} a' & b' \\ c' & d' \end{bmatrix} \tag{6.15.38}$$

The values of phenomenological coefficients can be evaluated through the expression

$$\begin{bmatrix} L_{22} & L_{23} \\ L_{32} & L_{33} \end{bmatrix} = \begin{bmatrix} D_{22} & D_{23} \\ D_{32} & D_{33} \end{bmatrix}\begin{bmatrix} a' & b' \\ c' & d' \end{bmatrix}^{-1}$$

$$= \begin{bmatrix} D_{22} & D_{23} \\ D_{32} & D_{33} \end{bmatrix}\left\{\frac{1}{\text{Det}}\begin{bmatrix} d' & -c' \\ -b' & a' \end{bmatrix}\right\} \tag{6.15.39}$$

where Det = $a'd' - b'c'$. Thus

$$L_{22} = \frac{d'D_{22} - b'D_{23}}{a'd' - b'c'}; \quad L_{23} = \frac{a'D_{23} - c'D_{22}}{a'd' - b'c'}$$

$$L_{32} = \frac{d'D_{32} - b'D_{33}}{a'd' - b'c'}; \quad L_{33} = \frac{a'D_{33} - c'D_{32}}{a'd' - b'c'}$$

For Onsager relation to hold good, it follows from the above expressions that we must have

$$a'\,D_{23} - c'\,D_{22} = d'\,D_{32} - b'\,D_{33} \tag{6.15.40a}$$

and $\quad a'd' - b'c' \neq 0 \qquad$ (6.15.40b)

From the limited experimental data available, it is verified that the Onsager reciprocal relation holds good.

From Eqs. (6.15.37b) and (6.15.37c), it follows that $D_{23} \neq D_{32}$ in a case where $L_{23} = L_{32}$ (Onsager reciprocal relation). Moreover, the requirement $L_{23} = L_{32} = 0$ does not lead to $D_{23} = D_{32} = 0$ unless $L_{22} = L_{33} = 0$.

6.16 ISOTHERMAL ULTRACENTRIFUGE SEDIMENTATION

Introduction

In the ultracentrifuge sedimentation, the solute particles migrate from the bulk of solution towards the bottom of a cell under the influence of a centrifugal force which is about 105 times greater than the gravitational force. The solution is taken in a transparent cell and is placed in the cavity of a rotor operating at very high speed in an apparatus which allows vibration-free operation at constant temperature.

If the sedimentation is carried over a longer time, eventually a state of equilibrium is reached where the forces acting in the opposite directions balance each other. Based on this, the equations applicable to solute particles at sedimentation equilibrium can be derived. However, the same equations are deriveable by treating the sedimentation on the basis of theory of irreversible processes.

Entropy Production

Since the solute particles flow under the influence of centrifugation, the expression of entropy production has the same form as that of diffusional process:

$$T\sigma = \sum_{i=1}^{n} J_i \ \text{grad}\,(-\mu_i) \tag{6.16.1}$$[†]

The chemical potential μ_i in Eq. (6.16.1) besides containing the concentration-dependent term includes a term which accounts for the kinetic energy acquired by the particles in the solution.

Kinetic Energy Acquired by the Particles

If ω is the angular velocity of the rotor, then the linear velocity of particles at a distane r from the centre of rotation is

$$v = \omega r \tag{6.16.2}$$

The kinetic energy acquired by the ith particles is

$$E_k = \frac{1}{2} m_i v^2 = \frac{1}{2} m_i (\omega r)^2 \tag{6.16.3}$$

[†] Equation 6.16.1 is considered to be applicable to solute particles only.

For one mole of the *i*th particles, the mass m_i is given by

$$m_i = M_i - \rho\, V_{i,\,\mathrm{pm}} \tag{6.16.4}$$

where M_i and $V_{i,\,\mathrm{pm}}$ are the molar mass and partial molar volume of *i*th particles, respectively, and ρ is the density of the solution. The term $\rho V_{i,\,\mathrm{pm}}$ in Eq. (6.16.4) accounts for the buoyance correction of mass of solvent displaced by the solute particles.

Substituting Eq. (6.16.4) in Eq. (6.16.3), we get

$$\begin{aligned} E_\mathrm{k} &= \frac{1}{2}\left(M_i - \rho\, V_{i,\mathrm{pm}}\right)\omega^2 r^2 \\ &= \frac{1}{2} M_i\left(1 - \rho\, v_{i,\mathrm{pm}}\right)\omega^2 r^2 \end{aligned} \tag{6.15.5}$$

where $v_{i,\,\mathrm{pm}}$ (= $V_{i,\,\mathrm{pm}}$ / M_i,) is the partial specific volume of the *i*th particles.

Chemical Potential of *i*th Particles The chemical potential of *i*th particles is lowered by the amount given by the kinetic energy acquired by one mole of particles and is thus given by

$$\mu_i = \mu_i^\circ + \mu_i^{(c)} - \frac{1}{2} M_i (1 - \rho v_{i,\,\mathrm{pm}})\, \omega^2 r^2 \tag{6.16.6}$$

where μ_i° is the standard chemical potential (dependent on temperature only) and $\mu_i^{(c)}$ is the concentration-dependent term.

Expression of grad ($-\mu_i$) Since the chemical potential varies with the distance r from the axis of rotation, the term grad ($-\mu_i$) is simply given by the expression $-\mathrm{d}\mu_i/\mathrm{d}r$. With this; Eq. (6.16.6) gives

$$-\frac{\mathrm{d}\mu_i}{\mathrm{d}r} = -\frac{\mathrm{d}\mu_i^{(c)}}{\mathrm{d}r} + M_i (1 - \rho v_{i,\,\mathrm{pm}})\, \omega^2 r \tag{6.16.7}$$

Phenomenological Equation For a solution containing one solute particles, the phenomenological equation is given by

$$\begin{aligned} J_2 &= L_2\left(-\frac{\mathrm{d}\mu_2}{\mathrm{d}r}\right) \\ &= -L_2\left[\left(\frac{\mathrm{d}\mu_2^{(c)}}{\mathrm{d}r}\right) - M_2 (1 - \rho v_{2,\mathrm{pm}})\, \omega^2 r\right] \end{aligned} \tag{6.16.8†}$$

The $\mathrm{d}\mu_2^{(c)}/\mathrm{d}r$ may be written as

$$\frac{\mathrm{d}\mu_2^{(c)}}{\mathrm{d}r} = \frac{\mathrm{d}\mu_2^{(c)}}{\mathrm{d}c_2}\,\frac{\mathrm{d}c_2}{\mathrm{d}r}$$

Assuming solution to be dilute, we have

$$\frac{\mathrm{d}\mu_2^{(c)}}{\mathrm{d}r} = \left(\frac{RT}{c_2}\right)\frac{\mathrm{d}c_2}{\mathrm{d}r} \tag{6.16.9}$$

[†] The solute is represented by the subscript 2.

Substitution of Eq. (6.16.9) in Eq. (6.16.8), we get

$$J_2 = -\left(\frac{L_2RT}{c_2}\right)\frac{dc_2}{dr} + L_2M_2\,(1 - \rho v_{2,\,\mathrm{pm}})\,\omega^2 r$$

$$= -D\,\frac{dc_2}{dr} + L_2M_2\,(1 - \rho v_{2,\,\mathrm{pm}})\,\omega^2 r \qquad (6.16.10)$$

where $D(= L_2RT/c_2)$ is the diffusion coefficient.

The term $M_2(1 - \rho v_{2,\,\mathrm{pm}})$ in Eq. (6.16.10) may be replaced in terms of sedimentation coefficient, s, defined by the expression

$$s = \frac{L_2M_2(1-\rho v_{2,\mathrm{pm}})}{c_2} \qquad (6.16.11)$$

With this, Eq. (6.16.10) becomes

$$J_2 = -D\frac{dc_2}{dr} + sc_2\omega^2 r \qquad (6.16.12)$$

Sedimentation Equilibrium

The term $sc_2\omega^2 r$ in Eq. (6.16.12) represents flow due to centrifugal sedimentation and $-D\,dc_2/\,dr$ is the flow in the opposite direction due to diffusion of solute. If the sedimentation is carried over a long period, a state of equilibrium is reached where the net flow J_2 becomes zero. At this stage, we have

$$D\,\frac{dc_2}{dr} = sc_2\omega^2 r \qquad (6.16.13)$$

Determination of Molar Mass of the Solute

Equation (6.16.13) forms the basis of determining the molar mass of solute. Separating the variables and integrating the resultant expression, we get

$$\int\frac{dc_2}{c_2} = \frac{s\omega^2}{D}\int r\,dr$$

i.e. $$\ln\frac{c_2}{c^\circ} = \frac{s\omega^2}{2D}\,r^2 + \text{constant.} \qquad (6.16.14)$$

Thus, a plot of $\ln(c_2 / c^\circ)$ versus r^2 is linear with slope equal to $s\omega^2/2D$. From the slope, s is evaluated which is used in Eq. (6.16.11) to determine the molar mass of the solute as described in the following.

Equation (6.16.11) is

$$s = \frac{L_2M_2(1-\rho v_{2,\mathrm{pm}})}{c_2}$$

Since $L_2RT/c_2 = D$ (Eq. 6.16.10), we get

$$\frac{s}{D} = \frac{M_2(1-\rho v_{2,\mathrm{pm}})}{RT}$$

or $$M_2 = \frac{(s/D)\,RT}{1-\rho v_{2,\mathrm{pm}}} \tag{6.16.15}$$

Equation (6.16.15) is known as Svedberg equation.

Evaluation of *s*/*D*.

The value of s/D in Eq. (6.16.15) may be determined by using Archibald suggestion which states that at the bottom end of the centrifugal cell (whose distance from the axis of rotation is r_b), the flow of solute is zero and as per Eq. (6.16.12) we will have

$$\frac{s}{D} = \frac{(\mathrm{d}c_2/\mathrm{d}r)_{r=r_\mathrm{b}}}{(c_2)_{r=r_\mathrm{b}}\,\omega^2 r_\mathrm{b}} \tag{6.16.16}$$

Knowing $(c_2)_{r=r_\mathrm{b}}$, $(\mathrm{d}c_2/\mathrm{d}r)_{r=r_\mathrm{b}}$ and ω, the value of s/D may be determined by using Eq. (6.16.16). This value can be substituted in Eq. (6.16.15) to determine the value of M_2.

6.17 TRANSPORT PROCESS BETWEEN TWO HOMOGENEOUS PHASES

Let the two compartments α and β of constant volumes (Fig. 6.17.1) contain the same gas (or fluid such as water) at temperatures T and $T + \Delta T$ and pressures p and $p + \Delta p$, respectively. Let the two compartments be connected through a small office (or a rigid membrane). Due to the temperature and pressure difference, energy (both heat and matter) will flow from the compartment α to the compartment β.

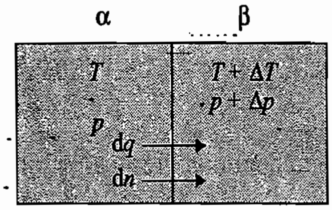

Fig. 6.17.1 Demonstration of transport process between two homogeneous phases

From the Gibbs relation ($\mathrm{d}U = T\,\mathrm{d}S - p\mathrm{d}V + \mu\,\mathrm{d}n$), we write the expression for the change in entropy at constant volume as

$$\mathrm{d}S = \frac{\mathrm{d}U}{T} - \frac{\mu}{T}\mathrm{d}n \tag{6.17.1}$$

Expression of Entropy Production

Since the compartments α and β taken together represents a closed system, the entropy production in the two compartments will be given by the expressions.

$$\mathrm{d_i}S^{(\alpha)} = -\frac{\mathrm{d}U}{T} + \frac{\mu^{(\alpha)}}{T}\mathrm{d}n$$

$$\mathrm{d_i}S^{(\beta)} = +\frac{\mathrm{d}U}{T+\Delta T} - \frac{\mu^{(\beta)}}{T+\Delta T}\mathrm{d}n$$

The total entropy production is

$$\begin{aligned}\mathrm{d_i}S &= \mathrm{d_i}S^{(\alpha)} + \mathrm{d_i}S^{(\beta)} \\ &= \mathrm{d}U\left(-\frac{1}{T} + \frac{1}{T+\Delta T}\right) + \mathrm{d}n\left(-\frac{\mu^{(\beta)}}{T+\Delta T} + \frac{\mu^{(\alpha)}}{T}\right)\end{aligned} \tag{6.17.2}$$

If ΔT is small in comparison to T, we may write

$$-\frac{1}{T}+\frac{1}{T+\Delta T}=\frac{-(T+\Delta T)+T}{T(T+\Delta T)}\simeq-\frac{\Delta T}{T^2} \tag{6.17.3}$$

Also, we have

$$-\frac{\mu^{(\beta)}}{T+\Delta T}+\frac{\mu^{(\alpha)}}{T}=\frac{-T\mu^{(\beta)}+(T+\Delta T)\,\mu^{(\alpha)}}{T(T+\Delta T)}\simeq-\frac{\mu^{(\beta)}-\mu^{(\alpha)}}{T}+\mu^{(\alpha)}\left(\frac{\Delta T}{T^2}\right)$$

$$=-\frac{V_{\mathrm{m}}\Delta p-S_{\mathrm{m}}\Delta T}{T}+(H_{\mathrm{m}}-T\,S_{\mathrm{m}})\left(\frac{\Delta T}{T^2}\right) \qquad \text{(Supersript } \alpha \text{ is dropped)}$$

$$=-\frac{V_{\mathrm{m}}\Delta p}{T}+H_{\mathrm{m}}\left(\frac{\Delta T}{T^2}\right) \tag{6.17.4}$$

Substituting Eqs (6.17.3) and (6.17.4) in Eq. (6.17.2), we get

$$\mathrm{d_i}S=\mathrm{d}U\left(-\frac{\Delta T}{T^2}\right)+\mathrm{d}n\left(-\frac{V_{\mathrm{m}}\Delta p}{T}+H_{\mathrm{m}}\frac{\Delta T}{T^2}\right) \tag{6.17.5}$$

The rate of entropy production is

$$\sigma=\frac{\mathrm{d_i}S}{\mathrm{d}t}=\left(\frac{\mathrm{d}U}{\mathrm{d}t}\right)\left(-\frac{\Delta T}{T^2}\right)+\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)\left(-\frac{V_{\mathrm{m}}\Delta p}{T}+H_{\mathrm{m}}\frac{\Delta T}{T^2}\right)$$

$$=J_UX_U+J_{\mathrm{m}}X_{\mathrm{m}} \tag{6.17.6}$$

where X_U $(-\Delta T/T^2)$ is the force correponding to the energy flow, J_U (= $\mathrm{d}U/\mathrm{d}t$) and X_{m} $(=-V_{\mathrm{m}}\Delta p/T+H_{\mathrm{m}}\Delta T/T^2)$ is the force corresponding to the matter flow, J_{m} (= $\mathrm{d}n/\mathrm{d}t$).

Phenomenological Equations

The phenomenological equations corresponding to Eq. (6.17.6) are

$$J_U=L_{11}X_U+L_{12}X_{\mathrm{m}}$$

$$=L_{11}\left(-\frac{\Delta T}{T^2}\right)+L_{12}\left(-\frac{V_{\mathrm{m}}\Delta p}{T}+H_{\mathrm{m}}\frac{\Delta T}{T^2}\right)$$

$$=(L_{11}-L_{12}H_{\mathrm{m}})\left(-\frac{\Delta T}{T^2}\right)+L_{12}\left(-\frac{V_{\mathrm{m}}\Delta p}{T}\right) \tag{6.17.7}$$

$$J_{\mathrm{m}}=L_{21}X_U+L_{22}X_{\mathrm{m}}$$

$$=L_{21}\left(-\frac{\Delta T}{T^2}\right)+L_{22}\left(-\frac{V_{\mathrm{m}}\Delta p}{T}+H_{\mathrm{m}}\frac{\Delta T}{T^2}\right)$$

$$=(L_{21}-L_{22}H_{\mathrm{m}})\left(-\frac{\Delta T}{T^2}\right)+L_{22}\left(-\frac{V_{\mathrm{m}}\Delta p}{T}\right) \tag{6.17.8}$$

A Few Derivations

When $\Delta T=0$ From Eq. (6.17.7), it is obvious that $J_U\neq 0$ even when $\Delta T=0$. From Eqs (6.17.7) and (6.17.18), we find that

$$\left(\frac{J_U}{J_{\mathrm{m}}}\right)_{\Delta T=0}=\frac{L_{12}}{L_{22}} \tag{6.17.9}$$

Equation (6.17.9) gives the energy tranferred for a unit flow of matter. This quantity is represented by the symbol U^*. Hence

$$U^* = \left(\frac{J_U}{J_\mathrm{m}}\right)_{\Delta T=0} = \frac{L_{12}}{L_{22}} \tag{6.17.10}$$

- **When $J_\mathrm{m} = 0$** The corresponds to the stationary state of the system which describes no flow of matter. From Eq. (6.17.8), we have

$$0 = (L_{21} - L_{22}\, H_\mathrm{m})\left(-\frac{\Delta T}{T^2}\right) + L_{22}\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

This gives

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_\mathrm{m}=0} = -\frac{L_{21} - L_{22}\, H_\mathrm{m}}{L_{22}\, V_\mathrm{m} T} = -\frac{(L_{21}/L_{22}) - H_\mathrm{m}}{V_\mathrm{m} T}$$

which in view of Eq. (6.17.10) gives

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_\mathrm{m}=0} = -\frac{U^* - H_\mathrm{m}}{V_\mathrm{m} T} = -\frac{q^*}{V_\mathrm{m} T} \quad (\text{since } L_{12} = L_{21}) \tag{6.17.11}$$[†]

where q^* is known as heat of transfer.

The pressure difference Δp for a given temperature differene to observe stationary state is known as thermomolecular pressure difference.

Alternative Choice of Flux and Force

Alternatively, Eq. (6.17.6) may be written as

$$\sigma = \frac{\mathrm{d_i}S}{\mathrm{d}t} = \left(\frac{\mathrm{d}U}{\mathrm{d}t} - H_\mathrm{m}\frac{\mathrm{d}n}{\mathrm{d}t}\right)\left(-\frac{\Delta T}{T^2}\right) + \left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

$$= \frac{\mathrm{d}}{\mathrm{d}t}(U - H_\mathrm{m}\mathrm{d}n)\left(-\frac{\Delta T}{T^2}\right) + \left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

$$= \left(\frac{\mathrm{d}q}{\mathrm{d}t}\right)\left(-\frac{\Delta T}{T^2}\right) + \left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

$$= J_q X_q + J_\mathrm{m} X'_\mathrm{m} \tag{6.17.12}$$

where $X_q (= -\Delta T/T^2)$ is the force corresponding to the heat flow, $J_q (= \mathrm{d}q/\mathrm{d}t)$ and X'_m $(= -V_\mathrm{m}\Delta p/T)$ is the force corresponding to the matter flow J_m $(= \mathrm{d}n/\mathrm{d}t)$. The phenomenological equations corresponding to Eq. (6.17.12) are

$$J_q = L'_{11} X_q + L'_{12} X'_\mathrm{m}$$

$$= L'_{11}\left(-\frac{\Delta T}{T^2}\right) + L'_{12}\left(-\frac{V_\mathrm{m}\Delta p}{T}\right) \tag{6.17.13}$$

$$J_\mathrm{m} = L'_{21} X_q + L'_{22} X'_\mathrm{m}$$

$$= L'_{21}\left(-\frac{\Delta T}{T^2}\right) + L'_{22}\left(-\frac{V_\mathrm{m}\Delta p}{T}\right) \tag{6.17.14}$$

[†] It may be mentioned here that to the terms U^* and H_m an arbitary constant can be added. In both cases the zero value has been assugned at $T = 0$. However, the quantity q^* is uniquely determined.

A Few Derivations

When $\Delta T = 0$ From Eq. (6.17.13), it is obvious that $J_q \neq 0$ even when $\Delta T = 0$. From Eqs (6.17.13) and (6.17.14), we find that

$$\left(\frac{J_q}{J_\mathrm{m}}\right)_{\Delta T=0} = \frac{L'_{12}}{L'_{22}} \tag{6.17.15a}$$

Equation (6.17.15) descibes the heat transferred for unit flow of matter. This quantity is known as heat of transfer and represented by the symbol q^*. Hence

$$q^* = \left(\frac{J_q}{J_\mathrm{m}}\right)_{\Delta T=0} = \frac{L'_{12}}{L'_{22}} \tag{6.17.15b}$$

- **When $J_\mathrm{m} = 0$** from Eq. (6.17.14), we get

$$0 = L'_{21}\left(-\frac{\Delta T}{T^2}\right) + L'_{22}\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

This gives

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_\mathrm{m}=0} = -\frac{L'_{21}}{L'_{22}}\frac{1}{V_\mathrm{m}T} \tag{6.17.16a}$$

which in view of Eq. (6.17.15b) gives

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_\mathrm{m}=0} = -\frac{q^*}{V_\mathrm{m}T} \tag{6.17.16b}$$

Reciprocity Relation

Making use of Eqs (6.17.15b) and (6.17.16b) in Eq. (6.17.15a), we get

$$\left(\frac{J_q}{J_\mathrm{m}}\right)_{\Delta T=0} = -V_\mathrm{m}T\left(\frac{\Delta p}{\Delta T}\right)_{J_\mathrm{m}=0} \tag{6.17.17}$$

Equation (6.17.17) is known as reciprocity relation. A second such relation is obtained with the conditions of (i) $\Delta p = 0$ in Eqs (6.17.13) and (6.17.14) and (ii) $J_q = 0$ in Eq. (6.17.13). We get

$$\left(\frac{J_q}{J_\mathrm{m}}\right)_{\Delta p=0} = \frac{L'_{11}}{L'_{21}} \quad \text{and} \quad \left(\frac{\Delta p}{\Delta T}\right)_{J_q=0} = -\frac{1}{V_\mathrm{m}T}\frac{L'_{11}}{L'_{12}} \tag{6.17.18}$$

Hence $$\left(\frac{J_q}{J_\mathrm{m}}\right)_{\Delta p=0} = -V_\mathrm{m}T\left(\frac{\Delta p}{\Delta T}\right)_{J_q=0} \tag{6.17.19}$$

Thermo-Osmosis

When the two compartments are separated with the help of a rigid membrane, the transfer of matter due to temperature difference is known as thermo-osmosis.

