Physical Chemistry



Ashish Kumar Nag

PHYSICAL CHEMISTRY Volume-I

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Ashish Kumar Nag completed his Master's degree in Science with Physical Chemistry as the special paper. He then joined as a research fellow at the Indian Association for the Cultivation of Science, Calcutta, under the supervision of Prof. Kankan Bhattacharrya (presently senior editor of Journal of Physical Chemistry). Prof. Nag studied the dynamics of molecules in the excited states using ultra-fast laser systems. During his tenure as a doctoral fellow (1986–1990), he published eight research papers in international journals.

After serving for 7 months as a lecturer at St. Xavier's College, Calcutta, the author joined as a senior lecturer at the erstwhile Bengal Engineering College, Howrah (now, Indian Institute of Engineering Science and Technology). Serving there for five years, he again joined at St. Xavier's College, where he is still working as Associate Professor.

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Currently, he is dedicatedly engaged in the teaching process and finding more innovative ways to teach the subject of Physical Chemistry to his students.

PHYSICAL CHEMISTRY Volume-I

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Dedicated to

The Memories of Binapani and Ananya To whom I owe so much

PREFACE

The field of Physical Chemistry has now become widespread that it has invaded all other branches of Science. This book is written not only to introduce the subject of Physical Chemistry to the students who aspire to become chemists, but also for many other students who will find the knowledge of subject matter essential at the later stages of their carriers.

The author has made every effort to represent the text in a lucid and easy-to-understand language. Significant time has been devoted for the development of the book so as to provide a strong foundation of the subject to the students studying it for the first time. Due care has been taken to ensure the coverage of recent trends in the field of Physical Chemistry. He has followed his principal objective of presenting the fundamentals of the subject as clearly as possible. For this reason, the book includes a number of worked out problems, so that the students apprehend the concepts covered in the respective chapters.

The students using this book are assumed to have a basic knowledge on the subjects of Chemistry, Physics and Calculus, as they usually gain in H.S. courses affiliated to different education boards (W.B.C.H.S.E., I.S.C., CBSE). Although the book is intended primarily for the conventional undergraduate course in Physical Chemistry; however, it covers more than that. It is believed to be equally efficient for more advanced courses and as a general reference book for those working in the fields that require a basic knowledge of Physical Chemistry.

Ashish Kumar Nag

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1 CHAPTER

THE EMPIRICAL GAS LAWS

1.1 INTRODUCTION: THE NATURE OF GASES

A gas may be defined as a homogeneous substance whose volume increases *without limit* when the pressure on it is reduced continuously, the temperature being kept fixed. Gases are further characterised by the fact that, when different gases in any proportion, whatsoever, are brought into contact, they diffuse rapidly into one another and form a homogeneous mixture. Temperature also has a profound influence on the volume of the gas.

The gaseous state is also characterised by the fact that, it has no bounding surface, and so, it has no definite shape; it takes the shape of the vessel in which it is contained. However, there is an important difference between a *gas* and a *liquid*. While the former has no surface at all, the latter has a surface. This places a limit on the volume it can occupy. Under ordinary conditions, gases are about one-thousandth as dense as liquids; nevertheless, there are conditions where the densities of the two states become comparable. We are often inclined to think that air weighs nothing; this is far from truth. If a cylindrical column of air, same in dimension as that of the Eiffel Tower (built wholly of steel) is imagined, then this column of air weighs more than the Eiffel Tower itself.

1.2 THE GAS LAWS

A very striking fact about the gases is that, independent of their chemical nature, they approximately obey certain very simple laws with regard to their physical properties. These are: (1) Boyle's law (2) Charles's or Gay-Lussac's law (3) Avogadro's law (4) Dalton's law of partial pressure, and (6) Graham's law of diffusion/effusion.

1.2.1 Boyle's Law

When the pressure of a gas is increased, at a fixed temperature, the volume decreases; a simple relation between the volume and the pressure was discovered by Robert Boyle (1662). He found that at a constant temperature, the volume of a definite mass of a gas is inversely proportional to the pressure, i.e.,

$$V \propto \frac{1}{P}$$
 (for a given mass of a gas at a fixed temperature)

 \Rightarrow

 \Rightarrow

(for a given mass of a gas at a fixed temperature) $PV = K_1$ (1.1)where K_1 is a constant depending upon the temperature and the mass of the gas and, also upon its nature. If V_1 is the volume of a given mass of gas at pressure P_1 and, V_2 is the volume at pressure P_2 , temperature remaining the same, then

$$P_1V_1 = K_1 = P_2V_2$$

$$P_1V_1 = P_2V_2 \quad \text{(for a given mass of a gas at a fixed T)} \quad (1.2)$$

This *P-V* relation is illustrated in Figure 1.1. Each curve corresponds to a given fixed temperature, and is called an isotherm ('iso' means 'the same'). The early experiments were crude, and we now know that gases obey this equation in the limit $P \to O$ and $T \to \infty$.

The understanding of the law is very clear. The pressure exerted by a gas is due to the bombardment of the molecules on the walls of the container. If the volume is doubled, the number density of the molecules is halved and therefore, the number of impacts on a unit area of the wall is also halved, and therefore, according to the Boyle's law, the pressure is also halved (everything at a fixed temperature).



Figure 1.1 (a) The pressure-volume dependence of a perfect gas at different temperatures (b) The projection of the ideal gas *P-V-T* surface onto the *P-V* plane. $(T_4 > T_3 > T_2 > T_1)$.

Another way to illustrate the Boyle's law is to plot 1/P against V (Figure 1.2). The advantage of this plot over the P-V plot is that, the linear relationship makes it easier to see any deviations from the law. For an ideal gas the plot of (1/P) versus v should be a straight line, passing through the origin.



Figure 1.2 A plot of 1/P against V for Boyle's original data. This linear plot, passing through the origin, shows that PV = constant.

Example 1.1

A given mass of gas occupies a volume of 120 mL at a pressure of 2.5 atm at a certain temperature. By how much the volume would be changed if the pressure were reduced to 1.5 atm under the isothermal condition?

Solution Applying the Boyle's law, we write

$$(1.5 \text{ atm}) V = (2.5 \text{ atm}) (120 \text{ mL})$$

 $V = (2.5 \text{ atm})(120 \text{ mL})$

 \Rightarrow

 $V = \frac{(2.5 \text{ atm})(120 \text{ mL})}{(1.5 \text{ atm})}$

 \Rightarrow V = 200 mL

The volume is therefore increased by (200 - 120) mL, i.e., 80 mL as a result of the pressure change.

Test Problem 1.1

A spherical bubble of radius 1×10^{-2} cm is formed deep inside the sea, where the pressure is 3.375 atm. Calculate the radius of the bubble when it comes up at the sea–air interface, where the pressure is 1 atm. Assume the isothermal condition.

1.3

(Ans: 1.5×10^{-2} cm)

1.2.2 Charles's Law; Gay Lussac's Law

The variation of the volume of a given mass of a gas with temperature, at a fixed pressure, is expressed by this law. The law states that, at a fixed pressure, the volume of a fixed mass

of a gas increases (or decreases) by $\frac{1}{273.15}$ of its volume at 0°C for every degree its rise

(or decrease) in temperature. If V_0 is the volume of a definite mass of gas at 0°C, then the volume V_t at t°C is given by

$$V_t = V_0 + \left(\frac{V_0}{273.15}\right)t$$
(1.3)

An alternative form of the law may be derived. If V_1 and V_2 are the volumes of a fixed mass of a gas at two temperatures t_1 and t_2 , measured at the same pressure then, it follows from Eq. (1.3)

$$V_1 = V_0 \bigg(1 + \frac{t_1}{273.15} \bigg)$$

 $V_2 = V_0 \left(1 + \frac{t_2}{273.15} \right)$

and

and finally,

$$\frac{V_1}{V_2} = \frac{(273.15 + t_1)}{(273.15 + t_2)} \tag{1.4}$$

1.2.3 Defining a New Scale of Temperature

Let us construct a *new scale of temperature* in which one degree is of the same size as one degree centigrade and, the zero is -273.15° below the zero of the centigrade scale. This means that the zero on this new scale is at -273.15° C (Figure 1.3).

Temperatures T on this new scale are then obtained by adding 273.15 to the celsius temperature t, viz.,

$$T/K = t/^{\circ}C + 273.15^{\circ}C$$
(1.5)

Temperatures on this new scale of temperature are called *absolute temperatures* because, there are reasons to believe that *the 'zero' on this new scale is the lowest conceivable temperature*. The symbol K is used to represent the absolute temperature, in honour of Lord Kelvin (Willian Thomson), who deduced an exactly the same scale of temperature from thermodynamic considerations and, which is shown to be *independent of the thermometric property of the substance used*. It is hence, called the Kelvin scale of temperature.



Figure 1.3 A plot of volume against temperature for argon, nitrogen and oxygen. The individual curves show the effect of a change in molar mass for the three gases. In each case one kilogram of gas is used at 1.00 atmosphere.

It may be noted that, according to the Charles's law, the volume of a gas should be zero at the *absolute zero*, i.e., at -273.15°C. However, apart from the fact that the gas would have liquefied and/or solidified, before this temperature is attained, it will be seen later that, this law fails to hold at such low temperatures.

Making use of this definition of the Kelvin scale of temperature, Eq. (1.4) changes to

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

$$\frac{V}{T} = K_2 \quad \text{(for a fixed mass of a gas at a fixed pressure)} \tag{1.6}$$

 \Rightarrow

where K_2 is a proportionality constant, depending upon the pressure and the mass of the gas and, also upon its nature. This equation may also be stated as: *the volume of a given mass of a gas, at a fixed pressure, is directly proportional to the absolute temperature*.

According to this law, a plot of V versus T for the given mass of a gas at a fixed pressure will be a straight line passing through the origin with a slope K_2 (Figure 1.4a). Such a line is called an ISOBAR. For each pressure, a different isobar is obtained. Higher the pressure lower is the slope K_2 (why?). The variation of the pressure of the fixed mass of a gas with temperature (at a fixed volume) is also shown (Figure 1.4b). These variations can be collectively illustrated as shown in Figure 1.5.



The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at T = 0 K, or t = -273°C.

The pressure also varies linearly with the temperature at constant volume and extrapolates to zero at T = 0 K (-273°C).





Figure 1.5 The variations, for a given mass of gas, of P and V with temperature. Compare this figure with Figure 1.6.

The Empirical Gas Laws

1.2.4 The Combined Gas Law

The laws of Boyle and Charles may be combined to get an equation of state, which represents the relationship among the parameters P, T and V for a given amount of a gas.

Let the gas has initially a volume V_i at pressure P_i and temperature T_i . Let these parameters are changed to V_f , P_f and T_f . This change can be made in two steps.

$$\begin{bmatrix} V_i, P_i, T_i \end{bmatrix} \xrightarrow[V_i]{\text{At fixed } T = T_i} \begin{bmatrix} V', P_f, T_i \end{bmatrix} \xrightarrow[V_f]{\text{At fixed pressure}} \begin{bmatrix} V_f, P_f, T_f \end{bmatrix} \xrightarrow[V_f]{\text{At fixed pressure}} \begin{bmatrix} V_f, P_f, T_f \end{bmatrix}$$

Applying the Boyle's law to the first step, we write

$$P_i V_i = P_f V'; \qquad \Rightarrow \quad V' = \frac{(P_i V_i)}{P_f}$$

$$\tag{1.7}$$

Then applying the Charles's law to the second step, we write

$$\frac{V'}{T_i} = \frac{V_f}{T_f} \qquad \Rightarrow \quad V' = \frac{(T_i V_f)}{T_f} \tag{1.8}$$

from these equations, we get

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}; \quad \Rightarrow \quad \frac{PV}{T} = K(\text{constant})$$
(1.9)

which shows that, for the given mass of a gas, any change in temperature and/or pressure will be accompanied by an adjustment of the volume, so that the quotient (PV/T) remains unaltered. This is demonstrated in Figure 1.6.



Figure 1.6 *P-v-T* surface for an ideal gas, showing the isothermals, isobars and isochores. Plot of Equation 1.9.

Example 1.2

A given mass of gas occupies 240 mL at 15°C and 1 atm. At what temperature will the volume be 360 mL, pressure remaining the same?

Solution

Using the Charles's law we write

 $\frac{T}{360 \text{ mL}} = \frac{288 \text{ K}}{240 \text{ mL}}$ $T = \frac{(288 \text{ K})}{(240 \text{ mL})}(360 \text{ mL})$ T = 432 K

 \Rightarrow

 \Rightarrow

Test Problem 1.2

A balloon is inflated to a volume of 1 L at room temperature (27°C) and atmospheric pressure. To what volume it will shrink if it is kept inside a refrigerator, at the same pressure. The temperature inside the refrigerator is -3° C. [Ans. 900 mL]

Example 1.3

A given mass of a gas occupies 11.2 L at 0°C and 1 atm. What will be the final pressure if it is expanded to 22.4 L by heating it to 100°C?

Solution

Using the combined gas [Eq. (1.9)]

$$P_{f} = \left(\frac{P_{i}V_{i}}{T_{i}}\right) \left(\frac{T_{f}}{V_{f}}\right) = \frac{(1 \text{ atm})(11.2 \text{ L})}{(273 \text{ K})} \frac{(373 \text{ K})}{(22.4 \text{ L})}$$

 \Rightarrow

$$P_f = 0.683 \text{ atm}$$

Test Problem 1.3

Starting out for a trip from the mountains (-5° C) you inflate your automobile tyres to a recommended pressure of 3×10^{5} Pa. As you drove into the seashore, the temperature rises to 38°C. Assuming that the volume of the tyre has increased by 2%, what would be the final pressure of the tyres? The manufacturer recommended that you should not exceed the pressure by 10%. Have you crossed the limit? If yes, by how much? [Ans: +13.67%]

1.2.5 The Ideal Gas Equation

The value of the constant K in Eq. (1.9) depends upon the mass and the nature of the gas; but, the introduction of the Avogadro's law makes a remarkable simplification.

Avogadro's Law Equal number of moles of all gases will occupy the same volume at a given temperature and pressure. (In the year 1811 !)

Mole: An Official Definition by IUPAC

A mole of a substance is defined as that amount of the substance which contains as many number of stable elementary entities as there are atoms in 0.012 kg of C-12 isotope. An essential feature to note is that, it is not just a number but, a quantity of a substance. Recently, the 'mole' has been included as one of the fundamental units of our measurements. It is the unit for measurement of the amount of the substance. The number of elementary units present in a mole is the Avogadro's number 6.022×10^{23} . We say, the Avogadro's constant $N_0 = 6.022 \times 10^{23}$ mol⁻¹.

Example 1.4

How many moles and molecules are there in 48 g oxygen?

Solution

The molecular weight of oxygen is 32; i.e., its molar mass is 32 g mol⁻¹. Therefore, the number of moles (n) in 48 g oxygen is

 $n = \frac{\text{mass}}{\text{molar mass}} = \frac{48 \text{g}}{32 \text{g} \text{mol}^{-1}} = 1.5 \text{ mol.}$

The number of oxygen molecules N present is then

 $N = 9.033 \times 10^{23}$

$$N = nN_0 = (1.5 \text{ mol}) (6.022 \times 10^{23} \text{ mol}^{-1})$$

 \Rightarrow

Test Problem 1.4

How many moles and atoms of sulfur are there in an 8 g sample of sulfur? After a controlled melting and re-crystallization, each set of eight sulfur atoms unite together to form a unit S_8 . If the entire sample turns into S_8 , then how many moles of S_8 will be formed? What will be the molar mass?

[Ans: 0.25 mol; 1.51×10^{23} atoms; 0.03125 mol; 256 g mol⁻¹]

Physical Chemistry

Hence, according to the Avogadro's law, for a mole of any gas, (PV/T) will be equal to a *universal constant R*, known as the gas constant. Its value will be the same for all gases. The general equation of state for any gas would be then

$$\frac{PV}{T} = R; \qquad \Rightarrow PV = RT \tag{1.10}$$

where V is the molar volume at the pressure P and temperature T. If v is the volume for nmoles, then the molar volume is V = v/n; we then write P(v/n) = RT

$$Pv = nRT \tag{1.11}$$

This is known as the ideal gas law. Another useful relation can be obtained by rearranging the above equation:

$$P = \frac{n}{v}RT = \left(\frac{W}{M}\right)\frac{RT}{v} = \rho\frac{RT}{M}$$

$$\rho = \frac{MP}{RT}$$
(1.12)

where *W* is the mass of the gas with molar mass *M* and ρ is the density.

This equation is of importance in

- (i) calculating the molar masses from density measurements and,
- (ii) determination of pressure high up in the altitudes by measuring the density and temperature.

Example 1.5

Find the density of NH_3 gas at 100°C and 1600 mmHg. Also calculate the number of molecules per unit volume.

Solution

The molar mass of NH_3 is 17 g mol⁻¹. Using Eq. (1.12)

$$\rho = \frac{MP}{RT} = \frac{(17 \text{ g mol}^{-1})(1600 \text{ mmHg})}{(0.082 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1})} \left(\frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \left(\frac{1}{373 \text{ K}}\right)$$
$$\rho = 1.17 \text{ gL}^{-1}$$

 \Rightarrow

 \Rightarrow

 \rightarrow

$$ho$$
 = 1.17 gL

If m be the mass of each molecule and n be the number of molecules per unit volume then.

$$\rho = mn$$

$$n = \frac{\rho}{m} = \frac{\rho}{M} N_0 = \frac{(1.17 \text{ g/} \text{L}^{-1})(6.022 \times 10^{23} \text{ mol}^{-1})}{17 \text{ g/mol}^{-1}}$$

 $n = 4.14 \times 10^{22}$ molecules L⁻¹

1.10

or,

 \Rightarrow

The Empirical Gas Laws

Test Problem 1.5

A cylinder filled with air is connected to a powerful vacuum pump to evacuate it and, the final pressure registered is 1×10^{-7} mm Hg (an excellent vacuum condition) at 27°C. Calculate the number of molecules present per cm³ of the cylinder. Can you find any of the postulates of the kinetic theory of gas with this result?

(Ans: 3.22×10^9 molecules cm⁻³)

..

1.2.6 The Absolute Zero of Temperature

The coefficient of volume expansion $\alpha = \left(\frac{1}{V}\frac{\partial V}{\partial t}\right)_p$, measured for a number of gases, *at* relatively high temperature and under extremely low pressure (this is the condition at which almost all gases behave ideally) has been found to be 0.0036609 (°C)⁻¹. Anticipating that V = 0 as $T \to O$ K, we make use of the equation, $V = V_0(1 + \alpha t)$, where *t* is in (°C) scale. This implies that, at the absolute zero of temperature

$$1 + \alpha t = 0 \qquad \Rightarrow \quad t = -\frac{1}{\alpha} = -\frac{1}{0.0036609} \circ C = -273.15 \circ C$$

The absolute zero is therefore – 273.15°.

Two different standard conditions are generally used to calculate different thermodynamical properties:

(i) **Standard Temperature and Pressure (STP):** The temperature is 0°C and the pressure 1 atm.

Under this condition, the molar volume of an ideal gas is 22.414 L.

(ii) Standard Ambient Temperature and Pressure (SATP): Here, the temperature chosen is 298.15 K and the pressure of 1 bar (that is, exactly 10⁵ Pa). Under this condition, the molar volume of an ideal gas is 24.787 L.

1.2.7 Evaluation of the Universal Gas Constant R

The most general definition of R is given by Eq. (1.11)

$$R = \frac{Pv}{nT}$$

So *R* has the dimensions of (pressure \times volume) divided by the (no. of moles \times Kelvin temperature). The dimensions of pressure are force \times (area)⁻¹ and area is (length)². Hence,

Pressure = force \times (length)⁻²

Physical Chemistry

Since the volume has the dimensions of $(length)^3$ and, the temperature is expressed in degrees, it follows from the above relations that

$$R = \frac{(\text{force})(\text{length})^{-2}(\text{length})^3}{(\text{degree})(\text{number of moles})} = \frac{(\text{force})(\text{length})}{\text{degree})(\text{number of moles})}$$

The product of force and length is energy; so

$$R = \frac{\text{energy}}{(\text{degree})(\text{number of moles})}$$
(1.13)

It is thus seen that the proper dimension of R is *energy per degree per mole*. The temperature is always expressed in kelvin but, the energy may be expressed as follows:

(i) Energy in Litre-Atmosphere

$$R = \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} = \boxed{0.08205 \text{ L atm } \text{K}^{-3} \text{mol}^{-1}}$$

- (ii) Energy in erg (CGS) or joule (SI) 1 atm is equivalent to 76 cm of Hg, whose density is 13.595 g cm⁻³ at 0°C. 1 atm = $h\rho g = (76 \text{ cm}) (13.595 \text{ g cm}^{-3}) (980.66 \text{ cm s}^{-2})$
- $\Rightarrow 1 \text{ atm} = 1.0132 \times 10^6 \text{ dyn cm}^{-2}; \text{ more accurately}$ $1 \text{ atm} = 1.01325 \times 10^6 \text{ dyn cm}^{-2}$

At 0°C and 1 atm, 1 mL = 1.000027 cm³. Therefore, in this system

$$R = \frac{(1.0132 \times 10^{6} \text{ dyn cm}^{-2}) (22414 \text{ mL})}{(1 \text{ mol})(273.15 \text{ K})} \left(\frac{1.000027 \text{ cm}^{3}}{1 \text{ mL}}\right)$$

or,
$$R = 8.314 \times 10^{7} \text{ erg K}^{-1} \text{ mol}^{-1}$$

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

or,
$$R = 8.314 \text{ Pa m}^{3} \text{ K}^{-1} \text{ mol}^{-1}$$

Again, 1 atm = 1.01325×10^5 Pa = 1.01325 bar (\because 1 bar = 1×10^5 Pa) Therefore, we also have

$$R = \frac{(1.01325 \text{ bar}) (22.414 \text{ dm}^3)}{(1 \text{ mol}) (273.15 \text{ K})}$$

or,

 $R = 8.314 \times 10^{-2} \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$

(iii) Energy in calorie

It is known from the joule's experiment that 1 cal = 4.184 J

The Empirical Gas Laws

 \Rightarrow

Therefore,

$$R = (8.314 \text{ J}^{-1} \text{ K mol}^{-1}) \left(\frac{1 \text{ cal}}{4.184 \text{ J}}\right)$$
$$R = 1.987 \text{ cal } \text{K}^{-1} \text{mol}^{-1} \text{ or, roughly}$$
$$R = 2 \text{ cal } \text{K}^{-1} \text{ mol}^{-1}$$

1.2.8a Mixture of Gases: Dalton's Law of Partial Pressure

When different gases are introduced into a container, they diffuse into one another and, form a homogeneous mixture. The total pressure exerted by this gas mixture *in a given volume at a fixed temperature* is given by the *Dalton's law of partial pressure*. The law states that *the total pressure of the mixture of gases is equal to the sum of the partial pressures of the constituent gases*. The partial pressure of each gas in the mixture is defined as the pressure the gas would exert if it alone had occupied the same volume as that of the mixture and, at the same temperature. Of course, in order for the law to be obeyed, no chemical reaction between the component gases may occur and, the component gases must behave ideally. Just to get an idea, let us take n_1 mole of a gas in a flask of a definite volume V at temperature T. The pressure exerted by the gas would be

..

$$p_1 = (n_1 RT)/V$$

If now, n_2 mole of a second gas be taken separately in the same flask (same V) at the same temperature T, the pressure would be

$$p_2 = (n_2 RT)/V$$

Similarly, if n_3 mole of another gas be taken separately in the same flask at the same temperature, the pressure would be

$$p_3 = (n_3 RT)/V$$

 n_t being the total number of moles of the mixture.

Now, if all these three gases of the same number of moles (i.e. n_1, n_2, n_3) are introduced into the same flask, then the pressure of the gas mixture P_{mix} (measured at the same T) is given by the Dalton's law as

$$P_{\text{mix}} = p_1 + p_2 + p_3$$

$$P_{\text{mix}} = (n_1 + n_2 + n_3) \frac{RT}{V} = \frac{n_t RT}{V}$$
(1.14)

 \Rightarrow

Physical Chemistry

Another form of the equation may be obtained as

$$\frac{p_1}{P_{\text{mix}}} = \frac{n_1}{n_t} = x_1; \text{ and } P_{\text{mix}} = \sum p_i$$
 (1.15)

where x_1 = the mole fraction of component 1 in the mixture; the sum is taken over all the components.

Example 1.6

A gas mixture consists of 10 g Ar (at. wt. 40) and 2 g He (at. wt. 4). The total pressure is 720 Torr. Calculate the partial pressure of the two components (1 Torr = 1 mmHg).

Solution

The number of moles of Ar, $n_{\rm Ar} = \frac{10 \text{ g}}{40 \text{ g} \text{ mol}^{-1}} = 0.25$ mole and that of He is,

$$n_{\text{He}} = \frac{\rho}{4 \text{ g' mol}^{-1}} = 0.5 \text{ mole.}$$
 The total number of moles in the mixture is:
 $n_t = n_{\text{Ar}} + n_{\text{He}} = 0.75 \text{ mole}$

The mole fractions of the two gases are:

$$x_{\rm Ar} = \frac{n_{\rm Ar}}{n_t} = \frac{0.25 \text{ mole}}{0.75 \text{ mole}} = \frac{1}{3}$$
$$x_{\rm He} = \frac{n_{\rm He}}{n_t} = \frac{0.5 \text{ mole}}{0.75 \text{ mole}} = \frac{2}{3}$$

The partial pressures of the two components are then

$$p_{\rm Ar} = x_{\rm Ar} P = \frac{1}{3}(720 \text{ Torr}) = 240 \text{ Torr}$$

 $p_{\rm He} = x_{\rm He} P = \frac{2}{3}(720 \text{ Torr}) = 480 \text{ Torr}$

and

Example 1.7

250 mL of gas *A* measured at 0.8 atm and 75 mL of another gas *B* at a pressure 8 atm, both measured at the same temperature, are introduced into a vessel of 2 L capacity. What is the total pressure of the mixture?

Solution

The partial pressure of gas *A* is the pressure the gas *A* would exert if it alone occupies the total volume of 2 L. By Boyle's law

$$p_A = \frac{(250 \text{ mL})(0.8 \text{ atm})}{(2000 \text{ mL})} = 0.1 \text{ atm}$$

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Similarly, the partial pressure of gas B is

$$p_B = \frac{(75 \text{ mL}) (8 \text{ atm})}{(2000 \text{ mL})} = 0.3 \text{ atm}$$

The total pressure, which is the sum of the two partial pressures is then

$$P = p_A + p_B = (0.1 + 0.3)$$
 atm = 0.4 atm

Example 1.8

A gas collected over water at 25°C becomes saturated with water vapour. The measured volume is 190 mL at a total pressure of 740 Torr. The vapour pressure of water at 25°C is 24 Torr. Calculate the volume the dry gas would occupy at a pressure of 760 Torr (1 atm).

Solution

The vapour pressure of water (24 Torr) will be the partial pressure of water vapour. So, the partial pressure of the dry gas is

$$p = (740 - 24)$$
 Torr = 716 Torr

This is the pressure of the dry gas when it occupies the entire volume of 190 mL. If this volume becomes V at 760 Torr, then by Boyle's law

V(760 mm Hg) = (716 mm Hg)(190 mL)

 \Rightarrow

$$V = 179 \text{ mL}$$

Assuming that the dry air contains 79% N_2 and 21% O_2 by volume, calculate the density of moist air at 25% and 1 atm pressure, when the relative humidity is 60%. The vapour pressure of water at 25°C is 23.76 mm Hg.

[*Hint:* Relative humidity is 60%; this means that the partial vapour pressure of water in the atmosphere is $p_{\rm H_2O} = (23.76 \text{ Torr}) (0.6) = 14.25 \text{ Torr.}$]

The sum of the partial pressures of O_2 and N_2 is then:

$$(p_{O_0} + p_{N_0}) = (760 - 14.25)$$
 Torr = 745.75 Torr.

The partial pressure of N₂ is then, p_{N_2} (745.75 Torr) (0.79) = 589.14 Torr and, that of O₂ is p_{O_2} = (745.75 Torr)(0.21) = 156.61 Torr. The mole fractions of the gases are then:

$$\begin{split} x_{\rm H_2O} &= \frac{14.25}{760} = 0.019; \quad x_{\rm N_2} = \frac{589.14}{760} = 0.775; \\ x_{\rm O_2} &= \frac{156.61}{760} = 0.206 \ \ ({\rm check\ that}, \, x_{\rm H_2O} + x_{\rm O_2} + x_{\rm N_2} = 1). \end{split}$$

The molar mass of air is then

$$\begin{split} M_{\rm air} &= 0.019(18~{\rm g~mol^{-1}}) + 0.775~(28~{\rm g~mol^{-1}}) + 0.206(32~{\rm g~mol^{-1}}) \\ M_{\rm air} &= 28.6~{\rm g~mol^{-1}} \end{split}$$

Then density is

$$\rho = \frac{MP}{RT} = \frac{(28.6 \text{ g mol}^{-1})(1 \text{ atm})}{(0.082 \text{ L atm} \text{ K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 1.17 \text{ gL}^{-1}$$

1.2.8b The Concept of Partial Pressure is not Just Mathematical; It has a Physical Significance.





It is a well known fact that $H_2(g)$ can pass through a palladium foil but, the others cannot. The mechanism for this passage of $H_2(g)$ through the palladium foil is very much intersecting; but here, we want to focus to another phenomenon, which would give us the realization that the concept of partial pressure of a component in a gas mixture is really a reality.

Consider Figure 1.7a, where a cubical box of a fixed volume V and, at a fixed temperature T is taken. The box is first filled up with $H_2(g)$ at 1 atm. As shown in Figure 1.7a, a manometer is attached to the box; the inside mouth being sealed with a thin Pd-foil. The other end is open to the atmosphere (1 atm).

As $H_2(g)$ can pass though the Pd-foil, at constant temperature, the equilibrium of $H_2(g)$ across the Pd-foil demands, equality of the pressure of $H_2(g)$; both of them are 1 atm. The height of the levels of Hg in the two limbs of the manometer will be the same (Figure 1.7a).

Some volume of $N_2(g)$ is then introduced into the same vessel (volume is fixed), at the same fixed temperature T, at 1 atm pressure. $N_2(g)$ cannot pass through the Pd-foil. Amazingly, it is found that, the heights of the Hg level in the two limbs remain the same; nothing changes.

1.16

 \Rightarrow

The Empirical Gas Laws

The reason is very clear; to attain the equilibrium at a fixed temperature, the partial pressure of $H_2(g)$ inside the box must be equal to the pressure of $H_2(g)$ on the other side of the Pd-foil; although the total pressure of the mixture is now 2 atm.

This proves convincingly that the concept of partial pressure of a component in a mixture is really a reality.

This physical concept, which is a reality, about the partial pressure of a component gas in a mixture of gases, I have found in the famous book of *Physical Chemistry* by Gilbert W. Castellan (3rd edition); slightly I have changed the methodology; nevertheless, I advise all the readers of this work to go through what has been written there.

1.2.8c Amagat's Law of Partial Volume

This law, which is very similar to the Dalton's Law of partial pressure, states that *the total volume of a mixture of non-reacting gases* is the sum of the *partial volumes* of the constituents of the mixture, at a fixed temperature, i.e.,

$$V = v_1 + v_2 + v_3 + \dots = \sum v_i$$

where V is the total volume of the mixture and v_i is the partial volume of the constituent 'i'. The partial volume *i* of a constituent 'i' is defined as the volume occupied by the pure constituent 'i' at the total pressure and temperature of the mixture.

From the ideal gas equation of state, we have

 $v_i = x_i V$

$$v_1 = n_1 \frac{RT}{P}; v_2 = n_2 \frac{RT}{P} \cdots$$
 etc,

where n_1, n_2, \dots are the number of moles of the components 1, 2, \dots respectively. Therefore,

$$(v_1 + v_2 + \cdots) = (n_1 + n_2 + \cdots) \frac{RT}{P} = n \frac{RT}{P} = V$$
 (1.16)

n being the total number of moles of the gases in the mixture; V is the total volume of the mixture. Moreover,

$$v_1 = n_1 \frac{RT}{P} = \frac{n_1}{n} V \implies v_1 = x_1 V$$
 (1.17)

and, similarly,

It is noteworthy that these equations are exactly equivalent to the equations of partial pressure.

Example 1.9

A container of volume 4.157×10^{-3} m³ maintained at 300 K contains 1.4×10^{-2} kg of N₂ and 3.2×10^{-2} kg of O₂ (it is assumed that at this temperature of 300 K, N₂ and O₂ do not react). Calculate the mole fraction of each gas in the mixture, their partial pressures and, the total pressure of the gas mixture.

(1.18)

Solution

Number of moles of N₂,
$$n_{N_2} = \frac{W_{N_2}}{M_{N_2}} = \frac{1.4 \times 10^{-2} \text{ kg}}{28 \times 10^{-3} \text{ kg mol}^{-1}} = 0.5 \text{ mole}$$

Number of moles of O₂,
$$n_{O_2} = \frac{W_{O_2}}{W_{O_2}} = \frac{3.2 \times 10^{-2} \text{ kg}}{32 \times 10^{-3} \text{ kg mol}^{-1}} = 1 \text{ mole}$$

Total number of moles in the gas mixture is then

$$n_{\rm T} = n_{\rm N_2} + n_{\rm O_2} = 1.5$$
 mole

The mole fractions of the gases are then

$$x_{N_2} = \frac{n_{N_2}}{n_T} = \frac{0.5}{1.5} = \frac{1}{3}; \ x_{O_2} = \frac{n_{O_2}}{n_T} = \frac{1}{1.5}$$

Check that: $x_{N_2} + x_{O_2} = 1$.

The total pressures of the mixture is

$$P_{T} = n_{T} \frac{RT}{V} = \frac{(1.5 \text{ pxol}) (0.082 \text{ L} \text{ atm } \text{K}^{-1} \text{ pxol}^{-1}) (300 \text{ K})}{(4.157 \times 10^{-3} \text{ px}^{3}) \left(\frac{10^{3} \text{ L}}{1 \text{ px}^{3}}\right)}$$

 \Rightarrow

 $P_T = 8.88 \text{ atm}$

The corresponding partial pressure are then:

$$P_{N_2} = x_{N_2} P_T = \frac{1}{3} \times 8.88 \text{ atm} = 2.96 \text{ atm}$$
$$P_{O_2} = x_{O_2} P_T = \frac{1}{1.5} \times 8.88 \text{ atm} = 5.92 \text{ atm}$$
$$\text{Total pressure} = 8.88 \text{ atm}.$$

and

This problem is an application of Dalton's law of partial pressure.

Example 1.10

 1.4×10^{-2} kg of N₂ and 3.2×10^{-2} kg of O₂, each taken at 1 atm and 300 K, are mixed together, so that the pressure of the mixture is also 1 atm and temperature 300 K. Calculate the partial volume of the components, the total volume, and the mole fraction of the components.

The Empirical Gas Laws

Solution

The number of moles of N₂, $n_{\rm H_2} = \frac{1.4 \times 10^{-2} \text{ kg}}{2.8 \times 10^{-3} \text{ kg mol}^{-1}} = 0.5 \text{ mole}$

at 1 atm and 300 K.