Problem 6.17.1

For transport process between two homogeneous phases, show that

(i) $(J_q)_{J_\mathrm{m}=0} = \left(L'_{11} - \dfrac{L'^2_{12}}{L'_{22}}\right)\left(-\dfrac{\Delta T}{T^2}\right) = \left(L'_{12} - \dfrac{L'_{11}\,L'_{22}}{L'_{21}}\right)\left(-\dfrac{V_\mathrm{m}\Delta p}{T}\right)$

(ii) $$(J_\mathrm{m})_{J_q=0} = \left(L'_{21} - \frac{L'_{11}L'_{22}}{L'_{12}}\right)\left(-\frac{\Delta T}{T^2}\right) = \left(L'_{22} - \frac{L'^2_{12}}{L'_{11}}\right)\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

Solution We have

(i) $$J_q = L'_{11}\left(-\frac{\Delta T}{T^2}\right) + L'_{12}\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$ (Eq. 6.17.13)

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_\mathrm{m}=0} = -\frac{L'_{21}}{L'_{22}}\frac{1}{V_\mathrm{m}T}$$ (Eq. 6.17.16a)

Eliminating Δp in Eq. (6.17.13) with the help of Eq. (6.17.16a), we get

$$(J_q)_{J_\mathrm{m}=0} = L'_{11}\left(-\frac{\Delta T}{T^2}\right) + L'_{12}\,\frac{V_\mathrm{m}}{T}\left(\frac{1}{V_\mathrm{m}T}\frac{L'_{21}}{L'_{22}}\Delta T\right)$$

$$= \left(L'_{11} - \frac{L'_{12}\,L'_{21}}{L'_{22}}\right)\left(-\frac{\Delta T}{T^2}\right) = \left(L'_{11} - \frac{L'^2_{12}}{L'_{22}}\right)\left(-\frac{\Delta T}{T^2}\right)$$

Eliminating ΔT in Eq. (6.17.13) with the help of Eq. (6.17.16a), we get

$$(J_q)_{J_\mathrm{m}=0} = L'_{11}\left(\frac{V_\mathrm{m}T\,(L'_{22}/L'_{21})}{T^2}\Delta p\right) + L'_{12}\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

$$= \left(L'_{12} - \frac{L'_{11}\,L'_{22}}{L'_{21}}\right)\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

(ii) $$J_\mathrm{m} = L'_{21}\left(-\frac{\Delta T}{T^2}\right) + L'_{22}\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$ (Eq. 6.17.14)

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_q=0} = -\frac{1}{V_\mathrm{m}T}\frac{L'_{11}}{L'_{12}}$$ (Eq. 6.17.18)

Eliminating Δp in Eq. (6.17.14) with the help of Eq. (6.17.18), we get

$$(J_\mathrm{m})_{J_q=0} = L'_{21}\left(-\frac{\Delta T}{T^2}\right) + L'_{22}\,\frac{V_\mathrm{m}}{T}\left(\frac{1}{V_\mathrm{m}T}\frac{L'_{11}}{L'_{12}}\Delta T\right)$$

$$= \left(L'_{21} - \frac{L'_{11}\,L'_{22}}{L'_{12}}\right)\left(-\frac{\Delta T}{T^2}\right)$$

Eliminating ΔT in Eq. (6.17.14) with the help of Eq. (6.17.18), we get

$$(J_\mathrm{m})_{J_q=0} = L'_{21}\left(\frac{V_\mathrm{m}T\,(L'_{12}/L'_{11})}{T^2}\Delta p\right) + L'_{22}\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

$$= \left(L'_{22} - \frac{L'_{21}\,L'_{12}}{L'_{11}}\right)\left(-\frac{V_\mathrm{m}\Delta p}{T}\right) = \left(L'_{22} - \frac{L'^2_{12}}{L'_{11}}\right)\left(-\frac{V_\mathrm{m}\Delta p}{T}\right)$$

Stationary State and Minimum Entropy Production

A system not in equilibrium involves fluxes and the forces. These fluxes and the forces move in a direction which help the system to attain equilibrium. In the latter state, all the fluxes and forces become zero. The system at equilibrium is said to be at the stationary state. However, there is another way of stationary state where one or more of the forces are held constant and allow to vary the other forces till the fluxes become zero. At this state, the system attains stationary state and it can be shown that this stationary state involves the minimum production of entropy. This principle may be illustrated with a system involving two forces, such as the phenomenon of thermo-osmosis.

The flux of matter as given by Eq. (6.17.14) is

$$J_{\mathrm{m}} = L'_{21} X_q + L'_{22} X'_{\mathrm{m}} \qquad \text{(Eq. 6.17.14)}$$

where $X_q = -\Delta T/T^2$ and $X'_{\mathrm{m}} = -V_{\mathrm{m}} \Delta p/T$.

Suppose ΔT is held constant and allow Δp to vary till it attains the value as governed by Eq. (6.17.16b) which is $\Delta p = -q^* \Delta T/V_{\mathrm{m}}T$. At this value, J_{m} becomes zero and the system attains the stationary state where

$$0 = L'_{21} X_q + L'_{22} X'_{\mathrm{m}} \qquad (6.17.20)$$

The entropy production is given by

$$\sigma = J_q X_q + J_{\mathrm{m}} X'_{\mathrm{m}} \qquad \text{(Eq. 6.17.12)}$$

Substituting the expressions of J_q and J_{m} from the phenomenological equations (Eqs 6.17.13 and 6.17.14), we get

$$\sigma = \left(L'_{11} X_q + L'_{12} X'_{\mathrm{m}}\right) X_q + \left(L'_{21} X_q + L'_{22} X'_{\mathrm{m}}\right) X'_{\mathrm{m}}$$

$$= L'_{11} X_q^2 + X'_{\mathrm{m}} X_q \left(L'_{12} + L'_{21}\right) + L'_{22} X'^2_{\mathrm{m}}$$

Since $L'_{12} = L'_{21}$, we have

$$\sigma = L'_{11} X_q^2 + 2L'_{21} X'_{\mathrm{m}} X_q + L'_{22} X'^2_{\mathrm{m}} \qquad (6.17.21)$$

For the entropy production to have a minimum value for fixed value of X_q, we get

$$\frac{\partial \sigma}{\partial X'_{\mathrm{m}}} = 0$$

and also we prove that $\partial^2 \sigma / \partial X'^2_{\mathrm{m}} > 0$.

Differentiating σ with respects to X'_{m} at constant X_q, we get

$$\frac{\partial \sigma}{\partial X'_{\mathrm{m}}} = 2L'_{21} X_q + 2L'_{22} X'_{\mathrm{m}} = 0$$

i.e. $$L'_{21} X_q + L'_{22} X'_{\mathrm{m}} = 0 \qquad (6.17.22)$$

which is identical to that given by Eq. (6.17.20). To show that the production of entropy is minimum, we find that

$$\frac{\partial^2 \sigma}{\partial X'^2_{\mathrm{m}}} = 2L'_{22} > 0 \qquad \text{(since } L_{22} \text{ is positive)}$$

Hence, the attainment of stationary state involves the production of minimum entropy. This fact, which have been established for a system involving two forces, is universally applicable to a system involving any number of flexes and forces. It can be broadly stated as follows.

Suppose a system involves a number of independent forces $X_1, X_2,..., X_n$. Let the forces $X_1\ X_2,...,X_k$ be held constant. The system moves in a direction where the fluxes corresponding to the rest the forces progressively become zero. The system attains stationary state when the forces $X_{k+1}, X_{k+2}, ..., X_n$ assume the values satisfying the condition of minimum entropy production or energy dissipation. The stationary state is set to be kth order since k forces are held constant. For example, the phenomenon of thermo-osmosis involves stationary state of the first order. The true thermodynamic equilibrium may be called a stationary state of zero order.

Knudsen Effect

Knudsen Gas

If the two compartments α and β at temperatures T and $T + \Delta T$, respectively, are connected through a capillary tube or a small hole, the developed thermomolecular pressure difference is known as Knudsen effect.

The gas is said to be Knudsen gas if the diameter of capillary or hole connecting two compartments is small compared to the mean free path of the gaseous molecules. The molecule of a Knudsen gas, when arrives at the opening of capillary or hole with a nonzero velocity component, passes freely through it. The number of such molecules striking the tiny hole in a unit time is given by

$$N' = \left(\frac{1}{4}\bar{u}\, N^*\right) A_{\text{hole}} \tag{6.17.23}$$

where $\bar{u}\left(= \sqrt{8k_BT/\pi m}\right)$ is the average speed of gaseous molecules, N^* $(= p/k_BT)$ is the number of gaseous molecules per unit volume and A_{hole} is the area of tiny hole. From Eq. (6.17.23), it follows that

$$N' \propto p/\sqrt{T} \tag{6.17.24}$$

In the stationary state, the number of molecules passing from the compartment β to the compartment α will be equal to those passing from the compartment α to the compartment β. Hence, we will have

$$\frac{p}{\sqrt{T}} = \frac{p + \Delta p}{\sqrt{T + \Delta T}} \tag{6.17.25}$$

Taking square on both sides and rearranging, we get

$$\frac{p^2}{T} = \frac{(p + \Delta p)^2}{(T + \Delta T)} \quad \text{i.e.} \quad p^2(T + \Delta T) = T(p^2 + \Delta p^2 + 2p\Delta p)$$

or $\quad p^2\Delta T = T(\Delta p^2 + 2p\Delta p)$

Neglecting Δp^2 term, we get

$$p^2\,\Delta T = 2pT\,\Delta p \quad \text{i.e.} \quad p\,\Delta T = 2T\,\Delta p$$

Thus, the expression of $\Delta p/\Delta T$ at the stationary state is

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_\mathrm{m}=0} = \frac{p}{2T} \qquad (6.17.26)$$

As per ideal gas equation ($pV_\mathrm{m} = RT$), Eq. (6.17.26) becomes

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_\mathrm{m}=0} = \frac{R}{2V_\mathrm{m}} \qquad (6.17.27)$$

Also, from Eq. (6.17.11), we get

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_\mathrm{m}=0} = -\frac{q^*}{V_\mathrm{m}T} \qquad (6.17.28)$$

Comparing Eqs (6.17.27) and (6.17.28), we get

$$-\frac{q^*}{V_\mathrm{m}T} = \frac{R}{2V_\mathrm{m}} \quad \text{i.e.} \quad q^* = -\frac{RT}{2} \qquad (6.17.29)$$

Since $q^* = U^* - H_\mathrm{m}$ (Eq. 6.17.11), we get

$$U^* - H_\mathrm{m} = -\frac{RT}{2} \quad \text{i.e.} \quad U^* = H_\mathrm{m} - \frac{RT}{2} \qquad (6.17.30)$$

Generalized Statement

For monatomic gas, $H_\mathrm{m} = (5/2)\,RT$. Hence

$$U^* = H_\mathrm{m} - \frac{RT}{2} = \frac{5}{2}RT - \frac{1}{2}RT = 2RT \qquad (6.17.31)^*$$

If the value of U^* is compared with the average kinetic energy per mole of gaseous molecules, we find that

$$U^* - \mathrm{KE} = 2RT - (3/2)RT = (1/2)\,RT \qquad (6.17.32)$$

that is, the gaseous molecules acquire an additional average kinetic energy of $(1/2)RT$ along the axis of the capillary tube or hole.

If the diameter of the capillary tube or hole is quite large, the gaseous molecules move in the bulk from one compartment to the other. Consequently, the pressure difference between the two compartments cannot be maintained and thus Δp becomes zero. According to Eq. (6.17.14), the stationary state can be established (i.e. $J_\mathrm{m} = 0$) provided $L'_{21} = 0$ and as per Eq. (6.17.16b), this requires that $q^* = 0$. Hence,

$$U^* = H_\mathrm{m} \qquad (6.17.33)$$

In actual practice, all possible values of q^* from $-RT/2$ to zero are observed depending upon the ratio of diameter of the capillary tube or hole and the mean free path of gaseous molecules.

6.18 THERMAL DIFFUSION IN A CONTINUOUS SYSTEM

Entropy Production

If there exists a temperature gradient in a continuous system, then there occurs a flow of matter caused by the nonconjugate force of temperature gradient. If the

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* See Annexure A-III at the end of this chapter for the derivation of the expression of energy of transfer on the basis of kinetic considerations.

system does not involve charged particles and if no reaction is involved, then the entropy production in the system due to the flow of matter in the direction of temperature gradient is given by

$$T\sigma = J_s \operatorname{grad}(-T) + \sum_{i=1}^{n} J_i \operatorname{grad}(-\mu_i) \qquad \text{(Eq. 6.6.10)}$$

where $$J_s = \frac{J_q - \sum_{i=1}^{n} \mu_i J_i}{T} \qquad \text{(Eq. 6.6.7)}$$

Reduced Heat Flow

Since $\mu_i = H_{i,\,\text{pm}} - TS_{i,\,\text{pm}}$, Eq. (6.6.7) may be written as

$$J_s = \frac{1}{T}\left[J_q - \sum_{i=1}^{n}(H_{i,\text{pm}} - TS_{i,\text{pm}})J_i\right]$$

$$= \frac{1}{T}\left[\left\{J_q - \sum_{i=1}^{n} H_{i,\text{pm}} J_i\right\}\right] + \sum_{i=1}^{n} S_{i,\text{pm}} J_i$$

$$= \frac{J_{q'}}{T} + \sum_{i=1}^{n} S_{i,\text{pm}}\, J_i \qquad (6.18.1)$$

where $$J_{q'} = J_q - \sum_{i=1}^{n} H_{i,\text{pm}}\, J_i \qquad (6.18.2)$$

The quantity $J_{q'}$ known as reduced heat flow. This is equal to the total heat flow minus the heat flow due to the flow of matter.

Expression of grad ($-\mu_i$)

We have

$$d\mu_i = -S_{i,\text{pm}} dT + V_{i,\text{pm}}\, dp + d\mu_i^{(c)}$$

where $\mu_i^{(c)}$ is the concentration-dependent term in the expression of μ_i. For a system at mechanical equilibrium, $dp = 0$. Hence

$$d\mu_i = -\,S_{i,\text{pm}}\, dT + d\mu_i^{(c)}$$

Thus, we can write

$$\text{grad}\,(-\mu_i) = -\,S_{i,\text{pm}}\,\text{grad}\,(-T) + \text{grad}\,(-\mu_i^{(c)}) \qquad (6.18.3)$$

Final Expression of Entropy Production

Substituting Eqs (6.18.1) and (6.18.3) in the expression of entropy production, we get

$$T\sigma = \left(\frac{J_{q'}}{T} + \sum_{i=1}^{n} S_{i,\text{pm}}\, J_i\right)\operatorname{grad}(-T)$$

$$+ \sum_{i=1}^{n} J_i \left(-S_{i,\text{pm}} \operatorname{grad}(-T) + \operatorname{grad}\left(-\mu_i^{(c)}\right)\right)$$

$$= \frac{J_{q'}}{T}\operatorname{grad}(-T) + \sum_{i=1}^{n} J_i \operatorname{grad}\left(-\mu_i^{(c)}\right) \qquad (6.18.4)$$

Diffusion of Solutes

Equation (6.18.4) includes the flows of both solvent and solutes. Representing solvent by the subscript 1 and solutes by 2, 3,..., etc., we may write Eq. (6.18.4) as

$$T\sigma = \frac{J_{q'}}{T}\,\mathrm{grad}\,(-T) + J_1\,\mathrm{grad}\left(-\mu_1^{(c)}\right) + \sum_{i=2}^{n} J_i\,\mathrm{grad}\left(-\mu_i^{(c)}\right) \tag{6.18.5}$$

The material flows and their forces mentioned in Eq. (6.18.5) are not independent. These are related to each other as mentioned in the following.

- The various forces are related through Gibbs-Duhem equation

$$\sum_{i=1}^{n} c_i\,\mathrm{grad}\left(-\mu_i^{(c)}\right) = 0 \tag{6.18.6}$$

- The various flows are related through the expression based on the fact that there occurs no flow of volume of the system. The volume of the system is

$$V = \sum_{i=1}^{n} n_i V_{i,\mathrm{pm}}$$

where $V_{i,\,\mathrm{pm}}$ is the partial molar volume of the ith constituent in the solution. Assuming these remain constants, the rate of flow of volume of the solution is

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \sum_{i=1}^{n}\left(\frac{\mathrm{d}n_i}{\mathrm{d}t}\right)V_{i,\mathrm{pm}} = \sum_{i=1}^{n} J_i V_{i,\mathrm{pm}}$$

Since $\mathrm{d}V/\mathrm{d}t = 0$ (the condition of no flow of volume of the solution), we have

$$\sum_{i=1}^{n} J_i V_{i,\,\mathrm{pm}} = 0 \tag{6.18.7}$$

Using Eqs (6.18.6) and (6.18.7), one can eliminate the dependent solvent term in Eq. (6.18.5). We will have

$$\mathrm{grad}\left(-\mu_1^{(c)}\right) = -\sum_{i=2}^{n}\left(\frac{c_i}{c_1}\right)\mathrm{grad}\,\left(-\mu_i^{(c)}\right)$$

$$J_1 = -\sum_{j=2}^{n} J_j\left(\frac{V_{j,\mathrm{pm}}}{V_{1,\mathrm{pm}}}\right)$$

Substituting these in Eq. (6.18.5), we get

$$T\sigma = \frac{J_{q'}}{T}\,\mathrm{grad}\,(-T) + \left[\sum_{j=2}^{n} J_j\left(\frac{V_{j,\,\mathrm{pm}}}{V_{1,\,\mathrm{pm}}}\right)\right]\left[\sum_{i=2}^{n}\left(\frac{c_i}{c_1}\right)\mathrm{grad}\left(-\mu_i^{(c)}\right)\right]$$

$$+\sum_{i=2}^{n} J_i\,\mathrm{grad}\left(-\mu_i^{(c)}\right)$$

$$= \frac{J_{q'}}{T}\,\mathrm{grad}\,(-T) + \sum_{j=2}^{n} J_j\left\{\sum_{i=2}^{n}\frac{V_{j,\mathrm{pm}}c_i}{V_{1,\mathrm{pm}}\,c_1}\,\mathrm{grad}\left(-\mu_i^{(c)}\right)\right\}$$

$$+\sum_{i=2}^{n} J_i\,\mathrm{grad}\left(-\mu_i^{(c)}\right)$$

$$= \frac{J_{q'}}{T}\,\text{grad}\,(-T) + \sum_{j=2}^{n} J_j \left\{ \sum_{i=2}^{n} \left(\delta_{ij} + \frac{V_{j,\text{pm}}\, c_i}{V_{1,\text{pm}}\, c_1} \right) \text{grad}\left(-\mu_i^{(c)}\right) \right\} \tag{6.18.8}$$

where δ_{ij} is Kronecker delta (it is equal to 1 for $i = j$ and is zero for $i \neq j$). Equation (6.18.8) may be written as

$$T\sigma = \frac{J_{q'}}{T}\,\text{grad}\,(-T) + \sum_{j=2}^{n} J_j\, Y_j \tag{6.18.9}$$

where $$Y_j = \sum_{i=2}^{n} \left(\delta_{ij} + \frac{V_{j,\text{pm}}\, c_i}{V_{1,\text{pm}}\, c_1} \right) \text{grad}\left(-\mu_i^{(c)}\right) \tag{6.18.10}$$

Thermal Diffusion in a Binary Continuous System

Entropy Production

A binary system involves a single solute dissolved in a system. For this system, Eq. (6.18.9) is

$$T\sigma = \frac{J_{q'}}{T}\,\text{grad}\,(-T) + J_2\, Y_2 \tag{6.18.11}$$

where $$Y_2 = \left(1 + \frac{V_{2,\text{pm}}\, c_2}{V_{1,\text{pm}}\, c_1}\right) \text{grad}\left(-\mu_2^{(c)}\right) = \left(\frac{V_{1,\text{pm}}\, c_1 + V_{2,\text{pm}}\, c_2}{V_{1,\text{pm}}\, c_1}\right) \text{grad}\,\left(-\mu_2^{(c)}\right)$$

$$= \frac{\text{grad}\left(-\mu_2^{(c)}\right)}{V_{1,\text{pm}}\, c_1} \tag{6.18.12†}$$

The term grad $\left(-\mu_2^{(c)}\right)$ may be expressed as

$$\text{grad}\,\left(-\mu_2^{(c)}\right) = \frac{\partial \mu_2}{\partial c_2}\,\text{grad}\,(-c_2)$$

With this, Eq. (6.18.12) becomes

$$Y_2 = \frac{\partial \mu_2 / \partial c_2}{V_{1,\text{pm}}\, c_1}\,\text{grad}\,(-c_2) \tag{6.18.13}$$

Phenomenological Equations

The phenomenological equations corresponding to Eq. (6.18.11) are

$$J_2 = L_{22}\, Y_2 + L_{2q'}\, \frac{\text{grad}(-T)}{T} \tag{6.18.14}$$

$$J_{q'} = L_{q'2}\, Y_2 + L_{q'q'}\, \frac{\text{grad}\,(-T)}{T} \tag{6.18.15}$$

[†] $c_1 V_{1,\text{pm}} + c_2 V_{2,\text{pm}} = (n_1/V) V_{1,\text{pm}} + (n_2/V) V_{2,\text{pm}} = (n_1 V_{1,\text{pm}} + n_2 V_{2,\text{pm}})/V = V/V = 1$

Accordig to Eq. (6.18.14), the flow of solute consists of two flows as mentioned in the following

- ***The diffusion of solute due the force Y_2 which, in turn, depends on (grad $(-c_2)$.***

The phenomenological coefficient may be identified with the diffusion coefficient D of the solute:

$$D = \frac{L_{22}}{c_1 V_{1,\text{pm}}}\left(\frac{\partial \mu_2}{\partial c_2}\right) \tag{6.18.16*}$$

For a dilute solution,

$$\left(\frac{\partial \mu_2}{\partial c_2}\right) = \frac{\partial (RT \ln c_2)}{\partial c_2} = \frac{RT}{c_2}$$

and $\quad c_1 V_{1,\text{pm}} \approx 1$

With these, Eq. (6.17.16) becomes

$$D = \frac{L_{22} RT}{c_2} \tag{6.18.17}$$

- ***The diffusion of solute due to the temperature gradient***

This diffusion is known as thermal diffusion. The corresponding phenomenological coefficient is generally dependent linearly on the concentration of solute. Hence

$$\frac{L_{2q'}}{T} \propto c_2 \qquad \text{i.e.} \qquad \frac{L_{2q'}}{T} = D_{\text{thermal}}\, c_2 \tag{6.18.18}$$

where D_{thermal} is known as thermal diffusion coefficient. In terms of D and D_{thermal} Eq. (6.18.14) becomes

$$J_2 = D \text{ grad } (-c_2) + D_{\text{thermal}}\, c_2 \text{ grad } (-T) \tag{6.18.19}$$

Thermal diffusion measurements can be made in a cell consisting of two parallel metal plates, with the warm plate at the top and the cold plate at the bottom. This arrangement of plates prevent convection currents. A homogeneous binary solution is introduced between the plates. A stationary temperature gradient is set up in the solution almost immediately. The time required to attain stationary temperature gradient is much less than the time for the diffusion of solute in the solution. Due to the temperature gradient in the solution, solute starts diffusing relative to the solvent in accordance to the Eq. (6.18.14) with $Y_2 = 0$, i.e.

$$J_2 = L_{2q'} \frac{\text{grad }(-T)}{T} = -\frac{L_{2q'}}{T} \text{ grad }(T)$$

$$= -D_{\text{thermal}}\, c_2 \text{ grad } (T)$$

The solute diffuses towards cold plate if the thermal diffusion is positive and will diffuse towards hot plate if the thermal diffusion is negative. For most of strong electrolytes in aqueous solution, the thermal diffusion is positive and thus solute diffuses towards cold plate.

---

* Equation (6.18.16) is obtained by making use of Eq. (6.18.14).

$$J_2 = L_{22}\, Y_2 = L_{22} \left(\frac{\partial \mu_2 / \partial c_2}{c_1 V_{1,\text{pm}}}\right) \text{grad } (-c_2) = D \text{ grad } (-c_2)$$

Soret Effect

The thermal diffusion produces a concentration gradient of the solute in the solution, which in turn causes a diffusion flux in the opposite direction to the thermal diffusive flow. After a while, the thermal diffusion exactly balances the counter diffusion due to the concentration gradient and the system attains a stationary state. The penomenon of establishing a concentration gradient as a result of a temperature gradient in condensed phases is known as Soret effect.

Soret Coefficient

Mathematically, Soret effect is described by setting $J_2 = 0$ in Eq. (6.18.19), which gives

$$0 = D \text{ grad } (-c_2) + D_{\text{thermal}}\, c_2 \text{ grad } (-T)$$

i.e.

$$s = \frac{D_{\text{thermal}}}{D} = -\frac{\text{grad}(-c_2)}{c_2 \text{ grad } (-T)} = -\frac{\text{grad } c_2}{c_2 \text{ grad } T} \tag{6.18.20}$$

where s is known as soret coefficient. According to Eq. (6.18.18), the soret coefficient is given as

$$s = \frac{D_{\text{thermal}}}{D} = \frac{L_{2q'}/Tc_2}{D} \tag{6.18.21}$$

Heat of Transfer

The heat of transfer is defined as the reduced heat flow per unit flow of matter at zero temperature gradient, i.e.

$$q^* = \left(\frac{J_{q'}}{J_2}\right)_{\text{grad } T = 0} \tag{6.18.22}$$

From Eqs (6.18.14) and (6.18.15), we get

$$q^* = \frac{L_{q'2}}{L_{22}} \tag{6.18.23}$$

Soret Coefficient Related to Heat of Transfer

The Soret coefficient is

$$s = \frac{L_{2q'}/Tc_2}{D} \qquad \text{(Eq. 6.18.21)}$$

and the heat of transfer is

$$q^* = \frac{L_{q'2}}{L_{22}} \qquad \text{(Eq. 6.18.23)}$$

If Onsager reciprocal relation ($L_{2q'} = L_{q'2}$) holds good, then it follows that

$$s = \frac{q^* L_{22}/Tc_2}{D}$$

Substituting the expression of D from Eq. (6.18.17), we get

$$s = \frac{q^* L_{22}/Tc_2}{L_{22}RT/c_2} = \frac{q^*}{RT^2} \tag{6.18.24}$$

The verification of Eq. (6.18.24) provides an experimental test of Onsager reciprocal relation.

Dufour Effect

The phenomenon of generating a temperature gradient as a result of concentration gradient is known as Dufour effect. Consider a system at uniform temperature (i.e. grad $(T) = 0$).

From Eq. (6.18.15), we find that

$$J_{q'} = L_{q'2}\, Y_2 = L_{q'2}\, \frac{\partial \mu_2 / \partial c_2}{c_1 V_{1,\mathrm{pm}}}\, \mathrm{grad}\,(-c_2)$$

For a dilute solution, we have $c_1 V_{1,\mathrm{pm}} \simeq 1$, and thus

$$J_{q'} \simeq L_{q'2}\, \frac{RT}{c_2}\, \mathrm{grad}\,(-c_2) = D_\mathrm{d}\, \mathrm{grad}\,(-c_2)$$

where D_d ($= L_{q'2}\, RT/c_2$) is known as Dufour coefficients. The ratio of Dufour and thermal cofficients is

$$\frac{D_\mathrm{d}}{D_\mathrm{thermal}} = \frac{L_{q'2}(RT/c_2)}{L_{2q'}/c_2 T} = RT^2 \qquad (\text{since} \quad L_{q'2} = L_{2q'}).$$

Dufour effect has been observed in mixing of two gases by diffusion into each other, initially at the same temperature. For liquids, Dufour effect has not yet observed due to insignificant Dufour coefficient.

6.19 TRANSPORT PROCESS IN AN ELECTROLYTIC SOLUTION

Entropy Production

For an electrolytic solution involving transport process in one direction at constant temperature without a chemical reaction, the entropy production is given by

$$T\sigma = \sum_{i=1}^{n} J_i\, \mathrm{grad}\,(-\tilde{\mu}_i) \tag{6.19.1}$$

where the electrochemical potential $\tilde{\mu}_i$ is given by the expression

$$\tilde{\mu}_i = \mu_i + z_i F \varphi \tag{6.19.2}$$

In this expression, μ_i is the chemical potential, z_i is the charge number (positive for cations, negative for anions and zero for nonelectrolytes), φ is the electrical potential and F is Faraday constant.

Flow of Solutes Relative to Solvent

Equation (6.19.1) involves the flow of solvent as well as solute species. However, the flow of solvent can be eliminated by expressing the flows of solutes relative to that of solvent. This is achieved by using Gibbs-Duhem equation

$$\sum_{i=1}^{n} c_i\, \mathrm{grad}\,(\tilde{\mu}_i) = 0 \tag{6.19.3}$$

Representing solvent by the subscript 1 and solute species by 2, 3, ..., etc., we write Eq. (6.19.3) as

$$c_1\, \mathrm{grad}\,(\tilde{\mu}_1) + \sum_{i=2}^{n} c_i\, \mathrm{grad}\,(\tilde{\mu}_i) = 0$$

i.e.

$$\mathrm{grad}(\tilde{\mu}_1) = -\sum_{i=2}^{n} (c_i/c_1)\, \mathrm{grad}\,(\tilde{\mu}_i) \tag{6.19.4}$$

Substitution of Eq. (6.19.4) in Eq. (6.19.1) gives

$$
\begin{aligned}
T\sigma &= J_1 \operatorname{grad}(-\tilde{\mu}_1) + \sum_{i=2}^{n} J_i \operatorname{grad}(-\tilde{\mu}_i) \\
&= J_1\left[-\sum_{i=2}^{n}\frac{c_i}{c_1}\operatorname{grad}(-\tilde{\mu}_i)\right] + \sum_{i=2}^{n} J_i \operatorname{grad}(-\tilde{\mu}_i) \\
&= \sum_{i=2}^{n}\left(J_i - \frac{c_i}{c_1}J_1\right)\operatorname{grad}(-\tilde{\mu}_i) \qquad (6.19.5)
\end{aligned}
$$

Transport Process in a Solution Involving a Single Electrolyte

Entropy Production Representing the positive and negative ions of an electrolyte by the subscripts "+" and "–", respectively, Eq. (6.19.5) gives

$$
\begin{aligned}
T\sigma &= \left(J_+ - \frac{c_+}{c_1}J_1\right)\operatorname{grad}(-\tilde{\mu}_+) + \left(J_- - \frac{c_-}{c_1}J_1\right)\operatorname{grad}(-\tilde{\mu}_-) \\
&= J_+^{(\mathrm{d})}\operatorname{grad}(-\tilde{\mu}_+) + J_-^{(\mathrm{d})}\operatorname{grad}(-\tilde{\mu}_-) \qquad (6.19.6)
\end{aligned}
$$

where $J_+^{(\mathrm{d})}$ and $J_-^{(\mathrm{d})}$ are known as diffusional flows of positive and negative ions, respectively.

Phenomenological Equations The phenomenological equations corresponding to Eq. (6.19.6) are

$$J_+^{(\mathrm{d})} = L_{++}\operatorname{grad}(-\tilde{\mu}_+) + L_{+-}\operatorname{grad}(-\tilde{\mu}_-) \qquad (6.19.7)$$

$$J_-^{(\mathrm{d})} = L_{-+}\operatorname{grad}(-\tilde{\mu}_+) + L_{--}\operatorname{grad}(-\tilde{\mu}_-) \qquad (6.19.8)$$

with Onsager reciprocal relation $L_{+-} = L_{-+}$.

Note: From Eq. (6.19.7), it is obvious that $J_+^{(\mathrm{d})}$ is not equal to zero if $\operatorname{grad}(-\tilde{\mu}_+)$ alone is zero. Similarly, $J_-^{(\mathrm{d})}$ is not zero if $\operatorname{grad}(-\tilde{\mu}_-)$ alone is zero. This indicates that the flow of negatively-charged species has a dragging effect on the positively charged species and vice-versa.

Expression for Electrical Conductivity The electric conductance is determined under isothermal condition with uniform concentration of electrolyte in a conductance cell. Under these conditions, we have

$$\operatorname{grad}\mu_i = 0 \qquad (6.19.9)$$

The electric conduction in the cell is due to the electric potential difference across the two electrodes. The local electric field intensity in the cell is given by

$$E = -\operatorname{grad}\varphi \qquad (6.19.10)$$

From Eq. (6.19.2), we get

$$\operatorname{grad}\tilde{\mu}_i = \operatorname{grad}\mu_i + z_i F \operatorname{grad}\varphi$$

which in view of Eqs (6.19.9) and (6.19.10) becomes

$$\operatorname{grad}\tilde{\mu}_i = -z_i F E \qquad (6.19.11)$$

Substituting Eq. (6.19.11) in the phenomenological equation (Eqs 6.19.7 and 6.19.8), we get

$$J_+^{(d)} = (z_+ L_{++} + z_- L_{+-})\, F\, E \qquad (6.19.12)$$

$$J_-^{(d)} = (z_+ L_{-+} + z_- L_{--})\, F\, E \qquad (6.19.13)$$

The electric current density (i.e. current per unit area) in the cell due to the flow of ions in the solution is given by

$$j = \sum_{i=2}^{n} z_i\, F\, J_i^{(d)} \qquad (6.19.14)^{\dagger}$$

In the present case, we have

$$j = \left[z_+ J_+^{(d)} + z_- J_-^{(d)}\right] F \qquad (6.19.15)$$

Substituting the expressions of $J_+^{(d)}$ and $J_-^{(d)}$ from Eqs (6.19.12) and (6.19.13), respectively, we get

$$\begin{aligned} j &= [z_+ (z_+ L_{++} + z_- L_{+-}) F\, E + z_- (z_+ L_{-+} + z_- L_{--})\, F\, E] F \\ &= [z_+^2 L_{++} + z_+ z_- (L_{+-} + L_{-+}) + z_-^2 L_{--}] F^2 E \\ &= K\, F^2\, E \qquad (6.19.16) \end{aligned}$$

where $K = z_+^2 L_{++} + z_+ z_- (L_{+-} + L_{-+}) + z_-^2 L_{--}$

$$= z_+^2 L_{++} + 2 z_+ z_- L_{+-} + z_-^2 L_{--} \qquad (\text{since } L_{+-} = L_{-+}) \qquad (16.19.17)$$

The expression of electrical conductivity (κ) is

$$\kappa = \frac{\text{Current density } (j)}{\text{Electrical field } (E)}$$

Substituting the expression j from Eq. (6.19.16), we get

$$\kappa = [z_+^2 L_{++} + z_+ z_- (L_{+-} + L_{-+}) + z_-^2 L_{--}]\, F^2 = KF^2 \qquad (6.19.18)$$

Expressions of Transport Number

The transport number of an ion in the solution is the fraction of current carried by the ion. Hence

$$t_+ = \frac{j_+}{j} = \frac{z_+ F J_+^{(d)}}{j} \qquad (6.19.19)$$

---

† It is immaterial to use diffusional flows or absolute flows in Eq. (6.19.14). This may be proved as follows.

$$\begin{aligned} J &= \left[z_+ J_+^{(d)} + z_- J_-^{(d)}\right] F \\ &= [z_+ (J_+ - (c_+/c_1) J_1) + z_- (J_- - (c_-/c_1) J_1)] \\ &= [(z_+ J_+ + z_- J_-) - (1/c_1)(z_+ c_+ + z_- c_-)] F \end{aligned}$$

The condition of electroneutrality requires that $z_+ c_+ + z_- c_- = 0$. Hence

$$j = (z_+ J_+ + z_- J_-) F = \sum_{i=2}^{n} z_i F\, J_i$$

Substituting $J_+^{(d)}$ and j from Eqs (6.19.12) and (6.19.16), respectively, we get

$$t_+ = \frac{z_+F[z_+L_{++} + z_-L_{+-}]FE}{\left[z_+^2 L_{++} + z_+z_-(L_{+-} + L_{-+}) + z_-^2 L_{--}\right]F^2E}$$

$$= \frac{z_+[z_+L_{++} + z_-L_{+-}]}{K} \qquad (6.19.20)$$

Similarly

$$t_- = \frac{z_-[z_+L_{-+} + z_-L_{--}]}{K} \qquad (6.19.21)$$

Derivation of Diffusion Coefficient

Considering the diffusion of ions without flow of current, we have from Eq. (6.19.15)

$$0 = \left[z_+ J_+^{(d)} + z_- J_-^{(d)}\right]F$$

which gives

$$z_+ J_+^{(d)} + z_- J_-^{(d)} = 0 \qquad (6.19.22)$$

Using Eqs (6.19.7) and (6.19.8) for $J_+^{(d)}$ and $J_-^{(d)}$, respectively, we get

$$z_+[L_{++}\,\text{grad}(-\tilde{\mu}_+) + L_{+-}\,\text{grad}\,(-\tilde{\mu}_-)] + z_-[L_{-+}\,\text{grad}\,(-\tilde{\mu}_+) + L_{--}\,\text{grad}\,(-\tilde{\mu}_-)] = 0$$

This gives

$$\text{grad}\,(\tilde{\mu}_+) = -\left(\frac{z_+L_{+-} + z_-L_{--}}{z_+L_{++} + z_-L_{-+}}\right)\text{grad}\,(\tilde{\mu}_-) \qquad (6.19.23)$$

Expressing grad (μ_+) and grad (μ_-) in Terms of grad (salt)

For the electrolyte $A_{\nu_+}B_{\nu_-}$ dissociating as

$$A_{\nu_+}B_{\nu_-} \rightleftharpoons \nu_+A^{z+} + \nu_-B^{z-} \qquad (6.19.24)$$

we have $\mu_{\text{salt}} = \nu_+\tilde{\mu}_+ + \nu_-\tilde{\mu}_-$

Thus $\text{grad}(\mu_{\text{salt}}) = \nu_+\,\text{grad}(\tilde{\mu}_+) + \nu_-\,\text{grad}\,(\tilde{\mu}_-)$ (6.19.25)†

To express $\text{grad}(\tilde{\mu}_+)$ in terms of grad (μ_{salt}), we eliminate $\text{grad}(\tilde{\mu}_-)$ in Eq. (6.19.23) with the help of Eq. (6.19.25). Thus, we get

$$\text{grad}\,(\tilde{\mu}_+) = -\left(\frac{z_+L_{+-} + z_-L_{--}}{z_+L_{++} + z_-L_{-+}}\right)\left[\frac{1}{\nu_-}\{\text{grad}(\mu_{\text{salt}}) - \nu_+\,\text{grad}(\tilde{\mu}_+)\}\right]$$

Rearranging this, we get

$$[\nu_-(z_+L_{++} + z_-L_{-+}) - \nu_+(z_+L_{+-} + z_-L_{--}]\,\text{grad}\,(\tilde{\mu}_+)$$

$$= -(z_+L_{+-} + z_-L_{--})\,\text{grad}\,(\mu_{\text{salt}}) \qquad (6.19.26)$$

---

† $\mu_{\text{salt}} = \nu_+\mu_+ + \nu_-\mu_- = \nu_+(\tilde{\mu}_+ - z_+F\varphi) + \nu_-(\tilde{\mu}_- - z_-F\varphi)$

$= (\nu_+\tilde{\mu}_+ + \nu_-\tilde{\mu}_-) - (\nu_+z_+ + \nu_-z_-)F\varphi$

$= \nu_+\tilde{\mu}_+ + \nu_-\tilde{\mu}_-$ (since $\nu_+z_+ + \nu_-z_- = 0$)

From the condition of electroneutrality ($\nu_+z_+ + \nu_-z_- = 0$), we get

$$\nu_- = -\nu_+\left(\frac{z_+}{z_-}\right) \tag{6.19.27}$$

Eliminating ν_- in Eq. (6.19.26) with the help of Eq. (6.19.27), we get

$$\left[-\nu_+\left(\frac{z_+}{z_-}\right)(z_+L_{++} + z_-L_{-+}) - \nu_+(z_+L_{+-} + z_-L_{--})\right]\operatorname{grad}(\tilde{\mu}_+)$$
$$= -(z_+L_{+-} + z_-L_{--})\operatorname{grad}(\mu_{\text{salt}})$$

This gives

$$\operatorname{grad}(\tilde{\mu}_+) = \frac{z_-}{\nu_+}\left[\frac{z_+L_{+-} + z_-L_{--}}{z_+^2L_{++} + z_+z_-(L_{-+} + L_{+-}) + z_-^2L_{--}}\right]\operatorname{grad}(\mu_{\text{salt}})$$
$$= \frac{z_-}{\nu_+}\left[\frac{z_+L_{+-} + z_-L_{--}}{K}\right]\operatorname{grad}(\mu_{\text{salt}}) \tag{6.19.28}$$