The number of moles of O₂,
$$n_{O_2} = \frac{3.2 \times 10^{-2} \text{ kg}}{32 \times 10^{-3} \text{ kg mol}^{-1}} = 1 \text{ mol}$$

at 1 atm and 300 K.

The partial volume of N_2 is

$$v_{\rm N_2} = n_{\rm N_2} \frac{RT}{P} = \frac{(0.5 \text{ mol})(0.082 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{1 \text{ atm}}$$

 \Rightarrow

$$v_{\rm N_2} = 12.3 \, {\rm L}$$

The partial volume O_2 is

$$v_{0_2} = n_{0_2} \frac{RT}{P} = \frac{(1 \text{ prof})(0.082 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{1 \text{ atm}}$$

 \Rightarrow

$$v_{0_2} = 24.6 \text{ L}$$

According to the law of partial volume, the total volume

 $V_t = (v_{N_2} + v_{O_2}) = (12.3 \text{ L} + 24.6 \text{ L}) = 36.9 \text{ L}$

The mole fractions are then [using Eq. (1.18)]

$$x_{\rm N_2} = \frac{v_{\rm N_2}}{v_t} = \frac{12.3 \ \text{L}}{36.9 \ \text{L}} = 0.333$$

and

The sum of the x_{N_2} and x_{O_2} is 0.333 + 0.667 = 1 This problem is an application of the Amagat's Law of partial volume.

(Students are advised to compare and study Examples 1.9 and 1.10.)

Example 1.11

 2×10^{-2} kg of H₂ and 3.2×10^{-2} kg O₂ are taken in a closed vessel of 1×10^{-2} m³ vessel, at 200°C. Calculate the total pressure of the mixture. If a spark ignites the mixture, what will be the final pressure?

$$x_{O_2} = \frac{v_{O_2}}{v_t} = \frac{24.6 \ \text{L}}{36.9 \ \text{L}} = 0.667$$

Solution

The number of moles of H₂,
$$n_{\text{H}_2} = \frac{2 \times 10^{-2} \text{ kg}}{2 \times 10^{-3} \text{ kg mol}^{-1}} = 10 \text{ mole}$$

The number of moles of
$$O_2$$
, $n_{O_2} = \frac{3.2 \times 10^{-2} \text{ kg}}{32 \times 10^{-3} \text{ kg mol}^{-1}} = 1 \text{ mole}$

The total number of moles of gases in the mixture is then $n_T = (10 + 1) 11$ moles.

The mol-fraction of H₂,
$$x_{H_2} = \frac{n_{H_2}}{n_T} = \frac{10 \text{ prof}}{11 \text{ prof}} = \frac{10}{11} = 0.9091$$

The mol-fraction of O₂, $x_{O_2} = \frac{n_{O_2}}{n_T} = \frac{1 \text{ mol}}{11 \text{ mol}} = \frac{1}{11} = 0.0909$

So that $x_{\rm H_2} + x_{\rm O_2} = 1$

The total pressure is

$$P_T + P_{H_2} + P_{O_2} = (n_{H_2} + n_{O_2}) \frac{RT}{V}$$

$$= (10 + 1) \mod \frac{(8.314 \text{ J K}^{-1} \mod^{-1}) (473 \text{ K})}{1 \times 10^{-2} \text{ m}^3}$$

$$= \frac{10 \times 8.314 \text{ Nm} (473)}{1 \times 10^{-2} \text{ m}^3} + \frac{1 \times (8.314 \text{ Nm}) (473)}{1 \times 10^{-2} \text{ m}^3}$$

$$\Rightarrow P_T = (3.93 \times 10^6 \text{ Nm}^{-2}) + (0.393 \times 10^6 \text{ Nm}^{-2})$$

$$P_T = 4.323 \text{ Pa}$$

The partial pressures are then: $p_{\rm H_2} = 3.93 \times 10^6$ Pa and, $p_{\rm O_2} = 0.393 \times 10^6$ Pa On sparking, the reaction which takes place is

$$2 \text{ H}_2 + \text{O}_2 \rightarrow 2 \text{ H}_2\text{O}$$

All the three constituents are in the gas phase, since the temperature is 200°C.

According to our problem, 1 mole of O_2 will react with 2 moles of H_2 ; producing 2 moles of H_2O and 8 moles of H_2 will remain unreacted. Therefore, the total number of moles of gases ($H_2(g)$ and $H_2O(g)$) is (8 + 2) = 10 mole

The final pressure is then:
$$P_f = \frac{nRT}{V} = \frac{(10 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(473 \text{ K})}{1 \times 10^{-2} \text{ m}^3}$$

 $\Rightarrow P_f = 3.93 \times 10^6 \text{ Pa}$

1.2.9 Diffusion of Gases: Graham's Law

The tendency of any substance to spread uniformly throughout the space available to it is called *diffusion*. Diffusion is exhibited by gases, liquids and, even by solids; but it is most rapid for gases. If a wide-mouthed jar of hydrogen is placed mouth to mouth with a jar of oxygen, it will be found, after a short time, that the two gases spread uniformly throughout the two jars. And, this will happen irrespective of whether the lighter gas is at the top or at the bottom. It is true that gravity has some influence on this distribution but, the effect is quite negligible unless a long column of gas, e.g., the atmosphere, is considered. A very similar process is the passage of the molecules of a gas through porous media or through small holes; this is *effusion*.

The law governing such diffusion or effusion was first stated by T. Graham (1829). The law states that at constant temperature and pressure, the rate of diffusion (or effusion) varies inversely as the square root of the density or the molar mass of the gas. If r_1 and r_2 represent the rates of diffusion of two gases under a given condition of P and T, whose densities are ρ_1 and ρ_2 , respectively, then

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$
(1.19)

..

As seen in Eq. (1.12), at a given P and T, the density $\underline{\rho}$ is directly proportional to the molar mass of the gas. Equation (1.19) may therefore, also be written as

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$
(1.20)

where M_1 and M_2 are the molar masses of the two gases. Equations (1.19) and (1.20) also reflect that lighter molecules will diffuse more rapidly than heavier gases. This fact was utilized in the separation of isotopes of different elements. The greatest success has been achieved in the separation of isotopes of hydrogen. The ratio of the rates of diffusion of hydrogen to deuterium is $\sqrt{2}:1$. It is also being said that the separation of $\binom{235}{92}u$ and $\binom{238}{92}u$ in the making of the atomic bombs had been done by this method of diffusion.

Example 1.12

The time required for a given volume of N_2 to effuse through an orifice is 35 s. Calculate the molar mass of a gas, an equal volume of which requires 50 s to effuse through the same orifice under identical conditions.

Solution

Let the volume of the gas that effuses be v. Then, according to the Graham's law

$$\frac{(v/35 \text{ s})}{(v/50 \text{ s})} = \sqrt{\frac{M}{28 \text{ g mol}^{-1}}}$$
$$M = 57.14 \text{ g mol}^{-1}$$

 \Rightarrow
Test Problem 1.6

The time required for a definite volume of oxygen to effuse through an orifice was found to be 135 s. Under exactly the same conditions, the same volume of another gas took 236 s to pass through. What is the molecular weight of the gas? (Ans: 97.8)

Example 1.13

A teacher enters a class room from the front door while a student from the back door. There are fifteen (15) equidistant rows of benches in the class room. The teacher releases N_2O , the laughing gas, from the first row, while the student releases the weeping gas, $C_6H_{11}OBr$ (Mol. wt 179) from the last row. At which row, the students will starts laughing and weeping simultaneously?

Solution

From the law of diffusion

$$\frac{(rate)_{N_2O}}{(rate)_{C_6 H_{11}OBr}} = \sqrt{\frac{179}{44}} \approx 2$$

Therefore N_2O diffuses at a rate twice as that of $C_6H_{11}OBr$.

Let n be the number of row from the front where the students laugh and weep simultaneously, then

$$\frac{n}{15-n} = 2 \quad \Rightarrow n = 30 - 2n \quad \Rightarrow 3n = 30$$

and finally, n = 10.

1.2.10 Limiting Density

From the equation of state of an ideal gas we have Eq. (1.12)

$$M = \frac{\rho}{P} RT$$

For a given gas at a fixed *T*, it is expected that the ratio (ρ/P) should be a constant. Experiments however, showed that, for any gas the ratio (ρ/P) varies with pressure at a fixed *T*. This is due to the non-ideality of the gases. Such a plot is shown for NH₃ in Figure 1.7, at 273.15 K. It is found that at pressure below 1 atm, the plot is very close to a straight line. This behaviour has also been observed for almost all gases. Hence, the line can be extrapolated to P = 0. In this limit, the gas behaves ideally. From Figure 1.7, it is found that for NH₃ at 273.15 K (0°C)

$$\lim_{P \to 0} \left(\frac{\rho}{P} \right) = 0.75988 \text{ g } \text{L}^{-1} \text{ atm}^{-1}$$

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Figure 1.7 Extrapolation of gas densities

Using the standard value of $R(0.08205 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1})$ and Eq. (1.12), we find

$$M = (0.75988 \text{ g } \text{L}^{-1} \text{ atm}^{-1})(0.08205 \text{ L atm} \text{ K}^{-1} \text{ mol}^{-1})(273.15 \text{K})$$
$$M = 17.03 \text{ g mol}^{-1}$$

 \Rightarrow

$$I = 17.03 \text{ g mol}^{-1}$$

which gives the accurate molar mass of ammonia. This method of determining the molecular weight is known as the *method of limiting density*.

Relative Density (Vapour Density) 1.2.11

The density of a gas measured relative to that of H₂ at a given P and T is called its relative density (older name is vapour density).

The relative density of gas $D = \frac{\rho}{\rho_{H_2}}$, where ρ and ρ_{H_2} are, respectively, the densities of the

gas in question and that of H_2 (both being measured under the same conditions of P and T). Using Eq. (1.12), we get

$$D = \frac{M}{M_{\rm H_2}} = \frac{M}{2}$$
(1.21)

where M and $M_{\rm H_2}$ are the molar masses of the gas and H₂, respectively. Note that D is dimensionless as it is a ratio of two molar masses.

1.2.12 Determination of Gas Density

There are various different methods for the determination of the density of gases. Most of them are now of historical interest. In the following, we shall look into some of them, which still are in use.

1.2.12.1 Dumas Method

Let us understand the method with an experimental result (27°C). A bulb made of glass is weighed (obviously filled with air); the weight is 52.30 g. Some amount of chloroform (whose density is to be measured) is taken, in the liquid phase, in the bulb and, is heated at least 20°C above the boiling point of the liquid (say, 100°C). It is to be ensured that, complete vapourisation took place and, which has expelled all the air from the bulb, so that, finally the bulb contains only the vapour of chloroform. The weight is taken (after cooling, with the bulb stoppered properly to 27°C). The weight of the bulb filled with the vapour is 52.96 g. Now the bulb is filled with water (27°C) and weighed. This weight is found to be 302 g. The atmospheric pressure is 752 Torr and, the density of air under ordinary conditions is 1.29 gL^{-1} . We now calculate the density of chloroform vapour as follows:

Mass of water in the bulb = mass of (bulb + water) – mass of (bulb + air) = (302 - 52.3) g = 249.7 g ≈ 250 g

Considering the density of water as 1 g cm⁻³, the volume is $v = (250 \text{ g})/(1 \text{ g cm}^{-3}) = 250 \text{ cm}^3$. The mass of air in the bulb is $(250 \text{ cm}^3) (1.29 \text{ gL}^{-1}) = 0.323 \text{ g}$. Therefore, the mass of the bulb is (52.30 - 0.323) g = 51.977 g.

The mass of the chloroform vapour in the bulb is then (52.96 - 51.977) g = 0.983 g. We now have the data set

$$\omega = 0.983$$
 g; $V = 0.25$ L; $T = 373$ K; $P = 752$ Torr.

Using the ideal gas Eq. (1.12)

 \Rightarrow

$$M = \frac{\omega RT}{vP} = \frac{(0.983 \text{ g})(0.082 \text{ }\text{L} \text{ atm } \text{K}^{-1} \text{ mol}^{-1})(373 \text{ }\text{K})}{(0.25 \text{ }\text{L})(752 \text{ Torr})} \times \frac{760 \text{ Torr}}{1 \text{ atm}}$$
$$M = 121.54 \text{ g mol}^{-1}$$

The molecular weight of chloroform is then calculated to be 121.54.

1.2.12.2 Victor-Meyer Method

In this method, a known amount of the sample (taken in the liquid phase) is vapourized completely in a closed flask and, an equal volume of air is expelled. This expelled air is then collected and the volume is then measured at the *corrected pressure* and, the temperature is recorded. Let us understand the method again with a problem.

In Victor-Meyer experiment, 0.241 g of chloroform expelled 47.9 mL air collected over water at 23°C. At this temperature, the vapour pressure of water is 18 Torr and, the

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pressure recorded is 782 Torr. The corrected pressure of chloroform vapour is (pressure recorded) – (v.p. of water) = (782 - 18) = 764 Torr using the same equation as before

$$M = \frac{\omega RT}{vP} = \frac{(0.241 \text{ g})(0.082 \text{ L} \text{ atm} \text{ K}^{-1} \text{ mol}^{-1})(296 \text{ K})}{(0.0479 \text{ L})(764 \text{ Torr})} \times \frac{(760 \text{ Torr})}{(1 \text{ atm})}$$
$$M = 121.48 \text{ g mol}^{-1}$$

 \Rightarrow

This is almost roughly the same value found as in the previous experiment. Students must also note that, the correction for the pressure would not have been necessary if the expelled air was collected over mercury.

1.2.13 Abnormal Vapour Density

1.2.13.1 Thermal Dissociation

It has been observed that in some vapour density measurements, the experimental values of the molecular weight are less than that expected and, the values decrease towards a limit as the temperature is raised. The vapour of N_2O_4 , NH_4Cl and PCl_5 , for example, gave molecular weights that approach *half the actual value* as the temperature is raised. This is clearly due to thermal dissociation. These gases undergo dissociation as

$$\begin{split} \mathrm{NH}_4\mathrm{Cl} &\rightleftharpoons \mathrm{NH}_3 + \mathrm{HCl}; \\ \mathrm{PCl}_5 &\rightleftharpoons \mathrm{PCl}_3 + \mathrm{Cl}_2 \\ \mathrm{N}_2\mathrm{O}_4 &\rightleftharpoons \mathrm{2NO}_2 \end{split}$$

In the vapour state, as the molecules of NH_4Cl (or PCl_5) dissociate, the total number of molecules increases and, at a fixed P and T, this increases the volume; but there is no change in the mass of the substance. This decreases the density and hence M, the mean molar mass. As the temperature is increased, the extent of dissociation increases and M decreases. At sufficiently high temperature, when the dissociation goes to 100 percent completion, M reaches at its lowest value.

Note that, it does not matter, whether the splitted molecules are similar or dissimilar. The question is, how many molecules are produced from a single molecule; the volume will increase proportionately. As an example, let one molecule of A splits up into n molecules of B (similar or dissimilar)

$$A \rightleftharpoons nB$$
 or, $A \rightleftharpoons n_1B_1 + n_2B_2 + ...; n_1 + n_2 + ... = n_1B_1 + n_2B_2 + ...; n_1 + n_2 + ... = n_2B_2 + ...; n_1 + n_2 + ... = n_2B_2 + ...; n_1 + n_2 + ... = n_2B_2 + ...; n_2B_2 + ...; n_2B_2 + ...; n_2B_2 + ... = n_2B_2 + ... = n_2B_2 + ...; n_2B_2 + ...; n_2B_2 + ... = n_2B_2 + ... = n_2B_2 + ...; n_2B_2 + ...; n_2B_2 + ... = n_2B_2 + ...$

Initial no. of mole 1

Number of moles at equilibrium are for $(1 - \alpha)$, for A, $n\alpha$ for B. the total number of moles at equilibrium is then $[1 + (n - 1)\alpha]$, where α is the degree of dissociation, i.e. fraction of the total number of molecular suffering dissociation. Let V be the molar volume at

0

the pressure and temperature of the experiment. If M_0 and M are the theoretical and experimental molar masses and, ρ_0 and ρ are the corresponding densities, then

$$\rho_0 V = \rho [1 + (n-1)\alpha] V \quad \text{with } \rho_0 = \frac{M_0 P}{RT} \text{ and } \rho = \frac{MP}{RT}$$

$$\Rightarrow \qquad \frac{\rho_0}{\rho} = \frac{M_0}{M} = 1 + (n-1)\alpha$$

$$\Rightarrow \qquad \alpha = \frac{(M_0 - M)}{(n-1)M} \quad \text{or} \quad \alpha = \frac{(\rho_0 - \rho)}{(n-1)\rho}$$
(1.22)

from which the degree of dissociation can be calculated. It is important to note that, whenever we find a low vapour density or, molecular weight, we suspect the case of dissociation. However, *the opposite is not true*. This is because, the decrease in the vapour density is due to an increase in the number of moles at equilibrium. If there is no change in the number of moles, e.g., when gaseous hydrogen iodide dissociates to form hydrogen and iodine vapour,

$$2HI \Longrightarrow H_2 + I_2$$

the volume, density and molecular weight remain unaffected (Why?).

Example 1.14

The vapour density of a sample of $\rm N_2O_4$ at 1 atm and 373 K is found to be 25. Calculate the equilibrium constant of the reaction

$$N_2O_4(g) \Longrightarrow 2NO_2(g)$$

Solution

The molecular weight of N_2O_4 is 92. So the relative vapour density should be (92/2) = 46. The experimental value, however, is 25. This indicates that the N_2O_4 molecules have dissociated partly into NO_2 . Let the degree of dissociation be α

$$N_2O_4(g) \Longrightarrow 2NO_2(g)$$

No. of moles initially 1 0

No. of moles at equilibrium $(1 - \alpha)$ 2α

Total number of moles at equilibrium is $(1 - \alpha + 2\alpha) = (1 + \alpha)$. Therefore

$$\frac{\rho_0}{\rho} = 1 + \alpha, \qquad \Rightarrow \quad \alpha = 0.84$$

1.26

=

_

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That is, 84 percent molecules have dissociated. The mole fractions are then:

$$x_{\mathrm{N_2O_4}} = \frac{(1-\alpha)}{(1+\alpha)} = \frac{0.16}{0.84}; \ x_{\mathrm{NO_2}} = \frac{2\alpha}{(1+\alpha)} = \frac{1.68}{1.84}$$

The partial pressures are then

$$p_{N_2O_4} = x_{N_2O_4}P = \frac{0.16}{1.84}(1 \text{ atm}) = \left(\frac{0.16}{1.84}\right) \text{atm}$$

and

$$p_{\text{NO}_2} = x_{\text{NO}_2} P = \frac{1.68}{1.84} (1 \text{ atm}) = \left(\frac{1.68}{1.84}\right) \text{atm}$$

The equilibrium constant for the thermal dissociation is then

$$K_P = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \left(\frac{1.68}{1.84}\right)^2 \left(\frac{1.84}{0.16}\right) atm$$

 \Rightarrow

$$K_P = 9.6$$
 atm

Example 1.15

In a vapour density experiment, 1.35 g N_2O_4 vapour was found to occupy a volume of 0.501 L at 45°C and 795 mm Hg. Calculate the fraction of the N_2O_4 molecules dissociated into NO_2 and, the equilibrium constant K_P of the thermal dissociation.

Solution

Considering the equilibrium

$$\begin{array}{c} N_2 O_4(g) \rightleftharpoons 2 NO_2(g) \\ \left(\frac{1.35}{92} \right) & 0 \end{array}$$

Initial no. of moles

No. of moles at equilibrium
$$\frac{1.35}{92}(1-\alpha) = 2\left(\frac{1.35}{92}\right)\alpha$$

Total number of moles at equilibrium is then

$$n_t = n_{\mathrm{N_2O_4}} + n_{\mathrm{NO_2}}$$

$$n_t = \left(\frac{1.35}{92}\right)(1+\alpha)$$
 mole

 \Rightarrow

Now using the ideal gas equation

$$Pv = n_t RT$$

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$$(795 \text{ pmm} \text{Hg}) \left(\frac{1 \text{ atm}}{760 \text{ pmm} \text{ Hg}} \right) (0.501 \text{ L}) = \left[\frac{1.35}{92} \times (1+\alpha) \text{ pmol} \right] \times (0.082 \text{ L} \text{ atm} \text{ K}^{-1} \text{ pmol}^{-1}) (318 \text{ K})$$

 $\alpha = 0.37$

That is, 37% dissociation took place. The students are now advised to calculate K_P following the same method given in Example 1.14. [Ans.: 0.664 (atm]

Test Problem 1.7

When PCl_5 vapour is heated in a closed flask to 200°C and 1.22 atm, the dissociation takes place by 42%. What are the mol-fractions and the partial pressures of the three components, PCl_5 , PCl_3 and Cl_2 ? Also calculate the equilibrium constant of the dissociation process. Also calculate the vapour density that would have been expected to get experimentally at this temperature.

(Ans: $x_{PCl_5} = 0.408$; $x_{PCl_3} = x_{Cl_2} = 0.296$ $p_{PCl_5} = 0.498$ atm; $p_{PCl_3} = p_{Cl_2} = 0.361$ atm $K_p = 0.262$ atm; $\rho = 73.42$

1.2.13.2 Molecular Association

There are examples where the molecules in the vapour phase associate pairwise to form dimers, which are in equilibrium with the monomers. More than two molecules may also associate, e.g., the formation of S_8 . Anyway, due to this kind of molecular association, the number of molecules in the vapour phase decreases (at a fixed *P* and *T*) and hence, the the volume decreases. The experimental vapour densities are then found to be more than the theoretical values. Formic acid, acetic acid and other carboxylic acids are well known examples forming dimers in the vapour phase.

Example 1.16

In a molecular weight determination, using acetic acid vapour, the experimental data suggests 100 g mol⁻¹ at 1 atm and 327°C. Calculate the degree of association of the molecules.

Solution

Let α be the degree of dimerization. Then the number of moles at equilibrium are: 2AcOH \longrightarrow (AcOH)₂

Initial no. of moles 1 0

 \Rightarrow

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No. of moles at equilibrium $(1 - \alpha)$ $\frac{\alpha}{2}$

Total number of moles at equilibrium is $\left(1-\alpha+\frac{\alpha}{2}\right) = \left(1-\frac{\alpha}{2}\right)$. If *V* be the molar volume at a given *P* and *T* and, ρ_0 and ρ are, respectively, the theoretical and experimental vapour densities, then

$$\rho_0 V = \rho \left(1 - \frac{\alpha}{2} \right) V$$

$$M_0 = M \left(1 - \frac{\alpha}{2} \right); \qquad \because \quad M \; \alpha \; \rho \text{ at a fixed } T \text{ and } P \left(\because \quad P = \frac{MP}{RT} \right)$$

$$\frac{M_0}{M} = \left(1 - \frac{\alpha}{2} \right)$$

 \Rightarrow

 \Rightarrow

 \Rightarrow

finally, $\alpha = 0.8$. The association is up to 80%.

 $\frac{60}{100} = 1 - \frac{\alpha}{2}$

Test Problem 1.8

A 0.1 g sample of acetic acid vapour was found to occupy 57.2 mL at 600 mm Hg pressure and 327°C. Calculate the degree of dimerisation at this pressure and temperature. Also calculate the apparent molecular weight and the relative vapour density of this acetic acid vapour.

(Ans.: *α* = 0.9; 109.09; 54.55)

PROBLEMS

- 1.1 6 g of C_2H_6 is taken in a closed container of volume 2.46 L at 2 atm and 27°C. Calculate the gas constant in cm³ atm K⁻¹ mol⁻¹, m³ bar K⁻¹ mol⁻¹ and JK⁻¹ mol⁻¹ units. [Ans.: 82 cm³ atm K⁻¹ mol⁻¹; 8.2 m³ bar K⁻¹ mol⁻¹; 8.31 JK⁻¹ mol⁻¹]
- **1.2** A cylinder fitted with a piston contains O_2 at 20°C and a pressure of 15 atm in a volume of 22 L. The piston is lowered, decreasing the volume of the gas to 16 L, and simultaneously raising the temperature to 25°C. Assuming ideal behaviour, calculate the final pressure of the gas. [Ans.: 21 atm]
- **1.3** Find the density of CO_2 gas at 77°C when confined by a pressure of 1 bar.

[Ans.: $1.53 \times 10^{-5} \text{ gL}^{-1}$]

1.4 At 0°C and 1000 mm Hg a given mass of N_2 occupies a volume of 1 L. At -100°C, the same mass of the gas under same pressure occupies a volume of

0.6313 L. Calculate the absolute zero in degree centigrade, and give reasons for the observed difference from the accepted value.

[*Ans.:* -271.2°C; the data at -100°C are not very reliable because a gas cannot be expected to behave ideally at as low as -100°C]

1.5 Calculate the pressure of the earth's atmosphere at a point where the barometer reads 76 cm Hg at 0°C and the acceleration of gravity g is 9.80665 ms^{-2} . The density of Hg at 0°C is $13.5951 \text{ g cm}^{-3}$ or $13.5951 \times 10^3 \text{ kg m}^{-3}$.

[Ans.: 101.325 kPa].

- **1.6** An ideal gas cannot be liquefied. Justify/Criticize.
- **1.7** In the derivation of PV = RT from the Boyle's law, the following steps may be followed:

(i)
$$PV = k_1$$
; (ii) $\frac{V}{T} = k_2$; (iii) $PT = k_3$

which step(s) is/are wrong?

[Ans.: (iii) is wrong]

[Ans.: 15.5 mol-percent]

1.8. From the relations between the variables for two ideal gases A and B, given below on the left, what can be concluded regarding the variables on the right?

	Given	Inference (>; = ; <)
(i)	Equal P, V, T ; $M_{\rm A} > M_{\rm B}$	$n_{\rm A} ? n_B$
(ii)	Equal P, V, ; $n_{\rm A} > n_{\rm B}$	$T_{ m A} ? T_B$
(iii)	Equal T, $n; P_{\rm A} > P_{\rm B};$	$V_{ m A} ~?~ V_B$
$[n_{\rm A} = n_{\rm B}; T_{\rm A} < T_{\rm B}; V_{\rm A} < V_{\rm B}]$		

1.9 A mixture of H_2 and O_2 is analyzed by passing it over hot copper oxide and, through a drying tube. H_2 reduces the CuO according to the equation

$$CuO + H_2 \rightarrow Cu + H_2O$$

oxygen then reoxidizes the Cu formed:

$$Cu + \frac{1}{2}O_2 \rightarrow CuO$$

100 cm³ of the mixutre measured at 25°C and 750 Torr yields 84.5 cm³ of dry oxygen measured under the same conditions of T and P after passage over CuO and the drying agent. What is the original composition of the mixture?

1.10 A vessel of volume 30 L contains ideal gas at temperature 0°C. After a portion of the gas has been let out, the pressure in the vessel decreased by $\Delta p = 0.78$ atm (the temperature remaining the same). Find the mass of the released gas. The density at 1.01325 atm is p = 1.3 gL⁻¹. [Ans.: 30 g]

- **1.11** A vessel contains a mixture of N_2 ($m_1 = 79$) and CO_2 ($m_2 = 11$ g) at a temperature T = 290 K and pressure 1 atm. Find the density of the mixture, assuming the gases to be ideal. [*Ans.*: 1.513 gL⁻¹]
- **1.12** A vessel of volume V = 7.5 L contains a mixture of ideal gases at a temperature T = 300 K; the number of moles of O_2 , N_2 and CO_2 are, respectively, 0.1, 0.2 and 0.3. Assuming the gases to be ideal, find:
 - (i) the pressure of the mixture, and
 - (ii) the mean molar mass of the mixture.

[Ans.: (i) 1.97 atm (ii) 36.67 g mol⁻¹]

- **1.13** Under what condition will a pure sample of an ideal gas not only exhibit a pressure of 1 atm but also a concentration of 1 mol L^{-1} ? [*Ans.:* 12.2 K]
- 1.14 Compare the times of diffusion through a given orifice, and under the same condition of P and T, of the gases H_2 , NH_3 , CO_2 relative to that of N_2 .

$$\left\lfloor \frac{t_{\rm H_2}}{t_{\rm N_2}} = 0.268 \ ; \frac{t_{\rm NH_3}}{t_{\rm N_2}} = 0.779 \ ; \frac{t_{\rm CO_2}}{t_{\rm N_2}} = 1.254 \right\rfloor$$

[*Ans.*: Degree of dissociation, $\alpha = 0.84$]

2 CHAPTER THE OF GASES

2.1 INTRODUCTION

Kinetic theory is a microscopic science, where an endeavour is made to explain the behaviour of gases by recognising that, a sample of a gas is made up of a very many numbers of elementary particles—atoms/molecules, obeying certain basic laws.

Clearly, the subject is extremely difficult to analyse. This is because, we do not know how the molecules look like, what are the forces operating between them and, what kind of laws they obey during their motion. One thing is clear: there is a *tremendous irregularity* in the motion of these elementary particles and, they are *fantastic in numbers*. These *two characteristics* will therefore require an extensive use of *probability and statistics* in the development of the theory.

A Brief History of Kinetic Theory of Gases

Although the idea of elementary particles and their ceaseless motion dates back to 450 B.C. due to Leukippos and Demokritos, Daniel Bernoulli may be honoured as the father of the kinetic theory. He first deduced a law, that today we know as the Boyle's law, by considering that, a gas is composed of an innumerable number of particles in ceaseless motion; between which no forces act and, which gives rise to the pressure of the gas in a container by the bombardment of the particles on the wall of the container (1738). For over hundred years Bernoulli's work was left ignored. J.J. Waterstone, a school teacher in Bombay (India) sent a paper to the Royal Society in 1845, explaining some concepts of the kinetic theory, but was not deemed worthy for publication until, Lord Rayleigh rediscovered it in 1892.

However, when Joule introduced the concept firmly that *heat is a hidden disordered motion of the atoms/molecules*, the idea of kinetic theory started receiving its acceptance. Thereafter, an excellent team of mathematical physicists: Clausius, Maxwell and Boltzmann led to an excellent development of the theory. Nevertheless, the development of kinetic theory had faced a strong opposition and, it is said that, the Boltzmann's suicide by drowning himself in 1906, came from the depression due to the attacks on the truth of the kinetic theory, which he could not retort.

Finally, the kinetic theory of gas considers that the atoms or molecules obey newtonian mechanics. However, since the elementary particles actually behave quantum mechanically, the theory is not fundamentally correct. For example, it cannot explain the temperature dependence of the heat capacity of gases. Nevertheless, the theory is excellent in explaining other properties, e.g. pressure, temperature, diffusion, etc.

2.2 BASIC ASSUMPTIONS OF KINETIC THEORY OF GASES

The basic materials behind the building up of the model are:

- 1. A gas consists of a very many number of molecules, considered as *perfectly elastic hard spheres*.
- 2. The molecules are in a state of complete molecular chaos, in which they move erratically along all possible directions, with all possible speeds from zero to infinity.
- 3. These movements are in straight lines (in the absence of any external force, like gravity), which are occasionally broken by collisions between themselves and, with the walls of the container. These collisions are all *perfectly elastic*, i.e., in which the *conservation of momentum as well as the kinetic energy hold*.
- 4. In the steady state, the collisions between the molecules do not affect the molecular density, i.e., the number of molecules per unit volume is uniform everywhere and, remains the same with time.
- 5. The distance traversed by a molecule between two successive collisions is called the free path. It is assumed that the size of the molecules is negligible in comparison to the *mean free path*. The molecules are therefore regarded as a point masses.
- 6. The time during which a collision lasts is negligible in comparison to the time required by a molecule to traverse the mean free path.
- 7. The forces between the molecules are neglected entirely, so that the energy of a gas is totally kinetic.
- 8. During the bombardment of the molecules on the wall of the container, a certain momentum is poured on the wall. The *net momentum poured normally*—*per unit area of the wall per second* is defined as the *pressure* of the gas.
- 9. The molecules move with different speeds, and hence, with different translation kinetic energies. The average translational kinetic energy of the molecules of a sample of gas is directly proportional to the kelvin temperature of the gas.

2.3 EXPERIMENTAL EVIDENCE IN SUPPORT OF THE KINETIC THEORY

That the molecules of a gas are in a state of complete erratic (i.e., random) movement can be supported by numerous experiments, of which the most conclusive evidence comes from the study of *Brownian motion*. While studying microscopic life, Robert Brown in 1827, noticed the fine particles of plant pollens jiggling all around in the water he was looking at through a microscope. These motions are perpetual and spontaneous. He correctly asserted that these motions are not living, and is not due to any chemical or electrical action. You can also observe this motion in smoke or dust particles through a microscope. The motion becomes more vigorous as you decrease the viscosity of the medium or increase the temperature. Later it was realised that the motions were due to an imbalance of force exerted by the solvent molecules on the solute particles. Thus, the incessant and random motion of the fundamental particles in a system becomes very much clear and, the motion of the molecules of a gas is exactly similar to this. Hence, all the laws of kinetic theory of gases are applicable to the Brownian particles and in fact, Einstein in 1905 developed a theory of Brownian motion on the basis of the kinetic theory of gases, which had also been verified by Perrin in 1908.

2.4 SOME CRITICS ON THE POSTULATES OF THE KINETIC THEORY

1. The assumption of perfectly elastic collision is necessary in order to account the following fact:

When an ideal gas is heated isothermally and reversibly, the heat absorbed by the gas is completely converted into the work of expansion by the gas, and when it is compressed back to the initial state, again isothermally and reversibly, exactly the same amount of work is destroyed and converted into heat. If the collisions were not perfectly elastic, then some of the kinetic energy of the molecules gained on heating, would lost in deforming the molecules and, this energy could not be given back into heat when the system is cooled. This is obviously a simplifying assumption and corresponds to reality only as a rough approximation.

2. Certainly, there are gravitational forces between the molecules (pair wise); these forces are very much weak in comparison to the kinetic energy. For example, the

average kinetic energy of the gas molecules at 300 K is about $10^{-21} J \left(\frac{3}{2} kT\right)$,

whereas the potential energy of gravitation between two H₂ molecules in contact (r = 1 Å) is about $10^{-54} \text{ J} (-Gm^2/r; G = 6.67 \times 10^{-11} \text{ Nm}^2 \text{ kg}^{-2}; m = 3.35 \times 10^{-27} \text{ kg}; r = 1 \times 10^{-10} \text{ m}).$

Gravitational force is
$$\frac{Gm^2}{r^2}$$
 Gravitational Potential Energy, $V = -\frac{Gm^2}{r}$
 $m_{H_2} = \frac{2.016 \times 10^{-3}}{6.023 \times 10^{23}} \text{ kg} \begin{vmatrix} G = 6.67 \times 10^{-11} \text{ Nm}^2 \text{kg}^{-2} \\ = 3.35 \times 10^{-27} \text{ kg} \end{vmatrix} = G = 6.67 \times 10^{-11} \text{ Nm}^2 \text{kg}^{-2}$
 $r = 1 \text{ Å} = 1 \times 10^{-10} \text{ m}$
∴ GPE, $V = -\frac{Gm^2}{r} = -\frac{(6.67 \times 10^{-11} \text{ Nm}^2 \text{kg}^{-2})(3.35 \times 10^{-27} \text{ kg})^2}{10 \times 10^{-10} \text{ m}}$
 $\Rightarrow V = -7.5 \times 10^{-54} \text{ J}$

Average translational K.E. =
$$\frac{3}{2}kT$$
 = 1.5 (1.38 × 10⁻²³ JK⁻¹)(300 K) or, = 6 × 10⁻²¹ JK⁻¹

Comparing these two results we can safely ignore the potential energy of the gas. However, the intermolecular forces of attraction are much greater and, the corresponding potential energy, although small under ordinary condition, becomes of the order of the kinetic energy near or below the critical temperature. These forces are neglected in the postulates by definition, which is again a simplifying assumption.