Proceeding similarly to express grad $(\tilde{\mu}_-)$ in terms of grad (μ_{salt}), we get

$$\operatorname{grad}(\tilde{\mu}_-) = \frac{z_+}{\nu_-}\left[\frac{z_-L_{-+} + z_+L_{++}}{z_+^2L_{++} + z_+z_-(L_{-+} + L_{+-}) + z_-^2L_{--}}\right]\operatorname{grad}(\mu_{\text{salt}})$$
$$= \frac{z_+}{\nu_-}\left[\frac{z_-L_{-+} + z_+L_{++}}{K}\right]\operatorname{grad}(\mu_{\text{salt}}) \tag{6.19.29}$$

Expressing $J_+^{(\text{d})}$ and $J_-^{(\text{d})}$ in terms of grad (μ_{salt})

Substituting Eqs (6.19.28) and (6.19.29) in Eq. (6.19.7), we get

$$J_+^{(\text{d})} = -\left[\frac{L_{++}(z_-/\nu_+)(z_+L_{+-} + z_-L_{--}) + L_{+-}(z_+/\nu_-)(z_-L_{-+} + z_+L_{++})}{K}\right]\operatorname{grad}(\mu_{\text{salt}})$$

$$= -\left[\frac{\left(\frac{z_+z_-}{\nu_+} + \frac{z_+^2}{\nu_-}\right)L_{++}L_{+-} + \frac{z_-^2}{\nu_+}L_{++}L_{--} + \frac{z_+z_-}{\nu_-}L_{+-}^2}{K}\right]\operatorname{grad}(\mu_{\text{salt}}) \tag{6.19.30}$$

where $L_{+-} = L_{-+}$ has been used in the numerator. Since $z_+\nu_+ + z_-\nu_- = 0$ (the condition of electroneutrality), we will have

$$\frac{z_+}{\nu_-} + \frac{z_-}{\nu_+} = 0$$

With this $\dfrac{z_+z_-}{\nu_+} + \dfrac{z_+^2}{\nu_-} = z_+\left(\dfrac{z_-}{\nu_+} + \dfrac{z_+}{\nu_-}\right) = 0$

and $$\frac{z_-^2}{\nu_+} = z_-\left(\frac{z_-}{\nu_+}\right) = z_-\left(-\frac{z_+}{\nu_-}\right) = -\frac{z_+z_-}{\nu_-}$$

With these, Eq. (6.19.30) becomes

$$J_+^{(\mathrm{d})} = \frac{z_+z_-}{\nu_-}\left[\frac{L_{++}L_{--}-L_{+-}^2}{K}\right]\mathrm{grad}\,(\mu_{\mathrm{salt}}) \tag{6.19.31}$$

Proceeding similarly for $J_-^{(\mathrm{d})}$, we have

$$J_-^{(\mathrm{d})} = \frac{z_+z_-}{\nu_+}\left[\frac{L_{++}L_{--}-L_{-+}^2}{K}\right]\mathrm{grad}\,(\mu_{\mathrm{salt}}) \tag{6.19.32}$$

Diffusion flow of the Salt

The diffusional flow of the salt is given by

$$J_{\mathrm{salt}}^{(\mathrm{d})} = \frac{J_+^{(\mathrm{d})}}{\nu_+} = \frac{J_-^{(\mathrm{d})}}{\nu_-}$$

$$= \frac{z_+z_-}{\nu_+\nu_-}\left[\frac{L_{++}L_{--}-L_{+-}^2}{K}\right]\mathrm{grad}\,(\mu_{\mathrm{salt}}) \tag{6.19.33}$$

The chemical potential of the salt in the solution changes point to point due to dependence of concentration on location, we will have

$$\mathrm{grad}\,(\mu_{\mathrm{salt}}) = \left(\frac{\mathrm{d}\mu_{\mathrm{salt}}}{\mathrm{d}c}\right)\mathrm{grad}\,(c)$$

With this, Eq. (6.19.33) becomes

$$J_{\mathrm{salt}}^{(\mathrm{d})} = \frac{z_+z_-}{\nu_+\nu_-}\left[\frac{L_{++}L_{--}-L_{+-}^2}{K}\right]\left(\frac{\mathrm{d}\mu_{\mathrm{salt}}}{\mathrm{d}c}\right)\mathrm{grad}\,(c) \tag{6.19.34}$$

Expression of Diffusion Constant Comparing Eq. (6.19.34) with Fick's law

$$J_{\mathrm{salt}}^{(\mathrm{d})} = -D\,\mathrm{grad}\,(c)$$

we get $$D = -\frac{z_+z_-}{\nu_+\nu_-}\left[\frac{L_{++}L_{--}-L_{+-}^2}{K}\right]\left(\frac{\mathrm{d}\mu_{\mathrm{salt}}}{\mathrm{d}c}\right) \tag{6.19.35}$$

Experimental Deterination of Phenomenological Coefficients

The expressions of conductivity, transference numbers and diffusion coefficient are

$$\kappa = K F^2 \qquad \text{(Eq. 6.19.18)}$$

$$t_+ = \frac{z_+(z_+L_{++}+z_-L_{+-})}{K} \qquad \text{(Eq. 6.19.20)}$$

$$t_- = \frac{z_-(z_-L_{--} + z_+L_{-+})}{K} \qquad \text{(Eq. 6.19.21)}$$

$$D = -\frac{z_+z_-}{\nu_+\nu_-}\left(\frac{L_{++}L_{--} - L_{+-}^2}{K}\right)\left(\frac{\mathrm{d}\mu_{\text{salt}}}{\mathrm{d}c}\right) \qquad \text{(Eq.6.19.35)}$$

where $K = z_+^2 L_{++} + z_+ z_- (L_{+-} + L_{-+}) + z_-^2 L_{--}$ (6.19.36)

From the electroneutrality condition ($\nu_+ z_+ + \nu_- z_- = 0$), we get

$$\frac{z_+}{\nu_-} + \frac{z_-}{\nu_+} = 0 \qquad \text{i.e.} \qquad \frac{z_+}{\nu_-} = -\frac{z_-}{\nu_+}$$

Hence $-\frac{z_+z_-}{\nu_+\nu_-} = \left(\frac{z_+}{\nu_-}\right)\left(-\frac{z_-}{\nu_+}\right) = \left(-\frac{z_-}{\nu_+}\right)^2 = \left(\frac{z_-}{\nu_+}\right)^2$

With this, the expression of diffusional constant becomes

$$D = \left(\frac{z_-}{\nu_+}\right)^2\left(\frac{L_{++}L_{--} - L_{+-}^2}{K}\right)\left(\frac{\mathrm{d}\mu_{\text{salt}}}{\mathrm{d}c_2}\right) \qquad (6.19.37)$$

From the expression of t_+, we get

$$\left(\frac{Kt_+}{z_+}\right)^2 = (z_+L_{++} + z_-L_{+-})^2 = z_+^2 L_{++}^2 + 2z_+z_-L_{++}L_{+-} + z_-^2L_{+-}^2 \qquad (6.19.38)$$

From the expression of D in Eq. (6.19.37), we get

$$\frac{\nu_+^2 K D}{\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c} = z_-^2 L_{++}L_{--} - z_-^2 L_{+-}^2 \qquad (6.19.39)$$

Adding Eqs (6.19.38) and (6.19.39), we get

$$\left(\frac{Kt_+}{z_+}\right)^2 + \frac{\nu_+^2 K D}{(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c)} = z_+^2 L_{++}^2 + 2z_+z_-L_{++}L_{+-} + z_-^2 L_{++}L_{--}$$

$$= L_{++}\left(z_+^2 L_{++} + 2z_+z_-L_{+-} + z_-^2 L_{--}\right)$$

$$= L_{++}K \qquad \text{(where } L_{+-} = L_{-+} \text{ is used)}$$

Cancelling K from both sides, we get

$$L_{++} = K\left(\frac{t_+}{z_+}\right)^2 + \frac{\nu_+^2 D}{(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c)}$$

which in view of Eq. (6.19.18) becomes

$$L_{++} = \kappa\left(\frac{t_+}{z_+F}\right)^2 + \frac{\nu_+^2 D}{(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c)} \qquad (6.19.40)$$

Proceeding similarly, it can be shown that

$$L_{--} = \kappa \left(\frac{t_-}{z_- F} \right)^2 + \frac{\nu_-^2 D}{(\mathrm{d}\mu_{\mathrm{salt}}/\mathrm{d}c)} \tag{6.19.41}$$

$$L_{+-} = \kappa \left(\frac{t_+ t_-}{z_+ z_- F^2} \right) + \frac{\nu_+ \nu_- D}{(\mathrm{d}\mu_{\mathrm{salt}}/\mathrm{d}c)} \tag{6.19.42}$$

Knowing the experimentally determined values of κ, t_+, t_-, D and $\mathrm{d}\mu_{\mathrm{salt}}/\mathrm{d}c$, Eqs (6.19.40) – (6.19.42) can be used to determine the values of phenomenological coefficients. The results on sodium chloride solutions have shown that the straight coefficients (L_{++} and L_{--}) are nearly linear functions of concentration, and the cross coefficient (L_{+-}) depends on concentration and decreases rapidly as the concentration of sodium chloride is decreased.

Reduced Phenomenological Mobilities

Ionic Mobility By definition, ionic mobility is the velocity acquired by the ion under the influence of unit magnitude of potential gradient, i.e.

$$u = \frac{v}{|\mathrm{d}(\Delta\phi/\mathrm{d}l))|} = \frac{v}{|E|} \tag{6.19.43)$^{[\dagger]}$ (}$$

where $|E|$ is the magnitude of electric field.[†]

Diffusional Flows The diffusional flows in terms of ionic mobilities are given by the expressions

$$J_+^{(\mathrm{d})} = c_+ (v_+ - v_{\mathrm{w}}) = c_+ u_+ \boldsymbol{E} \tag{6.19.44}$$

$$J_-^{(\mathrm{d})} = c_- (v_- - v_{\mathrm{w}}) = - c_- u_- \boldsymbol{E} \tag{6.19.45}$$

The negative sign in Eq. (6.19.45) is due to the fact that the negative ions move in the direction opposite to the electric field.

For the salt $A_{\nu_+} B_{\nu_-}$, we have

$$c_+ = \nu_+ c_{\mathrm{salt}} \quad \text{and} \quad c_- = \nu_- c_{\mathrm{salt}}$$

Reduced Phenomenological Mobilities With these, Eqs (6.19.44) and (6.19.45) become

$$J_+^{(\mathrm{d})} = (\nu_+ c_{\mathrm{salt}}) u_+ \boldsymbol{E} \tag{6.19.46}$$

$$J_-^{(\mathrm{d})} = - (\nu_- c_{\mathrm{salt}}) u_- \boldsymbol{E} \tag{6.19.47}$$

The phenomenological equations representing diffusional flows as

$$J_+^{(\mathrm{d})} = (z_+ L_{++} + z_- L_{+-}) F \boldsymbol{E} \qquad \text{(Eq. 6.19.12)}$$

$$J_-^{(\mathrm{d})} = (z_+ L_{-+} + z_- L_{--}) F \boldsymbol{E} \qquad \text{(Eq. 6.19.13)}$$

[†] The ionic mobility is the proportionality constant between ionic velocity and the electric field, i.e. $v = u\,E$. It is a scalar quantity. Here after, $|E|$ is simply represented as E.

Equating Eq. (6.19.46) with expression of $J_+^{(d)}$ given above, we get

$$\nu_+ c_{\text{salt}} u_+ E = (z_+ L_{++} + z_- L_{+-}) F E$$

Hence $$u_+ = \frac{(z_+ L_{++} + z_- L_{+-})F}{\nu_+ c_{\text{salt}}} = \frac{z_+^2 L_{++} F}{\nu_+ z_+ c_{\text{salt}}} + \frac{z_+ z_- L_{+-} F}{\nu_+ z_+ c_{\text{salt}}}$$

$$= u_{++} + u_{+-} \qquad (6.19.48)$$

where $$u_{++} = \frac{z_+^2 L_{++} F}{\nu_+ z_+ c_{\text{salt}}} \quad \text{and} \quad u_{+-} = \frac{z_+ z_- L_{+-} F}{\nu_+ z_+ c_{\text{salt}}} \qquad (6.19.49)$$

Proceeding similarly for $J_-^{(d)}$, we get

$$-\nu_- c_{\text{salt}} u_- E = (z_+ L_{-+} + z_- L_{--}) F E$$

Hence $$u_- = -\frac{(z_+ L_{-+} + z_- L_{--})F}{\nu_- c_{\text{salt}}} = -\frac{z_+ z_- L_{-+} F}{\nu_- z_- c_{\text{salt}}} - \frac{z_-^2 L_{--} F}{\nu_- z_- c_{\text{salt}}}$$

Using the condition of electroneutrality ($\nu_+ z_+ + \nu_- z_- = 0$), we get

$$u_- = \frac{z_+ z_- L_{-+} F}{\nu_+ z_+ c_{\text{salt}}} + \frac{z_-^2 L_{--} F}{\nu_+ z_+ c_{\text{salt}}}$$

$$= u_{-+} + u_{--} \qquad (6.19.50)$$

where $$u_{-+} = \frac{z_+ z_- L_{-+} F}{\nu_+ z_+ c_{\text{salt}}} \quad \text{and} \quad u_{--} = \frac{z_-^2 L_{--} F}{\nu_+ z_+ c_{\text{salt}}} \qquad (6.19.51)$$

Note that $u_{+-} = u_{-+}$, since $L_{+-} = L_{-+}$.

Molar Conductivity and Reduced Ionic Mobilities

The physical quantities u_{++} and u_{--} are known as reduced phenomenological mobilities of cation and anion, respectively, and the quantity u_{+-} is a measure of interaction between cation and anion of the salt in the solution.

The expressions relating ionic mobility and molar ionic conductivity are

$$u_+ = \frac{\lambda_+}{z_+ F} \quad \text{and} \quad u_- = \frac{\lambda_-}{|z_-| F} \qquad (6.19.52)$$

Molar conductivity in terms of molar ionic conductivities is

$$\Lambda_{\text{m}} = \nu_+ \lambda_+ + \nu_- \lambda_- \qquad (6.19.53)$$

Substituting λ_+ and λ_- from Eq. (6.19.52), we get

$$\Lambda_{\text{m}} = \nu_+ (u_+ z_+ F) + \nu_- (u_- |z_-| F)$$

$$= (\nu_+ z_+) u_+ F + (\nu_- |z_-|) u_- F$$

Since $\nu_+ z_+ = \nu_- |z_-|$ (the condition of electroneutrality), the above expression may be written as

$$\Lambda_{\text{m}} = \nu_+ z_+ F(u_+ + u_-) \qquad (6.19.54)$$

Since $\Lambda_{\text{m}} = \kappa / c$, the expression of conductivity is

$$\kappa = \Lambda_{\text{m}} c_{\text{salt}} = (\nu_+ z_+) c_{\text{salt}} F (u_+ + u_-) \qquad (6.19.55)$$

Using Eqs (6.19.48) and (6.19.50) in Eq. (6.19.54), we get

$$\Lambda_{\mathrm{m}} = \nu_+ z_+ F(u_{++} + 2u_{+-} + u_{--}) \tag{6.19.56}$$

Substituting the expression of u_{++}, u_{+-} and u_{--}, we get

$$\Lambda_{\mathrm{m}} = \frac{F^2}{c_{\mathrm{salt}}}\left(z_+^2 L_{++} + 2z_+z_- L_{+-} + z_-^2 L_{--}\right) \tag{6.19.57}$$

Similarly, Eq. (6.19.55) becomes

$$\kappa = (\nu_+ z_+)\, c_{\mathrm{salt}}(u_{++} + 2u_{+-} + u_{--}) \tag{6.19.58}$$

which on substituting the expressions of u_{++}, u_{+-} and u_{--} becomes

$$\kappa = F^2 (z_+^2 L_{++} + 2z_+z_- L_{+-} + z_-^2 L_{--}) \tag{6.19.59}$$

Note: Equation (6.19.59) is the same expression as given by Eq. (6.19.18).

Transport Numbers and Reduced Mobilities

We have

$$t_+ = \frac{\nu_+\lambda_+}{\Lambda_{\mathrm{m}}} \quad \text{and} \quad t_- = \frac{\nu_-\lambda_-}{\Lambda_{\mathrm{m}}} \tag{6.19.60}$$

Replacing λ's and Λ_{m} in terms of ionic mobilities, we get

$$t_+ = \frac{\nu_+ z_+ F u_+}{\nu_+ z_+ F(u_+ + u_-)} = \frac{u_+}{u_+ + u_-} = \frac{u_{++} + u_{+-}}{u_{++} + 2u_{+-} + u_{--}} \tag{6.19.61}$$

$$t_- = \frac{\nu_- |z_-| F u_-}{\nu_+ z_+ F(u_+ + u_-)} = \frac{u_-}{u_+ + u_-} = \frac{u_{--} + u_{-+}}{u_{++} + 2u_{+-} + u_{--}} \tag{6.19.62}$$

Diffusion Constant and Reduced Mobilities

From Eq. (6.19.35), we have

$$D = -\frac{z_+z_-}{\nu_+\nu_-}\left(\frac{L_{++}L_{--} - L_{+-}^2}{z_+^2 L_{++} + 2\, z_+z_- L_{+-} + z_-^2 L_{--}}\right)\left(\frac{\mathrm{d}\mu_{\mathrm{salt}}}{\mathrm{d}c}\right)$$

From Eqs (6.19.49) and (6.19.51), we find that

$$L_{++} = \frac{\nu_+ z_+ c_{\mathrm{salt}}}{F}\left(\frac{u_{++}}{z_+^2}\right)$$

$$L_{+-} = \frac{\nu_+ z_+ c_{\mathrm{salt}}}{F}\left(\frac{u_{+-}}{z_+ z_-}\right)$$

$$L_{--} = \frac{\nu_+ z_+ c_{\mathrm{salt}}}{F}\left(\frac{u_{--}}{z_-^2}\right)$$

Substituting these in the expression of D, we get

$$D = -\frac{c_{\mathrm{salt}}}{\nu_- z_- F}\left(\frac{u_{++}u_{--} - u_{+-}^2}{u_{++} + 2u_{+-} + u_{--}}\right)\left(\frac{\mathrm{d}\mu_{\mathrm{salt}}}{\mathrm{d}c}\right)$$

$$= \frac{c_{\mathrm{salt}}}{\nu_+ z_+ F}\left(\frac{u_{++}u_{--} - u_{+-}^2}{u_{++} + 2u_{+-} + u_{--}}\right)\left(\frac{\mathrm{d}\mu_{\mathrm{salt}}}{\mathrm{d}c}\right) \tag{6.19.63a}$$

Using Eq. (6.19.56), this becomes

$$D = c_{\text{salt}}\left(\frac{u_{++}u_{--} - u_{+-}^2}{\Lambda_{\text{m}}}\right)\left(\frac{\mathrm{d}\mu_{\text{salt}}}{\mathrm{d}c}\right) \tag{6.19.63b}$$

Expression of *D* for an ideal Solution

For an ideal solution, no interactions exist between cation and anions. Hence

$$u_{+-} = 0 \tag{6.19.64}$$

Also $\mu_{\text{salt}} = \nu_+ \mu_+ + \nu_- \mu_-$

$$= \nu_+ (\mu_+^\circ + RT \ln c_+) + \nu_-(\mu_-^\circ + RT \ln c_-)$$

$$= (\nu_+ \mu_+^\circ + \nu_- \mu_-^\circ) + RT (\nu_+ \ln c_+ + \nu_- \ln c_-)$$

Since $c_+ = \nu_+ c_{\text{salt}}$ and $c_- = \nu_- c_{\text{salt}}$ for $\mathrm{A}_{\nu_+}B_{\nu_-}$ electrolyte, we have

$$\mu_{\text{salt}} = \mu_{\text{salt}}^\circ + RT\,[\nu_+ \ln (\nu_+ c_{\text{salt}}) + \nu_- \ln(\nu_- c_{\text{salt}})]$$

Hence

$$\left(\frac{\mathrm{d}\mu_{\text{salt}}}{\mathrm{d}c_{\text{salt}}}\right) = RT\left(\frac{\nu_+}{c_{\text{salt}}} + \frac{\nu_-}{c_{\text{salt}}}\right) = \frac{(\nu_+ + \nu_-)RT}{c_{\text{salt}}} \tag{6.19.65}$$

Making use of Eqs (6.19.64) and (6.19.65) in Eq. (6.19.63a), we get

$$D = \frac{(\nu_+ + \nu_-)RT}{\nu_+ z_+ F}\left(\frac{u_{++}\,u_{--}}{u_{++} + u_{--}}\right) = \left(\frac{1}{z_+} + \frac{\nu_-}{\nu_+ z_+}\right)\frac{RT}{F}\left(\frac{u_{++}\,u_{--}}{u_{++} + u_{--}}\right)$$

$$= \left(\frac{1}{z_+} - \frac{1}{z_-}\right)\frac{RT}{F}\left(\frac{u_{++}\,u_{--}}{u_{++} + u_{--}}\right) \tag{6.19.66}$$

Evaluation of Reduced Mobilities

From Eq. (6.19.49), we have

$$u_{++} = \frac{z_+^2 F}{\nu_+ z_+ c_{\text{salt}}} L_{++}$$

Substituting for L_{++} from Eq. (6.19.40), we get

$$u_{++} = \frac{z_+^2 F}{\nu_+ z_+ c_{\text{salt}}}\left[\kappa\left(\frac{t_+}{z_+ F}\right)^2 + \frac{\nu_+^2 D}{(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c_{\text{salt}})}\right]$$

$$= \frac{1}{\nu_+ z_+ F}\left(\frac{\kappa}{c_{\text{salt}}}\right)\left(\frac{\nu_+ \lambda_+}{\Lambda_{\text{m}}}\right)^2 + \frac{\nu_+ z_+ FD}{c_{\text{salt}}(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c_{\text{salt}})}$$

$$= \frac{\nu_+}{z_+ F}\frac{\lambda_+^2}{\Lambda_{\text{m}}} + \frac{\nu_+ z_+ FD}{c_{\text{salt}}(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c_{\text{salt}})} \tag{6.19.67}$$

From Eq. (6.19.51), we get

$$u_{--} = \frac{z_-^2 F}{\nu_+ z_+ c_{\text{salt}}} L_{--}$$

Substituting for L_{--} from Eq. (6.19.41), we get

$$u_{--} = \frac{z_-^2 F}{\nu_+ z_+ c_{\text{salt}}}\left[\kappa\left(\frac{t_-}{z_- F}\right)^2 + \frac{\nu_-^2 D}{(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c_{\text{salt}})}\right]$$

$$= \frac{1}{\nu_+ z_+ F}\left(\frac{\kappa}{c_{\text{salt}}}\right)\left(\frac{\nu_-\lambda_-}{\Lambda_{\text{m}}}\right)^2 + \frac{\nu_-^2 z_-^2 F D}{\nu_+ z_+ c_{\text{salt}}(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c_{\text{salt}})}$$

$$= \frac{\nu_-^2}{\nu_+ z_+ F}\left(\frac{\lambda_-^2}{\Lambda_{\text{m}}}\right) + \frac{\nu_+ z_+ F D}{c_{\text{salt}}(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c_{\text{salt}})} \qquad (6.19.68)$$

In Eq. (6.19.68), the condition of electroneutrality ($\nu_+ z_+ + \nu_- z_- = 0$) has been used. From Eq. (6.19.49), we have

$$u_{+-} = \frac{z_+ z_- F}{\nu_+ z_+ c_{\text{salt}}} L_{+-}$$

Substituting for L_{+-} from Eq. (6.19.42), we get

$$u_{+-} = \frac{z_+ z_- F}{\nu_+ z_+ c_{\text{salt}}}\left[\kappa\left(\frac{t_+ t_-}{z_+ z_- F^2}\right) + \frac{\nu_+ \nu_- D}{(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c_{\text{salt}})}\right]$$

$$= \frac{1}{\nu_+ z_+ F}\left(\frac{\kappa}{c_{\text{salt}}}\right)\left(\frac{\nu_+\lambda_+}{\Lambda_{\text{m}}}\frac{\nu_-\lambda_-}{\Lambda_{\text{m}}}\right) + \frac{\nu_- z_- F D}{c_{\text{salt}}(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c_{\text{salt}})}$$

$$= \frac{\nu_-}{z_+ F}\frac{\lambda_+\lambda_-}{\Lambda_{\text{m}}} + \frac{\nu_- z_- F D}{c_{\text{salt}}(\mathrm{d}\mu_{\text{salt}}/\mathrm{d}c_{\text{salt}})} \qquad (6.19.69)$$

Knowing the quantities appeared in Eqs (6.19.67)—(6.19.69), the values of u_{++}, u_{--} and u_{+-} may be evaluated.

Expressions in Terms of Equivalent Conductivity

In Eqs (6.19.67)—(6.19.69), the quantities λ_+ λ_- and Λ_{m} stand for molar conductivities of positive ion, negative ion and salt, respectively. These may be changed to the respective equivalent conductivity by using the following expressions.

$$\lambda_{\text{m}}^{(+)} = z_+ \lambda_{\text{eq}}^{(+)} \;;\; \lambda_{\text{m}}^{(-)} = |z_-|\lambda_{\text{eq}}^{(-)}$$

$$\Lambda_{\text{m}} = \nu_+ \lambda_{\text{m}}^{(+)} + \nu_- \lambda_{\text{m}}^{(-)} = \nu_+ z_+ \lambda_{\text{eq}}^{(+)} + \nu_- |z_-| \lambda_{\text{eq}}^{(-)}$$

$$= \nu_+ z_+ \left(\lambda_{\text{eq}}^{(+)} + \lambda_{\text{eq}}^{(-)}\right) = \nu_+ z_+ \Lambda_{\text{eq}}$$

$$t_+ = \frac{\nu_+ \lambda_{\text{m}}^{(+)}}{\Lambda_{\text{m}}} = \frac{\nu_+\left(z_+ \lambda_{\text{eq}}^{(+)}\right)}{\nu_+ z_+ \Lambda_{\text{eq}}} = \frac{\lambda_{\text{eq}}^{(+)}}{\Lambda_{\text{eq}}}$$

$$t_- = \frac{\nu_- \lambda_{\text{m}}^{(-)}}{\Lambda_{\text{m}}} = \frac{\nu_-\left(|z_-| \lambda_{\text{eq}}^{(-)}\right)}{\nu_+ z_+ \Lambda_{\text{eq}}} = \frac{\lambda_{\text{eq}}^{(-)}}{\Lambda_{\text{eq}}}$$

When these expressions are used in Eqs (6.19.67) – (6.19.69), we get

$$u_{++} = \left(\frac{\lambda_{\text{eq}}^{(+)}}{\Lambda_{\text{eq}} F}\right)^2 + \frac{\nu_+ z_+ F D}{c_{\text{salt}} (\mathrm{d}\mu_{\text{salt}} / \mathrm{d}c_{\text{salt}})} \qquad (6.19.70)$$

$$u_{--} = \left(\frac{\lambda_{\text{eq}}^{(-)}}{\Lambda_{\text{eq}} F}\right)^2 + \frac{\nu_+ z_+ F D}{c_{\text{salt}} (\mathrm{d}\mu_{\text{salt}} / \mathrm{d}c_{\text{salt}})} \qquad (6.19.71)$$

$$u_{+-} = \frac{\lambda_{\text{eq}}^{(+)} \lambda_{\text{eq}}^{(-)}}{\Lambda_{\text{eq}} F} + \frac{\nu_- z_- F D}{c_{\text{salt}} (\mathrm{d}\mu_{\text{salt}} / \mathrm{d}c_{\text{salt}})} \qquad (6.19.72)$$

REVISIONARY EXERCISES

6.1 Show that the criterion of an irreversible process in a system is $\Delta_i S > 0$, where $\Delta_i S$ is the entropy production in the system.

6.2 Show that the rate of production of entropy during the progress of a chemical reaction is given by

$$\frac{\mathrm{d_i}S}{\mathrm{d}t} = \frac{A}{T}\frac{\mathrm{d}\xi}{\mathrm{d}t}$$

where A $(= -\Sigma_B \nu_B \mu_B)$ is the affinity of the chemical reaction.

6.3 Considering $\mathrm{d_i}S > 0$ for irreversible processes, show that the criteria of irreversibility can be expressed by any one of the following expressions

$$\mathrm{d}U_{S,V} < 0, \quad \mathrm{d}H_{S,p} < 0, \quad \mathrm{d}A_{T,V} < 0 \quad \text{and} \quad \mathrm{d}G_{T,p} < 0$$

6.4 Show that the affinity of a reaction can be expressed by any one of the following expressions

$$A = -\left(\frac{\partial U}{\partial \xi}\right)_{S,V} = -\left(\frac{\partial H}{\partial \xi}\right)_{S,p} = -\left(\frac{\partial F}{\partial \xi}\right)_{T,V} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p}$$

where the symbol F stands for Helmholtz function.'

6.5 Show that the affinity A of a chemical reaction is given by

(a) $A = T\left(\frac{\partial S}{\partial \xi}\right)_{T,V} - \left(\frac{\partial U}{\partial \xi}\right)_{T,V}$ (b) $A = T\left(\frac{\partial S}{\partial \xi}\right)_{T,p} - \left(\frac{\partial H}{\partial \xi}\right)_{T,p}$

6.6 Mention the salient features of thermodynamic treatment of irreversible process.

6.7 Show that for an elemental cell of volume v in a system, the following expressions hold good.

$$u_v = T s_v - p + \Sigma_i c_i \tilde{\mu}_i$$

$$\mathrm{d}u_v = T\,\mathrm{d}s_v - \Sigma_i \tilde{\mu}_i \mathrm{d}c_i = 0$$

6.8 Show that for an open system, the expression

$$\mathrm{d}u_v = \mathrm{d}q_v' - \Sigma_i h_{i,\,\text{pm}} \mathrm{d}c_i = 0$$

where $\mathrm{d}q_v'$ is the heat transfer and $h_{i,\,\text{pm}}$ is the heat due to the transfer of ith species into/from the system.

6.9 Show that the rate of entropy production in a system involving irreversible process is given by

$$\sigma = J_q \cdot \text{grad}\left(\frac{1}{T}\right) + \sum_i J_i \cdot \text{grad}\left(-\frac{\tilde{\mu}_i}{T}\right) + \frac{\tilde{A}}{T} J_r$$

$$\sigma = \frac{J_s}{T} \cdot \text{grad}\,(-T) + \sum_i \frac{J_i}{T} \cdot \text{grad}\,(-\tilde{\mu}_i) + J_r \frac{\tilde{A}}{T}$$

where the various symbols have their usual units.

6.10 Derive the following expressions.

For electrical conduction in a wire : $T\sigma = \left[\frac{1}{A}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)\right]\left[-\frac{\partial \varphi}{\partial x}\right]_T$

For heat conduction in a bar : $T\sigma = \frac{1}{A}\left(\frac{\mathrm{d}q}{\mathrm{d}t}\right)\left(-\frac{1}{T^2}\frac{\partial T}{\partial x}\right)$

Show that these expressions can be written as

$T\sigma = J X$

Explain the terms J and X in this expression.

6.11 What is a coupling phenomenon? Explain with examples.

6.12 What are phenomenolgical equations? State the Onsager symmetry principle for the cross phenomenological coefficients.

6.13 State and explain Curie-Prigogine principle as applicable to phenomenological equations.

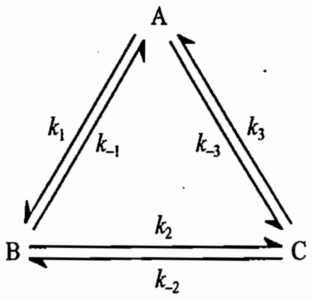
6.14 Show that the phenomenological coefficients satisfies the expressions:

$$L_{ii} > 0$$

$$\begin{vmatrix} L_{11} & L_{12} & \cdots & L_{1n} \\ L_{21} & L_{22} & \cdots & L_{2n} \\ \vdots & & & \\ L_{n1} & L_{n2} & \cdots & L_{nn} \end{vmatrix} \geq 0$$

6.15 For a reaction $0 = \Sigma_B \nu_B B$ near the equilibrium position, $L = r_{f,\,eq}/R$ and $\sigma = r^2/L$, where r is the rate of reaction and L is the phenomenological coefficient defining the expression $J_r = L\,X_r$ where $J_r = r$ and $X_r = A/T$.

6.16 For the reations



near to equilibrium, show that

$$L_{11} = (k_1\,[\mathrm{A}]_{eq} + k_3\,[\mathrm{C}]_{eq})/R$$

$$L_{21} = L_{12} = k_3\,[\mathrm{C}]_{\mathrm{eq}}\,/R$$
$$L_{22} = (k_2\,[\mathrm{B}]_{\mathrm{eq}} + k_3\,[\mathrm{C}]_{\mathrm{eq}})/R$$

6.17 (a) Describe the phenomenon of electro-osmosis. Show that the entropy production in this case may be expressed as

$$T\,\sigma = J_{\mathrm{m}} X_{\mathrm{m}} + I\,X_I$$

What are the expressions of J_{m}, X_{m} and X_I?

(b) Derive the expressions of the following physical quantities applicable to electro-osmosis in terms of phenomenological coefficients,
(i) Streaming potential, (ii) Streaming current, (iii) Electro-osmotic pressure, (iv) Electro-osmosis effect and (v) Saxen's relations.

6.18 (a) Describe the phenomenon of thermoelectricity highlighting (i) Seebeck effect and (ii) Peltier effect.

(b) How are the Seebeck effect and Peltier effect explained on the basis of theory of irreversible proceses?

(c) Define the terms (i) heat of transfer and relative thermoelectric power involved in the phenomenon of thermoelectricity.

(d) What is Thomson effect? Derive first and second equations of Thomson applicable to a thermocouple.

6.19 (a) Show that the entropy production in isothermal diffusion in a continuous system is given by the expression

$$T\,\sigma = \sum_{j=2}^{n} J_j Y_j$$

where $$Y_j = \sum_{i=2}^{n}\left(\delta_{ij} + \frac{V_j c_i}{V_1 c_1}\right)\mathrm{grad}\left(-\mu_i^{(\mathrm{c})}\right)$$

where V's stand for partial molar volumes. The subscript 1 stands for the solvent and subscripts 2, 3,..., stand for the solutes.

(b) Show that in a binary solution, the diffusion coefficient of solute is given by

$$D' = \frac{L_2 RT}{c_2}$$

(c) Show that in a ternary solution, the diffusion constants D_{23} is not equal to D_{32}, even though $L_{23} = L_{32}$.

6.20 On the basis of theory of irreversible processes, show that

$$J_2 = -D\,\frac{\mathrm{d}c_2}{\mathrm{d}r} + L_2\,M_2\,(1 - \rho\,v_2)\,\omega^2 r$$

for the isothemal ultracentrifuge sedimentation in a binary solution. How is this equation used for the determination of molar mass of the solute?

6.21. (a) For the two compartments containing the same gas and connected through a small orifice (or a rigid membrane), the transfer of heat (dq) and gas (dn) from the compartment T and p to $T + \Delta T$ and $p + \Delta p$ is associated with the entropy production given by the expression

$$\sigma = \left(\frac{\mathrm{d}U}{\mathrm{d}t}\right)\left(-\frac{\Delta T}{T^2}\right) + \left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)\left(-\frac{V_{\mathrm{m}}\,\Delta p}{T} + H_{\mathrm{m}}\,\frac{\Delta T}{T^2}\right)$$

By setting the phenomenological equations, derive the expressions of

(i) $(J_U/J_{\mathrm{m}})_{\Delta T=0}$ (ii) $(\Delta p/\Delta T)_{J_{\mathrm{m}}=0}$

(b) Show that the entropy production given in part (a) may be expressed as

$$\sigma = \left(\frac{\mathrm{d}q}{\mathrm{d}t}\right)\left(-\frac{\Delta T}{T^2}\right)+\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)\left(-\frac{V_{\mathrm{m}}\,\Delta p}{T}\right)$$

By setting the phenomenological equations, derive the expressions of

(i) $q^* = (J_q/J_{\mathrm{m}})_{\Delta T=0}$ (ii) $(\Delta p/\Delta T)_{J_{\mathrm{m}}=0}$

Also show that

$$(J_q/J_{\mathrm{m}})_{\Delta T=0} = -V_{\mathrm{m}}\,T\,(\Delta p/\Delta T)_{J_{\mathrm{m}}=0}$$

$$(J_q/J_{\mathrm{m}})_{\Delta p=0} = -V_{\mathrm{m}}\,T\,(\Delta p/\Delta T)_{J_q=0}$$

(c) Describe Knudsen effect. Show that

$$H^* - \mathrm{KE} = (1/2)\,RT$$

where H^* is the energy transferred due to the mirgation of 1 mol of the gas from the compartment at T to the compartment $T + \Delta T$.

6.22 (a) What is Soret effect. Show that the Soret coefficient is given by

$$s = \frac{L_{2q'}/Tc}{D}$$

where $L_{2q'}$ is cross phenomenological coefficient that represents interaction between the solute flow and the heat flow in a thermal diffusion in a continuous system.

(b) Show that in a thermal diffusion in a continous system, heat of transfer is given by

$$q^* = \left(\frac{J_{q'}}{J_2}\right)_{\mathrm{grad}\,T=0} = \frac{L_{q'2}}{L_{22}}$$

and it is related to the soret coefficient by the expression

$$q^* = s\,RT^2$$

6.23 (a) Show that the entropy production in the transport process in a solution involving a single electrolyte is given by

$$T\,\sigma = J_+^{(\mathrm{d})}\,\mathrm{grad}\,(-\tilde{\mu}_+) + J_-^{(\mathrm{d})}\,\mathrm{grad}\,(-\tilde{\mu}_-)$$

Set up the phenomenologival equations for the above expression and show that

(i) $\kappa = \left[z_+^2 L_{++} + 2z_+z_-L_{+-} + z_-^2 L_{--}\right]F^2$

(ii) $t_+ = \dfrac{z_+\left[L_{++}\,z_+ + L_{+-}z_-\right]}{z_+^2 L_{++} + 2z_+z_-L_{+-} + z_-^2 L_{--}}$

(iii) $D = -\dfrac{z_+z_-}{\nu_+\nu_-}\left[\dfrac{L_{++}L_{--} - L_{+-}^2}{z_+^2 L_{++} + 2z_+z_-L_{+-} + z_-^2 L_{--}}\right]\left(\dfrac{\partial\mu_{\mathrm{salt}}}{\mathrm{d}t}\right)$

(b) Express L_{++}, L_{--} in terms of κ, t_+, t_-, D, and $\mathrm{d}\mu_{\mathrm{salt}}/\mathrm{d}c$.

(c) Define reduced phenomenological mobilities and show that

$$u_{++} = \frac{z_+^2 L_{++} F}{\nu_+ z_+ c_{\text{salt}}}, \quad u_{--} = \frac{z_-^2 L_{--} F}{\nu_+ z_+ c_{\text{salt}}} \quad \text{and} \quad u_{++} = \frac{z_+ z_- L_{+-} F}{\nu_+ z_+ c_{\text{salt}}}$$

(d) Show that

$$\Lambda_{\text{m}} = \frac{F^2}{c_{\text{salt}}}\left(z_+^2 L_{++} + 2 z_+ z_- L_{+-} + z_-^2 L_{--}\right)$$

(e) Express t_+, t_-, and D in terms of redueced ionic mobilities. How are the reduced mobilities determined experimentally?

ANNEXURE I Basic Concepts Involved in the Treatment of Irreversible Processes

In this appendix, we describe a few concepts which are involved while treating with irreversible processes.

Gradient of a Scalar Function

For a scalar function $f(x, y, z)$, the gradient is defined as

$$\begin{aligned} \text{grad } f &= \frac{\partial f}{\partial x}\boldsymbol{i} + \frac{\partial f}{\partial y}\boldsymbol{j} + \frac{\partial f}{\partial z}\boldsymbol{k} \\ &= \nabla f \end{aligned} \tag{AI.1}$$

where ∇, a differential operator known as nabla or del, is

$$\nabla = \frac{\partial}{\partial x}\boldsymbol{i} + \frac{\partial}{\partial y}\boldsymbol{j} + \frac{\partial}{\partial z}\boldsymbol{k} \tag{AI.2}$$

For a scalar function f that is defined and differentiable in a domain D in space, the gradient of f at P on a level surface S of f in the domain D is perpendicular to S at P, provided it is a nonzero vector. Its direction coincides with the maximum increase in the value of f at P.

Divergence of a Vector Field

For a differentiable vector function $V(x, y, z)$, where x, y and z are the Cartesian coordinates, the divergence of V is defined as

$$\text{div } V = \frac{\partial v_1}{\partial x} + \frac{\partial v_2}{\partial y} + \frac{\partial v_3}{\partial_z} \tag{AI.3}$$

where v_1, v_2 and v_3 are the components of V alogn x, y, and z directions, respectively. The divergence of V can also be expressed as

$$\begin{aligned} \nabla \cdot V &= \left(\frac{\partial}{\partial x}\boldsymbol{i} + \frac{\partial}{\partial y}\boldsymbol{j} + \frac{\partial}{\partial z}\boldsymbol{k}\right) \cdot (v_1\boldsymbol{i} + v_2\boldsymbol{j} + v_3\boldsymbol{k}) \\ &= \frac{\partial v_1}{\partial x} + \frac{\partial v_2}{\partial y} + \frac{\partial v_3}{\partial z} \end{aligned} \tag{AI.4}$$

The Divergence Theorem

The divergence theorem, also known as Gauss's theorem, may be stated as follows. For a simple solid region D whose boundary S is oriented by the normal $\boldsymbol{n}$ directed outward from D, the vector field $\boldsymbol{F}$ whose component functions have continuous derivative on D satisfies the expression

$$\iint_{S} \boldsymbol{F} \cdot \boldsymbol{n} \, dS = \iiint_{D} \text{div } \boldsymbol{F} \, dV \tag{AI.5}$$

The divergence theorem helps evaluating a volume integral by replacing it by the surface integral and vice versa.