2.5 THE KINETIC INTERPRETATION OF THE PRESSURE OF A GAS

2.5.1 Definition

We know that a gas exerts pressure. Here, we want to know how is this pressure developed and, how much is that.

To analyse this, we take a gas in a cylindrical box, at one end of which there is a frictionless piston, which can move along either direction (Figure 2.1). There are a lot of molecules in perpetual erratic motion and, very often they hit the piston. There is, therefore, a continuous bombardments on the piston. What is the result then? Each time the piston receives a certain amount of momentum for each collision, it picks up speed. Let there be nothing on the other side of the piston, i.e., a vacuum outside.



Figure 2.1 *F* is the normal force required to hold the piston from moving out. The pressure of the gas *P* is then *F*/*A*, where *A* is the area of the piston.

Receiving a certain amount of momentum from each collision, the piston starts moving out of the box. In order to just keep it from moving out, we must therefore hold the piston with a certain force F. The magnitude of the force applied normally per unit area of the piston which is just sufficient to keep the piston at its position is defined as the pressure (P) of the gas.

2.5.2 Calculation

Let us first calculate how much momentum is poured normally per second on the wall by the bombarding molecules.

Let us fix-up the reference frame so that the x-axis of the coordinate system is perpendicular to the piston (Figure 2.1). If C_x be the velocity component of a molecule along the x-axis, then as it hits, the piston receives a momentum mC_x . What then? You can think that for a very short period of time, say 1 ns, the molecule is brought to rest and then, it bangs off the piston again with the speed C_x along the x-axis. During this return, the piston again receives mC_x momentum for the molecule. This thing you can realise if you press a rubber ball against a hard surface and, leave it; it bounces off. So the momentum the piston receives per collision is $2mC_x$. Now, how many collisions take place per second? Let n be the number of molecules per unit volume. To calculate how many molecules hit the piston in one second, we realise that the molecules which are beyond a distance C_x from the piston cannot reach in one second. So, all the molecules which are within a distance C_x from the piston will hit in one second (Figure 2.2). If the area of the piston is A, then all the molecules in the section of the volume C_xA will reach the piston in one second. The number is nAC_x . So, the total momentum imparted on the piston per second is



Figure 2.2 Only the molecules in the grey portion can reach the wall *WW* ' in one second; those in the white region cannot reach the wall in one second.

Force exerted = momentum change per second = $(2m C_x) (n A C_x) = 2m n A C_x^2$ The pressure (P) developed is then $P = \frac{F}{A} = 2m n C_x^2$ (2.1)

However, we have left one thing unnoticed; and that is, all the molecules are not moving with the same velocity component C_x . Let there be per unit volume, n_1 molecules with *x*-component velocity C_{x1} , n_2 molecules with C_{x2} and so on. So the pressure equation must be

$$P = 2m \left(n_1 C_{x1}^2 + n_2 C_{x2}^2 + \cdots \right)$$
(2.2)

Now, the average of C_x^2 is given by $\langle C_x^2 \rangle$,

where
$$\langle C_x^2 \rangle = \frac{n_1 C_{x1}^2 + n_2 C_{x2}^2 + \dots}{n_1 + n_2 + \dots} = \frac{\sum n_i C_{xi}^2}{\sum n_i} = \frac{\sum n_i C_{xi}^2}{n}$$

Physical Chemistry

$$\Rightarrow \qquad P = 2mn \langle C_r^2 \rangle$$

There is another point. In taking the average we have considered all positive C_x s (moving towards the piston) as well as all negative C_x 's (moving away from the piston). But, the force is developed on the piston only by, the molecules which are moving towards the piston. Due to the *isotropicity of the molecular movements*, we can correctly say that the pressure (P) is half (1/2) of the above expression, i.e.,

$$P = mn \left\langle C_x^2 \right\rangle \tag{2.3}$$

Now, there is nothing special along the x-direction. Molecules are also moving about back and forth (y direction) with mean squared velocity component $\langle C_y^2 \rangle$ and also up and down (z direction) with $\langle C_z^2 \rangle$. Again, due to the *isotropic movements*, we must have

$$\langle C_x^2 \rangle = \langle C_y^2 \rangle = \langle C_z^2 \rangle \tag{2.4}$$

and, if C be the velocity of a molecule in space, then since

$$\langle C^2 \rangle = \langle C_x^2 \rangle + \langle C_y^2 \rangle + \langle C_z^2 \rangle = 3 \langle C_x^2 \rangle$$
(2.5)

Using Eqs (2.4) and (2.5) in Eq. (2.3), we finally get

$$P = \frac{1}{3} mn \langle C^2 \rangle = \frac{1}{3} mn C_{\rm rms}^2$$

$$PV = \frac{1}{3} mN \langle C^2 \rangle = \frac{1}{3} mN C_{\rm rms}^2$$
(2.6)

or

where N is the total number of molecules contained in a container of volume V. Rewriting Eq. (2.6) in the form

$$P = \frac{2}{3} \frac{N}{V} \left\langle \frac{1}{2} m C^2 \right\rangle \tag{2.7a}$$

and realising that the average kinetic energy of the molecules is $\left\langle \frac{1}{2} \, m C^2 \right\rangle^1$, we find

$$PV = \frac{2}{3}U \tag{2.7b}^2$$

^{1.} The average translational kinetic energy of the molecules is not $\frac{1}{2}m\langle C\rangle^2$; it is $\frac{1}{2}m\langle C^2\rangle$. To

understand this, just write:
$$\varepsilon = \frac{1}{2} mc^2$$
, and then take the mean: $\langle \varepsilon \rangle = \frac{1}{2} m \langle C^2 \rangle$ or $\langle \varepsilon \rangle = \frac{1}{2} m C_{\text{rms}}^2$.

^{2.} For a mole of an ideal gas, we may write $U = \frac{3}{2}PV = \frac{3}{2}RT = N_o\left(\frac{3}{2}kT\right)$; the average translational

kinetic energy of the molecules is then $\langle \text{KE} \rangle_{\text{trans}} = \frac{3}{2} kT$. N_o is the Avogadro's constant and k is the Boltzmann constant.

where U is the total kinetic energy of translation of the molecules. Equation (2.6) may be considered as the fundamental equation of the kinetic theory of gases. On the left hand side of the equations we have the macroscopic parameters P and V which, relate with microscopic parameters m, N and $\langle C^2 \rangle$.

A few interesting points are listed below:

1. Thermodynamically we know that for *n* moles of a monoatomic ideal gas $U = n \cdot \frac{3}{2}RT$, which by using in Eq. (2.7) gives us the ideal gas equation

PV = n RT

- 2. For an ideal gas, the total kinetic energy of translation of the molecules U is a function of only T; there is no potential counterpart. So, *isothermally and reversibly* if an ideal gas is compressed, the work done on the gas is absorbed, but cannot be stored as U (as T is fixed); therefore, only the number of molecules per unit volume increases [cf. Eq. (2.6)], and therefore, the number of bombardments per unit area of the piston per second increases; this increases P.
- 3. If you take a sample of Li-vapour and a sample of an equal volume of uranium vapour at the same pressure, then their total translational kinetic energies are also equal. This means that the heavier uranium atoms move slowly than the lighter Li atoms.

2.6 SOME CRITICS ON THE PRESSURE EQUATION

1. Equation (2.6) has been derived with the assumption of perfectly elastic collision. So, what will be the fate of the equation if we take a gas where the collisions are not perfectly elastic?

To answer this, let us first take a monoatomic gas. In this case, the collisions had have to be perfectly elastic, for, if they were not, the piston would be heated up and, things would change. But eventually when equilibrium is attained, the collisions will be almost perfectly elastic. A gas does not cool down or, warm up on standing, provides support to the above discussion.

For a diatomic or triatomic molecule, *an inelastic collision* might decrease the translational kinetic energy and could turn up as the rotational and/or vibrational kinetic energy of the molecules; but the energy transfer can also take place in the reverse way, viz., from vibration into translation. Thus, the concept of perfectly elastic collision breaks down.

However, this does not invalidate the pressure equation. This is because the pressure has been calculated by taking the average over a many number of collisions and over all the molecules, which is also fantastic in number. This definitely will smoothe out the irregularities in the translation kinetic energies of the individual molecules after impact. That means, after collision some molecules will gain translational kinetic energy and the other will lose, and, on the average, no one neither gain nor loses any. Thus Eq. (2.6) still remains valid.

2. We have also assumed that the molecules do not collide with one another while they are on their way to hit a wall. Under condition of equilibrium, on the average, any deflection in the path of a molecule will be replenished by another collision which replaces the molecule.

2.7 WORK OF COMPRESSING A GAS

Here we want to understand from the kinetic theory point of view, the *PV* relation during a *reversible adiabatic compression of an ideal gas*, where there is *no heat exchange between the gas and its surroundings*. Our approach is therefore microscopic; later it will be proved macroscopically in thermodynamics.

Let us again consider a gas in a rectangular box as in Figure 2.1. Total force exerted by the molecules on the inner face of piston is PA. In order to maintain equilibrium, an external force of equal magnitude must also be applied on the piston from outside. But, if the external pressure applied on the piston is more than PA, the piston will move inward. Let us apply a pressure on the piston slightly more than the pressure P of the gas, so that the piston moves inward with a speed C', which is very small compared to the speed of the molecules. If C_x denotes the speed of the molecules along the x-axis, then with respect to the piston, a molecule hits the piston with the speed $(C_x + C')$ and, it also bounces off the piston with the same relative speed $(C_x + C')$. But a relative speed of $(C_x + 2C')$ speed of the molecules with respect to the inward moving piston of C' is equivalent to $(C_x + 2C')$ speed of the molecule with respect to the box. The increase in the kinetic energy of a molecule per collision with the moving wall is

$$\begin{split} \Delta (\mathbf{KE}) &= \frac{1}{2} m (C_x + 2C')^2 - \frac{1}{2} m C_x^2 \\ &= 2m \ C_x C' + 2m C'^2 \\ &= 2m \ C_x C' \bigg(1 + \frac{C'}{C_x} \bigg) \end{split}$$

Since $C' << C_x$ (to maintain reversibility), neglecting the second term we get $\Delta(\text{KE}) = 2m \ C_x C'$ per collision

The total kinetic energy change in time dt is therefore obtained by multiplying the above result by the total number of collisions during the same time dt; we get

Total change in the kinetic energy in time dt = $2m C_x C'(n C_x A) dt$ = $2 mn C_x^2 C' A dt$

2.8

and following the same procedure as before, to account for the different speeds of the molecules, we have

Total change in the kinetic
energy in time
$$dt$$
 = $2mn \frac{1}{2} \langle C_x^2 \rangle C'A dt$
= $\frac{1}{3} mn \langle C^2 \rangle C'A dt$
= $PC' A dt$ (2.8)
= $-PdV$ (:: dV is negative)

So we have the fundamental equation for a reversible adiabatic compression as $dU = -PdV \label{eq:update}$

Since dw = -PdV (no heat exchange), we can say that the increase in the energy of the gas is equal to the work done on the gas during a reversible adiabatic compression. It is also clear that if the speed of the piston were not too low so as to be neglected, i.e., if the compression were carried out irreversibly then, a greater amount of work would have been required than the reversible work; *or conversely*, a greater amount of work will be obtained from a *reversible expansion* than from an *irreversible expansion*.

Let us now derive the P-V relation during such a change. Equation (2.8) can be written as

$$d\left(N\frac{1}{2} m \langle C^2 \rangle\right) = \frac{1}{3} m \frac{N}{V} \langle C^2 \rangle C' A dt$$

realising that the total average translational kinetic energy is $N\left(rac{1}{2}\,m\,\langle C^2
angle
ight)$, where N is

the total number of molecules present in volume V. Using Eq. (2.7a), we find

$$d\left(\frac{3}{2}PV\right) = -PdV \qquad (\because C'Adt = -dV)$$

$$\Rightarrow \qquad \frac{3}{2}PdV + \frac{3}{2}VdP = -PdV$$

$$\Rightarrow \qquad \frac{5}{2}PdV + \frac{3}{2}VdP = 0$$

$$\Rightarrow \qquad \frac{5}{3}d\ln V + d\ln P = 0 \qquad [\text{multiplying by } \frac{2}{3} \text{ and dividing by } -PV]$$

$$\Rightarrow \qquad PV^{5/3} = \text{constant} \qquad (2.9)$$

If we use a standard result that the ratio of the two specific heats C_P and C_V is 5/3, i.e., $\gamma = 5/3$. Equation (2.9) therefore takes the form

$$PV^{\gamma} = \text{constant},$$

for a reversible adiabatic process with an ideal gas. This is excellent, because thermodynamically we can also prove this relation but, there we cannot see the internal machinery.

2.8 A DISTINCTION BETWEEN REVERSIBLE AND IRREVERSIBLE PROCESS

The basic idea is that if we want to compress the gas reversibly, C' must be made as small as possible. But if it is significant, the process will become irreversible.

In general, when C'/C_x is not negligible, the change in the kinetic energy in time dt can be written as

$$dU = \frac{1}{3} m \frac{N}{V} \langle C^2 \rangle C' \left(1 + \frac{C'}{C_x} \right) A dt \qquad \text{[from Eq. (2.8)]}$$

 \Rightarrow

$$dU = -P\left(1 + \frac{C'}{C_x}\right)dV \tag{2.10}$$

and, if the external pressure required to compress the gas $P_{\rm ext}$, then $P_{\rm ext}$ must be

1

$$P_{\rm ext} = P\left(1 \pm \frac{C'}{C_x}\right) \tag{2.11}$$

where the *negative sign is during expansion*, when the relative velocity of the molecule becomes $(C_x - C')$ instead of $(C_x + C')$. From Eq. (2.11), it is also clear that, if the process is to be conducted reversibly (i.e., $C'/C_x \approx 0$) then, the external and the internal pressures must be made virtually equal.

But if you want to compress irreversibly [the positive sign in Eq. (2.11)] an external pressure of magnitude greater than the internal pressure will be required ($P_{\text{ext}} > P$); and the difference ($P_{\text{ext}} - P$) increases as one increases the degree of irreversibility, i.e., to increase the speed of the piston C'. But, during irreversible expansion, the opposite thing will happen: P_{ext} is now less than P. Since the work is always given by $dw = -P_{\text{ext}} dV$, we find

during expansion: work is maximum in a reversible process. during compression: work is minimum in a reversible process.

2.9 THE KINETIC INTERPRETATION OF TEMPERATURE

Before introducing the concept of temperature, let us put some remark on the nature of collisions between two gas molecules. These are as follows:

- 1. The molecules will be assumed to be *smooth and perfectly elastic spheres*, i.e., *the kinetic energy* and *the momentum* of two colliding molecules *are conserved during a collision*.
- 2. If the centres of two colliding molecules are connected at the moment of collision by the 'Line of centres', the component of two velocities perpendicular to this line

remain unchanged, while the components along the line of centre after collisions are given by the expressions³,

$$C_{1f} = \frac{2m_2}{(m_1 + m_2)} C_{2i} + \frac{(m_1 - m_2)}{(m_1 + m_2)} C_{1i}$$
and
$$C_{2f} = \frac{2m_1}{(m_1 + m_2)} C_{1i} + \frac{(m_2 - m_1)}{(m_1 + m_2)} C_{2i}$$
(2.12)

3 Elastic collision between two molecules



Conservation of the momentum gives

$$\begin{split} m_1 C_{1i} + m_2 C_{2i} &= m_1 C_{1f} + m_2 C_{2f} \\ m_1 (C_{1i} - C_{1f}) &= m_2 (C_{2f} - C_{2i}) \\ & \dots (1) \end{split}$$

Conservation of the kinetic energy gives

$$\begin{aligned} &\frac{1}{2}m_1C_{1i}^2 + \frac{1}{2}m_2C_{2i}^2 = \frac{1}{2}m_1C_{1f}^2 + \frac{1}{2}m_2C_{2f}^2 \\ \Rightarrow & m_1(C_{1i}^2 - C_{1f}^2) = m_2(C_{2f}^2 - C_{2i}^2) \\ \Rightarrow & m_1(C_{1i} - C_{1f})(C_{1i} + C_{1f}) = m_2(C_{2f} - C_{2i})(C_{2f} + C_{2i}) \\ & \dots (2) \end{aligned}$$

Dividing Eq. (2) by Eq. (1),

$$\frac{m_1(C_{1i} - C_{1f})(C_{1i} - C_{1f})}{m_1(C_{1i} - C_{1f})} = \frac{m_2(C_{2f} - C_{2i})(C_{2f} + C_{2i})}{m_2(C_{2f} - C_{2i})}$$

$$C_{1i} + C_{1f} = C_{2f} + C_{2i}$$

$$(C_{1i} - C_{2i}) = -(C_{1f} - C_{2f}) \qquad \dots (3)$$

 \Rightarrow

 \Rightarrow

 \Rightarrow

$$C_{1i} + C_{1f} = C_{2f} + C_{2i}$$

(C_{1i} - C_{2i}) = -(C_{1f} - C_{2f}) ...(3)

This equation tells us that in an elastic one-dimensional collision, the relative velocity of approach before collision is equal and opposite to the relative velocity of separation after collision, no matter what the masses of the colliding molecules may be.

Multiplying Eq. (3) by m_2 gives

$$m_2(C_{1i} - C_{2i}) = m_2(C_{2f} - C_{1f}) \qquad \dots (4)$$

Equation (1) $\Rightarrow m_1(C_{1i} - C_{1f}) = m_2(C_{2f} - C_{2i})$

Subtracting

$$\Rightarrow$$

$$m_{2}C_{1i} - m_{2}C_{2i} - m_{1}C_{1i} + m_{1}C_{1f} = m_{2}C_{2f} - m_{2}C_{1f} - m_{2}C_{2f} + m_{2}C_{2i}$$

$$m_{1}C_{1f} + m_{2}C_{1f} = m_{1}C_{1i} + m_{2}C_{2i} - m_{2}C_{1i} + m_{2}C_{2i} = (m_{1} - m_{2})C_{1i} + 2m_{2}C_{2i}$$

 \Rightarrow

$$C_{1f} = \frac{(m_1 - m_2)}{(m_1 + m_2)} C_{1i} + \frac{2m_2}{(m_1 + m_2)} C_{2i}$$

Similarly, C_{1f} can be eliminated to find

$$C_{2f} = \frac{(m_2 - m_1)}{(m_1 + m_2)} C_{2i} + \frac{2m_1}{(m_1 + m_2)} C_{1i}$$

where the masses of the colliding molecules 1 and 2 are m_1 and m_2 , the velocity components being C_{1i} and C_{2i} before collision and, C_{1f} and C_{2f} after collision, along the line joining their centres at the time of impact.

To understand this, let us take an example (Figs 2.3a, 2.3b). Two molecules of mass m_1 and m_2 with speeds 300 ms⁻¹ and 500 ms⁻¹, respectively, hit one another as in Figure 2.3a. The molecule (2) came making an angle 30° with the line of centres and, the molecule (1) came at a direction of 60° with the line of centres from the opposite side. What will be their velocities of recoil?



Figure 2.3(a) $C_{1N} = C_1 \cos 30 = 259.8 \text{ ms}^{-1}$: $C_{1i} = C_1 \cos 60^\circ = 150 \text{ ms}^{-1} C_{2N} = C_2 \cos 60 = 250 \text{ ms}^{-1}$: $C_{2i} = C_2 \cos 30^\circ = 433 \text{ ms}^{-1}$. Where, $C_1 = 300 \text{ ms}^{-1}$ and $C_2 = 500 \text{ ms}^{-1}$.

Solution

The normal component of velocity of molecule 1, before collision is $C_{1\rm N} = (300 \text{ ms}^{-1}) \cos 30^\circ = 259.8 \text{ ms}^{-1}$ and, that of the second molecule is $C_{2\rm N} = (500 \text{ ms}^{-1}) \cos 60^\circ = 250 \text{ ms}^{-1}$. These two components will remain the same after the collision.

The two component velocities along the line of centres, before collision are

$$C_{1i} = (300 \text{ ms}^{-1}) \cos 60^\circ = 150 \text{ ms}^{-1}$$

and

$$C_{2i} = (500 \text{ ms}^{-1}) \cos 30^\circ = 433 \text{ ms}^{-1}$$

Therefore, after collision these components will change to

$$C_{1f} = \frac{(m_1 - m_2)}{(m_1 + m_2)} C_{1i} + \frac{2m_2}{(m_1 + m_2)} C_{2i}$$

$$\Rightarrow \qquad C_{1f} = \frac{1}{(m_1 + m_2)} \left[150 \ m_1 + 716 \ m_2 \right] \, \mathrm{ms}^{-1}$$

$$C_{2f} = \frac{(m_2 - m_1)}{(m_1 + m_2)} C_{2i} + \frac{2m_1}{(m_1 + m_2)} C_{1i}$$

 \Rightarrow

and

=

$$C_{2f} = \frac{1}{(m_1 + m_2)} [433 m_2 - 133 m_1] \,\mathrm{ms}^{-1}$$

Let molecule 1 be a CO₂ molecule and, molecule 2 be a H₂ molecule; the masses are then $m_1 = 7.3 \times 10^{-23}$ g and $m_2 = 0.33 \times 10^{-23}$ g. Therefore, $C_{1f} = 174.48$ ms⁻¹ and $C_{2f} = -108.5$ ms⁻¹. Therefore, after collision $C_{1N} = 259.8$ ms⁻¹ and $C_{1f} = 174.48$ ms⁻¹ and

$$\theta = \tan^{-1} \frac{259.8}{174.48} = 56.11^{\circ}$$

and similarly (see Figure 2.3b)

 \Rightarrow

$$\phi = \tan^{-1} \frac{250}{108.5} = 66.54^{\circ}$$

The two molecules will thus recoil away as shown in Figure 2.3b.



Figure 2.3(b) The directions of the recoil between two hard spheres; the collision is supposed to be perfectly elastic.

3. The velocity of the centre of mass of the two molecules is not changed by their collision. This is important to understand the nature of the collision. The momentum p of the system of two molecules can be written as

$$\vec{p} = m_1 \vec{C}_1 + m_2 \vec{C}_2 = (m_1 + m_2) \left\lfloor \frac{m_1}{(m_1 + m_2)} \vec{C}_1 + \frac{m_2}{(m_1 + m_2)} \vec{C}_2 \right\rfloor$$
$$\vec{p} = (m_1 + m_2) \vec{V}_{\text{CM}}$$

where \vec{V}_{CM} is the velocity of the centre of mass. Since \vec{p} is conserved during a collision, \vec{V}_{CM} remains constant. This means that the two molecules will recoil

according to the point 2 but, the centre of mass moves with uniform velocity; no change in speed; no change in direction.

2.9.1 What Determines the State of Thermal Equilibrium of Mixture of Two Different Gases?

We define the state of thermal equilibrium as that in which the temperature of the system is uniform throughout, and is also equal to that of the surroundings.

Let us take a box containing two different kinds of molecule of mass m_1 and m_2 with number density n_1 and n_2 . Let the molecules of the first kind were initially moving fast and, those of the second kind were moving slow. What will be the final picture?

There will be a continuous two body bombardments of all types: $m_1 \leftrightarrow m_1, m_2 \leftrightarrow m_2$ and $m_1 \leftrightarrow m_2$. For all these collisions, the total momentum and the total kinetic energy will remain the same. But, certainly there will be a *continuous exchange of momentum and*, *hence of velocity between the molecules*. The final picture will therefore be a *state in which thing will not change any more*. Let the two molecules approach one another with velocities (Figure 2.4(a)) \vec{C}_1 and \vec{C}_2 . They collide and fly off with a new combination of velocities. But the main idea is that (already explained) while all these things happen, *the centre of mass goes on moving, without any changes, with the velocity* (\vec{V}_{CM}) of the centre of mass:

$$\vec{V}_{\text{CM}} = \frac{(m_1 \vec{C}_1 + m_2 \vec{C}_2)}{(m_1 + m_2)}$$



Figure 2.4(a) The relative velocity of 1st molecule with respect to the second is $\vec{v} = \vec{c}_1 - \vec{c}_2$.



Figure 2.4(b) Assuming $m_1 = 3$ and $m_2 = 2$ the direction of centre of mass velocity is given by the vector *OP*, and its magnitude is given by the length of this OP vector.



Figure 2.4(c) For a given collision, the projection $\vec{V} \cdot \vec{C}_{CM}$ has a finite value.



Figure 2.4 (d) In a given volume, say 1 mL, these projections for the innumerable collisions are so widely distributed that $\langle \vec{V} \cdot \vec{C}_{CM} \rangle = 0$.

The relative velocity of their approach for a particular collision is $\vec{V} = \vec{C}_1 - \vec{C}_2$; and the direction of this vector \vec{V} could be at any possible direction with \vec{V}_{CM} . So, \vec{V}_{CM} obviously has a finite projection on \vec{V} at a single collision, i.e., $\vec{V} \cdot \vec{V}_{\text{CM}} \neq 0$ Fig 2.4(c). But, in the final state of equilibrium \vec{V} and \vec{V}_{CM} vectors are widely distributed that the average of $\vec{V} \cdot \vec{V}_{\text{CM}}$, i.e., $\langle \vec{V} \cdot \vec{V}_{\text{CM}} \rangle$ will be zero. That is

$$\langle \vec{V} \cdot \vec{V}_{CM} \rangle = 0$$

$$\vec{V} \cdot \vec{V}_{CM} = \frac{(\vec{C}_1 - \vec{C}_2) \cdot (m_1 \vec{C}_1 + m_2 \vec{C}_2)}{(m_1 + m_2)}$$
(2.13)

Now,

$$\Rightarrow \qquad \left\langle \vec{V} \cdot \vec{V}_{\rm CM} \right\rangle = \left\{ \left\langle \left(m_1 C_1^2 - m_2 C_2^2 \right) \right\rangle + m_2 \langle \vec{C}_1 \cdot \vec{C}_2 \rangle - m_1 \langle \vec{C}_2 \cdot \vec{C}_1 \rangle \right\} (m_1 + m_2) = 0 \text{ (fig 24(d))}$$

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$$\left\langle \vec{V} \cdot \vec{V}_{\rm CM} \right\rangle = \frac{1}{(m_1 + m_2)} \Big[\left\langle m_1 C_1^2 \right\rangle - \left\langle m_2 C_2^2 \right\rangle \Big] + (m_1 + m_2) \left\langle \vec{C}_1 \cdot \vec{C}_2 \right\rangle$$

How much is $\langle \vec{C}_1 \cdot \vec{C}_2 \rangle$? In the final state of equilibrium, the two vectors \vec{C}_1 and \vec{C}_2 could be oriented at all possible angles. So again, $\langle \vec{C}_1 \cdot \vec{C}_2 \rangle = 0$. Therefore, from the above equation it is clear that

$$\langle m_1 C_1^2 \rangle = \langle m_2 C_2^2 \rangle$$

$$\left\langle \frac{1}{2} m_1 C_1^2 \right\rangle = \left\langle \frac{1}{2} m_2 C_2^2 \right\rangle$$
(2.14)

or

This is the equation we are waiting for. If you take a mixture of two different gases under condition of thermal equilibrium, then the average kinetic energy of the two kinds of molecule is equal.

Now, instead of the gas mixture, if we take two boxes, one containing the gas A and other gas B, initially at different degrees of hotness, i.e., at different temperatures and, put them together into *thermal contact*, then what will be the final picture? Definitely, heat will flow from the hot gas (say gas A) to the cold one (gas B), and this exchange of energy will continue until their temperatures become equal, i.e., when they attain the state of thermal equilibrium. Now, what determines this state of thermal equilibrium between two different gases, each being present in the pure state?

We solve it as follows: Let us take a rectangular box (Figure 2.5) with two fixed membranes PP' and QQ'. The membrane PP' is permeable to the A molecules but, not to B, and the membrane QQ' is permeable to B molecules but, not to A. We first put A-gas molecules (Figure 2.5) in the left portion of PP' and the B-gas molecules in the right zone of QQ'. Initially they are taken at two different temperatures; say, A molecules were hotter than the B molecules. Definitely, the situation is not going to last. In the final stage, we will have a mixture of A and B molecules in the intermediate zone P QQ'P', the pure gas A to the left of PP' and pure gas B to the right of QQ'. But what about their energies?



Figure 2.5 In the final stage, the average hotness of all the molecules in all the three sections are equal.

2.16

In the intermediate zone, the hot A molecules will collide with the cold B molecules and, passing on some energy to the latter will return to the main body with less energy than that with which they have left. They will now suffer collision with the relatively hot molecules which have not left the compartment, and will take up a little energy from the latter. So, the result of this round trip will be a gradual cooling of the A molecules.

On the other hand, the B molecules after receiving energy from the A molecules in the intermediate zone will enter into their main B body, and again via collisions, will distribute their excess energy among them. The net result is therefore a gradual cooling of the A molecules and a gradual heating of the B molecules. This exchange of energy will continue until the hotness, i.e., the temperature of all parts of the entire system gets uniform, i.e., until the thermal equilibrium is attained. In this final state, the average kinetic energy of the A molecules and the B molecules are equal in the intermediate zone (we have proved it earlier). But since the A molecules in the intermediate zone are in thermal equilibrium with those in the left portion of PP', they must also have the same average kinetic energy (otherwise, thermal equilibrium could not have been established); and similarly, the average kinetic energy of the B molecules in the intermediate zone and, in the right portion of QQ' must also become equal.

Thus we have proved a very important concept:

Under condition of thermal equilibrium, i.e., at the same temperature, the average kinetic energy of the molecules of two gases (like or unlike) are equal.

This, in turn means that, the average kinetic energy of the molecules of a gas is a function of only temperature, no dependence upon anything, molar mass, atomicity, etc.

The result is amazing! If you take a H₂ gas and a CO₂ gas at the same temperature, then the molecules in both the systems will be moving with the same average kinetic energy. Now, how to set up the temperature scale ? The best way to do it would be to define this average kinetic energy itself as the temperature. But unfortunately, people have done it in a different way. They had put a constant factor of $\frac{3}{2}k$ (the Boltzmann constant: 1.38 × 10^{-23} JK⁻¹) between the average kinetic energy and the temperature in the kelvin scale. So, if T be the kelvin temperature of the gas, then the average translational kinetic energy

of the molecules is equal to $\frac{3}{2}kT$, i.e.,

$$\frac{1}{2}m\langle C^2\rangle = \frac{3}{2}kT \tag{2.15}$$

We shall prove this result later. Before going to the next section, we will discuss a little more about Eq. (2.15).

We have proved that the average kinetic energy of the molecules of a gas is $\frac{3}{2}kT$ (actually

we have not proved it; we have accepted the result logically, and will prove it later). The problem is we have been discussing only monoatomic gases. Naturally, we are now thinking about the result of diatomic or triatomic molecule.

The translation of a diatomic molecule may be pictured as the translation of two atoms; but now the two atoms are tied up with each other by a bond. So, although there are forces between the atoms of a diatomic molecule, the exchange of energy or momentum between the two atoms of the two diatomic molecules does not depend on the position of their counter atoms. So you can say that, if two atoms of masses m_A and m_B are held together by a bond, then although they may rotate or vibrate, *the condition of thermal equilibrium*

requires that each atom in a molecule has a mean translational kinetic energy of $\frac{3}{2}kT$.

That is $\frac{1}{2}m_A \langle C_A^2 \rangle = \frac{1}{2}m_B, \langle C_B^2 \rangle = \frac{3}{2}kT$. So what is the mean translational kinetic energy of the molecule as a whole, i.e., looking up at its motion along the motion of the centre of mass

the molecule as a whole, i.e., looking up at its motion along the motion of the centre of mass of m_A and m_B ?

The velocity of the centre of mass is

$$\vec{V}_{\rm CM} = \frac{m_A \vec{C}_A + m_B \vec{C}_B}{(m_A + m_B)}$$

The average translational kinetic energy of the molecule as a whole is then

 $\langle \text{KE} \rangle_{\text{trans}} = \frac{1}{2} M \langle V_{\text{CM}}^2 \rangle;$ *M* is the total mass of the molecule $M = (m_A + m_B)$

But, $V_{\rm CM}^2 = \vec{V}_{\rm CM} \cdot \vec{V}_{\rm CM} = (m_A \vec{C}_A + m_B \vec{C}_B) \cdot (m_A \vec{C}_A + m_B \vec{C}_B) / M^2$

$$\Rightarrow \qquad MV_{\rm CM}^2 = (m_A^2 C_A^2 + m_B^2 C_B^2 + 2m_A m_B C_A \cdot C_B)/M$$

$$\Rightarrow \qquad \qquad \frac{1}{2}M\left\langle V_{\rm CM}^{2}\right\rangle = \frac{1}{2M}\left[\left\langle m_{A}C_{A}^{2}\right\rangle + m_{B}\left\langle m_{B}C_{B}^{2}\right\rangle + 2m_{A}m_{B}\left\langle \vec{C}_{A}\cdot\vec{C}_{B}\right\rangle\right]$$

But, what is the value of $\langle \vec{C}_A \cdot \vec{C}_B \rangle$? Due to their random orientation, $\langle \vec{C}_A \cdot \vec{C}_B \rangle = 0$. Therefore,

$$\langle \text{KE} \rangle_{\text{trans}} = \frac{1}{2} M \left\langle V_{\text{CM}}^2 \right\rangle = \frac{1}{2M} [m_A(3kT) + m_B(3kT)]$$

$$\Rightarrow \qquad \langle \mathrm{KE} \rangle_{\mathrm{trans}} = \frac{1}{2M} \left(m_A + m_B \right) 3kT$$

 \Rightarrow

$$\langle \text{KE} \rangle_{\text{trans}} = \frac{3}{2} kT$$
 (2.16)

The result is amazing. If you have a diatomic molecule, the *average translational kinetic* energy is still $\frac{3}{2}kT$; but where is the rest of the energy? Because, you have calculated a total of $\frac{1}{2}m_A \langle C_A^2 \rangle + \frac{1}{2}m_B$, $\langle C_B^2 \rangle = 3kT$.

The rest of energy $3kT - \frac{3}{2}kT = \frac{3}{2}kT$ is now attributed to the rotational and vibrational kinetic energy of the molecule.

2.10 A MATHEMATICAL INTERLUDE

2.10.1 Spherical Coordinates

Instead of locating a point in space by specifying the Cartesian coordinates x, y and z, we can also locate the point by specifying the spherical coordinates, r, θ and ϕ . The relations between the two sets of coordinates are $x = r \sin \theta \cos \phi$: $y = r \sin \theta \sin \phi$; $z = r \cos \theta$ (Figure 2.6).



Figure 2.6 A representation of a point *P* in a spherical coordinate system. The length of the vector *OP* is *r*.

This coordinate system is called a *spherical coordinate system* because the graph of the equation r = c (constant) is a sphere of radius c centred at the origin. The limits of θ and ϕ are explained in Figure 2.7.



Figure 2.7(a) The radius vector r is rotated from $\theta = 0$ to $\theta = \pi$ at $\phi = 0$.