Explanation of Divergence of a Vector Field

By means of the Divergence theorem, it is possible to explain the divergence of a vector field in terms of fluid motion. Suppose (x_0, y_0, z_0) is a fixed point in space and D is a small volume element centred at (x_0, y_0, z_0) with boundary S and volume V. Let a fluid of density ρ flow through the space D and let $V(x_0, y_0, z_0)$ be the velocity of fluid particles at (x_0, y_0, z_0). Consider a small surface dS of S and let $\boldsymbol{n}$ be the outward normal vector to this area. The fluid will scan a volume $V(x, y, z) \cdot \boldsymbol{n}\, dS$ in a unit time. Multiplying this quantity with density ρ of fluid gives the mass of fluid flown in a unit time across the surface dS. The mass of fluid flowing outward through the entire area S is given by $\iint_S \rho\,(V \bullet \boldsymbol{n})\, dS$ and according to the Divergence theorem, we can write

$$\iint_S \rho(V \bullet \boldsymbol{n})\mathrm{d}S = \iiint_D \mathrm{div}\,(\rho V)\,\mathrm{d}V$$

If D is small, the integral on the right side of the above expression may be approximated as $[\mathrm{div}\,(\rho V(x_0, y_0, z_0))]V$. Hence

$$\iint_S \rho\,(V \bullet \boldsymbol{n})\,\mathrm{d}S = [\mathrm{div}\,(\rho V(x_0, y_0, z_0))]V$$

that is, $\mathrm{div}\,(\rho V(x_0, y_0, z_0))$ may be interpreted as the rate of mass flown per unit volume at (x_0, y_0, z_0) in the direction of outward normal. Hence, the name divergence of V at a point.

Two type of time-rate of change of a function may be identified in a physical system.

Local Time-Rate of Change of a Point Function

In a system, such as fluid in motion, there exists several point functions such as pressure, density and velocity. These point functions also depend upon time. In local time-rate of change of a point function, a point in the system is fixed and the change in the value of the function at this point within the time interval t and $t + \delta t$ is determined. Let the change be represented as $\Phi(x, y, z, t + \delta t) - \Phi(x, y, z, t)$. The limit

$$\lim_{\delta t \to 0} \frac{\Phi(x, y, z, t + \delta t) - \Phi(x, y, z, t)}{\delta t}$$

is known as the local time-rate of change of the function Φ. By convention, this change is represented as $\partial\Phi/\partial t$.

Total Time-Rate of Change of a Function

In total (also knowns as individual or substantial) time-rate of change of a function, focus is made on a particle and the change in the function Φ of the same particle is determined within the time interval t and $t + \delta t$. Let this change be represented as $\Phi(x + \delta x, y + \delta y, z + \delta z, t + \mathrm{d}t) - \Phi(x, y, z, t)$. The limit

$$\lim_{\delta t \to 0} \frac{\Phi(x + \delta x, y + \delta y, z + \delta z, t + \delta t) - \Phi(x, y, z, t)}{\delta t}$$

is known as the total time-rate of change of the function Φ. By convention, this change is represented as $\mathrm{d}\Phi/\mathrm{d}t$.

Relationship Between Local and Total Time-Rates

For a function $\Phi(x, y, z, t)$, we have

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)\left(\frac{\partial\Phi}{\partial x}\right) + \left(\frac{\mathrm{d}y}{\mathrm{d}t}\right)\left(\frac{\partial\Phi}{\partial y}\right) + \left(\frac{\mathrm{d}z}{\mathrm{d}t}\right)\left(\frac{\partial\Phi}{\partial z}\right) + \frac{\partial\Phi}{\partial t}$$

where $\mathrm{d}\Phi/\mathrm{d}t$ is the total derivative of Φ with respect to t, allowing for the variations in x, y and z as a result of change in time t, and $\partial\Phi/\partial x$, $\partial\Phi/\partial y$, $\partial\Phi/\partial z$, and $\partial\Phi/\partial t$

are the partial derivatives of Φ with respect to x, y, z and t, respectively. Equation (AI.10) may be written as

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = v_1\left(\frac{\partial \Phi}{\partial x}\right) + v_2\left(\frac{\partial \Phi}{\partial y}\right) + v_3\left(\frac{\partial \Phi}{\partial z}\right) + \left(\frac{\partial \Phi}{\partial t}\right)$$

$$= (\boldsymbol{V} \bullet \nabla)\Phi + \frac{\partial \Phi}{\partial t} \qquad \text{(AI.6)}$$

where $\boldsymbol{V}$ is the velocity of the particle and v_1 v_2 and v_3 are its components along x–, y– and z– axes, respectively. In the vector form

$$\boldsymbol{V} = v_1\,\boldsymbol{i} + v_2\boldsymbol{j} + v_3\boldsymbol{k}$$

where $v_1 = \mathrm{d}x/\mathrm{d}t$, $v_2 = \mathrm{d}y/\mathrm{d}t$ and $v_3 = \mathrm{d}z/\mathrm{d}t$.

Concept of Local Equilibrium

While dealing with a system undergoing reversible processes, the values of variables such as T, p, etc. have the same value throughout the system and thus one can express the changes in thermodynamic properties such as energy, enthalpy, entropy, etc. of the system in terms of independent variables. The same is also true regarding the thermodynamic properties of a system existing at equilibrium. However, this is not possible for a system undergoing irreversible processes because thermodynamic variables such as T, p, etc. may vary from point to point within the system. However such a system can be treated on the basis of local equilibrium in which the system is considered as an ensemble of large number of elemental cells of volume ΔV, each in equilibrium, exchanging energy and matter with neighbouring cells. The size of elemental cell is large enough to have a well defined temperature, density, etc., ignoring the influence of fluctuations on these variables and also describe the spatial variations of thermodynamic quantities. In local equilibrium, all thermodynamic intensive variables such as T and p are treated to be dependent on position x and time t, i.e. $T = f(x, t)$; $p = f(x, t)$.

The extensive variables are replaced by their densities (represented by the lower case symbols) which are also function of position x and time t, i.e., $u(x, t)$, $h(x, t)$, $s(x, t)$ and so on.

The total value of extensive variable, say entropy, is obtained by the expression

$$S = \int_V s(x,t)\mathrm{d}V \qquad \text{(AI.7)}$$

Equation of Continuity of Mass

Consider a fixed closed surface within a region of a moving fluid. Consider an elemental volume $\mathrm{d}V$ around a fixed point within the closed surface. Let ρ be the local density of the fluid at the chosen point. The mass of fluid within the closed surface at time t is given by

$$m = \int_V \rho\,\mathrm{d}V \qquad \text{(AI.8)}$$

where the integration is over the volume enclosed by the fixed surface. The time-rate of change of mass is

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{\partial}{\partial t}\left(\int_V \rho\,\mathrm{d}V\right) = \int_V \left(\frac{\partial \rho}{\partial t}\right)\mathrm{d}V \qquad \text{(AI.9)}$$

where $\partial\rho/\partial t$ is the time-rate of change of local density.

Consider now any element dS of the fixed surface and $\boldsymbol{n}$ be the unit vector drawn outwardly, normal to the surface dS at the point P. At time t, let V be the velocity of the fluid particles at the point P. The resolved part of the velocity V along the outward-drawn normal at P is $V\cdot \boldsymbol{n}$. and that along the inward normal at P is $-V\cdot\boldsymbol{n}$.

The mass of fluid entering per unit time across the area dS is

$$\frac{\mathrm{d}m'}{\mathrm{d}t}=-\rho(V\bullet\boldsymbol{n})\,\mathrm{d}S$$

The mass of fluid entering per unit time across the entire surface is

$$\frac{\mathrm{d}m}{\mathrm{d}t}=-\int_{\mathrm{S}}\rho(V\bullet\boldsymbol{n})\mathrm{d}S$$

According to the Divergence theorem

$$\int_{\mathrm{S}}\rho(V\bullet\boldsymbol{n})\,\mathrm{d}S=\int_V \mathrm{div}\,(\rho V)\mathrm{d}V$$

Hence, $\dfrac{\mathrm{d}m}{\mathrm{d}t}=-\int_V \mathrm{div}\,(\rho V)\mathrm{d}V$ (AI.10)

From Eqs (AI.9) and (AI.10), we get

$$\int_V\frac{\partial\rho}{\partial t}\,\mathrm{d}V=-\int_V \mathrm{div}\,(\rho V)\mathrm{d}V$$

or $$\int_V\left[\frac{\partial\rho}{\partial t}+\mathrm{div}(\rho V)\right]\mathrm{d}V=0$$

Since the surface is arbitrary, we must have

$$\frac{\partial\rho}{\partial t}+\mathrm{div}(\rho V)=0 \qquad \text{(AI.11)}$$

Equation (AI.11) is the required expression of continuity of mass which applies at any point (x, y, z) and at any time t. This equation is, in fact, the local equivalent of law of conservation of mass.

The vector ρV has the unit of

$$\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\left(\frac{\mathrm{m}}{\mathrm{s}}\right)=\mathrm{kg\,m^{-2}\,s^{-1}}$$

Thus, this vector represents the flow of mass through a unit area of the surface in a unit time. It is represented by the symbol $\boldsymbol{J}_m$ and is known as mass-flux density vector. In terms of the symbol $\boldsymbol{J}_m$, Eq. (AI.11) becomes

$$\frac{\partial \rho}{\partial t} + \operatorname{div} J_m = 0 \tag{AI.12}$$†

Comment on Eq. AI.12)

The divergence of J_m gives the flow of mass per unit volume in a unit time. A positive value of J_m implies the net outward flow of mass. This results in the negative value of $\partial\rho/\mathrm{d}t$ (i.e. a decrease in the value of local density per unit time) so that the sum of div J_m and $\partial\rho/\partial t$ is zero which is in agreement with the law of conservation of mass. On the other hand, a negative value of J_m implies the net inward flow of mass which causes an increase in the value of local density of the substance in the enclosed surface.

Equation of Continuity of Concentration

In terms of amount of substance, Eq. (AI.8) takes the form

$$n_i = \int_V c_i \,\mathrm{d}V$$

Hence $\dfrac{\mathrm{d}n_i}{\partial t} = \displaystyle\int_V \left(\frac{\partial c_i}{\partial t}\right) \mathrm{d}V$

The inward flow through a closed surface is

$$\frac{\mathrm{d}n_i}{\partial t} = -\int_S c_i \,(\boldsymbol{V} \bullet \boldsymbol{n})\,\mathrm{d}S$$

$$= -\int_V \operatorname{div}(c_i V)\,\mathrm{d}V \qquad \text{(Divergence theorem)}$$

Hence $\displaystyle\int_V \left(\frac{\partial c_i}{\partial t}\right)\mathrm{d}V = -\int_V \operatorname{div}(c_i V)\,\mathrm{d}V$

or $\displaystyle\int_V \left[\left(\frac{\partial c_i}{\partial t}\right) + \operatorname{div}(c_i V)\right]\mathrm{d}V = 0$

Hence $$\frac{\partial c_i}{\partial t} + \operatorname{div}(c_i V) = 0 \tag{AI.13a}$$

or $$\frac{\partial c_i}{\partial t} + \operatorname{div} J_i = 0 \tag{AI.13b}$$

where J_i represents the flow of amout of *i*th species through a unit area of the surface in a unit time.

Equation of Continuity of Energy

For any physical quantity, which obey the law of conservation, the equation of continuity can be written. For example, the total energy is conserved both locally and for the system as a whole as per the first law of thermodynamics. If ρ_u is the local energy density at a point, then the equation of continuity is

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† If the flowing fluid contains more than one constituent, the continuity equation holds good for each constituent leading to the expression

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div} J_i = 0$$

$$\frac{\partial \rho_u}{\partial t} + \text{div}\,(\rho_u V) = 0 \quad \text{i.e.} \quad \frac{\partial \rho_u}{\partial t} + \text{div}\, J_u = 0 \qquad \text{(AI.14)}$$

where J_u (= $\rho_u V$) is the energy flux density.

Equation of Continuty of Entropy

The total entropy of the system enclosed in the closed surface of volume V is

$$S = \int_V s_\upsilon \, \mathrm{d}V \qquad (s_\upsilon \text{ is the local entropy density})$$

Thus $$\frac{\mathrm{d}S}{\mathrm{d}t} = \int_V \left(\frac{\partial s_\upsilon}{\partial t} \right) \mathrm{d}V \qquad \text{(AI.15)}$$

The entropy entering per unit time across the entire surface of the system is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\int_S s_\upsilon \, (\boldsymbol{V} \bullet \boldsymbol{n}) \, \mathrm{d}S = -\int_S \boldsymbol{J}_s \bullet \boldsymbol{n} \, \mathrm{d}S \qquad \text{(AI.16)}$$

where J_s, the entropy flux vector, is $s_i V$. This vector coincides with the direction of entropy flow and has a magnitude equal to the entropy crossing per unit area perpendicular to the direction of flow in a unit time. As per the divergence theorem, Eq. (AI.16) becomes

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\int_V \text{div}\, J_s \, \mathrm{d}V \qquad \text{(AI.17)}$$

Equating Eqs (AI.15) and (AI.17), we get the equation of continuity of entropy.

$$\frac{\partial s_\upsilon}{\partial t} + \text{div}\, J_s = 0 \qquad \text{(AI. 18)}$$

Equation of Continuity for a Nonconservative system

A nonconservative system besides involving transportation of a substance (or a thermodynamic property) also involves the production or consumption of the substance (or a thermodynamic property). The production of a substance may be due to a chemical reaction occurring in the system and that of entropy may be due to some irreversible process occurring in the system.

System Involving a Chemical Reaction The consumption or generation of a substance in a chemical reaction is given by

$$r = \frac{1}{\nu_i} \frac{\mathrm{d}n_i}{\mathrm{d}t}$$

where ν_i is the stoichiometric number of ith substance in a balanced chemical equation. It has a negative value for a reactant and a positive value for a product of the chemical reaction. At constant volume, we have

$$\frac{\mathrm{d}\,(n_i/V)}{\mathrm{d}t} = \nu_i \frac{r}{V} \quad \text{or} \quad \frac{\mathrm{d}c_i}{\mathrm{d}t} = \nu_i J_r$$

With this, the equation of continuity (Eq. AI.13) becomes

$$\frac{\partial c_i}{\partial t} = -\text{div}\,(c_i\, V_i) + v_i J_r \tag{AI.19}$$

Equation (AI.19) is the local balance of amount of *i*th substance with a flux term and a source term.

Local Balance of Entropy If a system besides transportation of entropy also involves production of entropy due to some irreversible process occurring in the system, the equation of continuity as given by Eq. (AI.18) is modified to

$$\frac{\partial s_v}{\partial t} = -\text{div}\, J_s + \sigma \tag{AI.20}$$

where σ is the local entropy production per unit volume of the system in a unit time. Equation (AI.20) is the local balance of entropy with a flux term and a source term. For the entire system, we have

$$\int_V \frac{\partial s_v}{\partial t}\, \mathrm{d}V = -\int_V \text{div}\, J_s\, \mathrm{d}V + \int_V \sigma\, \mathrm{d}V \tag{AI.21}$$

In the above expression, we have

- The left side gives the overall rate of change of entropy of the system. It is represented by $\mathrm{d}S/\mathrm{d}t$.
- The first term on the right side gives the rate of transportation of entropy from/to the system. It is represented as $\mathrm{d_e}S/\mathrm{d}t$, where the subscript e to d stands for the "external" contribution.
- The second term on the right side gives the rate of production of entropy within the system. It is represented as $\mathrm{d_i}S/\mathrm{d}t$, where the subscript i to d stands for "internal" contribution.

With these, Eq. (AI.21) is often written as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d_e}S}{\mathrm{d}t} + \frac{\mathrm{d_i}S}{\mathrm{d}t} \tag{AI.22}$$

(Note: For a system involving reversible process, $\mathrm{d_i}S/\mathrm{d}t = 0$ while for an irreversible process, $\mathrm{d_i}S/\mathrm{d}t > 0$.)

Equation (AI.22) implies that

$$\mathrm{d}S = \mathrm{d_e}S + \mathrm{d_i}S \tag{AI.23}$$

Thermodynamic Force and Fluxes

A conservative force is equal to negative of change in potential energy and is given as

$$F = -\left(\frac{\partial U}{\partial x} i + \frac{\partial U}{\partial y} j + \frac{\partial U}{\partial z} k\right)$$

$$= -\,\text{grad}\; U \tag{AI.24}$$

A driving force occurs whenever there exists a difference in potential energy and its direction is the direction of maximum decrease in potential energy. In thermodynamic, the flow of a substance is due to the driving force governed by the difference in its chemical potential. This force is given by

$$X_i = -\text{grad}\,\mu_i \tag{AI.25}$$

Considering μ_i to be dependent on a single coordinate, say x-direction, we can write

$$X_i = -\boldsymbol{i}\frac{\partial \mu_i}{\partial x} \tag{AI.26}$$

Since $\mu_i = \partial G/\partial n_i$, we will have

$$X_i = -\boldsymbol{i}\frac{\partial}{\partial x}\left(\frac{\partial G}{\partial n_i}\right) \equiv -\boldsymbol{i}\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial x}\right) \tag{AI.27}$$

For a reversible process, $dG = dw_{\text{net}}$, where w_{net} stands for nonmechanical work. Also, the differential of work with distance represents force, we can write Eq. (AI.27) as

$$X_\text{i} = -\boldsymbol{i}\frac{\partial f}{\partial n_i} \tag{AI.28}$$

that is, the thermodynamic force X_i represents the force per unit amount of *i*th substance operating in the direction of unit vector $\boldsymbol{i}$ (which is the direction of greatest change in the chemical potential). The negative sign indicates that the force acts in the direction of maximum decrease in the chemical potential.

Forces and Fluxes in Theory of Irreversible Processes

The other examples of forces in the thermodynamic of irreversible processes are (i) a temperature gradient, (ii) a concentration gradient, (iii) a potential gradient and (iv) a chemical affinity. Theses forces are represented by the symbol X_i. These forces cause irreversible process of flow of heat, diffusion, electric current and chemical reaction, respectively. These are known as fluxes or flows and are represented by the symbol J_i.

ANNEXURE II Statistical Treatment of Fluctuation and Derivation of Onsager Symmetry Rule

Smoluchowski Method

Expression of Probability

The fluctuating number n of noninteracting particles in a volume element υ of a large volume V of a solution containing N particles may be determined by the method developed by Smoluchowski. The probability p of finding any particle in volume υ is

$$p = \frac{\upsilon}{V} \tag{AII.1}$$

Probability of finding the particle in the rest of the volume is

$$1 - p = 1 - \frac{\upsilon}{V} = \frac{V - \upsilon}{V} \tag{AII.2}$$

Probability of finding n particles in υ and $N - n$ particles in $V - \upsilon$ will be proportional to $p^n\,(1 - p)^{N-n}$

The number of ways of selecting n indistinguishable particles out of N particles is given by

$$^{n}C_N = \frac{N!}{n!(N-n)!} \tag{AII.3}$$

Hence, the total probability of finding n particles in the volume υ is

$$P_n = {}^{n}C_N p^n (1 - p)^{N-n} \tag{AII.4}$$

For a large value of N, Poisson has shown that the above probability takes the simple form

$$P_n = \frac{\nu^n\,\mathrm{e}^{-\nu}}{n!} \tag{AII.5}$$

where ν is the average value of n satisfying the relation

$$\frac{\nu}{\upsilon} = \frac{N}{V} \tag{AII.6}$$

Equation (AII.5) is the normalied expression satisfying the condition that the sum of all probabilities of finding any number of particles in υ is unity, that is

$$\sum_{n=0}^{\infty} P_n = \sum_{n=0}^{\infty} \frac{\nu^n\,\mathrm{e}^{-\nu}}{n!} = \mathrm{e}^{-\nu} \sum_{n=0}^{\infty} \frac{\nu^n}{n!} = \mathrm{e}^{-\nu}\,\mathrm{e}^{\nu} = 1 \tag{AII.7}$$

Proof ν being an Average Value of n

The average value of n is given by

$$\bar{n} = \sum_{n=0}^{\infty} n\,P_n \tag{AII.8}$$

$$= \sum_{n=0}^{\infty} n \left(\frac{\nu^n\,\mathrm{e}^{-\nu}}{n!} \right) = \mathrm{e}^{-\nu} \left[0 + \sum_{n=1}^{\infty} \frac{n\,\nu^n}{n!} \right]$$

$$= \mathrm{e}^{-\nu} \nu \sum_{n=1}^{\infty} \frac{\nu^{n-1}}{(n-1)!} = \mathrm{e}^{-\nu}\,\nu\left(\mathrm{e}^{\nu}\right) = \nu \tag{AII.9}$$

Average Fluctuation of the Value of *n*

The fluctuation in the number of particles in the volume v is defined as

$$f = n - \nu \qquad \text{(AII.10)}$$

The average value of fluctuation is

$$\bar{f} = \overline{n - \nu} = \sum_{n=0}^{\infty} (n-\nu)P_n$$

$$= \sum_{n=0}^{\infty} n\,P_n - \nu \sum_{n=0}^{\infty} P_n = \nu - \nu(1) = 0 \qquad \text{(AII.11)}$$

The average value of f equal to zero follows from the fact that the probabilities of positive and negative deviations will have identical values and thus their sum will be equal to zero.

Root Mean Square Average Value of Fluctuation

Since the average value of fluctuation is zero, the fluctuation in number is measured by the root mean square value of fluctuation, defined as

$$f_{\text{rms}} = \sqrt{\overline{(n-\nu)^2}} \qquad \text{(AII.12)}$$

The value of f_{rms} may be derived as follows.

$$\overline{(n-\nu)^2} = \overline{n^2} + \nu^2 - 2\bar{n}\nu$$

Now $$\overline{n^2} = \sum_{n=0}^{\infty} n^2\,P_n = \sum_{n=0}^{\infty} [(n(n-1) + n]P_n$$

$$= \sum_{n=0}^{\infty} n(n-1)\,P_n + \sum_{n=0}^{\infty} n\,P_n$$

$$= \sum_{n=0}^{\infty} n(n-1)\frac{\nu^n\,\mathrm{e}^{-\nu}}{n!} + \nu = \sum_{n=2}^{\infty} \frac{\nu^n\,\mathrm{e}^{-\nu}}{(n-2)!} + \nu$$

$$= \nu^2\,\mathrm{e}^{-\nu}\left(\sum_{n=2}^{\infty}\frac{\nu^{n-2}}{(n-2)!}\right) + \nu = \nu^2\,\mathrm{e}^{-\nu}\left(\mathrm{e}^{\nu}\right) + \nu$$

$$= \nu^2 + \nu$$

Also $\bar{n} = \nu$ (Eq. AII.9)

Hence $$\sqrt{\overline{(n-\nu)^2}} = \left[\left(\nu^2+\nu\right) + \nu^2 - 2(\nu)(\nu)\right]^{1/2} = \sqrt{\nu} \qquad \text{(AII.13)}$$

Relative Fluctuation in Number

In studing the fluctuation, the relative fluctuation plays more dominating role. This is defined as

$$f_{\text{r}} = \frac{\sqrt{\overline{(n-\nu)^2}}}{\nu} = \frac{\sqrt{\nu}}{\nu} = \frac{1}{\sqrt{\nu}} \qquad \text{(AII.14)}$$

The relative fluctuation decreases with increase in the square root of the average number of particle in the volume v.

Comment on Smoluchowski Method

The above analysis of fluctuation holds good for noninteracting independent particles. This treatment is not valid for interacting particles. While dealing with thermodynamic of irreversible processes, a statistics based on the interacting particle is required. Einstein's probability treatment provides such a method.

Einstein's Probability Treatment

Expression of Probability

Einstein's probability treatment is based on the entropy of the system. The Boltymann expression relating entropy with the number of configurations in which a system may be realized is given by

$$S = k_B \ln W \tag{AII.15}$$

where k_B is the Boltzmann constant. For a system at equilibrium, we write

$$S_0 = k_B \ln W_0 \tag{AII.16}$$

Fluctuation in the Entropy of a System

The fluctuation in the entropy of a system from its equilibrium value due to the parameter

$$\alpha_i = \xi_i - \xi_i^0 \tag{AII.17}$$

is given by the expression

$$\begin{aligned} \Delta S = S - S_0 &= k_B \ln \frac{W}{W_0} \\ &= k_B \ln \wp \end{aligned} \tag{AII.18}$$

In Eq. (AII.17), ξ_i and ξ_i^0 are the physical quantities (say, T, U, H, c) describing the given system and that at equilibrium, respectively.

Einstein Probability Expression

The symbol $\wp$ in Eq. (AII.18) represents probability of finding the system at a given state of fluctuation. Equation (AII.18) may be written as

$$\wp = K \exp(\Delta S/k_B) \tag{AII.19}$$

where K the normalizing factor satisfying the expression

$$\int \ldots \int \wp \, d\alpha_1, d\alpha_2 \ldots d\alpha_n = 1 \tag{AII.20}$$

that is, the total probability of finding the system in any state of fluctuation described by any physical quantity is unity.

For any fluctuation from the equilibrium position, the value of $\Delta S = S - S_0$) is negative because the system has a maximum value of entropy at equilibrium position and thus $S < S_0$.).

For the small fluctuation from the equilibrium position, one can express the entropy of the system in terms of entropy at the equilibrium position by using the Taylor's series:

$$S = S_0 + \sum_{i=1}^{n} \left(\frac{\partial S}{\partial \xi_i} \right) (\xi_i - \xi_i^0) + \frac{1}{2} \sum_{i,j=1}^{n} \left(\frac{\partial^2 S}{\partial \xi_i \, \partial \xi_j} \right) (\xi_i - \xi_i^0)(\xi_j - \xi_j^0) + \cdots$$

where the partial derivatives are evaluated at equilibrium position. Since S_0 has a maximum value at equilibrium, the first derivative $(\partial S/\partial \xi_i)_0$ will have a zero value.

Hence,

$$\Delta S = S - S_0 = \frac{1}{2}\sum_{i,j=1}^{n}\left(\frac{\partial^2 S}{\partial \xi_i \partial \xi_j}\right)_0 (\xi_i - \xi_i^0)(\xi_j - \xi_j^0)$$

$$= -\frac{1}{2}\sum_{i,j=1}^{n} g_{ij}\alpha_i\,\alpha_j \tag{AII.21}$$

where $g_{ij} = \left(\partial^2 S/\partial\xi_i\partial\xi_j\right)_0$ (AII.22)

Substitution of Eq. (AII.21) in Eq. (AII.19) gives

$$\wp = K\exp\left(-\sum_{i,j=1}^{n} g_{ij}\,\alpha_i\,\alpha_j\,/2k_B\right) \tag{AII.23}$$

Equation (AII.23) is the Einstein probability expression.

Average Value of Fluctuation of a Single Physical Quantity

For the fluctuation $\alpha = \xi - \xi^0$ of a single physical quantity, the expression of probability $\wp$ is

$$\wp = K\exp(-g\alpha^2/2k_B) \qquad \text{(Eq. AII.19)}$$

The average value of the fluctuation is

$$\bar{\alpha} = \int_{-\infty}^{+\infty} \alpha\,\wp\,d\alpha = K\int_{-\infty}^{+\infty}\exp\left(-g\alpha^2/2k_B\right)\alpha\,d\alpha \tag{AII.24}$$

Since the integrand in Eq. (AII.24) is an odd function, the value of integral will be equal to zero, i.e.

$$\bar{\alpha} = 0 \tag{AII.25}$$

Average of Square of Fluctuation of a Single Physical Quantity

The average value of α^2 is

$$\overline{\alpha^2} = \int_{-\infty}^{+\infty}\alpha^2\,\wp\,d\alpha = K\int_{-\infty}^{+\infty}\exp\left(-g\alpha^2/2k_B\right)\alpha^2\,d\alpha$$

$$= -\frac{k_B K}{g}\int_{-\infty}^{+\infty}\alpha\,d\left(e^{-g\alpha^2/2k_B}\right)$$

Carrying out the integration by parts, we have

$$\int\alpha\,d\left(e^{-g\alpha^2/2k_B}\right) = \alpha\,e^{-g\alpha^2/2k_B} - \int e^{-g\alpha^2/2k_B}\,d\alpha$$

Hence $$\overline{\alpha^2} = -\frac{k_B K}{g}\,\alpha\,e^{-g\alpha^2/2k_B}\Big|_{-\infty}^{+\infty} + \frac{k_B}{g}\int_{-\infty}^{+\infty}K\,e^{-g\alpha^2/2k_B}\,d\alpha$$

$$= 0 + \frac{k_B}{g}\int_{-\infty}^{-\infty} \wp\, d\alpha = \frac{k_B}{g}(1) = \frac{k_B}{g} \tag{AII.26}$$

(Note: The integral $\int_{-\infty}^{+\infty} \wp\, d\alpha = 1$ due to the normalization condition of $\wp$.)

From Eq. (AII.22), we have

$$g = g_{ii} = -\left(\frac{\partial^2 S}{\partial \xi_i^2}\right)_0$$

which in view of Eq. (AII.17) becomes

$$g = -\left(\frac{\partial^2 S}{\partial \alpha_i^2}\right) \tag{AII. 27}$$

Substituting this in Eq. (AII.26), we get

$$\overline{\alpha^2} = -\frac{k_B}{\left(\partial^2 S/\partial \alpha_i^2\right)_0} \tag{AII.28}$$

Fluctuation in a Subystem

For the fluctuation at constant T and p in a subsystem of volume v, the change in free energy accompanying the fluctuation is given by

$$dG = du - T\,ds + p\,dv \tag{AII.29}$$

where u and s are the energy and entropy, respectively, of the subsystem of volume v. The expression of dG in terms of U, S and V of the entire system may be derived as follows.

If u and s are energy and entropy of the subsystem of volume v, then in the remaining volume of the system, we will have

$$d(U - u) = T\,d(S - s) - p\,d(V - v) \tag{AII. 30}$$

where U and S are the energy and entropy of the entire system of volume V. Equation (AII.30) may be written as

$$du - T\,ds + p\,dv = dU - T\,dS + p\,dV$$

which in view of Eq. (AII.29) becomes

$$dG = dU - T\,dS + p\,dV$$

Hence, at constant U and V, we can write

$$dG = -T\,dS$$

Hence $$\left(\frac{\partial^2 G}{\partial \alpha^2}\right)_0 = -T\left(\frac{\partial^2 S}{\partial \alpha^2}\right)_0 \tag{AII.31}$$

With this, Eq. (AII.28) becomes

$$\overline{\alpha^2} = \frac{k_B T}{\left(\partial^2 G/\partial \alpha^2\right)_0} \tag{AII.32}$$

Value of $\overline{\alpha^2}$ for Noninteracting Particles

Let $\alpha = n - v$ be the fluctuation in the number of particles in the volume v of a system. We will have

$$\frac{\partial G}{\partial \alpha} = \frac{\partial G}{\partial n} = \mu$$

where μ is the chemical potential per particle. The expression of μ for an ideal system[†] is given by

$$\mu = \mu^\circ + p v_{\text{pm}} + k_B T \ln \frac{n}{v}$$

At constant T, p and v, we have

$$\frac{\partial \mu}{\partial n} = \frac{k_B T}{n}$$

With this, the expression of $(\partial^2 G / \partial \alpha^2)_0$ is given by

$$\left(\frac{\partial^2 G}{\partial \alpha^2}\right)_0 = \left(\frac{\partial^2 G}{\partial n^2}\right)_0 = \left\{\frac{\partial}{\partial n}\left(\frac{\partial G}{\partial n}\right)\right\}_0 = \left(\frac{\partial \mu}{\partial n}\right)_0 = \frac{k_B T}{n} \tag{AII.33}$$

At equilibrium $\alpha = 0$. Hence $n - v = 0$ i.e. $n = v$. thus

$$\left(\frac{\partial^2 G}{\partial \alpha^2}\right)_0 = \frac{k_B T}{v}$$

Substituting this in Eq. (AII.32), we get

$$\overline{\alpha^2} = \frac{k_B T}{k_B T / v} = v \tag{AII.34a}$$

which is identical to that obtained earlier from the Poisson distribution (Eq. AII.13). The root mean square of fluctuation is given by

$$\sqrt{\overline{\alpha^2}} = \sqrt{v} \tag{AII.34b}$$

The relative fluctuation is given by $\quad f_r = \dfrac{\sqrt{\overline{\alpha^2}}}{v} = \dfrac{\sqrt{v}}{v} = \dfrac{1}{\sqrt{v}}$ (AII.34c)

[†] In a solution, we have

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T, n_j \atop j \neq i} = v_{i,\text{pm}}$$

where $v_{i,\text{pm}}$ is the partial molar volume of the ith constituent in the solution. Assuming it to remain approximately constant, we will have

$$\int d\mu_i = v_{i,\text{pm}} \int dp \quad \text{i.e.} \quad \mu_i = v_{i,\text{pm}}\, p + \mu_i^{(c)}$$

where $\mu_i^{(c)}$ is constant of proportionality. It depends on T and composition of the solution. For a single particle in an ideal solution,

$$\mu_i^{(c)} = \mu_i^\circ + k_B T \ln c$$

where μ_i° is the standard chemical potential. It depends only on temperature. With this, the previous expression becomes

$$\mu_i = v_{i,\text{pm}}\, p + \mu_i^\circ + k_B T \ln c$$

Restoring Force of a Fluctuated System

The restoring force on a fluctuated system due to the fluctuated parameter α_i ($= \xi_i - \xi_i^{\circ}$; where ξ_i and ξ° are the parameters describing the given system and the system at equilibrium, respectively) is given by the expression

$$X_i = \left(\frac{\partial \Delta S}{\partial \alpha_i}\right) \qquad \text{(AIL.35)}^{\dagger}$$

where $\Delta S = S - S_0$. The force X_i restores the fluctuated system to equilibrium position.

Since $$\Delta S = -\frac{1}{2}\sum_{i,j=1}^{n} g_{ij}\,\alpha_i\,\alpha_j \qquad \text{(Eq. AII.21)}$$

it follows that

$$X_i = \frac{\partial \Delta S}{\partial \alpha_i} = -\sum_{j=1}^{n} g_{ij}\,\alpha_j \qquad \text{(AII.36)}^{\ddagger}$$

Since $$\wp = K\exp\left\{-\frac{1}{2k_B}\sum_{i,j=1}^{n} g_{ij}\,\alpha_i\,\alpha_j\right\} \qquad \text{(Eq. AII.23)}$$

it follows that

$$\frac{\partial \ln \wp}{\partial \alpha_i} = -\frac{1}{k_B}\sum_{j=1}^{n} g_{ij}\,\alpha_j \qquad \text{(AII.37)}$$

With this, Eq. (AII.36) becomes

$$X_i = k_B\,\frac{\partial \ln \wp}{\partial \alpha_i} = \frac{k_B}{\wp}\,\frac{\partial \wp}{\partial \alpha_i} \qquad \text{(AII.38)}$$

[†] For examples

Electrical conduction in a wire Equation (6.6.17) gives

$$X_i = \frac{\mathrm{d_i}S}{\mathrm{d}Q} = -\frac{\partial \varphi}{T} = -\frac{\operatorname{grad}\varphi}{T}$$

Heat conduction in a bar Equation (6.6.20) gives

$$X_i = \frac{\mathrm{d_i}S}{\mathrm{d}q} = -\frac{\partial T}{T^2} = \operatorname{grad}\left(\frac{1}{T}\right)$$

[‡] For example, for the two fluctuating parameters, we have

$$\Delta S = -\frac{1}{2}\left[g_{11}\,\alpha_1^2 + g_{12}\alpha_1\alpha_2 + g_{21}\alpha_2\alpha_1 + g_{22}\alpha_2^2\right]$$

$$\frac{\partial \Delta S}{\mathrm{d}\alpha_1} = -\frac{1}{2}\left[2g_{11}\,\alpha_1 + g_{12}\alpha_2 + g_{21}\alpha_2\right] = -(g_{11}\,\alpha_1 + g_{12}\,\alpha_2); \qquad (\text{since } g_{12} = g_{21})$$

With X_i defined by Eq. (AII.36), it can be shown that the entropy production expression is

$$\sigma = \frac{\mathrm{d}(\Delta S)}{\mathrm{d}t} = \sum_{i=1}^{n}\left(\frac{\partial \alpha_i}{\partial t}\right)\left(-\sum_{i=1}^{n} g_{ij}\,\alpha_j\right) \equiv \sum_{i=1}^{n} J_i X_i$$

where the flux $J_i = (\partial \alpha_i/\partial t)$.

Average of $X_i\,\alpha_J$

The average of $X_i\alpha_j$ (product of a fluctuating parameter α_j with the restoring force X_i) is given by

$$\overline{X_i\alpha_j} = \int\ldots\int (X_i\alpha_j)\,\wp\, \mathrm{d}\alpha_1\, \mathrm{d}\alpha_2 \ldots \mathrm{d}\alpha_n \qquad \text{(AII.39)}$$

where n is the total number of fluctuating parameters. Substituting X_i from Eq. (AII.38), we get

$$\overline{X_i\alpha_j} = k_\mathrm{B}\int\ldots\int \left(\frac{\partial\wp}{\partial\alpha_i}\right) \alpha_j\, \mathrm{d}\alpha_1\, \mathrm{d}\alpha_2 \ldots \mathrm{d}\alpha_n$$

$$= k_\mathrm{B}\int\ldots\int \mathrm{d}\alpha_1 \ldots \mathrm{d}\alpha_{i-1}\, \mathrm{d}\alpha_{i+1} \ldots \mathrm{d}\alpha_n \left(\alpha_j \frac{\partial\wp}{\partial\alpha_i}\right) \mathrm{d}\alpha_i \qquad \text{(AII.40)}$$

Carrying out the intergation $\int \alpha_j \frac{\partial\wp}{\partial\alpha_i}\, \mathrm{d}\alpha_i$ by parts, we get

$$\int_{-\infty}^{+\infty} \alpha_j \frac{\partial\wp}{\partial\alpha_i}\mathrm{d}\alpha_i = \alpha_j\wp \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \wp \frac{\partial\alpha_j}{\partial\alpha_i}\mathrm{d}\alpha_i$$

Since the probability $\wp$ of finding an infinite positive and negative fluctuations is zero, the first term on the right side of the above expression will be equal to zero. Moreover, α_i and α_j are independent parameters, the derivative $\partial\alpha_j/\partial\alpha_i = \delta_{ij}$ (Krönecker delta, $\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ij} = 1$ for $i \neq j$). With these, the above expression becomes

$$\int_{-\infty}^{+\infty} \alpha_j \frac{\partial\wp}{\partial\alpha_i}\mathrm{d}\alpha_i = -\delta_{ij} \int_{-\infty}^{+\infty} \wp\, \mathrm{d}\alpha_i \qquad \text{(AII.41)}$$

Substituting Eq. (AII.41) in Eq. (AII.40), we get

$$\overline{X_i\alpha_j} = -k_\mathrm{B}\,\delta_{ij}\int\ldots\int \wp\, \mathrm{d}\alpha_1\, \mathrm{d}\alpha_2 \ldots \mathrm{d}\alpha_n$$

$$= -k_\mathrm{B}\,\delta_{ij}(1) = -k_\mathrm{B}\,\delta_\mathrm{ij} \qquad \text{(AII.42)}$$

Thus, we have

- The average of fluctuating parameter multiplied by its conjugate force is equal to $-k_\mathrm{B}$.
- The average of fluctuating parameter multiplied by a nonconjugative force is equal to zero.

Principle of Microscopic Reversibility

The principle of microscopic reversibility states that under equilibrium conditions, a molecular process occurring at the microscopic level and its reverse take place on the average with the same probability.

The principle of microscopic reversibility has the following implications.

The equation of motion, $\boldsymbol{F} = m\,\boldsymbol{a}$, remains unaffected on replacing t by $-t$. In physical language, this implies that if the velocity of a given body is reversed at a given instant, say $t = t_0$, then the body will trace the path backward along the same sequence of configurations traversed by the body prior to that instant (i.e. at

$t = t_0$). Thus, to every direct solution of the equation of motion there corresponds a reverse solution and hence the equation of motion is said to be reversible.

Application to a Fluctuation in a System The principle of microscopic reversibility is also applicable to the fluctuations of a system from its equilibrium position. This implies that the values of fluctuating parameters are not affected on reversing the time. In other words, if one observes fluctuations about equilibrium and considers all the situations from which simultaneously the values of fluctuating parameters are given, then on an average the value of α_j computed in each case at time τ after the fluctuation α_1, α_2, ..., α_n have occurred will agree with the value of α_j computed at a time τ before the fluctuations have occurred. Mathematically, it may be expressed as

$$\left[\alpha_j(t+\tau)\right]_{\alpha_1(t),\ldots,\alpha_n(t)} = \left[\alpha_j(t-\tau)\right]_{\alpha_1(t),\ldots,\alpha_n(t)} \tag{AII.43}$$

If the above expression is multiplied by $\alpha_i(t)$ and take average of the products over all possible values of $\alpha_1(t)$, $\alpha_2(t)$, ..., we will get

$$\overline{\alpha_i(t)\,\alpha_j(t+\tau)} = \overline{\alpha_i(t)\,\alpha_j(t-\tau)} \tag{AII.44}$$

The averages in Eq. (AII.44) does not depend on the value of t. Thus, t in the right side of this equation may be replaced by $t + \tau$ to give

$$\overline{\alpha_i(t)\,\alpha_j(t+\tau)} = \overline{\alpha_i(t+\tau)\,\alpha_j(t)} \tag{AII.45}$$

Equation (AII.45) implies that the correlation in time between α_i and α_j, is independent of the direction of the time scale as shown in Fig. AII.1.