Figure 2.7(b) The semicircle in Fig 2.7(a) is then rotated about the z-axis through an angle $\phi = 0$ to $\phi = 2\pi$. The result is a sphere of radius r.

The differential volume element in the Cartesian coordinates is

$$d\tau = dx \, dy \, dz$$
 ...M1

In the spherical polar coordinates it is

$$d\tau = r^2 dr \sin \theta \, d\theta \, d\phi$$
 (Figure 2.8). ...M2

You can check the above equation within proper limits of find the volume of a sphere *V*, of radius *r*:



Figure 2.8 $O'P = a = OP \sin \theta a = \sin \theta \therefore PQ = r \sin \theta d\phi$ and $PS = rd\theta \therefore$ area, PQRS, $dA = r^2 \sin \theta d\theta d\phi$ If the differential area dA is swept radially by dr, the volume element becomes $d\tau = r^2 dr \sin \theta d\theta d\phi$.

$$V = \int d\tau = \int_{0}^{r} r^{2} dr \int_{0}^{\pi} \sin \theta \, d\theta \int_{0}^{2\pi} d\phi = \frac{4}{3} \pi r^{3} \gamma^{3}$$

If we integrate only over θ and ϕ , we get

$$dV = r^2 dr \int_0^\pi \sin\theta \ d\theta \int_0^{2\pi} d\phi = 4\pi r^2 dr \qquad \dots \text{M3}$$

which the volume of a spherical shell of radius r and thickness $dr: 4\pi r^2$ is surface area and dr is the thickness of the shell.

The area *PQRS* = *A* is $r^2 \sin\theta d\theta d\phi$

$$dA = r^2 \sin\theta \, d\theta \, d\phi \qquad \dots \mathrm{M4}$$

If we integrate dA over the entire range of $\theta(0 \rightarrow \pi)$ and $\phi(0 \rightarrow 2\pi)$,

$$A = \int dA = \left[\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \right] r^2$$
$$A = 4\pi r^2$$

 \Rightarrow

which is the area of the sphere.

We call the *solid enclosed* by the surface dA connecting the origin, *a solid angle* $d\Omega$, for a sphere of unit radius,

$$d\Omega = \sin \theta d\theta d\phi$$

The total solid angle is then

$$\Omega = \int d\Omega = \int_0^{\pi} \sin \theta \, d\theta \int_0^{2\pi} d\phi$$

$$\Omega = 4\pi$$
M5

2.10.2 Even and Odd Functions

We first define a function y = g(x) *even* if

$$g(x) = g(-x)$$
 for all x M6(a)

The graph of such a function is symmetric with respect to the y-axis (Figure 2.9a). A function h(x) is *odd* if



Figure 2.9 (a) Even function (b) Odd function.

Physical Chemistry

$$h(-x) = -h(x)$$
 (see Figure 2.9b)M6(b)

For example, the function $\cos nx$ is even while $\sin nx$ is odd. Three key factors for even and odd function are as follows:

1. If g(x) is an even function, then

$$\int_{-L}^{+L} g(x) dx = 2 \int_{0}^{L} g(x) dx \qquad (g \text{ even}) \qquad \dots M7$$

2. If h(x) is an odd function, then

$$\int_{-L}^{+L} h(x) dx = 0$$
 (*h* odd)M8

- 3. The product of an even and an odd function is odd.
- *Proof:* 1 and 2 are obvious from the graph. We generate a function q = gh with even g and odd h; q is then odd because

$$q(-x) = g(-x) h(-x) = -g(x) h(x) = -q(x)$$

2.10.3 The Gaussian Integral

It is given by

 \Rightarrow

$$I = \int_{-\infty}^{+\infty} e^{-x^2} dx; \ y = f(x) = e^{-x^2}$$
 (Figure 2.10(a))M9



Figure 2.10(a) The bell-shaped curve. Also called the normal or Gaussian function.

To evaluate this integral, we first square *I* and, write as

$$I^{2} = \int_{-\infty}^{+\infty} e^{-x^{2}} dx \int_{-\infty}^{+\infty} e^{-y^{2}} dy = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-(x^{2}+y^{2})} dx dy$$

Which is a double integral of the whole *xy*-plane. But this can also be written in the plane polar coordinate with the differential volume element $d(\pi r^2) = 2\pi r dr$ [Figure 2.10(b)] replacing the differential volume element dxdy in the cartesian coordinate as

$$I^{2} = \int_{0}^{\infty} e^{-r^{2}} (2\pi r dr) = \pi \int_{0}^{\infty} e^{-x} dx = \pi$$
$$I = \sqrt{\pi}$$

2.22



Figure 2.10(b) The circular strip of thickness dr and area $2\pi r dr$ replacing the area dxdy.

The integral $\int_0^{\infty} e^{-x^2} dx$ is therefore $\frac{1}{2}\sqrt{\pi}$, as the function e^{-x^2} is *even*. Obviously, we can also write

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}, \qquad \dots M10$$

where a is a constant.

 \Rightarrow

2.10.4 The Gamma Function

Another important function widely used in physical science introduced by Euler in the 1700s is the gamma function, and is defined by integral

$$\Gamma(n) = \int_0^\infty e^{-x} x^{n-1} dx \quad n > 0$$
 ...M11

Note that the integral is a function x and n, and the resulting integral is a function of n. If $n \ge 2$, we can integrate $\Gamma(n)$ by parts: using $e^{-x} dx dv$ and x^{n-1} as u

$$\begin{bmatrix} \int u dv = uv - \int v du \end{bmatrix}$$

$$\Gamma(n) = \begin{bmatrix} -x^{n-1} e^{-x} \end{bmatrix}_0^\infty + (n-1) \int_0^\infty x^{n-2} e^{-x} dx$$

$$\Gamma(n) = 0 + (n-1) \int_0^\infty x^{n-2} e^{-x} dx$$

$$\boxed{\Gamma(n) = (n-1) \overline{(n-1)}}$$
....M12

We can now write $\Gamma(n-1) = (n-2) \overline{(n-2)}$ and so on, and finally

$$\Gamma(n) = (n-1)(n-2)\dots\Gamma(1)$$

 \Rightarrow

 \Rightarrow

 \Rightarrow

$$\Gamma(n) = (n-1)! \qquad \therefore \qquad \Gamma(1) = \int_0^\infty e^{-x} \, dx = 1 \qquad \dots M13$$

Up to this point, Eq. M13 is restricted to integer values of $n \ge 2$; but we can also define factorials for other values of *n*. For n = 1, $\Gamma(1) = 1 = 0$!, which is interesting.

For other values of *n* (nonintegers). For $n = \frac{1}{2}$, using Eq. M11, we find

$$\Gamma\left(\frac{1}{2}\right) = \int_0^\infty e^{-x} x^{-1/2} dx$$

Let $ut x = u^2$; then $x^{-1/2} dx = 2du$

$$\Gamma\left(\frac{1}{2}\right) = 2\int_0^\infty e^{-u^2} du = \sqrt{\pi} \qquad \text{(cf. Eq. M10)} \qquad \dots \text{M14}$$

2.10.5 The Error Function

One of the most commonly occurring integrals that cannot be expressed in terms of elementary functions is the *error function:* it is defined as:

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du \qquad [-\infty < x < \infty]$$
M15

Since the function erf(x), cannot be expressed in terms of simple functions, it is a perfectly well-defined function of x and can be evaluated by numerical integration. Starting from Eq. M14, we can write

$$\frac{2}{\sqrt{\pi}}\int_0^\infty e^{-u^2} du = 1$$

which can be broken as

$$\frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du + \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du = 1$$
$$erf(x) + \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du = 1$$

 \Rightarrow

$$\frac{2}{\sqrt{\pi}}\int_{x}^{\infty}e^{-u^{2}}du=1-erf(x)$$

Defining the *complementary error function erfc* (x) as

$$\frac{2}{\sqrt{\pi}}\int_x^{\infty}e^{-u^2}du$$

we get

$$erfc(x) = 1 - erf(x)$$
M16

If the upper limit in the integral M15 is extended to ∞ , the result is: *erf* (∞) = 1. Therefore as *x* varies from zero to infinity, the *erf* (*x*) varies from zero to unity. We also find that

$$\int_{x}^{\infty} e^{-u^{2}} du = \frac{\sqrt{\pi}}{2} \operatorname{erfc}(x) \qquad \dots M17$$

These are illustrated in Figure 2.11 and Figure 2.12, and Table 2.1.



Figure 2.12(a) The error function *erf* (*x*) plotted against *x*.


x	erf (x)		x	erf (x)
0.0	0.000		2.0	0.9953
0.2	0.2227		2.2	0.9981
0.4	0.4284		2.4	0.9993
0.6	0.6039		2.6	0.9998
0.8	0.7421		2.8	0.9999
1.0	0.8427		3.0	1.0000
1.2	0.9103		3.2	1.0000
1.4	0.9523		3.4	1.0000
1.6	0.9763		3.6	1.0000
1.8	0.9891		3.8	1.0000
2.0	0.9953		4.0	1.0000

Table 2.1 Error function

2.11 HOW MANY MOLECULES STRIKE A *UNIT AREA* OF THE SURFACE OF THE CONTAINER?

When you take a gas in a container at a fixed temperature, there will be molecules with all possible speeds, moving in all possible directions.

Let us attach *to each molecule* a *vector*, whose length is equal to the speed of the molecule and, whose directions is along the direction of the motion. If we do it for all the molecules, at a particular times, we will get a random collection of as many vectors as there are molecules.



Figure 2.13 Vectors of all possible lengths (equivalent to molecules of all possible speeds) oriented in all possible directions (representing the random movement of the molecules). All these vectors are translated to a common origin.

Now, *translate* all these vectors (but, DO NOT ROTATE) to the origin of our coordinate system. The picture will be like that shown in Figure 2.13. Let us now draw two concentric

spheres, one of radius C and the other of radius C + dC. The number of vector tips lying in the infinitesimal shell (between the two spheres) will be equal to the number of molecules moving with speeds in the range C to C + dC (Figure 2.14). If we now consider an infinitesimal area on the surface of the sphere at angles $\theta \rightarrow \theta + d\theta$ and $\phi \rightarrow \phi + d\phi$ (Figure 2.15), then the solid angle described at the centre is $\sin \theta d\theta d\phi$. Since the total Nmolecules are distributed uniformly over the total solid angle 4π , the number of molecules moving with speeds in the range $C \rightarrow C + dC$ and, at angles θ and ϕ is

$$dN_{C,\theta,\phi} = \frac{N}{4\pi} \sin \theta \, d\theta d\phi \tag{2.17}$$

Figure 2.14 The number of dots in the spherical shell between radii c and c + dc is equal to the number of molecules having speeds between $c \leftrightarrow c + dc$. The dots are actually the tips of the velocity vectors. The volume of the shell is $4\pi c^2 dc$.



Figure 2.15 The number of vector tips in the solid angle described by θ and ϕ with tolerances $d\theta$ and $d\phi$ is $\frac{N}{4\pi}\sin\theta \, d\theta d\phi$.

Therefore, the number of molecules per unit volume, moving with speeds in the range $C \rightarrow C + dC$ and, along the direction described by θ and ϕ is

$$dn_{C,\theta,\phi} = \frac{dN_{C,\theta,\phi}}{V} = \frac{(N/V)}{4\pi} \sin\theta \ d\theta d\phi$$
$$dn_{C,\theta,\phi} = \frac{n}{4\pi} \sin\theta \ d\theta d\phi \qquad (2.18)$$

 \Rightarrow

where *n* is the number of molecules per unit volume. How many molecules strike a unit area placed at the origin on the *x*-*y* plane (Figure 2.16) along the θ , ϕ direction? In one second, the molecules can move over a distance *C*, and therefore, the number of molecules which are present in the slant cylinder of length *C*, positioned along θ , ϕ direction, will hit the unit area in one second. The volume of this cylinder is $C \cos \theta \times 1 = C \cos \theta$, and therefore, the number of strike will be



Figure 2.16 The number of molecules present in the slant cylinder of length *I*, and at angles θ and ϕ is $\frac{nC}{4\pi}$ sin $\theta \cos \theta \, d\theta \, d\phi$.

Number of moleclues striking a unit area placed at the origin on the x - y plane along the θ , ϕ direction per second = $dn_{C,\theta,\phi}$ (volume of the slant cylinder)

$$= \left(\frac{n}{4\pi}\sin\theta \ d\theta \ d\phi\right) (C\cos\theta)$$
$$= \frac{nC}{4\pi}\sin\theta\cos\theta \ d\theta \ d\phi \qquad (2.19)$$

Therefore, the total number of striking on this unit area by the molecules moving in the speed range $C \rightarrow C + dC$ from all directions in one second, but from one side of the *x*-*y* plane is

Striking Rate =
$$\frac{nC}{4\pi} \int_0^{\pi/2} \sin\theta \cos\theta d\theta \int_0^{2\pi} d\phi = \frac{1}{4} nC$$

The angle θ is varied from $0 \rightarrow \pi/2$ because we want to cover the surface on one hemisphere; all directions above the *x*-*y* plane (Figure 2.17).

Finally, we realise that there are molecules in different speed ranges: n_1 molecules per unit volume in the speed range $C_1 \rightarrow C_1 + dC$, n_2 in the range $C_2 \rightarrow C_2 + dC$... etc., the net striking rate is then



Figure 2.17 Number of molecules striking a unit area placed at the origin of the x-y plane from one hemispherical side.

Striking Rate =
$$\frac{1}{4}[n_1C_1 + n_2C_2 + \cdots] = \frac{1}{4}n\langle C \rangle$$

where the average speed is

$$\langle C \rangle = \frac{(n_1 C_1 + n_2 C_2 + \cdots)}{n}$$

The wall collision frequency is therefore given by

$$z_{\text{wall}} = \frac{1}{4} n \langle C \rangle \tag{2.20}$$

2.12 CALCULATION OF PRESSURE OF A GAS

What happens when a molecule hits the wall? As shown in Figure 2.18, there is no change in the tangential component of the velocity of the molecule; only the normal component of the velocity of the molecule is changed from $C \cos \theta$ to $-C \cos \theta$.



Figure 2.18 During a wall collision, the tangential velocity component remains unchanged; only the normal component of velocity is changed from $C \cos \theta$ to $-C \cos \theta$, for the given collision shown.

Therefore, per blow the momentum imparted is $2mC \cos \theta$. Hence, the momentum change dp per second per unit area of the wall along the $\theta - \phi$ direction is [using Eq. (2.19)]

$$dp = (2mC\cos\theta) \left(\frac{nC}{4\pi}\sin\theta\cos\theta d\theta d\phi\right)$$
$$dp = \frac{mnC^2}{2\pi}\sin\theta\cos^2\theta \ d\theta d\phi$$

and realising that the pressure P is developed due to the momentum blow of the bombarding molecules, from all possible directions per unit area per second but, from one side of the hemisphere, we can write

$$P = \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} dp$$
$$P = \frac{1}{3} mnC^{2}$$

 \Rightarrow

 \Rightarrow

Finally, considering molecules of all possible speeds

$$P = \frac{1}{3} m \sum n_i C_i^2$$

$$P = \frac{1}{3} mn \langle C^2 \rangle, \text{ or } P = \frac{1}{3} m \frac{N}{V} C_{\text{rms}}^2, \text{ or } P = \frac{1}{3} mn C_{\text{rms}}^2$$
(2.21)

where the root mean square speed defined as

$$C_{\rm rms}^2 = \frac{1}{n} \sum n_i C_i^2 = \langle C^2 \rangle$$

 $\langle C^2 \rangle$ is the mean squared speed and $C_{\rm rms}$ is the root mean square speed [compare with Eqs (2.15) and (2.16)]. We can, therefore, write the average translational kinetic energy

$$\frac{1}{2}m\langle C^2 \rangle = \frac{1}{2}m C_{\rm rms}^2 = \frac{3}{2}kT$$

It is mentioned earlier, that the average translational kinetic energy is not $\frac{1}{2}m\langle C\rangle^2$; it is

$$\langle \epsilon \rangle = \frac{1}{2}m C_{\rm rms}^2$$
, and the $C_{\rm rms}$ may be defined as the speed with which the molecules move

with the average translational kinetic energy.

$$C_{\rm rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$
(2.22)

m is the molecular mass, M is the molar mass, $R=kN_0\,(k$ is the Boltzmann constant, N_0 is the Avogadro's constant).

Equation (2.21) now can also be transformed as

$$P = \frac{1}{3} mnC_{\rm rms}^2 = \frac{1}{3} mn \frac{3kT}{m}$$

or

 \Rightarrow

$$P = nkT$$

The ideal gas equation.

2.13 DERIVATION OF IDEAL GAS LAWS FROM KINETIC THEORY

2.13.1 Boyle's Law

Differentiating PV with respect to pressure at constant temperature [Eq. (2.21)]

$$\begin{split} \left[\frac{\partial(PV)}{\partial P}\right]_T &= \frac{\partial}{\partial P} \left[\frac{1}{3} m N \langle C^2 \rangle \right]_T \\ &= \frac{2}{3} N \left[\frac{\partial}{\partial P} \left(\frac{1}{2} m \langle C^2 \rangle \right)\right]_T + \frac{1}{3} m \langle C^2 \rangle \left(\frac{\partial N}{\partial P}\right)_T \end{split}$$

Since the average translational kinetic energy, $\frac{1}{2}m\langle C^2\rangle$, is a function of only temperature, the first differential on the right-hand side is zero. Now, if the molecules do not undergo

any association or dissociation, then N is also fixed, i.e., $\left(\frac{\partial N}{\partial P}\right)_T = 0$. So we have, for a given mass of a gas

$$\left[\frac{\partial(PV)}{\partial P}\right]_T = 0$$

which is the Boyle's law.

2.13.2 Charles's Law

Again we start by recognising that the average translational kinetic energy of the molecules of an ideal gas is directly proportional to the kelvin temperature

$$\langle \epsilon \rangle = \frac{1}{2} m \langle C^2 \rangle = \frac{3}{2} kT \\ \left[\frac{\partial}{\partial T} \left(\frac{1}{2} m \langle C^2 \rangle \right) \right]_P = \frac{3}{2} k$$

 \Rightarrow

_

Therefore,

$$\begin{split} \left[\frac{\partial}{\partial T}\left(PV\right)\right]_{P} &= \frac{3}{2} N \left[\frac{\partial}{\partial T} \left(\frac{1}{2}m\langle C^{2} \rangle\right)\right]_{P} + \frac{1}{3} m \langle C^{2} \rangle \left(\frac{\partial N}{\partial T}\right)_{P} \\ &= Nk + \frac{1}{3} m \langle C^{2} \rangle \left(\frac{\partial N}{\partial T}\right)_{P} \end{split}$$

If the molecules do not undergo any association or dissociation then, $\left(\frac{\partial N}{\partial T}\right)_P = 0$; hence, for a given mass of a gas (N is fixed),

$$\left(\frac{\partial(PV)}{\partial T}\right)_P = \text{ constant}$$

Under condition of fixed pressure,

$$\left[\frac{\partial(PV)}{\partial T}\right]_{P} = P\left(\frac{\partial V}{\partial R}\right)_{P} = \text{ constant}$$

$$\left(\frac{\partial V}{\partial T}\right)_{P} = \text{ constant.}$$

i.e., the rate of change of the product *PV* with the kelvin temperature at a fixed pressure is constant or, if the pressure is held fixed for a given mass of an ideal gas, the volume varies linearly with the kelvin temperature; this is the Charles's law.

2.13.3 Avogadro's Law

If we take equal volumes of two different gases under the same conditions of pressure and temperature, we have from Eq. (2.7)

$$U_{1} = U_{2}$$

$$N_{1} \left\langle \frac{1}{2} m_{1} C_{1}^{2} \right\rangle = N_{2} \left\langle \frac{1}{2} m_{2} C_{2}^{2} \right\rangle$$

$$\left\langle \frac{1}{2} m_{1} C_{1}^{2} \right\rangle = \left\langle \frac{1}{2} m_{2} C_{2}^{2} \right\rangle$$

But,

because each of them is equal to $\frac{3}{2}kT$. This implies

$$N_1 = N_2$$

i.e., they contain an equal number of molecules. This is Avogadro's law.

2.13.4 Dalton's Law of Partial Pressure

If several gases are separately contained in a volume V for each, and if $N_1, N_2,...$ etc. are the number of molecules of masses m_1, m_2 , etc., then

$$\begin{split} P_1 = & \frac{1}{3} \frac{m_1 N_1}{V} \left\langle C_1^2 \right\rangle; P_2 = \frac{1}{3} \frac{m_2 N_2}{V} \left\langle C_2^2 \right\rangle \dots \text{etc.} \\ P_1 = & \frac{2}{3} U_1; P_2 = \frac{2}{3} U_2; \dots \text{etc.} \end{split}$$

or

where P_1 , P_2 , etc. are the pressures of the gases; $\langle C_1^2 \rangle$, $\langle C_2^2 \rangle$... etc. are their mean square speeds and, U_1 , U_2 , etc. are their kinetic energies per unit volume. Now, if all the gases are mixed together to occupy the same volume V, then it is found experimentally that, no heat is absorbed or liberated (this is actually true for ideal gases)⁴. The total energy of the mixture is equal to the sum of those of the separate gases, i.e.,

$$U_{\rm mix} = U_1 + U_2 + \dots$$

 $\frac{3}{2}P = \frac{3}{2}P_1 + \frac{3}{2}P_2 + \cdots$

If P be the pressure of the mixture, then

 \Rightarrow or

$$P = \sum P_i$$

 $P = P_1 + P_2 + \dots$

which is the law we wanted to prove.

2.12.5 Graham's Law of Diffusion/Effusion

Equation (2.20) gives us the rate of striking of the molecules on the wall. If there be a tiny hole of area A on the wall, then the molecules which are going to hit the area A, will effuse

⁴ This result was quite expected, because, by definition, there is no interaction between the molecule of an ideal gas.

out. The number of molecules effusing out of the hole of area A per second is therefore

$$\frac{dN}{dt} = \frac{1}{4}n\langle C\rangle A$$
$$= \frac{1}{4}A\frac{PN_0}{RT}\sqrt{\frac{8RT}{\pi M}}$$

where we have used the equation, $\langle C \rangle = \sqrt{\frac{8RT}{\pi M}}$

 $\Rightarrow \qquad \qquad \frac{dN}{dt} = \frac{PN_0A}{\left(2\pi MRT\right)^{1/2}}$

The escape of gas molecules through a tiny hole is called effusion. The rate of effusion is therefore directly proportional to $M^{-1/2}$, which is the Graham's law of effusion. Two conditions are, however, to be mentioned:

- (i) The hole must be tiny; if it is big, then there will be a rapid flow of the gas, destroying the distribution of velocity of the molecules.
- (ii) The size of the hole must be much smaller than the average distance traversed by the molecules between two successive collisions; otherwise, it would not be a free flow (effusion is a free flow), because the molecules will collide many times with one another, while passing through the hole and, a hydrodynamic flow would be set up throughout the container, towards the hole.

2.14 KINETIC THEORY APPLIED TO THE ATMOSPHERE

2.14.1 Barometric Distribution

In this section, we shall learn: how are the molecules distributed in space subjected to a static field of force, at thermal equilibrium. For example, if we consider our atmosphere as a column of gas, and which is subjected to the gravity field along the Z axis, say, and which is at thermal equilibrium then, here we want to know, how the number of molecules per unit volume changes with altitude?

Before taking up the mathematical steps, let us first analyse the situation by physical reasoning. When you put a column of gas on the earth surface, two distinct forces act on the molecules:

- $(i) \quad The \ kinetic \ molecular \ force \ and$
- (ii) The gravity force

You are well acquainted with the character of the kinetic molecular force; this tends to randomise the molecules uniformly all over the space available. But the effect of the gravity force is something different; it tends to pull down all the molecules at the bottom. So, one tries to bring an order (the gravity force) and the other, the kinetic molecular force, tries to bring a disorder in the system. The final picture will therefore be some sort of compromise between these two opposing forces. While the gravity force will try to pull down all the molecules to the bottom, the kinetic molecular force will knockout some of them and kick them off to the higher altitudes. Thus, the number of molecules per unit volume will decrease as we go up and up and, obviously will be the pressure. We now want to make the discussion quantitative.

Let us fix up our reference frame so that the z-axis points vertically up. Also, let us consider a reference level at Z = 0. All these are required to represent the various altitudes of our atmosphere which is at rest at thermal equilibrium (Figure 2.19).



Figure 2.19 The isothermal atmosphere.

Consider an element of the fluid of thickness *z* at an altitude *z*. The element is like a thin disc of unit area. Since the element is at rest, the vertical upward force acting on the lower face of the slab is more than the vertical downward force acting on the upper face by an amount, which is the force due to the mass of the slab itself. If P be the pressure at height Z and P + dP at height Z + dZ, then

$$P - (P + dP) = \rho g dZ$$

$$dP = -\rho g dZ$$
(2.23)

 \Rightarrow

п

where
$$\rho$$
 is the density of the fluid at the height Z. If *m* be the mass of each molecule and *n* be the number of such molecules present per unit volume at the height Z then, $\rho = mn$, with which Eq. (2.23) changes to

$$dP = -mngdZ \tag{2.24}$$

Applying the ideal gas law, we write

$$P = nkT; \Rightarrow dP = kTdn \ (k \text{ is the Boltzmann constant})$$
 (2.25)

Combining Eqs (2.24) and (2.25), we get

$$\frac{dP}{P} = -\frac{mg}{kT}dZ \tag{2.26}$$

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and also,

$$\frac{dn}{n} = -\frac{mg}{kT}dZ \tag{2.27}$$

Finally, integration of these two equations between limits: $P = P_0$; $n = n_0$ at Z = 0 and, at an altitude *Z* the pressure is *P* and the number density is *n*, we get

$$P = P_0 \exp\left[-\frac{mgZ}{kT}\right]$$
(2.28)

and

 $n = n_0 \, \exp\!\left[\frac{-\,mgZ}{kT}\right] \tag{2.29}$

We now got the answer. Two factors are responsible for the pressure: (i) the momentum blow by each molecule and (ii) the number of molecules per unit volume. As we assumed an *isothermal atmosphere*, the momentum blow at any altitude is the same but, the *number density* of the molecules *decreases exponentially with altitude* [Eq. (2.29)]. The second factor then makes the difference. Remembering that P = nkT, it is clear to understand that as the number density of the molecules decreases exponentially [Eq. (2.29)], the pressure also follows the same rule [Eq. 2.28)]. Equation (2.29) is therefore the reason and Eq. (2.28) is the result.

Another interesting feature of the differential Eq. (2.26) is that the relative decrease in pressure (-dP/P) is directly proportional to the increase in height dZ. This means that if you observe a 10% decrease in the atmospheric pressure after 10 km, you will observe again a 10% decrease after another 10 km, i.e., (1 atm) (0.9) = 0.9 atm at an altitude 10 km, (1 atm) (0.9) (0.9) = 0.81 atm pressure at an altitude 20 km (ground level pressure is 1 atm) and so on.

2.14.2 Who Keeps the Temperature of the Atmosphere Constant?

A molecule moving vertically up will behave like a stone thrown upwards. It will rise up with decreasing kinetic energy and with an equal gain in the potential energy. It will finally come to rest, where its potential energy is maximum and kinetic energy zero; it will then start falling down when its potential energy will be converted into kinetic energy. Hence, the atmosphere becomes gradually tenuous with increasing altitude.

However, there is an apparent difficulty: since the mean kinetic energy is proportional to the kelvin temperature, it might seem that the temperature of the atmosphere should fall off with height. This difficulty can be removed if we realise that the molecules which can reach the upper layers have had higher kinetic energies than the average value and, therefore, the molecules which are in the lower layers have had a lesser kinetic energy

than the average value $\left(\frac{3}{2}kT\right)$. There is thus a compensation; the average kinetic energy remains throughout the same. Had there been a temperature gradient vertically along the height of the atmosphere, a Carnot engine could have been operated which would extract

heat from some lower altitude and, rejects heat at some higher altitude, producing some work at each cycle. This would be definitely against the second law of thermodynamics. This is called the '*Sama Effect*'; attempts to detect it has failed, and it is claimed that, a flow of gas had been detected by a light vane.

Most probably you are thinking that why we really feel cold when we move up to a hill station? *There is a fundamental difference between our atmosphere in this book and, our real atmosphere*. Here, we have assumed that the atmosphere is in thermal equilibrium and, is not exchanging any energy with the surroundings. But, our real atmosphere is in continuous energy exchange with the sun; and, if you apply again the barometric formula [Eqs. (2.28) and (2.29)], you may get the answer. At higher altitudes the density of the air is low and hence, it can hold a very little of the energy it receives from the sun, and hence we feel cold. Let us make it quantitative:

Considering the cooling of dry atmosphere with altitude as adiabatic, we may write

$$T^{\gamma}P^{(1-\gamma)} = \operatorname{constant}\left(\gamma = \frac{C_{P}}{\overline{C}_{V}}\right)$$
$$(1-\gamma) T^{\gamma}P^{-\gamma}dP + \gamma P^{(1-\gamma)}T^{(\gamma-1)}dT = 0$$
$$(1-\gamma) T^{\gamma}dP + \gamma PT^{(\gamma-1)}dT = 0$$
$$(1-\gamma) T^{\gamma}\frac{dP}{P} + \gamma T^{(\gamma-1)}dT = 0$$

 \Rightarrow

 \Rightarrow

Using Eq. (2.26),

$$-(1-\gamma) T^{\gamma} \frac{mg}{kT} dZ + \gamma T^{(\gamma-1)} dT =$$

$$\Rightarrow \qquad -\frac{(\gamma-1)}{\gamma} \frac{mg}{k} dZ = dT$$

$$\Rightarrow \qquad \frac{dT}{dZ} = -\frac{(\gamma-1)}{\gamma} \frac{mg}{k}$$

which on integration

=

=

$$\int_{T_0}^T dT = -\frac{(\gamma - 1)}{\gamma} \frac{mg}{k} \int_0^Z dZ$$

we find

$$T = T_0 - \frac{(\gamma - 1)}{\gamma} \frac{mg}{k} Z$$
(2.30a)

0

where T is the temperature at an altitude Z and T_0 is the surface temperature. We got a nice result. How is then the pressure of our atmosphere varies with altitude?

Starting from Eq. (2.30) and dividing throughout by T_0 we find

$$\frac{T}{T_0} = 1 - \frac{(\gamma - 1)}{\gamma} \frac{mgZ}{kT_0}$$

Again, considering the cooling as adiabatic we may write

$$\left(\frac{T}{T_0}\right) = \left(\frac{P}{P_0}\right)^{\frac{(\gamma-1)}{\gamma}}$$

and, substituting this equation, the above equation reads

$$\begin{split} \left(\frac{P}{P_0}\right)^{\frac{(\gamma-1)}{\gamma}} &= 1 - \frac{(\gamma-1)}{\gamma} \frac{mgZ}{k T_0} \\ \frac{P}{P_0} &= \left(1 - \frac{(\gamma-1)}{\gamma} \frac{mgZ}{k T_0}\right)^{\frac{\gamma}{(\gamma-1)}} \end{split}$$

 \Rightarrow

 \Rightarrow

 \Rightarrow

Considering ideal behaviour:

$$\frac{(\gamma-1)}{\gamma} = \frac{(\overline{C}_P - \overline{C}_V)/\overline{C}_V}{\overline{C}_P/\overline{C}_V} = \frac{(\overline{C}_P - \overline{C}_V)}{\overline{C}_P} = \frac{R}{\overline{C}_P}$$

and using this, we have

$$\frac{P}{P_0} = \left(1 - \frac{R}{\overline{C}_P} \frac{mgZ}{kT_0}\right)^{\frac{\gamma}{(\gamma-1)}}$$

$$\frac{P}{P_0} = \left(1 - \frac{k N_0}{\overline{C}_P} \frac{mgZ}{kT_0}\right)^{\frac{\gamma}{(\gamma-1)}} (\because R = kN_0)$$

$$P = P_0 \left(1 - \frac{MgZ}{\overline{C}_P T_0} \right)^{\frac{\gamma}{(\gamma - 1)}}$$
(2.30b)

where M is the molar mass: $M = mN_0$. Students must understand that Eqs (2.28) and (2.29) are applicable only for an isothermal atmosphere. The pair of Eq. (2.30) takes care of the decrease in temperature in the variation of pressure with altitude.

- (i) the pressure of our atmosphere decreases with altitude according to Eq. (2.30b), and
- (ii) the temperature of our atmosphere decreases linearly with altitude [Eq. 2.30(a)].

2.14.3 Barometric Distribution in a Mixture of Gases

The barometric Eqs (2.28) and (2.29) also apply to a mixture of gases like our atmosphere; but *m* must now be replaced by the mean molecular mass: $m_{\text{mix}} = \sum x_i m_i$, where x_i is the mole-fraction of the component *i*, whose molecular mass is m_i . Equation (2.28) can also be applied to the individual components in a mixture, e.g.

$$P_{i,Z} = P_{i,Z}^{0} \exp\left[-\frac{m_{i}gZ}{kT}\right]$$
(2.31)

where $P_{i,Z}$ and $P_{i,Z}^0$ are the partial pressures of the component *i* at an altitude *Z* and at the ground level.

2.14.4 Effect of Temperature on Distribution

Writing Eq. (2.28) as

$$\frac{P}{P_0} = \exp\left[-\frac{mgZ}{kT}\right]$$

We find that fraction of the ground level pressure (P/P_0) at some altitude Z increases with increase in temperature. The exponential decrease in pressure with altitude becomes sluggish with increasing T (Figure 2.20). The reason is clear: on increasing the temperature, the kinetic molecular motion increases which, knockout more molecules from the lower altitudes to higher altitudes against the pull of the gravity.



Figure 2.20 Two decays for a given gas at two different temperatures, T_1 and T_2 ($T_2 > T_1$).

The subject matter may be made a little bit more mathematical: starting from Eq. (2.28),

$$\frac{P}{P_0} = \exp\left[-\frac{\mathrm{mg}\,Z}{kT}\right]$$

We note that the right hand side of the above equation gives the fraction of the ground level pressure (P_0) at height Z. Now, the effect of temperature on the distribution is deduced as follows: If, instead of the temperature T_i , the gas is maintained at some higher temperature $T_f(T_f > T_i)$, the height Z_f , at which the exponent and therefore, the exponential term has the same value previously determined by Z_i and T_i is given by

$$\frac{\operatorname{mg} Z_i}{T_i} = \frac{\operatorname{mg} Z_f}{T_f}$$

Since

$$T_f > T_i, \ Z_f > Z_i$$

which means that, the fall in pressure to some definite fraction of the ground level pressure at low temperature demands higher altitude at higher temperature.

Example 2.1

Calculate the change in pressure of the atmosphere at a height 8.5 km from the earth surface due to a change in temperature from 27° C to -36° C. Assume the air to be an ideal gas with molar mass $0.0289 \text{ kg mol}^{-1}$. Consider the ground level pressure to be 1 atm.

Solution

Using Eq. (2.28) at the two temperatures

$$P_{8.5 \text{ km}} (237 \text{ K}) = P_0 \exp\left[-\frac{MgZ}{RT}\right]; \left(\frac{m}{k} = \frac{mN_0}{kN_0} = \frac{M}{R}\right)$$
$$= (1 \text{ atm}) \exp\left[-\frac{(0.0289 \text{ kg mol}^{-1})(9.8 \text{ ms}^{-2})(8.5 \times 10^3 \text{ m})}{(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(237 \text{ k}))}\right]$$

 $\Rightarrow P_{8.5 \text{ atm}}(237 \text{ K}) = (1 \text{ atm}) \exp[-1.2218] = 0.2947 \text{ atm}$

Similarly, $P_{8.5 \text{ km}}$ (300 K) = (1 atm) exp[-0.965] = 0.3810 atm

The change in pressure is

$$P_{8.5 \text{ atm}}(237 \text{ K}) - P_{8.5 \text{ km}}(300 \text{ K}) = (0.2947 - 0.3810) \text{ atm} = -0.0863 \text{ atm}$$

The pressure at 8.5 km altitude is decreased by 0.0863 atm due to the temperature change from 27°C to -36°C.

2.14.5 Effect of Molecular Mass on Distribution

Again, starting from Eq. (2.28),

$$\frac{P}{P_0} = \exp\left[-\frac{mgZ}{kT}\right]$$

We find that the pressure falls off more rapidly for a gas of heavier molecules compared to a gas of lighter molecules (Figure 2.21). The reason is very clear: at a fixed temperature, the average kinetic energy of the molecules of any gas is the same, i.e. the knocking out effect is the same. The heavier molecules are therefore more strongly pulled towards the earth surface compared to the lighter molecules.

You know that N_2 and O_2 exist on the earth surface in the mol-ratio 4:1. Since N_2 molecules are relatively lighter than the O_2 molecules, the number density of the latter will drop down more rapidly than the former with increase in altitude. So we may expect that the proportion of N_2 to O_2 will increase with altitude. In fact, this does not happen in our atmosphere, at least at reasonable heights. This is because (i) our atmosphere is not isothermal and (ii) it is not at rest; they are mixed up again. However, the *lightest gases definitely predominate at upper levels*.



Figure 2.21 Heavier molecules are more denser at the lower levels than the lighter molecules.

Example 2.2

If mol-percentages of O_2 and He in the air at the earth surface are 20.93 and 0.0001, respectively, then calculate the height after which He will predominate O_2 . Temperature is 300 K.

Solution

Let their number densities become equal at altitude h. Therefore, we may write

$$\frac{n}{n_0} \times 100 = 20.93 \exp \left[-\frac{(0.032 \text{ kg mol}^{-1}) \text{ gh}}{RT} \right]$$

$$= 0.0001 \exp \left[-\frac{(0.004 \text{ kg mol}^{-1}) \text{ gh}}{RT} \right]$$

$$\Rightarrow \qquad 209300 = \exp \left[\frac{(0.028 \text{ kg mol}^{-1}) \text{ gh}}{RT} \right]$$

$$\Rightarrow \qquad \ln 209300 = \frac{(0.028 \text{ kg mol}^{-1}) (9.8 \text{ m/s}^{-2}) h}{(8.314 \text{ M/m mol}^{-1} \text{ K}^{-1}) (300 \text{ K})}$$

$$\Rightarrow \qquad h = \frac{8.314 \times 300 \times \ln(209300)}{0.028 \times 9.8} \text{ m}$$

or

h = 111,362.06 m = 111.36 km

Comment Students must always take care of the units and their cancellations to get the desired unit of the parameter/property asked for.

Example 2.3

Consider an isothermal atmosphere. If the pressure is decreased to 90% of the ground level pressure after 9 km, then to what extent it would decrease after 27 km?

Solution

Using Eq. (2.28),

$$\begin{split} P_{\rm 27\,km} &= P_0 \, \exp\!\!\left[-\frac{mg(27\,\,{\rm km})}{kT}\right] \\ &= P_0 \, \left\{ \exp\!\!\left[-\frac{mg(9\,\,{\rm km})}{kT}\right] \right\}^{27\,\,{\rm km}/9\,\,{\rm km}} \\ P_{\rm 27\,\,{\rm km}/P_0} &= \!\left(\frac{P_{9\,\,{\rm km}}}{P_0}\right)^3 = (0.9)^3 = 0.729 \end{split}$$

 \Rightarrow

Example 2.4

The mol-ratio of N_2 to O_2 in the atmosphere at the ground level is 4:1. Calculate the total pressure at 10 km altitude at 27°C, if that at the ground level be 1 atm. Average molar mass of air is 0.0289 kg mol⁻¹.

Solution

The mol-fractions of O_2 and N_2 at the ground level are $x_{O_2} = 0.2$ and $x_{N_2} = 0.8$, respectively.

Therefore, the ground level pressures of these two gases are: $P_{O_2}(O) = 0.2$ atm. and $P_{N_2}(O) = 0.8$, using Eq. (2.31)

$$P_{\rm N_2} = P_{\rm N_2}(\rm O) \exp \left[-\frac{(0.028 \text{ kg mol}^{-1})(9.8 \text{ ms}^{-2})(10,000 \text{ m})}{(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(300 \text{ k})}\right]$$

 \Rightarrow

 $P_{N_2}(10 \text{ km}) = 0.266 \text{ atm}$

and similarly, $P_{O_2}(10 \text{ km}) = 0.057 \text{ atm.}$

The total pressure at an altitude of 10 km is the sum of these two partial pressures, i.e. 0.323 atm.

Example 2.5

A balloon having a capacity of 15,000 m³ is filled with He gas at 27°C an 1 atm pressure. If the balloon is loaded with 90% of the load, that it can lift at the ground level, at what height will the balloon come to rest? Assume that the volume of the balloon is constant, with mass 1500 kg and the atmosphere isothermal at 27°C. The molar mass of air is $0.0289 \text{ kg mol}^{-1}$ and the ground level pressure is 1 atm.

Solution

Volume of the balloon = 15,00 m³; T = 300 K (isothermal condition) and the ground level pressure P = 1 atm = 101325 Pa (1 Pa = 1 Nm⁻²).

Mass of the He in the balloon is

$$W_{\rm He} = \frac{PvM}{RT} = \frac{(101325 \text{ M m}^{-2}) (15,000 \text{ m}^3) (0.004 \text{ kg mol}^{-1})}{(8.314 \text{ M M M}^{-1} \text{ mol}^{-1}) (300 \text{ K})}$$

 \Rightarrow

$$W_{\rm He} = 2437.45 \; \rm kg$$

.

Mass of the balloon

 \Rightarrow

$$W_{\rm B} = 1500 \text{ kg}$$

 $W_{\rm He} + W_{\rm B} = (2437.45 + 1500) \text{ kg} = 3937.45 \text{ kg}$

Mass of the displaced air at the ground level

$$W_{\rm air} = \frac{PvM}{RT} = \frac{(101325 \text{ M m}^{-2}) (15,000 \text{ m}^{3}) (0.0289 \text{ kg mol}^{-1})}{(8.314 \text{ M m} \text{ K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}$$

 $W_{\rm air} = 17,610.6 \ {\rm kg}$

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lifting power at the ground level is then

$$[W_{air} - (W_{He} + W_B) = (17,610.6 - 3937.45) \text{ kg} = 13673.15 \text{ kg}$$

90% of this lifting power = (13673.15×0.9) kg = 12,305.84 kg. The net downward load is then

$$(W_{\text{He}} + W_{\text{B}} + 12,305.84) \text{ kg} = 16,243.29 \text{ kg}$$
 ...(a)

The net upward force is then

 $[W_{air} - 16,243.29 \text{ kg}] = 1367.31 \text{ kg}$

Let *P* be the pressure at the altitude *h*, where the balloon comes to rest. The mass of the displaced air at this altitude is

$$\frac{P \times 15,000 \times 0.0289}{8.314 \times 300} = 0.1738 P \text{ (P is in Pa)} \qquad \dots \text{(b)}$$

Equations (a) and (b) are now equated

P

 \Rightarrow

 \Rightarrow

Finally, using the barometric equation

$$h = \frac{RT}{Mg} \ln \frac{P_0}{P} = \frac{(8.314 \text{ Mm K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(0.0289 \text{ kg mol}^{-1})(9.81 \text{ ms}^{-2})} \ln \frac{1 \text{ atm}}{0.922 \text{ atm}}$$

 \Rightarrow

 \Rightarrow

h = 714 m.

How to Calculate the Total Number of Molecules 2.14.6 in the Atmosphere?

Equation (2.29) gives us the variation in the number of molecules per unit volume with altitude (assumed isothermal). We will now calculate the total number of molecules in the entire atmosphere.

Consider a cylindrical atmosphere of uniform cross-section A, we then focus our attention to the portion of the atmosphere between heights Z and Z + dZ. The volume of this section is AdZ. Since dZ is infinitesimally small, the number density of the molecules in this section can be regarded as constant [Eq. (2.29)]; the total number of molecules in this section is therefore n AdZ. The total number of molecules present in the entire atmosphere is therefore

$$N(0, \infty) = \int_0^\infty n \ AdZ = n_0 \ A \int_0^\infty \exp(-mgZ / kT) \ dZ$$
$$N(0, \infty) = n_0 \ AkT / mg$$
(2.32)

Similarly, the total number of molecules within an altitude Z from the earth surface is

$$N(0, Z) = \frac{n_0 AkT}{mg} \left[1 - \exp\left(-\frac{mgZ}{kT}\right) \right]$$
(2.33)

The fraction of the total number of molecules present within the altitude Z is therefore,

$$f(0,Z) = \frac{N(0,Z)}{N(0,\infty)} = 1 - \exp\left(-\frac{mgZ}{kT}\right)$$
 (2.34)

Example 2.6

Calculate the fraction of the total number of O_2 molecules which lies below an altitude of 8550 m. Consider the atmosphere to be isothermal at 27°C.

Solution

Using Eq. (2.34), the fraction is

 $f(0,8550 \text{ m}) = 1 - \exp\left[-\frac{(0.032 \text{ kg } \text{ mol}^{-1})(9.8 \text{ ms}^{-1})(8550 \text{ m})}{(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(300 \text{ k})}\right]$

 \Rightarrow

$$f(0, 8550 \text{ m}) = 0.659$$

The height of Mt. Everest is about 8550 m. This means that, at the top of Mt. Everest the percentage of O_2 goes down to 0.659 factor of that present at the ground level; the drop in temperature is neglected. Had it been considered the percent factor will become further lesser.

Example 2.7

Calculate the mass of our atmosphere around our earth. The mean radius of the earth is 6.4×10^3 km and the ground level pressure is 1 atm.

Solution

The total number of molecules present in the atmosphere is obtained from Eq. (2.32):

$$N(0,\infty) = \frac{n_0 \ AkT}{mg}$$
 (A is the area of the surface of the earth)

Therefore, the total mass is

Mass
$$(0, \infty) = \frac{n_0 AkT}{g} = \frac{AP_0}{g}$$

Where we have used the ground level pressure $P_0 = n_0 kT = 1$ atm.

$$\Rightarrow \qquad \text{Mass}(0,\infty) = \frac{4\pi r^2 P_0}{g} = \frac{4(3.14)(6.4 \times 10^3 \,\text{m})^2 (1 \,\text{atm})}{(9.8 \,\text{ms}^{-2})}$$

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$$\Rightarrow \qquad \text{Mass} (0, \infty) = \frac{4(3.14)(6.4 \times 10^6 \text{ m})^2(1 \text{ atm})}{9.8 \text{ ms}^{-2}} \times \frac{(101325 \text{ Pa})}{1 \text{ atm}}$$
$$\text{Mass} (0, \infty) = 5.32 \times 10^{18} \text{ kg}$$

Example 2.8

Calculate the mean potential energy of the molecules in the atmosphere at 300 K.

Solution

The number of molecules in the section of the atmosphere between the altitudes Z to Z+dZ is n AdZ; each of them has potential energy mgZ. The average potential energy is therefore given by

$$\langle \varepsilon_{\rm Pot} \rangle = \frac{1}{N(0,\infty)} \int_0^\infty \varepsilon_{\rm Pot} dN$$

 \Rightarrow

$$\Rightarrow \qquad \langle \varepsilon_{\rm Pot} \rangle = \frac{Am^2 g^2 n_0}{n_0 AkT} \int_0^\infty e^{-mgZ/kT} Zdt \quad [\text{using Eq. (2.32)}]$$

 $\langle \varepsilon_{\rm Pot} \rangle = \frac{1}{N(0,\infty)} \int_0^\infty (mgZ) A ndZ$

$$\Rightarrow$$

(using the gamma function; see Sec. 2.10.4; M.11)

 $\Rightarrow \qquad \langle \varepsilon_{\rm Pot} \rangle = kT = (1.38x^{-23} \text{ JK}^{-1}) (300 \text{ K})$

$$\Rightarrow \qquad \langle \mathcal{E}_{\rm Pot} \rangle = 4.14 \times 10^{-21} \, \rm{J}$$

This is sometimes referred to as the *thermal energy* of the molecules.

 $\langle \varepsilon_{\rm Pot} \rangle = \frac{m^2 g^2}{kT} \left(\frac{kT}{mg} \right)^2$

Example 2.9

Show that the height H, at which the pressure is (1/e)th of the ground level value is equal to that imaginary height within which the entire exponential atmosphere is present but, with the ground level pressure uniform throughout from zero to H.

Solution

The total number of molecules in the exponential atmosphere is given by $An_0 \frac{kT}{mg}$ [Eq. (2.32)]; and if this is assumed to be present within an altitude *H* uniformly with the ground level pressure P_0 (= $n_0 kT$), then

$$An_0 \,\frac{kT}{mg} = A H n_0$$

$$\Rightarrow$$
 $H =$

Using Eq. (2.28),

$$= P_0 \ e^- \ \frac{mg \ Z}{kT}$$

 $\frac{kT}{mg}$

Р

e

 \Rightarrow

$$\frac{(mgH - kT)}{kT} = 1 = e^0 \implies mgH - kT = 0$$

 $\frac{1}{2} P_0' = P_0' e^{-\frac{mg H}{kT}} \implies e^{\frac{mg H}{kT}} e^{-1} = 1 = e^0$

 \Rightarrow

and finally, our answer $H = \frac{kT}{mg}$.

Example 2.10

When Julius Caesar expired, his last exhalation had a volume of about 500 cm³. This expelled air was, 1 mol% argon. Assume that the temperature was 300 K and the ground level pressure 1 atm. Assume that the temperature and pressure are uniform over the earth's surface and still have the same values. If Caesar's argon molecules have all remained in the atmosphere and have been completely mixed throughout the atmosphere, how many inhalations, 500 cm³ each, must we make on average to inhale one of Caesar's argon molecules? The mean radius of the earth is 6.37×10^6 m.

Solution

If n and n_0 are the number of Ar molecules per unit volume at an altitude Z and, on the earth's surface, respectively, then

z + dz

z = 0

area A

(2.29)]

$$n = n_0 \exp\left(-\frac{mgZ}{kT}\right)$$
 [cf. Eq. (

The total number of Ar molecules in the atmosphere $(Z = 0 \text{ to } Z \rightarrow \infty)$ is then

$$n_{\text{total}} (Ar) = N(0, \infty) = \int_{0}^{\infty} nAdZ$$

 $n_{\text{total}} (Ar) = n_0 A \int_{0}^{\infty} e^{\frac{mgZ}{kT}} dZ$

 \Rightarrow

 \Rightarrow

$$n_{\text{total}} (Ar) = \frac{n_0 \ AkT}{mg}$$
 [cf Eq. (2.32)] ...(a)

m is mass of a Ar-atm.

This total number of molecules in his last exhalation may also be written as

$$n_{\text{(total)}} = \frac{P_{v}}{RT} N_{0}$$

$$= \frac{(1 \text{ atm}) (500 \text{ cm}^{3}) (6.022 \times 10^{23} \text{ atoms } \text{ mol}^{-1})}{(82.05 \text{ cm}^{3} \text{ atm} \text{ K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}$$

$$= 1.223 \times 10^{22} \text{ atoms}$$

Therefore, the total number of Ar atoms is

$$n_{\text{total}} (\text{Ar}) = 1.223 \times 10^{22} \times 0.01 = 1.223 \times 10^{20} \text{ atoms}$$
 ...(b)

Now, equating Eqs (a) and (b), we find

 $\frac{n_0 \ AkT}{mg} = 1.223 \times 10^{20} \text{ atoms} = \frac{n_0 \ ART}{Mg} \qquad (M \text{ is the molar mass of Ar})$ $n_0 = \frac{(1.223 \times 10^{20} \text{ atoms}) (0.04 \text{ kg } \text{mol}^{-1}) (9.81 \text{ m/s}^{-2})}{4\pi \ (6.37 \times 10^6 \text{ m})^2 \ (8.314 \text{ M m } \text{ K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}$ $= 37.75 \text{ atoms } \text{m}^{-3} \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3}\right)$ $= 37.75 \text{ atom } 10^{-6} \text{ cm}^{-3} = 37.75 \text{ atom}/10^6 \text{ cm}^3$

37.75 atoms of He present in 10^6 cm³

1 atom of He will be found in 0.0265×10^6 cm³ = 2.65×10^4 cm³

To take a single of Caesar's Ar atoms, number of inhalations required is

$$\frac{2.65 \times 10^4 \text{ cm}^3}{500 \text{ cm}^3} = 53$$

Example 2.11

Calculate the change in the ground level pressure of the atmosphere if the temperature is increased by *x* times.

Solution

Let n_0 be the number of molecules per unit volume at the ground level at temperature *T*. The ground level pressure is then $P_0 = n_0 kT$. The total number of molecules present in the whole atmosphere is then $An_0 kT/mg$ [Eq. (2.32)]. If n_0' be the population density at the ground level when, the temperature is increased to xT, then we must have, from the conservation of the number of molecules:

$$\frac{An_0 \ kT}{mg} = \frac{An'_0 \ k(xT)}{mg}$$
$$n'_0 = \frac{n_0}{mg}$$

 \Rightarrow

The ground level pressure at this increased temperature is therefore

$$P_0' = n_0' k(xT) = n_0 kT = P_0$$

The ground level pressure therefore remains unchanged.

x

Comment When the temperature is increased x times, the gas becomes dilute at the ground level but, they are now hitting more harder. So the pressure remains the same.

Example 2.12

A balloon having a capacity of 10,000 m³ is filled with He at 20°C and 1 atm pressure. If the balloon is loaded with 80% of the load that it can lift at ground level, at what height will the balloon come to rest? Assume that the volume of the balloon is constant, the atmosphere isothermal at 20°C, the molar mass of air is 28.9 g mol⁻¹, and the ground level pressure is 1 atm. The mass of the balloon is 1.3×10^6 g.

Solution

The mass of He in the balloon is

$$W_{\rm He} = \frac{PvM}{RT}$$
$$W_{\rm He} = \frac{(101325 \text{ M/m}^{-2})(10,000 \text{ m}^{3})(0.004 \text{ kg mol}^{-1})}{(8.314 \text{ M/m} \text{ k}^{-1} \text{ mol}^{-1})(293 \text{ k})}$$

or,

$$W_{\rm He}$$
 = 1663.8 kg

The mass of the balloon $W_{\rm B}$ is 1300 kg.

The sum of the masses of He and balloon is

$$(W_{\text{He}} + W_{\text{B}}) = (1663.8 + 1300)\text{kg} = 2963.8 \text{ kg}$$

The mass of the displaced air at the ground level is

$$W_{air} = \frac{PvM}{RT}$$

$$W_{air} = \frac{(101325 \text{ M m}^{-2})(1 \times 10^4 \text{ m}^3)(0.0289 \text{ kg mol}^{-1})}{(8.314 \text{ M m} \text{ k}^{-1} \text{ mol}^{-1})(293 \text{ k})}$$

$$W_{air} = 12,020.89 \text{ kg}$$

or

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Therefore, the lifting power at the ground level is

(12,020.89 - 2963.8) kg = 9057.1 kg.

The mass of the load is (0.8×9057.1) kg = 7245.68 kg.

The net downward load is then $W_L = (2963.8 + 7245.68)$ kg wt. = 10,209.48 kg wt.

The net upward force is then

 $W \uparrow = W_{\rm air} - W_L = (12,020.89 - 10,209.48) \; \rm kg \; wt$ $W \uparrow = 1,811.41 \; \rm kg \; wt.$

or

Let h be the altitude where the balloon comes to rest and the pressure at height h be P. The mass of the displaced air at the altitude h is

$$\frac{P \times 10^4 \times 0.0289}{8.314 \times 293} = 0.1186 P \text{ (the pressure } P \text{ is in Pa)}$$

and this must be equal to the net downward load, i.e.

$$\Rightarrow \qquad 0.1186 P = 10,209.48$$

$$\Rightarrow \qquad P = 86,083.31 Pa$$

$$\Rightarrow \qquad P = (86,083.31 Pa) \left(\frac{1 \text{ atm}}{101325 Pa}\right)$$

$$\Rightarrow \qquad P = 0.8496 \text{ atm}$$

We now apply the barometric equation

$$P = P_0 \exp\left(-\frac{mgh}{kT}\right)$$

$$\Rightarrow \qquad h = \frac{RT}{Mg} \ln \frac{P_0}{P}$$

$$\Rightarrow \qquad = \frac{(8.314 \text{ Nm } \text{k}^{\text{-1}} \text{ mol}^{-1})(293 \text{ k})}{(0.0289 \text{ kg mol}^{-1})(9.8 \text{ m s}^{\text{-2}})} \ln\left(\frac{1 \text{ atm}}{0.8496 \text{ atm}}\right)$$
or
$$h = 1,401.9 \text{ m}$$
or
$$h \approx 1.4 \text{ km}$$

Example 2.13

Calculate the change in the ground level pressure of the atmosphere if the temperature is increased to x times the initial temperature.

Solution

Let n_0 be the number of molecules per unit volume at the ground level at temperature T. The ground level pressure is then $P_0 = n_0 kT$. The total number of molecules present in the whole atmosphere is $An_0 \frac{kT}{mg}$ [cf. Eq. (2.32)]. If the population density at the ground level be n_0' when, the temperature i = increased then, we may write:

$$\frac{An_0 kT}{mg} = \frac{An_0' K(xT)}{mg}$$

 \Rightarrow

 \Rightarrow

$$n_0' = \frac{n_0}{x}$$

The ground level pressure at this increased temperature is then

$$P_0' = n_0' k(xT) = \frac{n_0}{x} kxT = n_0 kT = P_0$$

The ground level pressure therefore remains unchanged. The reason behind this interesting result is that, when the temperature is increased x times, the gas becomes dilute at the ground level but, they are now bombarding more harder; so the pressure remains the same.

2.14.7 Barometric Distribution as a Special Case of More Generalised Boltzmann Distribution

In the barometric equation, we note an interesting fact that the number density of the particles at any altitude is proportional to

exp [- gravitational potential energy of each particle at that altitude/kT]

Now, the question is: do the equation also works when the molecules/particles are subjected to any potential field other than the gravity?

To find the answer, let us apply the system in a potential field where F force acts on each particle along the x axis (F is a function of x). As we have done earlier, let us take two parallel planes of unit area at distances x and x + dx from some reference point. If the number density of the particles at the level x be n, then the total number of particles between the two chosen planes is ndx; the net force on this assembly is, therefore, Fn dx; and this must also be the pressure difference dP across this section; i.e.

$$Fndx = dP = k Tdn$$
$$\frac{dn}{n} = \frac{Fdx}{kT}$$

We know that, for a conservative force, $F = -\frac{dV}{dx}$, where *V* is the potential energy at the point *x* and *dV* is its change over the distance *dx*. Then we can write

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$$\frac{dn}{n} = -\frac{dV}{kT}$$

and integrating between limits

$$\int_{n_0}^{n} \frac{dn}{n} = -\frac{1}{kT} \int_{0}^{V} dV$$

$$n = n_0 \exp\left(-\frac{V}{kT}\right)$$
(2.35)

which is nothing different from Eq. (2.29), where we had V = mgZ.

Equation (2.35) is the Boltzmann distribution and now we understand that the barometric distribution is a special case of the more generalised Boltzmann distribution. Suppose, we take an aqueous solution of NaCl. Concentrate on a particular Na⁺ ion. How are the other Na⁺ and Cl⁻ ions arranged about this central ion? The answer is given by Eq. (2.35). *They are arranged exponentially*: the concentration of the Na⁺ ions increases exponentially and that of the Cl⁻ ions decreases exponentially with increasing distance from the central cation. We will find an ingenious application of this principle later.

Example 2.14

The potential energy of the particles of a system in a certain central field depends on the distance from the centre of the field as $V = ar^2$, where 'a' is a positive quantity. The temperature is T and the number of particles per unit volume at the centre is n_0 . Calculate

- (i) the number of molecules located between distances r and r+dr from the centre of the field.
- (ii) the fraction of the total number of molecules located between distances r and r + dr.
- (iii) the most probable distance separating the molecules from the centre of the field.
- (iv) by how many times the number density of the molecules at the centre of the field changes if the temperature is changed by a factor (1/x)?
- (v) the number of particles whose potential energy lies within the interval $V \to V + dV,$ and
- (vi) the most probable value of the potential energy of a particle. Compare this value with the potential energy of a particle located at the most probable distance.

Solution

The distribution of the particles in the space is given by Eq. (2.35)

$$n = n_0 \, \exp\!\left(-\frac{ar^2}{kT}\right)$$

2.52

 \Rightarrow

where n and n_0 , respectively, are the population densities of the particles at the distance r and at the centre.

(i) To solve this part, we have first to find the volume of the shell between two concentric spheres of radii r and r + dr; and then multiply this with the population density at r. The volume of the shell is $d(V) = d\left(\frac{4}{3}\pi r^3\right) = 4\pi r^2 dr$. Therefore, the

number of particles located between distances r to r + dr is

$$dN_r = (4\pi r^2)n = 4\pi n_0 \exp\left(-\frac{ar^2}{kT}\right)r^2 dr$$

(ii) To find the fraction, we have to calculate the total number of particles present. This is

$$N(0,\infty) = \int_0^\infty dN_r = 4\pi n_0 \int_0^\infty e^{-\frac{ar^2}{kT}} r^2 dr$$

 \Rightarrow

$$N(0, \infty) = n_0 \left(\frac{\pi kT}{a}\right) \qquad (\text{see Sec. 1.9.4; M11})$$

 $(10)^{3/2}$

The fraction of the total number of particles lying between r to r + dr is therefore

$$f(r \to r + dr) = \frac{dN_r}{N(0, \infty)} = 4\pi \left(\frac{a}{\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{ar^2}{kT}\right) r^2 dr$$
(iii)
$$\frac{dN_r}{dr} = 4\pi N(0, \infty) \left(\frac{a}{\pi kT}\right)^{3/2} r^2 \exp\left(-\frac{ar^2}{kT}\right)$$

Figure 2.22(a) shows that there is an exponential decrease in the density of the particles with r. Figure 2.22(b) shows the parabolic increase in the volume of the shell. Figure 2.22(c) gives the combined effect of these two variations. The function first increases and then, forming a maximum, decays down. The distance corresponding to this maximum is called the most probable distance, because at this distance the differential spherical shell contains the maximum number of molecules. To find this distance, we differentiate $\frac{dN_r}{dr}$ with respect to r and equate it to zero:

$$\frac{d}{dr}\left(\frac{dN_r}{dr}\right) = 8\pi n_0 r \exp\left(-\frac{ar^2}{kT}\right) \left[1 - \frac{ar^2}{kT}\right] = 0$$

Three solutions are there:

(i) r = 0 (ii) $r \to \infty$ and (iii) $r = \sqrt{\frac{kT}{a}}$

You can easily find from Figure 2.22(c) that at r = 0 and as $r \to \infty$, there are no particles. So the only physically acceptable solution is $r_{mp} = \sqrt{\frac{kT}{a}}$.



Figure 2.22 The combined effect of the two opposing factors.

(iv) Let n'_0 be the concentration at the centre of the field at temperature T/x. Then we can write

$$n_0 \left(\frac{\pi kT}{a}\right)^{3/2} = n'_0 \left(\frac{\pi kT}{xa}\right)^{3/2}$$
 (of sec. 1.9.4; M 11)

as the total number of particles remain the same.

 $\Rightarrow \qquad \qquad n_0' = n_0 \ x^{3/2}$

which means that the number of particles per unit volume will change by a factor of $x^{3/2}$.

(v) If V and V + dV are the potential energies of the particles at distances r and r + dr, then the number is exactly the same as dN_r ; writing it as dN_V , we get

$$dN_V = 4\pi n_0 \, \exp\!\left(-\frac{ar^2}{kT}\right) r^2 dr$$

Since

 \Rightarrow

$$dN_V = 4\pi n_0 \, \exp\left(-\frac{V}{kT}\right) \frac{V}{a} \frac{1}{2\sqrt{aV}} \, dV$$

 $V = ar^2, dr = \frac{1}{2\sqrt{aV}} dV$

$$\Rightarrow \qquad \qquad dN_V = \frac{2\pi n_0}{a^{3/2}} V^{1/2} \exp\left(-\frac{V}{kT}\right) dV$$

The distribution function is therefore

$$\frac{dN_V}{dV} = \frac{2\pi n_0}{a^{3/2}} V^{1/2} \exp\left(-\frac{V}{kT}\right)$$

and is shown in Figure 2.23.



Figure 2.23 Variation of the distribution function with the potential energy V.

To find the most probable value of the potential energy, we differentiate $\frac{dN_V}{dV}$ (vi) and, equate it to zero.

$$\frac{d}{dV}\left(\frac{dN_V}{dV}\right) = \frac{2\pi n_0}{a^{3/2}} V^{1/2} \exp\left(-\frac{V}{kT}\right) \left[\frac{1}{2V} - \frac{1}{kT}\right] = 0$$

The physically acceptable solution is

$$V_{mp} = rac{1}{2} kT$$

The potential energy at the most probable distance is

 $\overline{2}$

$$V_{r=r_{mp}} = a r_{mp}^2 = a \frac{kT}{a} = kT$$
$$\frac{V_{mp}}{V_{r=r_{mp}}} = \frac{1}{2}$$

...

2.15 MAXWELL'S DISTRIBUTION OF MOLECULAR SPEED

2.15.1 Introduction

We have finished a long section of a topic which describes a single feature of a gaseous sample at rest in thermal equilibrium. The barometric distribution function gives us the distribution of the particles in a potential field in space, *irrespective of their speeds*. That is, it estimates how many particles are here and how many of them are there. But there is another important feature of the system, that we want to know.

Suppose, we calculate the total number of molecules in between two altitudes h and h + dh from the earth's surface. We then ask, are all the molecules in this section moving with the same speed? Definitely not. For, even if we have started off with this section, having all the molecules therein, moving with the same speed, the random erratic collisions among the molecules would continuously change their velocities and ultimately, a steady state will be attained in which the molecules will be distributed *indistinguishably* over the entire velocity spectrum. The adjective 'indistinguishable' means that a particular molecule would not become restricted to move in a given speed zone; rather, they will be certainly, constantly changing their speed but, the number of molecules moving in a given speed range will be fixed, after the steady state is attained. We now want to find out the rule according to which the molecules are distributed over the entire speed range: $0 \rightarrow \infty$. However, before we start, it would be nice to prove that, if all the molecules move with the same speed, the behaviour of the gas would be quite different from that required by thermodynamics.

Consider a one-dimensional gas in which all the molecules move vertically up and down, i.e. along the *z*-axis only. Suppose the molecules start rising up from the earth's surface with velocity V_0 ; as they go up, they lose their kinetic energy according to the equation

$$\frac{1}{2} m v_0^2 = \frac{1}{2} m v^2 + m g Z$$

where v is the velocity of the molecules at height Z from the earth's surface. Definitely, a

height $Z_m = \frac{v_0^2}{2g}$ will be attained at which, all the molecules would stop and drop down

towards the earth's surface. What is the result?

Firstly, our atmosphere should have a finite sharp upper limit, and secondly, since you know that the average kinetic energy of the molecules is a linear function of temperature, the atmosphere will also experience a linear drop in temperature until the upper limit is reached, where the temperature goes to the absolute zero. Thirdly, the density would increase with altitude. This is because, in the higher altitudes the molecules move slowly and require a longer time to traverse a given length. All these conclusions are going against our knowledge. The first and the third points violate the barometric distribution; and the

second point violates the 2nd and 3rd laws of thermodynamics, according to which, the attainment of OK is an impossibility. The molecules therefore cannot move with the same speed.

2.15.2 Postulates and Criticisms

James Clerk Maxwell solved this problem first in 1859. His deduction was based on the following assumptions:

- (i) The distribution of velocity is the same along any direction.
- (ii) The number of molecules per unit volume remains the same in the course of time in every volume element throughout the gas.
- (iii) The probability of occurrence of any velocity component, say v_x , is independent of the values of the other two velocity components v_y and v_z .

Assumption (iii), which is one form of what has been called the 'Principle of Molecular Chaos', was, however, the main objection raised, against the theory, by the opposite schools, particularly, the mathematical purists. Moreover, Maxwell's original proof did not take account the effect of molecular collisions. Later, Maxwell himself, Boltzmann, Jeans and others have derived the same equation by taking into account the effect of molecular collisions and, some assumptions which seemed more plausible. In fact, the best justification of the distribution law is to consider it as a special case of the more generalised Boltzmann distribution law, which can be proved from the statistical mechanical principles. Finally, in spite of so little satisfaction to the mathematical purists, one can just only wonder at the genius of Maxwell who proposed such a *fundamental and accurate* physical law, probably from his intuition. We shall now move to explore the distribution function.

2.15.3 Distribution Law

We consider a sample of a gas where the molecules are moving randomly, i.e. along all possible direction in space. As we know from our elementary knowledge, *a velocity vector* v can be broken into its three rectangular components v_x , v_y and v_z . Let '*n*' be the total number of molecules per unit volume.

If dn_{v_x} be the number of molecules per unit volume whose x-component velocities lie in the range $v_x \rightarrow v_x + dv_x$ then, we may write:

The fraction of the total number of molecules whose x-component velocities lie in the range $v_x \rightarrow v_x + dv_x$ is (dn_{v_x}/n) . This fraction must depend on some function of v_x , say $f(v_x)$ and, must be directly proportional to the interval dv_{x_i} ; because, if this interval in the infinitesimal scale is doubled, the number of molecules must also be doubled. We write for the velocity distribution along the v_x axis as

$$\frac{dn_{v_x}}{n} = f(v_x) \, dv_x$$

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and, the velocity distribution function $f(v_x)$ as

$$\frac{1}{n}\frac{dn_{v_x}}{dv_x} = f(v_x) \tag{2.36}$$

Due to the *isotropic nature* of the movement of the molecules, the velocity distribution functions along v_y and v_z axes will be similar exactly as that along v_x axis, i.e.

$$f(v_y) = \frac{1}{n} \frac{dn_{v_y}}{dv_y} \text{ and } f(v_z) = \frac{1}{n} \frac{dn_{v_z}}{dv_z}$$

If we now define the velocity distribution function $F(v_x, v_y, v_z)$ representing the probability of the occurrence of the x-component velocities in the range $v_x \rightarrow v_x + dv_x$ and simultaneously, the y and z component velocities in the ranges $v_y \rightarrow v_y + dv_y$ and $v_z \rightarrow v_z + dv_z$, respectively, then

$$F(v_x, v_y, v_z) dv_x dv_y dv_z = \frac{dn_{v_x, v_y, v_z}}{n}$$
$$= f(v_x)f(v_y)f(v_z)dv_x dv_y dv_z$$

where dn_{v_x,v_y,v_z} is the number of molecules per unit volume whose x, y and z component velocities lie simultaneously, in the ranges $v_x \rightarrow v_y + dv_x$, $v_y \rightarrow v_y + dv_y$ and $v_z \rightarrow v_z + dv_z$, respectively.