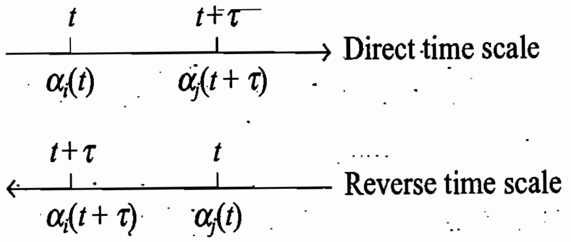

Fig. AII.1 The correlation in time between α_i and α_j is independent of the direction of the time scale

If $\overline{\alpha_i(t)\,\alpha_j(t)}$ is subtracted from both sides of Eq. (AII.45), we get

$$\overline{\alpha_i(t)\,\alpha_j(t+\tau) - \alpha_i(t)\,\alpha_j(t)} = \overline{\alpha_i(t+\tau)\,\alpha_j(t) - \alpha_i(t)\,\alpha_j(t)}$$

or $$\overline{\alpha_i(t)\left[\alpha_j(t+\tau) - \alpha_j(t)\right]} = \overline{\alpha_j(t)\left[\alpha_i(t+\tau) - \alpha_i(t)\right]}$$

Dividing both sides by τ, we get

$$\overline{\alpha_i(t)\left[\frac{\alpha_j(t+\tau) - \alpha_j(t)}{\tau}\right]} = \overline{\alpha_j(t)\left[\frac{\alpha_i(t+\tau) - \alpha_i(t)}{\tau}\right]}$$

Let $\tau \to 0$, we get

$$\overline{\alpha_i(t)\left(\mathrm{d}\alpha_j(t)/\mathrm{d}t\right)} = \overline{\alpha_j(t)\left(\mathrm{d}\alpha_i(t)/\mathrm{d}t\right)} \tag{AII.46}$$

In deriving Eq. (AII.46), it is assumed that $\tau \to 0$. This does not imply that τ is zero, but τ should be sufficiently small satisfying the requirement

$$\tau_0 << \tau << \tau_r$$

where τ_0 is time for a single collision process and τ_r is the relaxation time of the fluctuation. In fact, the time interval $\tau_r - \tau_0$ should be sufficiently wide so as to unaffect the validity of Eq. (AII.46).

Onsager Hypothesis

In order to derive Onsager law of symmetry of phenomenological coefficients, Onsager made the following hypothesis.

The rate of change of a fluctuating variable, or the average rate of decay of a fluctuation, $d\alpha_i/dt$, has the same linear dependence on the thermodynamic forces as is observed in macroscopic flows.

According to this hypothesis, we must have

$$\left(\frac{\overline{d\alpha_i}}{dt}\right) = \sum_{k=1}^{n} L_{ik} X_k \qquad \text{(AII.47)}^{\dagger}$$

Derivation of Onsager Symmetry Rule

Substituting Eq. (AII.47) in Eq. (AII.46), we get

$$\overline{\alpha_i \sum_{k=1}^{n} L_{jk} X_k} = \overline{\alpha_j \sum_{k=1}^{n} L_{ik} X_k}$$

or $$\sum_{k=1}^{n} L_{jk} \overline{(\alpha_i X_k)} = \sum_{k=1}^{n} L_{ik} \overline{(\alpha_j X_k)}$$

which on using Eq. (AII.42) becomes

$$-k_B \sum_{k=1}^{n} L_{jk}\, \delta_{ik} = -k_B \sum_{k=1}^{n} L_{ik}\, \delta_{jk}$$

$$-k_B L_{ji} = -k_B L_{ij}$$

or $$L_{ji} = L_{ij} \qquad \text{(AII.48)}$$

where k_B in the above expression is Boltzmann constant. Equation (AII.48) represents Onsager symmetry rule.

Comment The Onsager symmetry rule is based on the application of hypothesis made by Eq. (AII.47), that is, the regression of fluctuation follows the same law as macroscopic irreversible processes. The validity of the Onsager symmetry rule has been verified by several types of irreversible processes and may be regarded as the established law.

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† The basis of Eq. (AII.47) may be rationalized as follows.

The recovery of an equilibrium state, in most cases, follows a linear law in accordance to the expression

$$\left(\frac{\overline{d\alpha_i}}{dt}\right) = \sum\nolimits_j p_{ij}\, \alpha_j$$

where the terms α_j on the right side, besides α_i, allows for the possibility of coupling amongst different fluctuations. Since the fluctuating variables are related to the restoring force (Eq. AII.35), the above expression may be written as Eq. (AII.47).

ANNEXURE III Kinetic Considerations of Energy of Transfer

Collision Frequency with the Side of the Vessel

Considering the side of a vessel as xy-plane, we imagine an oblique cylinder of slant height $u\,\mathrm{d}t$ with an base area A as shown in Fig. AIII.1. The cylinder will include all the molecules with velocity u coming from the direction (θ, φ) that strike the base area A in the time interval $\mathrm{d}t$. The volume of the cylinder is

$$V = \text{(base area) (vertical height)}$$

$$= A\{(u \cos \theta)\,\mathrm{d}t\} \qquad \text{(AIII.l)}$$

If N^* is the number density of gaseous molecules (i.e. number of molecules per unit volume of the vessel), then the number of molecules contained in the volume of cylinder is

$$N = N^*[A\{u \cos \theta\}\mathrm{d}t] \qquad \text{(AIII.2)}$$

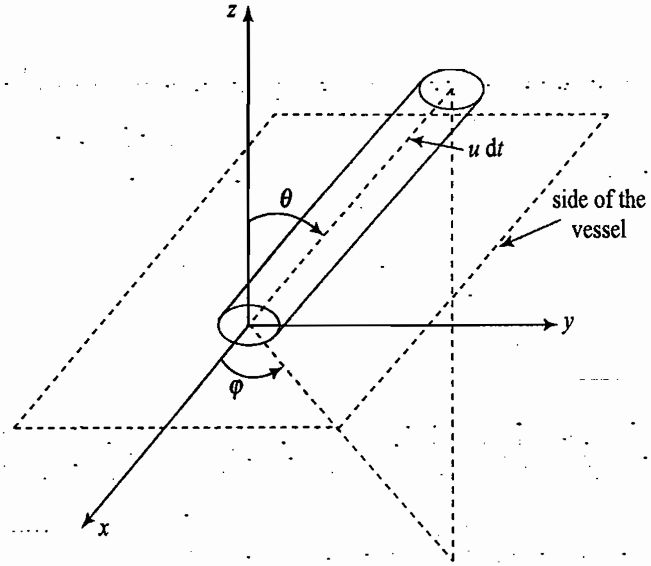

Fig. AIII.1 Computation for the collisions with the side of a vessel

The probability of a molecule having velocities between u and $u + \mathrm{d}u$ in the volume element $\mathrm{d}\tau$ situated in the direction (θ, φ) as given by Maxwell velocity distribution function is

$$P = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} \exp\left(-\frac{mu^2}{2k_{\mathrm{B}}T}\right)\mathrm{d}\tau$$

Since $\mathrm{d}\tau = u^2\,\mathrm{d}u \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$, we have

$$P = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} \exp\left(-\frac{mu^2}{2k_{\mathrm{B}}T}\right)u^2\,\mathrm{d}u \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi \qquad \text{(AIII.3)}$$

Hence, the number of molecules reaching the base area A of the cylinder is

$$\mathrm{d}N = NP = N^*[A\{u \cos \theta\}\,\mathrm{d}t]\left[\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} \exp\left(-\frac{mu^2}{2k_{\mathrm{B}}T}\right)u^2\,\mathrm{d}u \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\right]$$

(AIII.4)

The number of molecules reaching per unit area in a unit time is given by

$$\frac{1}{A}\frac{\mathrm{d}N}{\mathrm{d}t} = N^*\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2}\exp\left(-\frac{mu^2}{2k_\mathrm{B}T}\right)u^2\,\mathrm{d}u\sin\theta\cos\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi \qquad \text{(AIII.5)}$$

If the above expression is integrated over all possible velocities and directions, we get the total number of molecules striking the base area A per unit time interval. Thus,

$$z = N^*\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2}\int_0^\infty \exp\left(-\frac{mu^2}{2k_\mathrm{B}T}\right)u^2\,\mathrm{d}u\int_0^{\pi/2}\sin\theta\cos\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\varphi \qquad \text{(AIII.6)}$$

Nofe that the integration over θ is carried over from 0 to $\pi/2$ because the molecules strike the side of the vessel from one side only. The result of the above integrations is

$$z = N^*\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2}\left[\frac{1}{2}\left(\frac{2k_\mathrm{B}T}{m}\right)^2\right]\left(\frac{1}{2}\right)(2\pi)$$

$$= \frac{N^*}{4}\left(\frac{8k_\mathrm{B}T}{\pi m}\right)^{1/2} = \frac{1}{4}N^*u_\mathrm{av} \qquad \text{(AIII.7)}$$

Mean Kinetic Energy of Kundsen Gas

If the diameter of a hole in a vessel containing a gas is small as compared to the mean free path of gaseous molecules, the molecules on arriving at the hole are effused freely through the hole. The gas involving such a effusion is known as Knudsen gas. Let the base area shown in Fig. AIII.1 represent such a hole in the vessel.

The number of molecules reaching the hole within the considered hole as given by Eq. (AIII.4) is

$$\mathrm{d}N = N^*\,[A\,(u\cos\theta)\,\mathrm{d}t]\left[\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2}\exp\left(-\frac{mu^2}{2k_\mathrm{B}T}\right)u^2\,\mathrm{d}u\sin\theta\,\mathrm{d}\theta\,d\varphi\right]$$

The kinetic energy associated with the molecules is

$$\mathrm{d}E_\mathrm{k} = \left(\frac{1}{2}mu^2\right)\mathrm{d}N$$

$$= \left(\frac{1}{2}mu^2\right)\left[N^*\{A(u\cos\theta)\mathrm{d}t\}\right]\left[\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2}\exp\left(-\frac{mu^2}{2k_\mathrm{B}T}\right)u^2\,\mathrm{d}u\sin\theta\,\mathrm{d}\theta\,d\varphi\right] \qquad \text{(AIII.8)}$$

Hence

$$\frac{1}{A}\frac{\mathrm{d}E_\mathrm{k}}{\mathrm{d}t} = \left(\frac{m}{2}\right)N^*\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2}u^3\exp\left(-\frac{mu^2}{2k_\mathrm{B}T}\right)u^2\,\mathrm{d}u\sin\theta\cos\theta\,\mathrm{d}\theta\,d\varphi \qquad \text{(AIII.9)}$$

If the above expression is integrated over all possible velocities and directions, we get the total kinetic energy of gaseous molecules striking the hole per unit area in a unit time interval. Thus

$$\text{KE} = \left(\frac{mN^*}{2}\right)\left(\frac{m}{2\pi\, k_{\text{B}}T}\right)^{3/2} \int_0^\infty u^5 \exp\left(-\frac{mu^2}{2k_{\text{B}}T}\right) \mathrm{d}u \int_0^{\pi/2} \sin\theta\cos\theta\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\varphi$$

$$= \left(\frac{mN^*}{2}\right)\left(\frac{m}{2\pi\, k_{\text{B}}T}\right)^{3/2} \left(\frac{2k_{\text{B}}T}{m}\right)^3 \left(\frac{1}{2}\right)(2\pi) \qquad \text{(AIII.10)}^\dagger$$

The number of molecules reaching the hole per unit area in a unit time interval as given by Eq. (AIII.7) is

$$z = N^*\left(\frac{m}{2\pi\, k_{\text{B}}T}\right)^{3/2} \left[\frac{1}{2}\left(\frac{2k_{\text{B}}T}{m}\right)^2\right]\left(\frac{1}{2}\right)(2\pi) \qquad \text{(AIII.11)}$$

The average kinetic energy of molecules that strike the hole and effuse freely through the hole is obtained by dividing Eq. (AIII.10) by Eq. (AIII.11). Hence

$$\overline{\text{KE}} = \frac{\text{KE}}{z} = \frac{(m/2)\,(2k_{\text{B}}T/m)^3}{(1/2)\,(2k_{\text{B}}T/m)^2} = 2\,k_{\text{B}}T \qquad \text{(AIII.12)}$$

For the effusion of 1 mol of the gas, we have

$$U^* = N_{\text{A}}\,\overline{\text{KE}} = 2(N_{\text{A}}k_{\text{B}})T = 2\,RT \qquad \text{(AIII.13)}$$

[†] The integral over u in Eqs (AIII.6) and (AIII.10) is $\int_0^\infty x^n\, \mathrm{e}^{-\alpha x^2}\,\mathrm{d}x$. Its value is $1/2\,a^2$ for $n = 3$ and is $1/a^3$ for $n = 5$.

APPENDIX Units and Conversion Factors

SI Units

There are seven base quantities in SI units. These are described in Table AI.1.

Table AI.1 Seven Basic Quantities in SI Units

Physical quantity	*Name of unit*	*Symbol of unit*	*Definition*
Length	meter	m	1650 763.73 wavelengths in vacuum of the radiation corresponding to the transition $2p_{10}$–$5d_5$ of the krypton–86
Mass	kilogram	kg	A cylinder of platinum-irridium alloy kept by the International Bureau of weights and Measures in Paris
Time	second	s	The duration of 9 192 631 770 cycles of the radiation associated with the transition between the two hyperfine levels of the ground caseium–133 atom
Electric current	ampere	A	The magnitude of the current that, when flowing through each of two long parallel wires separated by one 1 m in free space, results in a force between the two wires of 2×10^{-7} N for each meter of length.
Thermodynamic temperature	kelvin	K	Origin is at absolute zero and the triple point of water is 273.16 K
Amount of substance	mole	mol	Amount of substance that contains as many elementary entities (atoms, molecules, ions, etc.) as there are carbon atoms in 0.012 kg of carbon–12
Luminous*	candela	cd	The luminous intensity, in the perpendicular direction, of a surface of 1/600 000 sq m of a black body at the temperature of freezing platinum under a pressure of 101.325 kPa

Units Derived from the Base SI Units

Physical quantity	*Name of unit*	*Symbol and definition*
Force	newton	N = kg m s^{-2} or J m^{-1}
Energy	joule	J = kg m^2 s^{-2} or N m
Electric charge	coulomb	C = A s
Potential difference	volt	V = kg m^2 s^{-3} A^{-1} or J A^{-1} s^{-1}
Resistance	ohm	Ω = kg m^2 s^{-3} A^{-2} or V A^{-1}
Frequency	hertz = cycle per second	Hz = s^{-1}
Area	square metre	m^2
Volume		cubic metre m^3
Density		kilogram per cubic metre kg m^{-3}
Velocity	metre per second	m s^{-1}
Angular velocity	radian per second	rad s^{-1}
Acceleration	metre per square second	m s^{-2}
Pressure	newton per square metre or pascal	N m^{-2} or Pa
Conductivity	siemen	S = Ω^{-1}
Magnetic fluid density	tesla	T = Wb m^{-2} = V s m^{-2}
Electric capacitance	farad	F = C V^{-1}
Magnetic flux	weber	Wb = V s
Inductance	henry	H = Wb A^{-1}

CGS Units vis-á-vis SI Units

Physical quantity	*CGS units*		*SI units*	
	Name	*Symbol*	*Name*	*Symbol*
Length	centimetre	cm	metre	m
	Angstrom (10^{-8} cm)	Å		
Mass	gram	g	kilogram	kg
Time	second	sec	second	s
Temperature	celsius kelvin	°C °K	kelvin	K
Energy	calorie	cal	joule	J
	kilocalorie	kcal	kilojoule	kJ
	litre-atmosphere	lit-atm		
	ergs	erg		
Electric current	ampere	A	ampere	A

Conversion of CGS Units to SI Units

Quantity	*Units*	*Equivalent*†
Length	Angstron, Å	10^{-10} m = 10^{-1} nm = 10^{2} pm
	micron, μ	10^{-6} m
Volume	litre	10^{-3} m^{3} = dm^{3}
Force	dyne	10^{-5} N
Energy	erg	10^{-7} J
	cal	4.184 J
	eV	$1.602\,1 \times 10^{-19}$ J
	eV/mole	98.484 kJ mol^{-1}
Pressure	atmosphere	101.325 kN m^{-2}
	mmHg (or Torr)	133.322 N m^{-2}
	bar (10^{6} dyn/cm^{2})	10^{5} N m^{-2}
Viscosity	poise	10^{-1} kg m^{-1} s^{-1}
Magnetic flux density (magnetic induction)	gauss	10^{-4} T

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† Symbols used for fractions and multiples are given in the next Table.

SI Prefixes

Fraction	*Prefix*	*Symbol*	*Multiples*	*Prefix*	*Symbol*
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^{2}	hecto	h
10^{-3}	milli	m	10^{3}	kilo	k
10^{-6}	micro	μ	10^{6}	mega	M
10^{-9}	nano	n	10^{9}	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P

Values of Some Physico-Chemical Constants

Constant	*CGS units*	*SI units*
Acceleration of gravity, g	980.66 cm sec^{-2}	9.806 65 m s^{-2}
Avogadro's constant, N_A	$6.022\ 05 \times 10^{23}$ molecules $mole^{-1}$	$6.022\ 05 \times 10^{23}$ mol^{-1}
Bohr magneton, μ_B	9.2741×10^{-21} erg $gauss^{-1}$	9.27408×10^{-24} A m^2
Bohr radius, a_0	0.529 177 Å	$5.291\ 77 \times 10^{-11}$ m
Boltzmann constant, k	$1.380\ 66 \times 10^{-16}$ erg (degree $K)^{-1}$ $molecule^{-1}$	$1.380\ 60 \times 10^{-22}$ J K^{-1}
Debye	10^{-18} esu·cm	$3.335\ 6 \times 10^{-30}$ C m
Electronic charge, e	$4.802\ 98 \times 10^{-10}$ esu	$1.602\ 16 \times 10^{-19}$ C
Electronic rest mass, m_e	$9.109\ 53 \times 10^{-28}$ g	$9.109\ 53 \times 10^{-31}$ kg
Faraday, F	96 487 coulomb $equiv^{-1}$	$9.648\ 46 \times 10^4$ C mol^{-1}
Gas constant R	8.31441×10^7 ergs (degree $K)^{-1}$ $mole^{-1}$ 8.31441 Joules (degree $K)^{-1}$ $mole^{-1}$ 0.082 054 litre-atm (degree $K)^{-1}$ $mole^{-1}$ 1.987 cal (degree $K)^{-1}$ $mole^{-1}$	8.314 41 J K^{-1} mol^{-1} 8.314 41 N m K^{-1} mol^{-1} 8.314 41 Pa m^3 K^{-1} mol^{-1} 8.314 41 kPa dm^3 K^{-1} mol^{-1} 8.314 41 MPa cm^3 K^{-1} mol^{-1}
Molar volume of ideal gas at 0 °C can 1 atm, V_m	22.414 litres	$2.241\ 4 \times 10^{-2}$ m^3 mol^{-1}
Permittivity of vacuum, $\varepsilon_0 = \mu_0^{-1} c^{-2}$		$8.854\ 188 \times 10^{-12}$ C^2 s^2 kg^{-1} m^{-3}
Permeability of vacuum, μ_0		$4\pi \times 10^{-7}$ H m^{-1}
Planck's constant, h	$6.626\ 18 \times 10^{-27}$ erg sec	$6.626\ 18 \times 10^{-34}$ J s
Proton rest mass, m_p	1.67265×10^{-24} g	$1.672\ 65 \times 10^{-27}$ kg
Vacuum speed of light, c	$2.997\ 925 \times 10^{10}$ cm sec^{-1}	$2.997\ 925 \times 10^8$ m s^{-1}
Standard atmospheric pressure	76 cm Hg 760 mm Hg (or torr) 1.1032×10^6 dynes/cm^2	101.325 kPa 1.0132 5 bar

Greek Alphabets

	Symbol					Symbol			
Name	Roman	Italic	Roman	Italic	Name	Roman	Italic	Roman	Italic
Alpha	Α	*Α*	α	*α*	Nu	Ν	*Ν*	ν	*ν*
Beeta	Β	*Β*	β	*β*	Xi	Ξ	*Ξ*	ξ	*ξ*
Gamma	Γ	*Γ*	γ	*γ*	Omicron	Ο	*Ο*	ο	*ο*
Delta	Δ	*Δ*	δ	*δ*	Pi	Π	*Π*	π	*π*
Epsilon	Ε	*Ε*	ε	*ε*	Rho	Ρ	*Ρ*	ρ	*ρ*
Zeta	Ζ	*Ζ*	ζ	*ζ*	Sigma	Σ	*Σ*	σ	*σ*
Eta	Η	*Η*	η	*η*	Tau	Τ	*Τ*	τ	*τ*
Theta	Θ	*Θ*	θ	*θ*	Upsilon	Υ	*Υ*	υ	*υ*
Iota	Ι	*Ι*	ι	*ι*	Phi	Φ	*Φ*	ϕ	*ϕ*
Kappa	Κ	*Κ*	κ	*κ*	Chi	Χ	*Χ*	χ	*χ*
Lambda	Λ	*Λ*	λ	*λ*	Psi	Ψ	*Ψ*	ψ	*ψ*
Mu	Μ	*Μ*	μ	*μ*	Omega	Ω	*Ω*	ω	*ω*

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