All the differentials cancel so that we conclude that

$$F(v_x, v_y, v_z) = f(v_x) f(v_y) f(v_z)$$
(2.37)

This means that the probability that the velocity v (with components v_x , v_y and v_z) lies in the range between v and v + dv is just the product of the probabilities that the velocity components lie in their respective ranges. Thus, the individual velocity components behave like statistically independent quantities.

Taking the natural logarithm of Eq. (2.37),

$$\ln F = \ln f(v_{r}) + \ln f(v_{r}) + \ln f(v_{z})$$
(2.38)

Now, taking the derivative with respect v_x

$$\frac{\partial \ln F}{\partial v_x} = \frac{d \ln f(v_x)}{dv_x} + 0 + 0$$
(2.39)

and since $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$, we get

$$\frac{\partial v}{\partial v_x} = \frac{2v_x}{2\sqrt{(v_x^2 + v_y^2 + v_z^2)}}$$

$$\frac{\partial v}{\partial v_x} = \frac{v_x}{v}$$
(2.40)

or

 \Rightarrow

Equation (2.39) can then be rewritten as

$$\frac{d\ln F}{dv} \cdot \frac{\partial v}{\partial v_{x}} = \frac{d\ln f(v_{x})}{dv_{x}}$$

and, using Eq. (2.40)

$$\frac{d\ln F}{dv} \cdot \frac{v_x}{v} = \frac{d\ln f(v_x)}{dv_x}$$
$$\frac{1}{v} \frac{d\ln F}{dv} = \frac{1}{v_x} \frac{d\ln f(v_x)}{dv_x}$$
(2.41a)

If we have differentiated $\ln F$ with respect to v_y or v_z , similar equation (due to isotropicities) would be obtained:

$$\frac{1}{v}\frac{d\ln F}{dv} = \frac{1}{v_x}\frac{d\ln f(v_y)}{dv_y} = \frac{1}{v_z}\frac{d\ln f(v_z)}{dv_z}$$
(2.41b)

finally leading us to

$$\frac{1}{v}\frac{d\ln F}{dv} = \frac{1}{v_x}\frac{d\ln f(v_x)}{dv_x} = \frac{1}{v_y}\frac{d\ln f(v_y)}{dv_y} = \frac{1}{v_z}\frac{d\ln f(v_z)}{dv_z}$$
(2.42)

In Eq. (2.42), v_x , v_y and v_z are completely independent of each other. That is, you can put in any values you wish for v_x , v_y and v_z , and the equation must remain valid. There is only one way that this can be true and, that is if all the terms in Eq. (2.42) are equal to a same constant. For reasons which we will see in a moment, let this constant be (-b), where b > 0. Therefore

$$\frac{1}{v_x} \frac{d \ln f(v_x)}{dv_x} = -b$$
$$d \ln f(v_x) = -bv_x dv_x$$

 \Rightarrow

and, on integration with the constant $\ln a$

$$\ln f(v_x) = -\frac{b}{2} v_x^2 + \ln a$$

$$f(v_x) = a \ e^{-\frac{b}{2} v_x^2}$$
(2.43)

or

Equation (2.43) is the functional form of $f(v_x)$. We find that it is Gaussian and hence an even function. The function goes to zero at $v_x = \pm \infty$, which means that the integral is finite. If we had made the original constant +b instead of -b (b > 0), then the function would shoot to infinite at $v_x = \pm \infty$, and would not be integrable. Our next objective is to find expressions for 'a' and 'b'. From Eq. (2.36), we find that $f(v_x) dv_x$ is the fraction of the total number of molecules having velocities in the range $v_x \rightarrow v_x + dv_x$ ($-\infty \le v_x \le \infty$). The sum of all possible fractions must be unity, i.e.

$$\int_{-\infty}^{+\infty} f(v_x) dv_x = 1$$

$$\Rightarrow \qquad a \int_{-\infty}^{+\infty} e^{-\frac{bv_x^2}{2}} dv_x = 1 \qquad \text{(using equation 2.43)}$$

$$\Rightarrow \qquad a \sqrt{\frac{2\pi}{b}} = 1 \qquad \text{(see the Gaussian integral; 2.10.3)}$$
or
$$a = \sqrt{\frac{b}{2\pi}} \qquad (2.44)$$

Then we calculate $\langle v_x^2 \rangle$; this we obtain as

$$\left\langle v_x^2 \right\rangle = \int_{-\infty}^{+\infty} v_x^2 f(v_x) \, dv_x = a \int_{-\infty}^{+\infty} e^{-\frac{bv_x^2}{2}} v_x^2 \, dv_x$$

= $2a \int_0^{\infty} e^{-\frac{bv_x^2}{2}} v_x^2 \, dv_x \quad (\because \text{ even function})$
= $a \int_0^{\infty} e^{-\frac{bv_x^2}{2}} (v_x^2)^{\frac{3}{2}-1} \, d(v_x^2) = a \frac{\left[\left(\frac{3}{2}\right)\right]}{\left(\frac{b}{2}\right)^{3/2}}$

and simplifying

$$\langle v_x^2 \rangle = \frac{1}{b}$$

The average translational kinetic energy in one dimension is therefore

$$\frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} \frac{m}{b} = \frac{1}{2} kT$$

 \Rightarrow

and, using this result in Eq. (2.44)

$$a = \sqrt{\frac{m}{2\pi kT}} \;$$

 $b = \frac{m}{kT}$

The Maxwell's distribution function of molecular velocity along the *x*-axis is therefore [using Eqs (2.43) and (2.45)]

$$f(v_{x}) = \frac{1}{n} \frac{dn_{v_{x}}}{dv_{x}} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_{x}^{2}/2kT}$$

$$dn_{v_{x}} = n \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_{x}^{2}/2kT} dv_{x}$$
(2.46a)

or

This equation is one of the most fundamental equations of the kinetic theory.

Again, due to the isotropicity of the movements of the gas molecules (i.e. the molecular motion is completely random), there is no difference among the velocity distributions along the three axes. This is also corroborated from the assumption (i) of Maxwell. We can write, therefore

$$\begin{aligned} f(v_y) &= \frac{1}{n} \frac{dn_{v_y}}{dv_y} = \left(\frac{m}{2\pi kT}\right)^{1/2} e \frac{-mv_y^2}{2kT} \\ f(v_z) &= \frac{1}{n} \frac{dn_{v_z}}{dv_z} = \left(\frac{m}{2\pi kT}\right)^{1/2} e \frac{-mv_z^2}{2kT} \end{aligned}$$
(2.46b)

and

Equations (2.46a) and (2.46b) represent the velocity distribution of the molecules in a gas along the three rectangular axes. Figure 2.24 shows this distribution along the v_x axis for N_2 at 25°C and 1025°C. The area under the curve within the interval range $v_x' \rightarrow v_x' + dv_x$ is $f(v_x) \cdot dv_x$, i.e. $\frac{1}{n} \frac{dn_{v_x}}{dv_x} \cdot dv_x$ or $\frac{1}{n} dn_{v_x}$, i.e., the fraction of the total number of molecules moving with velocities in the range v_x' to $v_x' + dv_x$ along the x axis. The total area under each curve must therefore be unity. It is noted that the fraction of the total number of molecules moving along a given axis, say v_x , with velocities in the range $v_x' + dv_y$ and $v_y' + dv_y' + dv_y'$

 $v_x' + dv_x$ decreases at first, very slowly, and then very rapidly as the velocity is increased. So far $\frac{1}{2}m\langle v_x^2\rangle < kT$, this decrease is slow but, as $\frac{1}{2}m\langle v_x^2\rangle$ becomes of the order of 10 kT, the fraction becomes almost zero (Figure 2.24). This can therefore be concluded that only

a negligibly few molecules are there in a gas, whose energy is much greater than kT. With increase in temperature, the distribution becomes more broader and more flatter because of the normalization.

(2.45)


Figure 2.24 Molecular velocity distribution in one dimension for N₂ at 25°C and at 1025°C.

Example 2.15

Show that $\langle v_x \rangle = 0$.

Solution

The number of molecules per unit volume moving with x-component velocities in the range $v_x \rightarrow v_x + dv_x$ is

 $dn_{v_x} = (\text{total no. of molecules per unit volume}) \times \text{fraction of the total no. of molecules having x-component velocities in the range } v_x \rightarrow (v_x + dv_x)$

 \Rightarrow

$$dn_{v_x} = n \times f(v_x) dv_x$$

The average of v_x is then

$$\langle v_x \rangle = \frac{1}{n} \int_{-\alpha}^{+\infty} v_x dn_{v_x} = \int_{-\infty}^{+\infty} \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/2kT} \cdot v_x dv_x$$

i.e.

 $\langle v_x \rangle = 0,$

Since the function $v_x e^{-mv_x^2/2kt}$ is an odd function (Sec. 1.9.2; Eq. M8).

The result is quite expected: number of molecules moving with speeds in the range, say (50 to 50.001) ms⁻¹ to the east, is exactly the same as those to the west. The velocity, being a vector, therefore cancels out. Although average velocity along the *x*-axis $\langle v_x \rangle$ is zero,

we must get a finite value of the x-component velocity along one direction, say, to the east. The limits of integration are now from 0 to ∞ and, the total number of molecules per unit volume should be halved as before, i.e. (n/2). Therefore, the average of the x-component velocity towards east is

$$\langle v_{x,+} \rangle = \frac{2}{n} \int_0^\infty v_x \, dn_{v_x} = \frac{2}{n} n \left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^\infty v_x \, e^{-mv_x^2/2kt} \, dv_x$$

$$\langle v_{x,+} \rangle = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^\infty e^{-mv_x^2/2kt} \, d(v_x^2)$$

$$\langle v_{x,+} \rangle = \sqrt{\frac{2kT}{\pi m}}$$

$$(2.47a)$$

or

 \Rightarrow

The average of x component (or y or, z) velocity along the positive (right) direction is finite.

It is now a very easy job to find that how many molecules strike a unit area held perpendicular to the *x*-axis per second. As shown in Figure 2.25, all the molecules, which are within the cylinder of unit are and length $\langle v_{x,+} \rangle$, held normal to the *yz* plane would strike per second the result is (Figure 2.25)



Figure 2.25 The number of molecules in this column is $\frac{n}{2} \langle v_{x,+} \rangle$ that are moving towards right, and, they will hit the area A (unit).

 $\left. \begin{array}{l} \text{Number of molecules striking} \\ \text{a unit area of the wall of the} \\ \text{container per second} \end{array} \right\} \\ = \frac{n}{2} \left\langle v_{x\,,\,+} \right\rangle = \frac{1}{2} n \sqrt{\frac{2kT}{\pi m}} \end{array}$

$$= \frac{1}{4} n \sqrt{\frac{8kT}{\pi m}}$$
$$= \frac{1}{4} n \langle c \rangle$$
(2.47b)

a result, that we got earlier [cf. Eq. (2.20)].

Physical Chemistry

2.15.4 Speed Distribution and Energy Distribution in One Dimension

Due to the isotropicity in the movement of the molecules, the number of molecules moving with speeds in the range $C_x \rightarrow C_x + dC_x$ towards east must be equal to those moving west. Therefore, if dn_{v_x} be the number of molecules per unit volume, found moving in the velocity range $v_x \rightarrow v_x + dv_x$ then, the number of molecules per unit volume, moving in the speed range $C_x \rightarrow C_x + dC_x$, where $|v_x| = C_x$ and $dv_x = dC_x$ is $dn_{C_x} = 2dn_{v_x}$. We can write, therefore, $dn_{C_x} = 2dn_{v_x}$. This is explained in Figure 2.26. The speed distribution function in one dimension is therefore

$$dn_{C_x} = 2dn_{v_x} = 2n \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mC_x^2}{2kT}} dC_x$$
(2.48)

A plot of $f(C_x)$, i.e. $\frac{1}{n} \frac{dn_{C_x}}{dC_x}$ versus C_x would be exactly, the same as the right part of

Figure 2.26, but being multiplied by 2.



Figure 2.26 The sum of the two strips is equal to the fraction of the total molecules with velocities in the range $v_x \rightarrow v_x + dv_x$ irrespective of direction; so $dn_{c_v} = 2(dn_{v_v})$.

The average speed in one dimension is then

$$\langle C_x \rangle = \frac{1}{n} \int_0^\infty C_x dn_{C_x} = 2 \left(\frac{m}{2\pi kT} \right)^{1/2} \int_0^\infty C_x e^{-mC_x^2/2kT} dC_x$$

$$\langle C_x \rangle = \sqrt{\frac{2kT}{\pi m}} \tag{2.49}$$

exactly the same result as in Eq. (2.47). If the energy corresponding to the speed C_x is ε_x , then

$$\in_{\mathbf{x}} = \frac{1}{2} m C_{\mathbf{x}}^2 \text{ ; } d \in_{\mathbf{x}} = m C_{\mathbf{x}} d C_{\mathbf{x}} \text{ and } d C_{\mathbf{x}} = \frac{1}{\sqrt{2m \in_{\mathbf{x}}}} d \in_{\mathbf{x}}.$$

Equation (2.48) then transforms to

$$dn_{\epsilon_{x}} = dn_{C_{x}} = 2n \left(\frac{1}{2\pi kT}\right)^{1/2} e^{-\epsilon_{x}/kT} d\epsilon_{x}$$
$$dn_{\epsilon_{x}} = n \left(\frac{1}{\pi kT}\right)^{1/2} \epsilon_{x}^{-1/2} e^{-\epsilon_{x}/kT} d\epsilon_{x}$$
(2.50)

or

 \Rightarrow

which is the distribution of energy in one dimension. The average kinetic energy of the molecules in one dimension is therefore

$$\begin{aligned} \langle \epsilon_x \rangle &= \frac{1}{n} \int_0^\infty \epsilon_x \ dn_{\epsilon_x} \\ \Rightarrow & \langle \epsilon_x \rangle = \left(\frac{1}{\pi kT}\right)^{1/2} \int_0^\infty \epsilon_x^{1/2} \ e^{-\epsilon_x/kT} d \ \epsilon_x \\ \Rightarrow & \langle \epsilon_x \rangle = \left(\frac{1}{\pi kT}\right)^{1/2} \int_0^\infty e^{-\epsilon_x/kT} (\epsilon_x)^{\frac{3}{2}-1} \ d \ \epsilon_x \end{aligned}$$

and, using the gamma function

$$\langle \epsilon_x \rangle = \frac{1}{2} kT \tag{2.51}$$

Finally, using the isotropicity of the movement of the molecules we may write

$$\langle \boldsymbol{\in}_{\boldsymbol{x}} \rangle = \langle \boldsymbol{\in}_{\boldsymbol{y}} \rangle = \langle \boldsymbol{\in}_{\boldsymbol{z}} \rangle = \frac{1}{2} \, \boldsymbol{k} T$$

and therefore, the total translational kinetic energy of the molecules

$$\begin{split} &\langle \in \rangle = \langle \in_x \rangle + \langle \in_y \rangle + \langle \in_z \rangle \\ &\langle \in \rangle = \frac{3}{2} \, kT \end{split}$$

Example 2.16

Calculate the root mean square velocity of the molecules of a gas along the *x*-axis. **Solution**

First, we calculate the mean square velocity of the molecules along the *x*-axis:

$$\langle v_x^2 \rangle = \frac{1}{x} \int_{-\infty}^{+\infty} v_x^2 + (v_x) \, dv_x = \frac{1}{n} \int_{-\infty}^{+\infty} \left(\frac{m}{2\pi \, kT}\right)^{1/2} e^{-\frac{mv_x^2}{2kT}} \, v_x^2 \, dv_x$$

$$\langle v_x^2 \rangle = \left(\frac{m}{2\pi \, kT}\right)^{1/2} \int_{-\infty}^{+\infty} e^{-\frac{mv_x^2}{2kT}} \, v_x^2 \, dv_x$$

 \Rightarrow

 \Rightarrow

Since the function is even, we may write

$$\langle v_x^2 \rangle = 2 \left(\frac{m}{2\pi kT} \right)^{1/2} \int_0^\infty e^{-\frac{mv_x^2}{2kT}} v_x^2 dv_x$$

and, to apply the rule of gamma function, we rewrite it as

$$\langle v_x^2 \rangle = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^\infty e^{-\frac{mv_x^2}{2kT}} (v_x^2)^{\frac{3}{2}-1} d(v_x^2)$$
$$\langle v_x^2 \rangle = \left(\frac{m}{2\pi kT}\right)^{1/2} \frac{\sqrt{\frac{3}{2}}}{(m/2kT)^{3/2}} = \frac{kT}{m}$$

The root mean square velocity along the *x*-axis is therefore

$$(v_x)_{\rm rms} = \sqrt{\langle v_x^2 \rangle} = \sqrt{\frac{kT}{m}}$$
(2.52)

Example 2.17

Calculate the most probable velocity of the molecules along the *x*-axis.

Solution

The most probable velocity is defined as the velocity at which the velocity distribution function $\left(\frac{1}{n}\frac{dn_{v_x}}{dv_x}\right)$ is maximum. From Figure 2.26, it is clear that the maximum of the curve occurs at $v_x = 0$. So, the most probable velocity of the molecules along the *x*-axis is zero. Mathematically you can prove it by differentiating the function with respect to v_x and then, equating the result to zero. Do it yourself.

Example 2.18

Calculate the average speed and the root mean square speed of the molecules of N_2 at 27°C along the *x*-axis. Note that root mean square speed and root mean square velocity are the same. Why? How much is the average translational kinetic energy along this axis?

Solution

The average speed is

$$\begin{split} \langle C_x \rangle &= \sqrt{\frac{2kT}{\pi m}} = \sqrt{\frac{2RT}{\pi M}} \\ &= \sqrt{\frac{2(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{3.14 (0.028 \text{ kg mol}^{-1})}} \end{split}$$

 \Rightarrow

 $\langle C_x \rangle = 238.2 \text{ ms}^{-1}$

The root mean square speed is

$$(v_x)_{\rm rms} = \sqrt{\frac{kT}{m}} = \sqrt{\frac{RT}{M}}$$
$$(v_x)_{\rm rms} = \sqrt{\frac{(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(300 \text{ K})}{0.028 \text{ kg mol}^{-1}}} = 298.46 \text{ ms}^{-1}$$

 \Rightarrow

 \Rightarrow

You can directly use Eq. (2.51):

$$\langle \epsilon_x \rangle = \frac{1}{2} kT = \frac{1}{2} (1.38 \times 10^{-23} \text{ JK}^{-1}) (300 \text{ K})$$

 $\langle \epsilon_x \rangle = 2.07 \times 10^{-21} \text{ J}$

We may also do it as

$$\langle \epsilon_x \rangle = \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} m \langle v_x \rangle_{\rm rms}^2$$
$$= \frac{1}{2} \frac{(0.028 \text{ kg mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1})} \times (298.46 \text{ ms}^{-1})^2$$
$$\langle \epsilon_x \rangle = 2.07 \times 10^{-21} \text{ J}$$

exactly the same result we got earlier. Note that

$$\begin{split} &\frac{1}{2} \ m \langle C_x \rangle^2 = \frac{1}{2} \frac{(0.028 \ \text{kg mol}^{-1})}{(6.022 \times 10^{23} \ \text{mol}^{-1})} \times (238.2 \ \text{ms}^{-1})^2 \\ &\frac{1}{2} \ m \langle C_x \rangle^2 = 1.32 \times 10^{-21} \ \text{J} \end{split}$$

is not the average kinetic energy. The average kinetic energy is always obtained from the rms speed (It has already been mentioned earlier).

2.15.5 Speed Distribution and Energy Distribution in Two Dimension

Speed Distribution We now consider a gas where the molecules are restricted to move on the x-y plane, i.e. the distribution in two dimension. Again, due to the isotropicity of the movement of the molecules (postulate (i); 4.8.2), we may write

$$\frac{dn_{v_x}}{n} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x$$
(2.53a)

$$\frac{dn_{v_y}}{n} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_y^2/2kT} dv_y$$
(2.53b)

and

where Eq. (2.53a) gives the probability that the molecules have their *x*-component velocities in the range v_x to $v_x + dv_x$ and Eq. (2.53b) represents the same but, along the *y*-axis. Since the probability that a molecule has its *x*-component velocity in the rang v_x to $v_x + dv_x$ is in no way dependent on the probability that, its *y*-component velocity would be in the range v_y to $v_y + dv_y$ (postulate iii; article: 2.15.2), we may write

$$\frac{dn_{v_xv_y}}{n} = \left(\frac{dn_{v_x}}{n}\right) \times \left(\frac{dn_{v_y}}{n}\right)$$
(2.54)

where $dn_{v_xv_y}$ is the number of molecules per unit volume, whose *x*-component velocities are in the range v_x to $v_x + dv_x$ and, simultaneously, the *y*-component velocities in the range v_y to $v_y + dv_y$. This is gives us

$$dn_{v_x,v_y} = n \left(\frac{m}{2\pi kT}\right) e^{-\frac{m(v_x^2 + v_y^2)}{2kT}} dv_x dv_y$$
(2.55)

which is the velocity distribution function in two-dimensions. The equation is exemplified in Figs 2.27(a) and 2.27(b). In Figure 2.27(a), the $v_x - v_y$ plane is a two dimensional velocity space. Each point on the plane represents a simultaneous occurrence of the given v_x and v_y and, can also be interpreted as the tip point of the vector, representing the velocity of the molecule, whose projections on the v_x and v_y axes are the given specified values of v_x and v_y . The number of points in the infinitesimal rectangular area $dv_x dv_y$ is obviously $dn_{v_x v_y}$.

Figure 2.27(b) shows the two-dimensional velocity distribution function $\frac{1}{n} \frac{dn_{v_x v_y}}{dv_x dv_y}$ versus v_x and v_y .



Figure 2.27(a) The velocity in two dimension. The number or tip points of the velocity vectors, originating from the origin (0, 0), that are present in the infinitesimal area $dv_x dv_y$ is dn_{v_x,v_y} . The total number of tip points of the velocity vectors \vec{v} lying within the annular space between the two concentric circles of radii *C* and *C* + *dC* is dn_{c} .



Figure 2.27(b) The velocity distribution function versus v_x and v_y .

As shown in Figure 2.27(a), the distribution of the speed $C = \sqrt{(v_x^2 + v_y^2)}$ is obtained by collecting all the velocity vector tip points in the two-dimensional velocity space which lie within the annular space of the two concentric circles of radii C and C + dC (C = |v|). The area of the annular space is $d(\pi C^2)$, i.e. $2\pi C dC$. The number of tip points in this area is

 $\frac{dn_{v_xv_y}}{dv_x dv_y} \times 2\pi C dC: \text{ If } dn_C \text{ be the number of molecules per unit volume, moving with speeds}$

in the range $C \rightarrow C + dC$ (irrespective of direction), then it is given by

$$dn_{C} = \frac{dn_{v_{x}v_{y}}}{dv_{x}dv_{y}} \times 2\pi C dC$$

$$dn_{C} = \frac{mn}{hT} e^{-mc^{2}/2kT} C dC \qquad (2.56)$$

 \Rightarrow

which is the speed distribution of the molecules in two dimensions. A plot of the speed distribution.



Figure 2.28 The speed distribution function for N_2 in two dimensions at 25°C and 1025°C .

function of N_2 at two different temperatures is shown in Figure 2.28. An important feature that students should not miss is that as the temperature is increased, the curve becomes more wider (also compare it with Figure 2.24.) This means that on increasing the temperature, the molecules move over more wider range of speed. The height of the maximum is depressed because, the function $\frac{1}{n} \frac{dn_c}{dc}$ is normalised, i.e. the total area under each curve must be unity.

The average speed is then evaluated as

$$\langle C \rangle = \frac{1}{n} \int_0^\infty c dn_C = \frac{m}{kT} \int_{kT}^\infty e^{-mc^2/2kT} C^2 dC$$
$$\langle C \rangle = \sqrt{\frac{\pi kT}{2m}}$$
(2.57)

 \Rightarrow

The mean square speed is evaluated as

$$\langle C^2 \rangle = \frac{1}{n} \int_0^\infty c^2 dn_c = \frac{2kT}{m}$$

and therefore, the rms speed is now

$$C_{\rm rms} = \sqrt{\langle C^2 \rangle} = \sqrt{\frac{2kT}{m}}$$
 (2.58)

The most probable speed in two dimensions is then obtained by differentiating the speed distribution function $\frac{1}{n} \frac{dn_C}{dC}$, with respect to *C* and then, equating the result to zero.

$$\frac{d}{dC} \left(\frac{1}{n} \frac{dn_c}{dC} \right) = \frac{m}{kT} \frac{d}{dC} \left[Ce^{-mc^2/2kT} \right]$$
$$\frac{d}{dC} \left(\frac{1}{n} \frac{dn_c}{dC} \right) = \frac{m}{kT} e^{-mc^2/2kT} \left(1 - \frac{mc^2}{kT} \right)$$

or

Equating the left-hand side to zero, two solutions come out: (i) $C \rightarrow \infty$ and (ii) $C = \sqrt{kT/m}$. The first solution being physically unacceptable, the most probable speed of the molecules in two dimensions is

$$C_{\rm mps} = \sqrt{\frac{kT}{m}} \tag{2.59}$$

Energy Distribution To find the energy distribution function $f(\varepsilon)$, defined as $\frac{1}{n} \frac{dn_{\varepsilon}}{d\varepsilon}$, where dn_{ε} is the number of molecules per unit volume, moving with energy in the range ε to $td\varepsilon$, ε is the energy corresponding to the speed c, i.e. $\varepsilon = \frac{1}{2}mC^2$ and $dC = \frac{1}{\sqrt{2m\varepsilon}}d\varepsilon$. We then transform Eq. (2.56) as

$$dn_{\varepsilon}(=dn_{c}) = \frac{mn}{kT} e^{-\frac{\varepsilon}{kT}} \sqrt{\frac{2\varepsilon}{m}} \frac{1}{\sqrt{2m\varepsilon}} d\varepsilon$$
$$dn_{\varepsilon} = \frac{n}{kT} e^{-\varepsilon/kT} d\varepsilon$$
(2.60)

or

The nature of this distribution function and the effect of temperature on the distribution is shown in Figure 2.29.

The average energy of the molecules in two dimensions is then evaluated as

$$\langle \varepsilon \rangle = \frac{1}{n} \int_{0}^{\infty} \varepsilon d\varepsilon = \frac{1}{kT} \int_{0}^{\infty} \varepsilon e^{-\varepsilon/kT} d\varepsilon$$

 \Rightarrow

 \Rightarrow

$$\langle \varepsilon \rangle = \frac{1}{kT} \int_0^\infty e^{-\varepsilon/kT} \cdot \varepsilon^{2-1} \, d\varepsilon$$

$$\langle \varepsilon \rangle = kT$$
 (using the gamma function) (2.61)

This result was quite expected; for one dimension, we got the average energy as $\frac{1}{2}kT$; therefore, in two dimensions it becomes $\left(\frac{1}{2}kT + \frac{1}{2}kT\right) = kT$.



Figure 2.29 The effect of temperature on the distribution function of energy with increase in temperature; the number of molecules in the higher energy zone increases.

2.15.5.1 Fraction of the Molecules having Energy More than a Specific Value ε^*

The number of molecules having energy greater than or equal to ε^* is evaluated from Eq. (2.60) as

$$n(\geq \varepsilon^*) = \int_{\varepsilon^*}^{\infty} dn_{\varepsilon} = \frac{n}{kT} \int_{\varepsilon^*}^{\infty} e^{-\varepsilon^*/kT} d\varepsilon$$
$$n(\geq \varepsilon^*) = ne^{-\varepsilon^*/kT}$$
(2.62a)

 \Rightarrow

Therefore, the fraction of the total number of molecules with energy more than ε^* is

$$f(\geq \varepsilon^*) = \frac{n(\geq \varepsilon^*)}{n} = e^{-\varepsilon^*/kT}$$
(2.62b)

Gradually, we shall see the importance of Eq. (2.62b).

2.15.6 Speed Distribution and Energy Distribution in Three Dimension

Speed Distribution If $\left(\frac{dn_{v_x}}{n}\right)$ be the probability that the molecules have their *x*-component velocities in the range $v_x \rightarrow v_x + dv_x \left(\frac{dn_{v_y}}{n}\right)$ be the probability of having their *y*-component

velocities in the range $v_y \to v_y + dv_y$ and $\left(\frac{dn_{v_z}}{n}\right)$ be the probability of having their

z-component velocities in the range $v_z \rightarrow v_z$ + dv_z , then these probabilities are given by

$$\left(\frac{dn_{v_x}}{n}\right) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x$$

$$\left(\frac{dn_{v_y}}{n}\right) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_y^2/2kT} dv_y$$

$$\left(\frac{dn_{v_z}}{n}\right) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_z^2/2kT} dv_z$$

$$(2.63)$$

and

Therefore, the probability $\left(rac{dn_{v_xv_yv_z}}{n}
ight)$ of finding a molecule with velocity components,

simultaneously in the ranges v_x to $v_x + dv_x$, v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$ is given by the product of the individual probabilities

$$\frac{dn_{v_x v_y v_z}}{n} = \left(\frac{dn_{v_x}}{n}\right) \left(\frac{dn_{v_y}}{n}\right) \left(\frac{dn_{v_z}}{n}\right)$$
(2.64)

where $dn_{v_xv_yv_z}$ is the number of molecules per unit volume, whose velocity components are simultaneously in the ranges v_x to $v_x + dv_x$, v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$. Using Eqs (2.63) and (2.64) we have

$$dn_{v_x v_y v_z} = n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)} dv_x \, dv_y \, dv_z \tag{2.65a}$$

which is the velocity distribution equation in three dimensions. A three dimensional velocity space is constructed (Figure 2.30). A point with coordinate values v_x , v_y and v_z represents a molecule whose velocity components are v_x , v_y and v_z .



Figure 2.30 The number of representative points in the cuboid $d\tau$ is equal to the number of molecules given by Eq. (2.65).

In spherical polar coordinate, Eq. (2.65) can also be written as

$$dn_{c,\theta,\phi} = n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mC^2}{2kT}} C^2 dC \sin\theta \, d\theta \, d\phi \tag{2.65b}$$

See Section 2.10.1 M2. Here, the volume element dv_x , dv_y and dv_z has just been replaced by $C^2 dC \sin \theta d\theta d\phi$.

The cuboid of volume (dv_x, dv_y, dv_z) is drawn at a distance $C\left[=(v_x^2 + v_y^2 + v_z^2)^{1/2}\right]$ from the origin, with side lengths dv_x , dv_y and dv_z . The number of representative points in this cuboid is nothing but $dn_{v_xv_yv_z}$, i.e. the number of molecules per unit volume whose velocity components are simultaneously in the ranges v_x to $v_x + dv_x$, v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$. The number of such points per unit volume of the velocity space is

Number density of the velocity representative point ρ

$$\rho = \frac{dn_{v_x v_y v_z}}{dv_x dv_y dv_z}$$

$$\rho = n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mC^2/2kT}$$
(2.66)

or

It is interesting to see that this number density ρ does not depend on the direction of the velocity vectors, but, only on their lengths, i.e. their speed *C*. This is in accordance with the isotropicity of the movement of the molecules; all directions are equally probable for their movement. Therefore, if we count the total number of representative points within the spherical shell between two concentric spheres of radii *C* and *C* + *dC* (Figure 2.31) then, we get the number of molecules per unit volume which are moving with speeds in the

range *C* to *C* + *dC*, irrespective of direction. If the number of such molecules per unit volume be dn_C , then $dn_C = (number density of the$ velocity representative points) × (volume of theshell)

$$\Rightarrow dn_C = \left[n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mC^2/2kT} \right] d \left(\frac{4}{3} \pi C^3 \right)$$

or
$$dn_C = 4\pi n \left(\frac{m}{2\pi kT}\right)^{-1} C^2 e^{-mC^2/2kT} dC$$
 (2.67)

which is the famous Maxwell's distribution of molecular speed.

We shall now discuss about the nature and characteristic features of the distribution:



Figure 2.31 The spherical shell between two concentric spheres of radii *C* and *C* + *dC*. Collecting all the velocity vectors of length *C*, but oriented along all possible directions in space we get *dn_C*.

 dn_C is the number of molecules per unit volume which move with speeds in the range C to C + dC. Therefore, $\frac{1}{n} \frac{dn_c}{dC}$ is the fraction of the total number of molecules per unit speed range. This is the speed distribution function f(c)

$$f(C) = \frac{1}{n} \frac{dn_c}{dC} = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} C^2 e^{-\frac{mC^2}{2kT}}$$
(2.68)

A plot of f(c) versus C is shown in Figure 2.32. There are two opposing functions on the righthand side: the parabolic function C^2 and the Gaussian function $\exp\left(-\frac{mC^2}{2kT}\right)$. Initially, the curve rises from zero at C = 0, a most parabolically, because the factor C^2 is dominant in this region and the Gaussian factor remains almost unity. But, as C is increased, the Gaussian factor starts becoming the dominant factor. Due to this competing effect of these two opposing factors, the curve passes through a maximum. The corresponding speed is called the *most probable speed*, $C_{\rm mps}$. When C is increased beyond the $C_{\rm mps}$, due to the more dominant Gaussian factor, the curve decays.

The most probable speed is evaluated as follows.

The slope of the curve is $\frac{d}{dC}\left(\frac{1}{n}\frac{dn_c}{dC}\right)$, which is

$$\frac{d}{dC}\left(\frac{1}{n}\frac{dn_c}{dC}\right) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mC^2}{2kT}} C\left(2 - \frac{mC^2}{kT}\right)$$



Figure 2.32 A plot of the speed distribution function $f(c) = \frac{1}{n} \frac{dn_c}{dC}$ against C. The relative positions of C_{msr} (c) and C_{rms} is also shown.

Equating the slope of the curve in Figure 2.32 to zero, we find three solutions: (i) C = 0, (ii) $C \to \infty$ and (iii) $c = \sqrt{\frac{2kT}{m}}$. The first two solutions are not physically acceptable because, at these two limits there are no molecules. So, the most probable speed is given by

 \Rightarrow

$$C_{\rm mps} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$
(2.69)

The first two solutions (C = 0 and $C \to \infty$) are also of importance; they help us to know that the curve in Figure 2.32 rises with zero slope and, also glances to zero as $C \to \infty$. The curve has therefore, altogether three horizontal slopes.

The average speed of the molecules $\langle c \rangle$ is evaluated as

$$\begin{split} \langle C \rangle &= \frac{1}{n} \int_0^\infty C dn_c = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{mC^2}{2kT}} \ C^3 dC \\ \langle C \rangle &= 2\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{mC^2}{2kT}} \ (C^2)^{2-1} \ d(C^2) \end{split}$$

$$\Rightarrow \qquad \langle C \rangle = 2\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \frac{\overline{|2|}}{\left(\frac{m}{2kT}\right)^{2}}$$

or $\langle C \rangle = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$ (using the gamma function) (2.70)

The mean square speed $\langle c^2 \rangle$ is evaluated similarly as follows:

$$\begin{split} \langle C^2 \rangle &= \frac{1}{n} \int_0^\infty C^2 dn_c = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{mC^2}{2kT}} C^4 dC \\ \Rightarrow & \langle C^2 \rangle = \frac{2\pi}{\pi \sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{mC^2}{2kT}} (C^2)^{\frac{5}{2}-1} d(C^2) \\ \Rightarrow & \langle C^2 \rangle = \frac{2\pi}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \frac{\left|\frac{5}{2}\right|}{\left(\frac{m}{2kT}\right)^{\frac{5}{2}}} \\ \Rightarrow & \langle C^2 \rangle = \frac{\cancel{2}}{\sqrt{\pi}} \frac{\cancel{2}kT}{m} \frac{3}{\cancel{2}} \cdot \frac{1}{\cancel{2}} \sqrt{\cancel{\pi}} \end{split}$$

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or

$$\langle C^2 \rangle = \frac{3kT}{m}$$
, and the root mean square speed

$$C_{rms} = \sqrt{\langle C^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}^5$$
(2.71)

The relative positions of $C_{rms}, \langle C \rangle$ and C_{mps} are shown in Figure 2.32. The root mean

square $C_{\rm rms}$ has a special feature.

The root mean square speed of the molecules is the speed with which the molecules move with the average translational kinetic energy:

$$\frac{1}{2}mC_{\rm rms}^{\ 2} = \frac{1}{2}m\frac{3kT}{m} = \frac{3}{2}kT$$

We now assemble the different features of the speed distribution function as follows:

- 1. The distribution is dynamic in nature: This means that in the steady state, the number of molecules moving in a given speed range is constant, but their identities are constantly changing due to the continuous random elastic collisions between them. In other words, the number of molecules which fly off from a given speed range in a given time period is exactly equal to the number of molecules which come into that region of speed in the same time period.
- 2. The area under the curve, in Figure 2.32, between C to C + dC is the fraction of the total number of molecules moving with speeds in the range $C \rightarrow C + dC$. The total area under the curve is then obviously unity.
- 3. *The temperature* has a profound influence on the distribution curve. With rise in temperature, the curve becomes more broader (Figure 2.33); the position of the maximum (at the most probable speed) is shifted to the right, but the height of the maximum is depressed. This is because of the fact that the distribution function is normalized, and therefore, the area under the three curves are equal and is unity. This is explained in Figure 2.33. With increase in temperature, the number of slow moving molecules decreases and that of the faster moving molecules increase. The width of the curve is a direct measure of the absolute temperature.

$$\begin{split} C_{mps} : \left< C \right> : C_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} \\ = 1.414 : 1.596 : 1.73 \\ = 1 : 1.29 : 1.223 \end{split}$$

⁵ The ratio of the there characteristic speeds is then (using equations 2.69, 2.70 and 2.71)



Figure 2.33 The effect of temperature on the speed distribution function.

4. Figure 2.34 shows the distribution curve of two different gases at the same temperature. The curve is narrower for the heavier molecules and broader for the lighter molecules. This is because *the average translational kinetic energy is the*

same for the molecules of both the gases at the same temperature $\left(\frac{3}{2} kT\right)$ and this

is $\frac{1}{2}mC_{\rm rms}^2$. Therefore, heavier molecules move slowly and the lighter molecules

move faster.



Figure 2.34 Comparison of the speed distribution function of O₂ and He at the same temperature.

5. If the temperature is increased gradually from very low value, the number of molecules in any given speed range C to C + dC will increase and then it becomes maximum at $T = \frac{mC^2}{3k}$, after which the population decreases monotonously.

6. Finally, note that the most probable velocity is zero along any direction but the most probable speed (in three dimensions) is $\sqrt{2RT/M}$. The reason is that the number of speed representing points is obtained by multiplying the density of velocity representing points ρ with the volume of the spherical shell $4\pi c^2 dC$ [see Eqs. (2.66) and (2.67)]. From Eq. (2.66) it is seen that ρ is maximum at C = 0 and afterwards, decreases in the Gaussian manner with increase in C. On the other hand, the volume of the spherical shell increases parabolically. Since this volume element is zero at C = 0, we conclude that there are no molecules at rest, i.e., with C = 0. Caught in between these two competing factors (ρ decreases and $4\pi c^2$ increases), the speed distribution function first increases, almost parabolically from C = 0 and then passes through a maximum, where the two opposing factors cancel each other; thereafter the curve slopes down due to the dominance of the Gaussian factor over the parabolic factor. We thus get the most probable speed C_{mps} corresponding to the maximum of the curve. This is explained in Figure 2.35.



Figure 2.35 The competing effects of the parabolic factor and the Gaussian factor.

7. Finally, an interpretation of the absolute temperature can be suggested from the distribution curve. It is seen that the lower the temperature, the narrower would be the width of the distribution curve. Therefore, if it is possible to reduce the temperature to 0 K, then the distribution curve would become an infinitely long vertical strip of practically zero width. But, this contradicts the Heisenberg's uncertainly Principle; 'attainment of zero kelvin is an impossibility'.

2.15.6.1 Explanation of Some Interesting Facts by the Maxwell's Speed Distribution Function

1. The rate of all elementary reactions increases exponentially with increase in temperature.

For every elementary reaction there is a certain activation energy, which the reactant molecules must posses in order to be converted into the product molecules. On increasing the temperature, since the speed distribution curve flattens off, the number of such activated molecules increases, resulting into an increase in the reaction rate. You can also present a similar argument to explain the rise of vapour pressure of a pure liquid on increasing the temperature.

2. The atmosphere of the moon is very dilute compared to that of our atmosphere. When a particle of mass m leaves the Earth's surface with escape speed v_e , it has

the kinetic energy $\frac{1}{2}mv^2$ and the gravitational potential energy $\left(\frac{-GMm}{R}\right)$, where \underline{G} is the gravitational constant (6.67 × 10⁻¹¹ Nm² kg⁻²), M is the mass of the Earth ($M = 5.98 \times 10^{24}$ kg) and R its radius ($R = 6.37 \times 10^6$ m). When the particle reaches infinity, it stops and has no kinetic energy. It also has no potential energy because this is our zero-potential energy state. The total energy of the particle at infinity is therefore, zero. From the conservation of energy principle, its total energy at the Earth's surface must also have been zero; therefore

$$(\text{KE}) + (\text{PE}) = \left(\frac{1}{2} m v_e^2\right) + \left(-\frac{GMm}{R}\right) = 0$$

$$v_e = \sqrt{\frac{2GM}{R}}$$
(2.72)

 \Rightarrow

 \Rightarrow

On the earth surface

$$\begin{split} v_{e(E)} = & \sqrt{\frac{2(6.67\times10^{-11}~\mathrm{Nm}^2~\mathrm{kg}^{-2})~(5.98\times10^{24}~\mathrm{kg})}{6.37\times10^6~\mathrm{m}}} \\ \hline v_{e(E)} = & 11.2~\mathrm{km~s}^{-1} \end{split}$$

Similarly, it can be shown that the escape speed on the Moon surface is 2.38 km s⁻¹. Do it yourself: Gravitational acceleration $g_{\text{moon}} = \frac{1}{6} g_{\text{earth}}$; $M_{\text{moon}} = 7.36 \times 10^{22}$ kg; $R_{\text{moon}} = 1.74 \times 10^6$ m; $g = \frac{GM}{R^2}$.

$$v_{e(m)} = 2.38 \times \text{km s}^{-1}$$

From the above calculations, we find the escape speed on the Earth's surface and the Moon surface as 11.2 km s^{-1} and 2.38 km s^{-1} , respectively. Therefore, a substantial fraction of the total number of molecules leaves the Moon surface, leaving a very dilute atmosphere on its surface; this fraction present over the Earth's surface is relatively much denser.

2.15.7 Extension of the Maxwell's Distribution Law to Boltzmann Distribution Law

First, we shall show that the Maxwell's distribution holds in different parts of a force field, e.g. the gravitational field.

Consider the velocity distribution along the *Z*-direction and let the law holds at the level $z = h_1$. We then write

$$dn_{v_{z}} = n_{1} \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_{z}^{2}}{2kT}} dv_{z}$$
(2.73)

as the velocity distribution, as applied to the altitude $z = h_1$; n_1 is the total number of molecules per unit volume at height h_1 . The number of molecules crossing this layer, per unit area per second, in the upward direction with velocities in the range v_z to $v_z + dv_z$ is then

$$n_1 \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_z^2}{2kT}} v_z dv_z^{7}$$
(2.74)

and each of these molecules on reaching an upper altitude $z = h_2$ will have an extra potential energy $mg (h_2 - h_1)$, and hence, if the primed symbols are used for the h_2 -level then

$$\frac{1}{2}mv_z^{2\prime} + mg(h_2 - h_1) = \frac{1}{2}mv_z^2$$
(2.75)

 \Rightarrow

$$v_z' dv_z' = v_z \, dv_z \tag{2.76}$$

⁶ Hint: $g = \frac{GM}{r^2}$; $g_{\text{moon}} = \frac{1}{6} \times 9.8 \text{ ms}^{-2}$; then from known values of M_{moon} and r_{moon} , find G_{moon} . Finally, use Eq. (2.72) to get $v_{e(m)}$.

 \Rightarrow

 $^{^7}$ (because, a swarm of molecules contained in the volume element $(v_z\cdot 1)$ will cross this level in one second)

Using Eqs (2.75) and (2.76), Eq. (2.74) changes to

$$n_1 \ e^{-mg(h_2 - h_1)/kT} \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-mv_z'^2/2kT} \ v_z' dv_z' \tag{2.77}$$

but $n_1 e^{-mg(h_2 - h_1)/kT} = n_2$, where n_2 is the number of molecules per unit volume at the altitude $z = h_2$. Equation (2.77) then changes as

$$n_2 \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_z'^2}{2kT}} v_z' dv_z'$$
(2.78)

It is now seen that Eqs (2.78) and (2.74) are the same expressions for the conditions which apply to the heights h_1 and h_2 , and hence, Maxwell's law is valid to the altitude h_2 also. Not only the gravity field, the velocity and the speed distribution function is also valid for all field of forces, even those in which the change in the potential energy is large upon traversing a distance of the order of molecular diameter.

The Maxwell-Boltzmann distribution may then be written as

$$dn = 4\pi n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 \exp\left[-\frac{\left(\frac{1}{2}mv^2 + \varepsilon_P\right)}{kT}\right] dv$$
(2.79)

<u>,</u> п

where ε_P is the potential energy of the molecules, measured from a given reference, and *n* is the number of molecules per unit volume at the given reference.

At any given altitude, ε_P is constant, so that $e^{-\frac{\varepsilon_P}{kT}}$ is also a constant; this constant times 'n' is the population density at that level (according to the Boltzmann distribution):

$$dn_v = 4\pi (n \ e^{-\varepsilon_P/kT}) \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv$$
$$dn_v = 4\pi n' \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \ e^{-\frac{mv^2}{2kT}} \ dv$$

where n' is number of molecules per unit volume at the altitude where dn_v is estimated; this equation is simply the Maxwell's speed distribution function at an altitude where dn_v is to be evaluated. This means that at any altitude the speed distribution is always Maxwellian, irrespective of the potential energy.

For example, if we take a gas and place it on the Earth's surface, then the number density of the molecules at an upper level is always less than that at a lower level, but the fraction of the total number of molecules moving in any given speed range is exactly equal at both the altitudes. The distribution function is also applicable to polyatomic molecules for which rotational and vibrational kinetic energies are present in addition to the translational kinetic energy.

Equation (2.79) is also applicable to real gases; here, ε_P is the potential energy of each molecule arising out of the attractive and/or repulsive interaction between the molecules. Since the ε_P term is again a function of position coordinates only, *the speed distribution function of the molecules of a real gas is again Maxwellian*.

Example 2.19

Calculate the most probable, average and the root mean square speed of the molecules of a sample of O_2 gas at 27°C.

Solution

The most probable speed is [Eq. (2.69)]

$$C_{\rm mps} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{(0.032 \text{ kg mol}^{-1})}}$$

Cancellation of the units is important; we do it as

$$C_{\rm mps} = \sqrt{\frac{2(8.314 \text{ kg ms}^{-2} \text{ mK}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(0.032 \text{ kg mol}^{-1})}}$$
$$C_{\rm mps} = 394.83 \text{ ms}^{-1}$$

 \Rightarrow

Note that the desired unit comes out correctly. The average speed [Eq. (2.70)]

$$\langle c \rangle = \sqrt{\frac{8RT}{\pi M}}$$

 $\langle c \rangle = \sqrt{\left[\frac{8(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(3.14)(0.032 \text{ kg mol}^{-1})}\right]}$

or

 \Rightarrow

$$\langle c \rangle = 445.63 \text{ ms}^{-1}$$

Similarly, $C_{\rm rms}$ is [Eq. (2.71)]

$$C_{\rm rms} = \sqrt{\frac{3RT}{M}} = 483.56 \ {\rm ms}^{-1}$$

Example 2.20

Calculate the most probable, average and the rms speed of the molecules of a gas whose density at 1 atm pressure is 1 gL^{-1} .

Solution

The pressure-temperature-density relation of an ideal gas is

$$\rho = \frac{MP}{RT} \Rightarrow \frac{RT}{M} = \frac{P}{\rho}$$

Therefore,

$$egin{aligned} C_{ ext{mps}} &= \sqrt{rac{2RT}{M}} = \sqrt{2rac{P}{
ho}} \ C_{ ext{mps}} &= \sqrt{rac{2 imes 1 ext{ atm}}{1 ext{ gL}^{-1}}} \end{aligned}$$

 \Rightarrow

Cancellation of the units is done as

$$C_{\rm mps} = \sqrt{\frac{2 \times 1 \, \text{atm} \left(\frac{101325 \, Pa}{1 \, \text{atm}}\right)}{(1 \, \text{g/L}^{-1}) \left(\frac{1 \, \text{L}}{1 \times 10^{-3} \, \text{m}^{3}}\right) \left(\frac{1 \, \text{kg}}{1 \times 10^{3} \, \text{g}}\right)}}$$

 \Rightarrow

$$C_{\rm mps}$$
=450 ms⁻¹ = 0.45 km s⁻¹

you yourself show that all the units finally come to ms^{-1} . In the same way, using proper expressions, show that

$$\langle C \rangle = 0.510 \text{ ms}^{-1} \text{ and } C_{\text{rms}} \approx 0.55 \text{ km s}^{-1}.$$

Comment Note that if the pressure and density are given then, your need not require the molar mass M and the temperature T of the gas.

Example 2.21

Calculate the most probable, average and the root mean square speed of the He atoms at 327° C, where the atoms are restricted to move on the *x*-*y* plane.

Solution

Here, the movement of the molecules is on the x-y plane. Therefore, we use Eqs (2.57), (2.58) and (2.59), as applied to the two-dimensional movements:

The most probable speed [Eq. (2.59)] is

$$C_{\rm mps} = \sqrt{\frac{RT}{M}} = \sqrt{\frac{(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (600 \text{ K})}{(0.004 \text{ kg mol}^{-1})}}$$

 \Rightarrow

$$C_{\rm mps} = 1.12~{\rm km~s^{-1}}$$

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The average speed is [Eq. (2.57)]

$$\langle C \rangle = \sqrt{\frac{\pi RT}{2 M}} = \sqrt{\frac{3.14(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(600 \text{ K})}{2(0.004 \text{ kg mol}^{-1})}}$$

or

 $\langle C \rangle \,{=}\,1.4~{\rm km~s^{-1}}$

The root mean square speed is

$$C_{\rm rms} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (600 \text{ K})}{0.004 \text{ kg mol}^{-1}}}$$

or

$$C_{\rm rms} = 1.6 \ {\rm km \ s^{-1}}$$

Example 2.22

The Maxwell's speed distribution function depends on the molar mass of the gas and the temperature. Show that, in terms of the reduced speed, defined as $C_r = \frac{C}{C_{\text{mps}}}$, the distribution function is independent of M and T.

Solution

 $C = C_{\text{mps}} C_r$; therefore, $dC = C_{\text{mps}} dC_r$, we then write the speed distribution function as

$$dn_{C_r} (= dn_C) = 4\pi n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} C^2 e^{-\frac{mC^2}{2kT}} dC$$

 \Rightarrow

$$dn_{C_r} = rac{4n}{\sqrt{\pi}} \left(rac{m}{2kT}
ight)^{rac{3}{2}} C_{
m mps}^2 C_r^2 \ e^{-rac{m}{2kT}C_{
m mps}^2 C_r^2} C_{
m mps} \ dC_r$$
 $dn_{C_r} = rac{4n}{\sqrt{\pi}} \left(rac{m}{2kT}
ight)^{rac{3}{2}} \left(rac{2kT}{m}
ight) C_r^2 \ e^{-C_r^2} \left(rac{2kT}{m}
ight)^{rac{1}{2}} \ dC_r$

9

 \Rightarrow

or
$$dn_{C_r} = \frac{4n}{\sqrt{\pi}} C_r^2 e^{-C_r^2} dC_r$$

and, finally in terms of the reduced speed C_r , the speed distribution function becomes

$$\frac{1}{n} \frac{dn_{C_r}}{dC_r} = \frac{4}{\sqrt{\pi}} C_r^2 \ e^{-C_r^2}$$

which is independent of the molar mass of the gas (M) and the temperature T.

Example 2.23

Find the fraction of the gas molecules whose speeds differ by less then 1.00% from the value of

- (a) the most probable speed.
- (b) the root mean square speed.

Solution

(a) The fraction of the total number of molecules moving with speeds in the range C to C + dC is

$$\frac{dn_c}{n} = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} C^2 \ e^{-\frac{mC^2}{2kT}} \ dC$$

By the problem,

$$C = C_{\rm mps} = \sqrt{\frac{2kT}{m}}; \, dC = 2 \times 0.01 \, C_{\rm mps} = 0.02 \sqrt{\frac{2kT}{m}}$$

The factor 2 is taken because the speeds may be less than, as well as more than $C_{\rm mps}.$ Therefore,

$$\frac{dn_c}{n} = \frac{4\pi}{\pi\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \left(\frac{2kT}{m}\right) e^{-1} (0.02) \left(\frac{2kT}{m}\right)^{\frac{1}{2}}$$
$$\frac{dn_c}{n} = \frac{0.08}{\sqrt{\pi}} e^{-1} = 0.0166, \text{ i.e. } 1.66\%$$

(b) Exactly in the same way

$$\frac{dn_c}{n} = \frac{4\pi}{\pi\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \left(\frac{3kT}{m}\right) e^{-\frac{3}{2}} (2) (0.01) \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$$

Comment Since the range of speed given is very small, we have directly used the differential form. If the span of speed range is large, we have to integrate dn_C (see Example 2.23).

Example 2.24

 \Rightarrow

Calculate the temperature at which

- (a) the root mean square speed of $\rm H_2$ molecules exceeds their most probable speed by 400 $\rm ms^{-1}.$
- (b) the speed distribution function of O_2 molecules has its maximum at the speed $C = 420 \text{ ms}^{-1}$.

Solution

(a) According to the problem

$$\sqrt{\frac{3RT}{M}} - \sqrt{\frac{2RT}{M}} = 400 \text{ ms}^{-1}$$

Physical Chemistry

 \Rightarrow

$$\sqrt{T} \left(\sqrt{\frac{3(8.314 \text{ JK}^{-1} \text{ mol}^{-1})}{(0.002 \text{ kg mol}^{-1})}} - \sqrt{\frac{2(8.314 \text{ JK}^{-1} \text{ mol}^{-1})}{(0.002 \text{ kg mol}^{-1})}} \right) = 400 \text{ ms}^{-1}$$

Cancellation of the units gives

$$\sqrt{T} \left(111.67 \text{ ms}^{-1} \text{ K}^{-\frac{1}{2}} - 91.18 \text{ ms}^{-1} \text{ K}^{\frac{1}{2}} \right) = 400 \text{ ms}^{-1}$$
$$\sqrt{T} = 19.52 \text{ K}^{\frac{1}{2}}$$

or

 \Rightarrow

 $T = 381 {
m K}$

(b) The speed distribution shows its maximum at the most probable speed; therefore

$$\begin{split} C_{mps} &= \sqrt{\frac{2RT}{M}} = 420 \text{ ms}^{-1} \\ T &= \frac{(420 \text{ ms}^{-1})^2 \ (0.032 \text{ kg mol}^{-1})}{2 \ (8.314 \text{ JK}^{-1} \text{ mol}^{-1})} \end{split}$$

or

 \Rightarrow

$$\underline{T} = 339.47 \text{ K}$$

Example 2.25

Calculate the number of O_2 molecules moving in the range $0 - 200 \text{ ms}^{-1}$ at 1 atm, 0°C.

Solution

Using the speed distribution function [Eq. (2.68)]

$$dn_c = 4\pi n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} C^2 e^{-\frac{mC^2}{2kT}} dC$$

We estimate the number of molecules over the speed range $0 \rightarrow C * (C * = 200 \text{ ms}^{-1})$ as

$$n(0 \rightarrow C^*) = \int_0^{C^*} dn_C$$

 \Rightarrow

 \Rightarrow

$$n(0 \to C^*) = 4\pi n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^{C^*} C^2 \ e^{-\frac{mC^2}{2kT}} \ dC$$

$$n(0 \to C^*) = 2\pi n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^{C^*} C \ e^{-\frac{mC^2}{2kT}} \ d(C^2)$$

 \Rightarrow

 \Rightarrow

 \Rightarrow

 \Rightarrow

$$\Rightarrow \qquad n(0 \to C^*) = 2\pi n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \left(\frac{2kT}{m}\right)^{\frac{3}{2}} \int_0^{C^*} \sqrt{\frac{m}{2kT}} C e^{-\left(\sqrt{\frac{m}{2kT}}C\right)^2} \times d\left[\left(\sqrt{\frac{m}{2kT}} C\right)^2\right]$$
$$\Rightarrow \qquad n(0 \to C^*) = \frac{2n}{\sqrt{\pi}} \int_0^{C^*} x \ e^{-x^2} d(x)^2 \ ; \ x = \sqrt{\frac{m}{2kT}} C$$

Now,

...

$$\begin{split} n(0 \to C^*) &= -\frac{2n}{\sqrt{\pi}} \int_{x=0}^{x=\sqrt{\frac{mC^{*2}}{2kT}}} x \ d(e^{-x^2}) \\ n(0 \to C^*) &= \frac{-2n}{\sqrt{\pi}} \left[|xe^{-x^2}|_0^{\sqrt{\frac{mC^{*2}}{2kT}}} - \int_0^{\sqrt{\frac{mC^{*2}}{2kT}}} e^{-x^2} \ dx \right] \\ n(0 \to C^*) &= \frac{2n}{\sqrt{\pi}} \left[\sqrt{\frac{mC^{*2}}{2kT}} \exp\left[-\frac{mC^{*2}}{2kT} \right] - \int_0^{\sqrt{\frac{mC^{*2}}{2kT}}} e^{-x^2} \ dx \right] \\ n(0 \to C^*) &= n \left[\frac{2}{\sqrt{\pi}} \int_0^{\sqrt{\frac{mC^{*2}}{2kT}}} e^{-x^2} \ dx - \sqrt{\frac{2mC^{*2}}{\pi kT}} \ e^{-\frac{mC^{*2}}{2kT}} \right] \end{split}$$

The first integral is the error function discussed in Section 2.10.5. Therefore

$$\frac{n(0 \to C^*)}{n} = erf\left(\sqrt{\frac{mC^{*2}}{2kT}}\right) - \sqrt{\frac{mC^{*2}}{\pi kT}} \exp\left(-\frac{mC^{*2}}{2kT}\right)$$
$$\frac{mC^{*2}}{2kT} = \frac{MC^{*2}}{2RT} = \frac{(0.032 \text{ kg mol}^{-1})(200 \text{ ms}^{-1})^2}{2(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(273 \text{ K})} \approx 0.3$$
$$\sqrt{\frac{mC^{*2}}{2kT}} \approx 0.5 \text{ and } \sqrt{\frac{2mC^{*2}}{\pi kT}} \approx 0.6$$

Therefore,

$$\frac{n(0 \to C^*)}{n} = erf(0.5) - 0.6 \ e^{-0.3}$$

and finally, $\frac{n(0 \rightarrow C^*)}{n} = 0.521 - 0.44 = 0.08$. Therefore, about 80 molecules out of one thousand, move in the speed range $(0 - 200 \text{ ms}^{-1})$.

Example 2.26

Estimate, how the numbers in the above Problem 2.23 changes when *the temperature in the kelvin scale* is double i.e. at 546 K.

Physical Chemistry

Solution At 546 K,

$$\frac{mC^{*2}}{2kT} = 0.14 ; \Rightarrow \sqrt{\frac{mC^{*2}}{2kT}} = 0.375 \sim 0.4$$

and

$$\sqrt{\frac{2mC^{*2}}{\pi kT}} = 0.4$$

Therefore,

$$\frac{n(0 \to 200 \text{ ms}^{-1})}{n} = erf(0.4) - 0.4 \ e^{-0.14} = 0.078$$

Therefore, on increasing the temperature from 273 K to 546 K, the number of molecules moving with speeds in the range $0 - 200 \text{ ms}^{-1}$ changes from 80 to 78 out of 1000. This corresponds to 0.2% decrease.

Comment At 273 K, $\frac{1}{2}mC^{*2} = 1.06 \times 10^{-21}$ J and $kT = 3.77 \times 10^{-21}$ J. Within the speed range 0-200 ms⁻¹, the kinetic energy of the molecules is significantly less than the thermal energy kT. Remember that, whenever this is the case, i.e. $\frac{1}{2}mc^2 < kT$, the number of molecules either decreases or remains almost the same as the temperature is increased.

Example 2.27

Calculate the fraction of the O_2 molecules moving with speeds more than 600 ms⁻¹ at 273 K and find corresponding number at 546 K.

Solution

To solve this problem you could have started as

$$\frac{n(C^* \to \alpha)}{n} = \frac{1}{n} \int_{C^*}^{\infty} dn_C$$

but, it is more convenient to find

$$\frac{n(0\to C^*)}{n} = \frac{1}{n} \int_0^{C^*} dn_C$$

and then, subtract it from unity

$$\frac{n(0 \to 600 \text{ ms}^{-1})}{n} = erf\left(\sqrt{\frac{mC^{*2}}{2kT}}\right) - \sqrt{\frac{2mC^{*2}}{\pi kT}} \exp\left(-\frac{mC^{*2}}{2kT}\right)$$

where $C^* = 600 \text{ ms}^{-1}$. Now, $\frac{mC^{*2}}{2kT} = 2.54$; $\sqrt{\frac{mC^{*2}}{2kT}} = 1.6$ and $\sqrt{\frac{2mC^{*2}}{\pi kT}} = 1.8$ at 273 K

Therefore, at 273 K

$$\frac{n \ (0 \to 600 \text{ ms}^{-1})}{n} = erf(1.6) - 1.8 \ \exp(-2.54)$$
$$= 0.836$$

Therefore.

$$\frac{n(>600 \text{ ms}^{-1})}{n} = 0.164$$

i.e. 164 molecules out of 1000 with speeds more than 600 $\rm ms^{-1}.$ Similarly at 546 K, we find

$$\frac{n(>600 \text{ ms}^{-1})}{n} = 0.477$$

Therefore, on increasing the temperature from 273 K to 546 K $n(>600 \text{ ms}^{-1})$ changes from 164 to 477, out of 1000; it is an increase by 31.3%.

Comment This is story if
$$\left|\frac{1}{2}mc^2 > kT\right| \cdot kT$$

Example 2.28

Calculate the fraction of the total number of O_2 molecules moving in the speed range $(C_{\rm mos} \pm 10^{-3}) \,{\rm ms}^{-1}$ at 273 K. Also find out the number at 546 K.

Solution

Since the range of speed ($dC = 2 \times 10^{-3} \text{ ms}^{-1}$) is small compared to the speed of interest, we use the differential form

$$\frac{dn}{n} = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} C_{\rm mps}^2 \exp\left(-\frac{mC_{\rm mps}^2}{2kT}\right) dC$$

$$\frac{dn}{n} = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \left(\frac{2kT}{m}\right) \exp\left(-1\right) 2 \times 10^{-3}$$

or

or

$$\frac{dn}{n} = 4.4 \times 10^{-6} \text{ (at 273 K)}$$

Similarly, at 546 K

$$\frac{dn}{n} = 3.12 \times 10^{-6}$$

Comment On doubling the temperature, the most probable speed increases to 1.414 times, but the fractional number of molecules moving in that speed range decreases to 0.709 times. $(3.12 \div 4.4 = 0.709)$

Example 2.29

For gaseous N_2 find:

- (a) the temperature at which the speeds of the molecules $c_1 = 300 \text{ ms}^{-1}$ and $c_2 = 600 \text{ ms}^{-1}$ are associated with equal values of Maxwell's speed distribution function.
- (b) the speed of the molecules c at which the value of the speed distribution function at a temperature T will be the same as that for the temperature x times higher.

Solution

(a) Equating the speed distribution function at the speed c_1 and c_2 at the same temperature, we get

$$\begin{aligned} &4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c_1^2 \exp\left(-\frac{mc_1^2}{2kT}\right) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c_2^2 \exp\left(-\frac{mc_2^2}{2kT}\right) \\ \Rightarrow & c_1^2 \exp\left(-\frac{mc_1^2}{2kT}\right) = c_2^2 \exp\left(-\frac{mc_2^2}{2kT}\right) \\ \Rightarrow & \exp\left[\frac{m(c_2^2 - c_1^2)}{2kT}\right] = \left(\frac{c_2}{c_1}\right)^2 = \left(\frac{600 \text{ ms}^{-1}}{300 \text{ ms}^{-1}}\right)^2 = 4 \\ \Rightarrow & \frac{m(c_2^2 - c_1^2)}{2kT} = \ln 4 \\ \Rightarrow & T = \frac{m(c_2^2 - c_1^2)}{2k \ln 4} = \frac{M(c_2^2 - c_1^2)}{2R \ln 4} \quad (\because M = \text{mN}_0 \text{ and } \text{kN}_0 = R) \\ \Rightarrow & T = \frac{(0.028 \text{ kg mol}^{-1})(600^2 - 300^2) \text{ m}^2 \text{s}^{-2}}{2(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \ln 4} \end{aligned}$$

 \Rightarrow

T = 328 K

(b) According to the problem

$$4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c^2 \exp\left(-\frac{mC^2}{2kT}\right) = 4\pi \left(\frac{m}{2\pi kxT}\right)^{\frac{3}{2}} c^2 \exp\left(-\frac{mC^2}{2kxT}\right)$$
$$\Rightarrow \qquad \exp\left(-\frac{mC^2}{2kT}\right) = x^{-\frac{3}{2}} \exp\left(-\frac{mC^2}{2kxT}\right)$$

Simplifying, we get

$$C = \sqrt{\frac{3kT}{m} \frac{x\ln x}{(x-1)}}$$

Example 2.30

At what temperature of an N_2 and O_2 mixture do the most probable speeds of N_2 and O_2 molecules differ by 30 ms⁻¹?

Solution

According to the problem

$$\sqrt{\frac{2RT}{M_{N_2}}} - \sqrt{\frac{2RT}{M_{O_2}}} = 30 \text{ ms}^{-1}$$

$$\Rightarrow \qquad \sqrt{2RT} \left(\frac{1}{\sqrt{M_{N_2}}} - \frac{1}{\sqrt{M_{O_2}}}\right) = 30 \text{ ms}^{-1}$$

$$\Rightarrow \qquad \sqrt{2RT} (0.386) \text{ kg}^{-\frac{1}{2}} \text{ mol}^{\frac{1}{2}} = 30 \text{ ms}^{-1}$$

$$\Rightarrow \qquad (2 \times 8.314 \text{ JK}^{-1} \text{ mol}^{1} T) (0.386 \text{ kg}^{-\frac{1}{2}} \text{ mol}^{-\frac{1}{2}})^{2} = 900 \text{ m}^{2} \text{ s}^{-2}$$

$$\Rightarrow \qquad 2.478 T \text{ m}^{2} \text{ s}^{-2} \text{ K}^{-1} = 900 \text{ m}^{2} \text{ s}^{-2}$$

$$\Rightarrow \qquad T = 363 \text{ K}$$

Example 2.31

The temperature of a mixture of H_2 and He is 300 K. At what value of the molecular speed will the speed distribution function yield the magnitude for both the gases?

Solution

Equating the speed distribution functions of the two gases, we find

$$(m_{\rm He} - m_{\rm H_2}) \frac{C^2}{2kT} = \frac{3}{2} \ln 2 = 1.039$$
$$C^2 = \frac{1.039 \times 2 \times 8.314 \times 300}{(0.004 - 0.002)} \,\mathrm{m^2 s^{-2}}$$

 \Rightarrow

 \Rightarrow

$$C = 1.61 \ \mathrm{km s^{-1}}$$

Example 2.32

At what temperature of a gas will the number of molecules, whose speeds fall within a given interval $C \rightarrow C + dC$ be the greatest?

Solution

The speed distribution function is

$$\frac{1}{n} \frac{dn_c}{dC} = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} C^2 e^{-\frac{mC^2}{2kT}}$$

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$$\Rightarrow \qquad \qquad \frac{1}{n} \frac{dn_c}{dC} = 4\pi \left(\frac{m}{2\pi k}\right)^{\frac{3}{2}} C^2 T^{-\frac{3}{2}} e^{-\frac{mC^2}{2kT}}$$

Let

 \Rightarrow

 \Rightarrow

$$y = T^{-\frac{3}{2}} \exp\left(-\frac{mC^2}{2kT}\right)$$

 $\frac{dy}{dT} = T^{-\frac{3}{2}} e^{-\frac{mC^2}{2kT}} \left(-\frac{3}{2T} + -\frac{mC^2}{2kT^2} \right)$

At the maximum, the left-hand side is zero; therefore

$$\left(-\frac{3}{2T} + -\frac{mC^2}{2kT^2}\right) = 0$$
$$T = \frac{mC^2}{3k}$$

Example 2.33

Find the fraction of molecules whose velocity projection on the v_x axis falls within the interval v_x to $v_x + dv_x$, while the moduli of the perpendicular velocity components fall within the interval v_{\perp} to $v_{\perp} + dv_{\perp}$.

Solution

The fraction of the total number of molecules whose *x*-component velocities fall within the range v_x to $v_x + dv_x$ is

$$\frac{dn_{v_x}}{n} = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}} dv_x$$

The fraction of the total number of molecules whose *y*- and *z*-component velocities lie in the range in the range v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$ simultaneously along all possible directions is

$$\frac{dn_{v_{y}v_{z}}}{n} = \left(\frac{m}{2\pi kT}\right)e^{-\frac{(v_{y}^{2} + v_{z}^{2})}{2kT}} d(\pi v_{\perp}^{2})$$

where $v_{\perp}^2 = v_y^2 + v_z^2$. Therefore, the required fraction is

$$\frac{dn_{v_{\perp},v_x}}{n} = \left(\frac{dn_{v_x}}{n}\right) \left(\frac{dn_{v_y,v_z}}{n}\right)$$
$$\frac{dn_{v_{\perp},v_x}}{n} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} (2\pi v_{\perp}) dv_{\perp} dv_x$$

or

Example 2.34

Using the Maxwell's speed distribution function, calculate the number of molecules bombarding a unit area of the wall per second.

Solution

The Maxwell's distribution of molecular velocity, [Eq. (2.65)], may be put in terms of the spherical polar coordinate as

$$dn_{c,\theta,\phi} = n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mC^2}{2kT}} C^2 dC \sin\theta d\theta d\phi$$

where the volume element in the cartesian coordinate (dv_x, dv_y, dv_z) is replaced by $c^2 dc \sin \theta d\theta d\phi$ in the spherical polar coordinate (see Figure 2.8).

Referring to Figure 2.16, the volume of the slant cylinder is $C \cos \theta$; and it has ($C \cos \theta$) $dn_{C, \theta, \phi}$ number of molecules. All these molecules will hit the unit area placed on the $v_x - v_y$ plane situated at the origin along this $\theta - \phi$ direction. Therefore, the total number of bombardments on this unit area from one side of the $v_x - v_y$ plane is

$$\begin{split} &\int_{C=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} (C \cos \theta) \, dn_{C,\theta,\phi} \\ &= \frac{n}{\pi \sqrt{\pi}} \left(\frac{m}{2kT} \right)^{\frac{3}{2}} \int_{0}^{\infty} e^{-\frac{mC^{2}}{2kT}} C^{3} dC \int_{0}^{\pi/2} \sin \theta \cos \theta \, d\phi \int_{0}^{2\pi} d\phi \\ &= \frac{n}{\pi \sqrt{\pi}} \left(\frac{m}{2kT} \right)^{\frac{3}{2}} \frac{1}{2} \int_{0}^{\infty} e^{-\frac{mc^{2}}{2kT}} (C^{2})^{2-1} d(C^{2}) \times \frac{1}{2} \times 2\pi \\ &= \frac{1}{4} \sqrt[n]{\frac{8kT}{\pi m}} = \frac{1}{4} n \langle C \rangle \end{split}$$

The same result we got earlier in two different ways [Eqs. (2.20) and (2.47b)].

Example 2.35

From the Maxwell's distribution of molecular speed, arrive at the expression of the pressure of a gas at temperature T and number density n.

Solution

Again referring to Figure 2.16, we consider a slant cylinder of length *C* and area unity, at the direction θ and ϕ .

The speed distribution function in the spherical polar coordinate is

which is the number of molecules per unit volume moving with speeds in the range C to C + dC and at the direction determined by the angles θ and ϕ . The volume of this slant cylinder is $C \cos \theta$ and, it contains $(C \cos \theta) dn_{c, \theta, \phi}$ number of molecules. The momentum delivered normally per strike on a unit area placed at the origin, on the *x*-*y* plane is $(2m, C \cos \theta)$.

Therefore, remembering that the total momentum blow normally, per unit area on the x-y plane per second from all possible directions (but, from one side of the x-y plane) and with all possible speeds is the pressure of the gas, P, we write

$$\begin{split} P &= \int_{0}^{\infty} \int_{0}^{\pi/2} \int_{0}^{2\pi} (C \cos \theta) (dn_{c,\theta,\phi}) \left(2mC \cos \theta \right) \\ P &= 2mn \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_{c=0}^{\infty} c^{4} e^{-\frac{mc^{2}}{2kT}} dc \int_{\theta=0}^{\pi/2} \sin \theta \cos^{2} \theta \, d\theta \times \int_{\phi=0}^{2\pi} d\phi \\ P &= \frac{mn}{\pi \sqrt{\pi}} \left(\frac{m}{2kT} \right)^{\frac{3}{2}} \int_{0}^{\infty} e^{-\frac{mc^{2}}{2kT}} (c^{2})^{\frac{5}{2}-1} d(c^{2}) \times \frac{1}{3} \times 2\pi \end{split}$$

$$P = \frac{mn}{\pi\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \frac{\left|\frac{5}{2}\right|}{\left(\frac{m}{2kT}\right)^{5/2}} \times \frac{2\pi}{3}$$

and simplifying

$$P = nkT$$

The ideal gas equation.

Example 2.36

The distribution of the molecules of a beam coming out of a hole in a vessel is described by ${}_{mC^2} {}^8$

the function $f(c) = Ac^3 e^{-\frac{mC^2}{2kT} \cdot 8}$ Find the most probable values of

- (a) the speed of the molecules in the beam; compare the result obtained with the most probable speed of the molecules in the bulk.
- (b) the kinetic energy of the molecules in the beam.

Solution

(a)
$$f(c) = Ac^3 e^{-\frac{mC^2}{2kT}}$$

 $\Rightarrow \frac{df}{dc} = Ae^{-\frac{mC^2}{2kT}} \left[3c^2 - \frac{mC^4}{kT} \right]$

 \Rightarrow

 \Rightarrow

 \Rightarrow

 $[\]overline{^{8}}$ You will find it later in the article 2.15.7.2 and an example of it.

At the most probable speed, $\frac{df}{dC} = 0$, whose physically acceptable solution is obtained by

$$\left(3C_{mps}^2 - \frac{mC_{mps}^4}{kT}\right) = 0$$

otherwise C has to be infinity. We then have at the surface, $C_{\rm mps} = \sqrt{\frac{3kT}{m}}$. In the bulk $C_{\rm mps} = \sqrt{\frac{2kT}{m}}$.

(b) The function f(C) can be written as

$$f(C) = \frac{1}{n} \frac{dn_c}{dC} = A C^3 e^{-\frac{mC^2}{2kT}}$$

where dn_c is the number of molecules per unit volume whose speeds are in the range C to C + dC.

The corresponding energy distribution function is

$$f(C) = \frac{1}{n} \frac{dn_c}{dC} = AC^3 \ e^{-\frac{mC^2}{2kT}}$$

$$\varepsilon = \frac{1}{2} mC^2 \implies d\varepsilon = mCdC \implies dC = \frac{1}{mC} dC$$

$$C^2 = \frac{2\varepsilon}{m}; \quad \therefore \quad C = \sqrt{\frac{2\varepsilon}{m}} \implies C^3 = \left(\frac{2\varepsilon}{m}\right)^{\frac{3}{2}}$$

$$C^3 = \left(\frac{2\varepsilon}{m}\right)^{\frac{3}{2}}; \ dC = \frac{1}{m\sqrt{\frac{2\varepsilon}{m}}} \ d\varepsilon = \frac{1}{\sqrt{2m\varepsilon}} \ d\varepsilon$$

$$dn_c = nAC^3 \ e^{-\frac{mC^2}{2kT}} \ dC$$

Now,

 \Rightarrow

=

$$dn_{\varepsilon} = nA \left(\frac{2\varepsilon}{m}\right)^{\frac{2}{3}} e^{-\frac{\varepsilon}{kT}} \frac{1}{\sqrt{2m\varepsilon}} d\varepsilon$$

$$\Rightarrow \qquad \qquad dn_{\varepsilon} = nA\left(\frac{2\varepsilon}{m^2}\right)e^{-\frac{\varepsilon}{kT}} d\varepsilon$$

$$\therefore \qquad f(\varepsilon) = \frac{1}{n} \frac{dn_{\varepsilon}}{d\varepsilon} = \left(\frac{2A}{m^2}\right) \varepsilon \, e^{-\frac{\varepsilon}{kT}}$$
$$dn_{\varepsilon} = rac{2nA}{m^2} \varepsilon \ e^{-\varepsilon/kT} \ d\varepsilon$$

This implies, the energy distribution function

$$f(\varepsilon) = \frac{1}{n} \frac{dn_{\varepsilon}}{d\varepsilon} = \frac{2A}{m^2} \varepsilon e^{-\frac{\varepsilon}{kT}}$$
$$\frac{d}{d\varepsilon} f(\varepsilon) = \frac{2A}{m^2} e^{-\frac{\varepsilon}{kT}} \left(1 - \frac{\varepsilon}{kT}\right)$$

To get the most probable value of the kinetic energy ε , we set

$$\frac{d}{d\varepsilon}f(\varepsilon) = 0$$
$$\varepsilon_{mn\varepsilon} = kT$$

 \Rightarrow

 \Rightarrow

Example 2.37

Using the Maxwell's distribution function find the number of molecules striking a unit area of the wall of the vessel at angles between θ to $\theta + d\theta$. The gas is at temperature *T*, population density of the molecules is *n* and the molecular mass is *m*.

Solution

In spherical polar coordinates, the speed distribution function of Maxwell is (see Figure 2.8)

$$dn_{c,\,\theta,\,\phi} = n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} c^2 \, dc \sin\theta \, d\theta \, d\phi$$

Therefore, according to the problem, the striking rate on a unit area of the wall between angles θ to $\theta + d\theta$ is = $\int_{c=0}^{\infty} \int_{\phi=0}^{2\pi} (C \cos \theta) dn_{c, \theta, \phi}$

Striking rate
$$= \frac{n}{\pi\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \left[\int_{c=0}^{\infty} e^{-\frac{mC^2}{2kT}} C^3 dC \int_{\phi=0}^{2\pi} d\phi \right] \sin\theta \cos\theta d\theta$$

Striking rate
$$= \frac{n \not\pi}{\not\pi \sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{mC^2}{2kT}} (C^2)^{(2-1)} d(C^2) (\sin\theta\cos\theta \,d\theta)$$

$$= \frac{n}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \left[2\left(\frac{2kT}{m}\right)^2 \sin\theta\cos\theta \,d\theta\right]$$

and finally, the striking rate is

$$n\sqrt{\frac{2kT}{\pi m}}\sin\theta\cos\theta\;d\theta$$

Example 2.38

Find the number of molecules striking a unit area of the wall with speeds in the range *C* to C + dC, irrespective of direction.

Solution

Starting from the expression of the striking rate as obtained in the previous problem;

Striking rate $= \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} (C \cos \theta) \, dn_{c,\,\theta,\,\phi}$

which covers all possible directions but, from one side of the plane. That is

the striking rate
$$= \frac{n}{\pi\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \left[c^3 e^{-\frac{mC^2}{2kT}} dC\right] \times \int_0^{\pi/2} \sin\theta \cos\theta \, d\theta \int_0^{2\pi} d\phi$$

Working out the integrals, we find

striking rate
$$= n\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} C^3 e^{-\frac{mC^2}{2kT}} dC$$

2.15.7.1 Energy Distribution

The Maxwell's energy distribution in three dimensions is obtained as follows. The speed distribution equation is

$$dn_{c} = 4\pi n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} C^{2} \exp\left(-\frac{mC^{2}}{2kT}\right) dC$$

where dn_c is the number of molecules per unit volume moving with speeds in the range *C* to C + dC and *n* is the population density of the molecules.

If the corresponding energy range is ε to ε + $d\varepsilon$, i.e.

$$\varepsilon = \frac{1}{2} mC^2$$
 and $mCdC = d\varepsilon$

then, if the number of molecules per unit volume in this energy range ε to $(\varepsilon + d\varepsilon)$ is dn_{ε} (where $d\varepsilon$ corresponds to dc), we may write

$$dn_{\varepsilon} = dn_{c} = 4\pi n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \left(\frac{2\varepsilon}{m}\right) e^{-\frac{\varepsilon}{kT}}$$

$$dn_{\varepsilon} = 2\pi n \left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} e^{\frac{1}{2}} e^{\frac{-\varepsilon}{kT}} d\varepsilon$$
(2.80)

This is the Maxwell's energy distribution in three dimensions. A plot of $\left(\frac{1}{n}\frac{dn_{\varepsilon}}{d\varepsilon}\right)$ versus ε

is shown in Figure 2.36. There are three main characteristic differences between the speed distribution and the energy distribution function.



Figure 2.36 The distribution of the translational energies of gas molecules at 298 K and 1000 K.

- (i) The initial slope of the energy distribution curve is infinite whereas that of the speed distribution function is zero.
- (ii) As a consequence of (i), the energy distribution curve rises up more steeply than the speed distribution curve, and, beyond the maximum the energy distribution curve falls of more sluggishly than the speed distribution curve.
- (iii) The energy distribution function is independent of the molar mass of the gas.

Example 2.39

Show that the average kinetic energy of the molecules of a gas at equilibrium, at a fixed temperature T is $\frac{3}{2}kT$.

Solution

 \Rightarrow

Using the rule of averaging, the average energy $\langle \varepsilon \rangle$ is

$$\begin{split} \langle \varepsilon \rangle &= \frac{1}{n} \int_0^\infty \varepsilon dn_\varepsilon = 2\pi \left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{\varepsilon}{kT}} \varepsilon^{\frac{3}{2}} d\varepsilon \\ \langle \varepsilon \rangle &= 2\pi \left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{\varepsilon}{kT}} (\varepsilon)^{\frac{5}{2}-1} d\varepsilon \end{split}$$

2.100

 $\langle \varepsilon \rangle = 2\pi \left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} \frac{\left(\frac{3}{2}\right)\left(\frac{1}{2}\right)\sqrt{\pi}}{\left(\frac{1}{kT}\right)^{\frac{5}{2}}} = \frac{3}{2}kT$

Example 2.40

Show that the energy corresponding to the most probable speed is twice that of the most probable energy.

Solution

 \Rightarrow

Differentiating $\frac{1}{n} \frac{dn_{\varepsilon}}{d\varepsilon}$ [Eq. (2.80)] with respect to ε and, equating the result to zero, to get the most probable energy $\varepsilon_{mp\varepsilon} = \frac{1}{2}kT$. The most probable speed is $C_{mps} = \sqrt{\frac{2kT}{m}}$; the corresponding energy is therefore,

$$\left\langle arepsilon
ight
angle_{C_{mps}} = rac{1}{2} \, m igg(rac{2kT}{m} igg) = kT$$

$$\frac{\langle \varepsilon \rangle_{C=C_{mps}}}{\langle \varepsilon \rangle_{mpe}} = \frac{kT}{\frac{1}{2}kT} = 2$$

 \Rightarrow

What fraction of the molecules move with energy more than a specified value ε^* ? Starting from Eq. (2.80), we write

$$\int_{\varepsilon^*}^{\infty} \frac{dn_{\varepsilon}}{n} = 2\pi \left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} \int_{\varepsilon^*}^{\infty} \varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{kT}} d\varepsilon$$
$$\frac{n(\varepsilon^*)}{n} = \frac{2\pi}{\pi\sqrt{\pi}} \left(\frac{1}{kT}\right)^{\frac{3}{2}} \int_{\varepsilon^*}^{\infty} \varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{kT}} d\varepsilon$$

 \Rightarrow

Substituting $\varepsilon = kTx^2$, so that $d\varepsilon = kTd(x^2)$ and $\sqrt{\varepsilon} = \sqrt{kT} x$, we have

$$\frac{n(>\varepsilon^*)}{n} = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT}\right)^{\frac{3}{2}} \int_{x=\sqrt{\varepsilon^*/kT}}^{\infty} \sqrt{kT} \ x \ e^{-x^2} \ kT \ d(x^2)$$

$$\Rightarrow$$

$$\frac{n(>\varepsilon^*)}{n} = \frac{2}{\sqrt{\pi}} \int_{x=\sqrt{\varepsilon^*/kT}}^{\infty} x e^{-x^2} d(x^2)$$

and integrating by parts

$$\frac{n(>\varepsilon^*)}{n} = -\frac{2}{\sqrt{\pi}} \left[\left| x e^{-x^2} \right|_{\sqrt{\varepsilon^*/kT}}^{\infty} - \int_{\sqrt{\varepsilon^*/kT}}^{\infty} e^{-x^2} dx \right]$$

$$\Rightarrow \qquad \qquad \frac{n(>\varepsilon^*)}{n} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{\varepsilon^*}{kT}} \exp\left(-\frac{\varepsilon^*}{kT}\right) + \frac{2}{\sqrt{\pi}} \int_{\sqrt{\varepsilon^*/kT}}^{\infty} e^{-x^2} dx$$

The last integral is the complementary error function (see Eq. M16 of Sec. 2.10.5 and Table 2.1). Therefore

$$\frac{n(>\varepsilon^*)}{n} = 2\sqrt{\frac{\varepsilon^*}{kT}} \exp\left(-\frac{\varepsilon^*}{kT}\right) + erfc\left(\frac{\varepsilon^*}{kT}\right)$$

Referring to the Table 2.1, we find that at $x = 2.2 \ erf(2.2) = 0.9981$ and therefore, *erfc* (2.2) = 1 - 0.9981, i.e. 0.0019. If x is increased further, the *erf*(x) is increased and the *erfc* (n) is decreased and becomes less and less significant. We can thus argue that, if ε^* is more than twice of $kT(\varepsilon^* > 2kT)$, then the last integral can be neglected, with the result

$$\frac{n(>\varepsilon^*)}{n} = 2\left(\frac{\varepsilon^*}{\pi kT}\right)^{\frac{1}{2}} \exp\left(-\frac{\varepsilon^*}{kT}\right); (\varepsilon^* > 2kT)$$
(2.81)

2.15.7.2 The Speed Distribution of the Molecules at the Surface of the Container is Different from that in the Bulk

In Example 2.33 it was given that the distribution of the speed of the molecules in a beam coming out of a tiny hole is given by the function $Ac^3 e^{-\frac{mc^2}{2kT}}$. The reason is very simple: near the hole at the surface of the vessel, the fraction of the total number of molecules moving with speed in the range C to C + dC varies as $c^2 e^{-\frac{mc^2}{2kT}}$ (the Maxwellian way). The rate of which the molecules will effuse out will therefore depend on this factor and, also the number of molecules which comes to the surface per second; this number is directly proportional to the speed of the molecules C. Therefore, the speed distribution of the molecules in the beam should be C times the Maxwellian factor $c^2 e^{-\frac{mc^2}{2kT}}$, i.e. $c^3 e^{-\frac{mc^2}{2kT}}$. We

have also seen that the most probable speed of the molecules in the beam is $\sqrt{\frac{3k\overline{T}}{m}}$ while, that in the bulk is $\sqrt{\frac{2kT}{m}}$.

Example 2.41

Calculate the average speed of the molecules striking a small surface on the wall of the container. Compare the result with that in the bulk.

Solution

From the foregoing discussion we found that the speed distribution of the molecules in a beam is given by

$$f(c)_{\text{beam}} = Ac^3 e^{-\frac{mc^2}{2kT}}$$

and this distribution would guide the rate at which the molecules strike an area of the wall. Therefore, the average speed at which the molecules strike the wall is

$$\left\langle c \right\rangle_{\text{surface}} = \frac{\int_{0}^{\infty} cf(c)_{\text{beam}}}{\int_{0}^{\infty} f(c)_{\text{beam}}}$$

the denominator is necessary for the normalization of the function $f(c)_{\text{beam}}$. Then

$$\langle c \rangle_{\text{surface}} = \frac{\int_0^\infty A \, c^4 \, e^{-\frac{mc^2}{2kT}} \, dc}{\int_0^\infty A \, c^3 \, e^{-\frac{mc^2}{2kT}} \, dc}$$

$$\Rightarrow \qquad \langle c \rangle_{\text{surface}} = \frac{\int_0^\infty e^{-\frac{mc^2}{2kT}} (c^2)^{\frac{5}{2}-1} d(c^2)}{\int_0^\infty e^{-\frac{mc^2}{2kT}} (c^2)^{2-1} d(c^2)}$$

$$\Rightarrow \qquad \langle c \rangle_{\text{surface}} = \frac{\left| \frac{5}{2} \left(\frac{m}{2kT} \right)^2}{\left(\frac{m}{2kT} \right)^{\frac{5}{2}} |\overline{2}} = \sqrt{\frac{9\pi kT}{8m}}$$

The $\langle c \rangle_{\text{bulk}}$ is $\langle c \rangle_{\text{bulk}} = \sqrt{\frac{8kT}{\pi m}}$

Therefore,
$$\frac{\langle c \rangle_{\text{surface}}}{\langle c \rangle_{\text{bulk}}} = \sqrt{\frac{8\pi kT}{8m}} \sqrt{\frac{\pi m}{8kT}} = \frac{3\pi}{8}$$

Example 2.42

Calculate the root mean square speed of the molecules in a molecular beam.

Solution

As we have done in Example 2.39, we first find $\left< c^2 \right>_{\rm surface}\,$ as

$$\langle c^2 \rangle_{\text{surface}} = \frac{\int_0^\infty c^2 f(c)_{\text{beam}}}{\int_0^\infty f(c)_{\text{beam}}} = \frac{\int_0^\infty e^{-\frac{mc^2}{2kT}} c^5 dc}{\int_0^\infty e^{-\frac{mc^2}{2kT}} c^3 dc}$$

$$\Rightarrow \qquad \langle c^2 \rangle_{\text{surface}} = \frac{\int_0^\infty e^{-\frac{mc^2}{2kT}} (c^2)^{3-1} d(c^2)}{\int_0^\infty e^{-\frac{mc^2}{2kT}} (c^2)^{2-1} d(c^2)}$$

$$\langle c^2
angle_{
m surface} = rac{\overline{\left| 3 \left(rac{m}{2kT}
ight)^2}
ight|^2}{\left(rac{m}{2kT}
ight)^3 \overline{\left| 2
ight|^2}} = rac{4kT}{m}$$

Therefore, $C_{\text{rms(surface)}} = \sqrt{\langle c^2 \rangle_{\text{surface}}} = \sqrt{\frac{4kT}{m}}$

2.16 EQUIPARTITION OF ENERGY PRINCIPLE: DEGREES OF FREEDOM

2.16.1 Degrees of Freedom of a Dynamical System

Consider an atom constrained to move along the x-axis. At any instant, the position of the atom can be specified by a single position coordinate x; the associated momentum p_x is

then also defined by the equation, $p_x = m\dot{x}\left(\dot{x} = \frac{dx}{dt}\right)$. We say that the particle (the atom)

has one degree of freedom; because, the specification of one position coordinate and, hence the corresponding linear momentum $m\dot{x}$, the dynamical system of the atom is completely defined. If the particle is constrained to move on a plane, say, the x - y plane, then we require *two position coordinates* x and y and hence, two momentum coordinates p_x and p_y to define the dynamical state of the system. Extending the story to three dimensions, we need *three position coordinates* and hence, *three momentum coordinates*.

We define the degrees of freedom (f) of an atomic/molecular system as the minimum number of position coordinates and hence, an equal number of momentum coordinates required to define the dynamical state of the system.

How many degrees of freedom a diatomic molecule has? For each atom we require three position coordinates, and hence, altogether we need six position coordinates. Moreover, the molecule now has rotational and vibrational motion. We analyse the system by looking at its centre of mass; for this we require *three position coordinates* (x, y, z) to represent *the translational motion of the centre of mass of the molecule*. This specification of the position of the centre of mass is not sufficient; we did not specify the orientation of the molecule. We do it as follows: We place one of the two atoms of the molecule at the centre of the coordinate system and specify the value of the angles θ and ϕ (Figure 2.37). Still the description is not complete; because, the two atoms are oscillating against one another

and are constantly changing their positions relative to the centre of mass. So, we then specify an extra coordinate r, the distance between the two atoms. Altogether we then have six position coordinates: x, y, z; $r \theta$ and ϕ . This defines completely the dynamical state of the system (see Figure 2.37).



Figure 2.37 Six independent coordinates are required to specify the state and position of a diatomic molecule. *x*, *y*, *z*,; the coordinates of the centre of mass, and *r*, $\theta \phi$ to define the bond length and the orientation of the molecule in space.

In general, an *n*-atomic molecule has 3n degrees of freedom (three for each atom and hence, 3n for the molecule). To define the translation, specification of *three position coordinates* of the centre of mass is just sufficient, always. Therefore, the translational degree of freedom is always 3; $f_t = 3$ for any molecule.

We have just seen that *two* generalised coordinates are required to define the rotational motion of a linear molecule. The rotational degree of freedom f_r is then always two for linear molecules ($f_r = 2$) The rest (3n - 5) goes to define the vibrational motion; $f_v = (3n - 5)$ for linear molecules. For non-linear molecules, say a non-linear tri-atomic molecule (Figure 2.38), we first choose an axis joining any two atoms and, then specify θ and ϕ ; finally we specify the angle of rotation ϕ of the third atom about the chosen axis. Non-linear molecules, therefore, have three rotational degrees of freedom; $f_r = 3$. The number of vibrational degrees of freedom is then $f_v = (3n - 6)$.



Figure 2.38 For a non-linear n-atomic molecule rotation needs 3 degrees of freedom; number of vibrational degrees of freedom is then (3n - 6).

2.16.2 Principle of Equipartition of Energy

How much is the translational kinetic energy of a molecule ε_{tr} in space?

$$\varepsilon_{tr} = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 = \frac{1}{2m} p_x^2 + \frac{1}{2m} p_y^2 + \frac{1}{2m} p_z^2$$

where v_x , v_y and v_z are the components of the velocity v of the molecule along the three axes x, y and z and, p_x , p_y and p_z are the corresponding linear momenta along the three axes, respectively. ε_{tr} can therefore be put in the form

$$\varepsilon_{tr} = a_1 p_1^2 + a_2 p_2^2 + a_3 p_3^2$$

$$a_1 = a_2 = a_3 = \frac{1}{2m} \text{ and, } p_1 = p_x; p_2 = p_y; p_3 = p_z$$
(2.82)

where,

This is all the energy for a monoatomic molecule (no rotational and vibrational motion is present). Note that there are *three square terms of momentum in the expression of the translational kinetic energy;* recognize that a molecule has only three translational degrees of freedom ($f_t = 3$). But polyatomic molecules can also rotate and vibrate.

For linear molecules

$$\varepsilon_{\rm rot} = \frac{1}{2I} (Iw_x)^2 + \frac{1}{2I} (Iw_y)^2 = a_4 P_4^2 + a_5 P_5^2$$

and, for non-linear molecules

$$\varepsilon_{\rm rot} = \frac{1}{2I_x} (I_x w_x)^2 + \frac{1}{2I_y} (I_y w_y)^2 + \frac{1}{2I_z} (I_z w_z)^2 \bigg\}$$
(2.83)
$$\varepsilon_{-x} = \frac{1}{2I_x} (I_x w_x)^2 + \frac{1}{2I_y} (I_y w_y)^2 + \frac{1}{2I_z} (I_z w_z)^2 \bigg\}$$

or

$$\varepsilon_{\rm rot} = \frac{1}{2I_x} P_x^2 + \frac{1}{2I_y} P_y^2 + \frac{1}{2I_z} P_z^2 = a_6 P_x^2 + a_7 P_y^2 + a_8 P_z^2$$

where I_x , I_y and I_z are the moments of inertia about the three axes *x*-, *y*- and *z*; w_x , w_y and w_z are the corresponding angular velocities and, P_x , P_y and P_z are the corresponding angular momenta (all the *a*-terms are constants).

It is important to note that the rotational kinetic energy expression is given by two square terms for linear and three for non-linear molecules; these are found to be the same as the corresponding number of rotational degrees of freedom f_r .

The vibrational energy of a bond connecting two atoms of a polyatomic molecule is given by

$$\varepsilon_{\text{vib/mode}} = a_i p_i^2 + b_i q_i^2$$

For each mode (assumed to be harmonic); p_i is the momentum coordinate and q_i is the corresponding position coordinate. The first term represents the kinetic energy and the second term represents the potential energy. The total energy of vibration of a polyatomic molecule is therefore

$$\varepsilon_{\rm vib} = \sum_{i=1}^{(3n-5)} a_i p_i^2 + \sum_{i=1}^{(3n-5)} b_i q_i^2 \quad \text{for linear molecules}$$

$$\varepsilon_{\rm vib} = \sum_{i=1}^{(3n-6)} a_i p_i^2 + \sum_{i=1}^{(3n-6)} b_i q_i^2 \quad \text{for non-linear molecules}$$

$$(2.84)$$

and,

 \Rightarrow

How much is then the total energy of a molecule on an average? Summing up Eqs (2.82), (2.83) and (2.84), we find

 $\perp c$

$$\varepsilon_{\text{total}} = \varepsilon_{\text{tr}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}}$$

$$\varepsilon_{\text{total}} = \sum_{j=1}^{3n} a_j p_j^2 + \sum_{j=1}^{(3n-5) \text{ or } (3n-6)} b_j q_j^2 \qquad (2.85)$$

where the first term represents the total kinetic energy of translation plus rotation, plus vibration; the number of square terms is [(3 + 2 + (3n - 5))], i.e. for linear molecules and [3+3+(3n-6)], i.e. 3n for non-linear molecules. The second term represents the potential energy (3n - 5 for linear and 3n - 6 for non-linear molecules). Therefore, we find that the number of square terms required to define the total kinetic energy of a molecule is 3n, the degrees of freedom of the molecule. The principle of the equipartion of energy indicates that when the energy is proportional to the square of a given position coordinate or momentum,

the average energy due to that coordinate or momentum is simply $\frac{1}{2}kT$ per molecule.

$$\begin{array}{l} \textit{Proof: Suppose } \varepsilon_{i} = \frac{p_{i}}{2m}; \text{ the average of } \varepsilon_{i} \text{ is} \\ & \langle \varepsilon_{i} \rangle = \frac{\int \ldots \int \varepsilon_{i} \; e^{-\varepsilon_{i}/kT} \; dq_{1} \ldots dq_{r} \, dp_{1} \ldots dp_{r}}{\int \ldots \int \; e^{-\varepsilon_{i}/kT} \; dq_{1} \ldots dq_{r} \; dp_{1} \ldots dp_{r}} \\ \Rightarrow & \langle \varepsilon_{i} \rangle = \frac{\int \ldots \int \left(\frac{p_{i}^{2}}{2m}\right) e^{-p_{i}^{2}/2mkT} \; dq_{1} \ldots dq_{r} \; dp_{1} \ldots dp_{r}}{\int \ldots \int \; e^{-p_{i}^{2}/2mkT} \; dq_{1} \ldots dq_{r} \; dp_{1} \ldots dp_{r}} \end{array}$$

 n^2

Since the first two factors in the integrand of the numerator and the first in the denominator depend on p_i alone, the rest of the variables can be integrated out in both numerator and denominator without affecting these factors. It is obvious that the result yields factors all of which cancel from the numerator and denominator; we then have

$$\langle \varepsilon_i \rangle = \frac{\int_{-\infty}^{+\infty} \left(\frac{p_i^2}{2m}\right) e^{-\frac{p_i^2}{2mkT}} dp_i}{\int_{-\infty}^{+\infty} e^{-\frac{p_i^2}{2mkT}} dp_i}$$

$$\langle arepsilon_i
angle = rac{\sqrt{\pi}}{4\pi} (2\pi kT)^{rac{3}{2}} = rac{1}{2} kT$$

The total energy of a dynamical system in thermal equilibrium is equally partitioned among its degrees of freedom and the contribution towards the energy is $\frac{1}{2}kT$ per degree of freedom.

It is interesting, particularly, for the vibrational motion of a molecule. Consider two diatomic molecules, the bond of one being much stiffer than the other; till then, the vibrational kinetic energies are exactly equal at the same temperature.

However, note that potential energy of a molecular system is not always quadratic, e.g. in the gravity field, the gravitational potential energy is mgh; its contribution is then not

 $\frac{1}{2}kT$.

Example 2.43

From the velocity distribution function in three dimensions show that the average translational kinetic energy of the molecules of a gas is $\frac{3}{2}kT$.

Solution

 \Rightarrow

 \Rightarrow

$$\langle \varepsilon \rangle_{\text{kinetic }(tr)} = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left(\frac{1}{2} mv^{2}\right) dn_{v_{x} v_{y} v_{z}}}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dn_{v_{x} v_{y} v_{z}}} \qquad \text{[using Eq. (2.65)]}$$

$$\langle \varepsilon \rangle_{\text{kinetic }(tr)} = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left(\frac{1}{2} mv^{2}\right) e^{-\frac{mv^{2}}{2kT}} dv_{x} v_{y} v_{z}}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{mv^{2}}{2kT}} dv_{x} v_{y} v_{z}}$$

$$\langle \varepsilon \rangle_{\text{kinetic }(tr)} = \frac{2 \int_{0}^{\infty} \left(\frac{1}{2} mv^{2}\right) e^{-\frac{mv^{2}}{2kT}} v^{2} dv \int_{0}^{\pi} \sin\theta \, d\theta \int_{0}^{2\pi} d\phi}{2 \int_{0}^{\infty} e^{-\frac{mv^{2}}{2kT}} v^{2} dv \int_{0}^{\pi} \sin\theta \, d\theta \int_{0}^{2\pi} d\phi }$$

as the functions are even. Therefore,

$$\begin{split} \langle \varepsilon \rangle_{\text{kinetic } (tr)} = & \frac{\left(\frac{m}{2}\right) \int_{0}^{\infty} v^{4} \ e^{-\frac{mv^{2}}{2kT}} dv}{\int_{0}^{\infty} v^{2} \ e^{-\frac{mv^{2}}{2kT}} dv} \\ \langle \varepsilon \rangle_{\text{kinetic } (tr)} = & \frac{3}{2} \ kT \end{split}$$

 \Rightarrow

Example 2.44

Show that for a one-dimensional harmonic oscillator with a force constant $k (= 4\pi^2 v^2 m)$, where v is the frequency of oscillation and m is the mass of the oscillator, the average energy of vibration is kT.

Solution

The kinetic energy of the oscillator is $\frac{1}{2}mv^2$ (v is the velocity). The potential energy V is obtained as

$$\frac{dV}{dx} = -(\text{force}) \Rightarrow \frac{dV}{dx} = kx \text{ (by Hooke's law)}$$

$$\int_{0}^{V} dV = k \int_{0}^{x} x dx \text{ or } V = \frac{1}{2} kx^{2} \text{ (Harmonic)}$$

The average energy of a one-dimensional harmonic oscillator is then

$$\langle \varepsilon \rangle_{\text{vib}} = \frac{\int_{v=-\infty}^{+\infty} \int_{x=-\infty}^{+\infty} \left(\frac{1}{2}mv^2 + \frac{1}{2}kx^2\right) dn_{v,x}}{\int_{v=-\infty}^{+\infty} \int_{x=-\infty}^{+\infty} dn_{v,x}}$$

$$\Rightarrow$$

$$\langle \varepsilon \rangle_{\rm vib} = \frac{\int\limits_{-\infty}^{+\infty+\infty} \left(\frac{1}{2}mv^2 + \frac{1}{2}kx^2\right) n \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{\left(\frac{1}{2}mv^2 + \frac{1}{2}kx^2\right)}{k_B T}} dv \, dx \\ \int\limits_{-\infty}^{+\infty+\infty} \int\limits_{-\infty}^{+\infty+\infty} n \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{\left(\frac{1}{2}mv^2 + \frac{1}{2}kx^2\right)}{k_B T}} dv \, dx$$

 k_B is the Boltzmann constant.

or

$$\langle \varepsilon \rangle_{\text{vib}} = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{\infty} \left(\frac{1}{2} m v^2\right) e^{-\frac{m v^2}{2k_B T}} e^{-\frac{k x^2}{2k_B T}} dv \, dx}{\int_{-\infty}^{+\infty} e^{-\frac{m v^2}{2k_B T}} dv \int_{-\infty}^{+\infty} e^{-\frac{k x^2}{2k_B T}} dx} + \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left(\frac{1}{2} k x^2\right) e^{-\frac{m v^2}{2k_B T}} e^{-\frac{k x^2}{2k_B T}} dv \, dx}{\int_{-\infty}^{+\infty} e^{-\frac{m v^2}{2k_B T}} dv \int_{-\infty}^{+\infty} e^{-\frac{k x^2}{2k_B T}} dx}$$

$$\Rightarrow \qquad \langle \varepsilon \rangle_{\text{vib}} = \frac{\int_{-\infty}^{+\infty} \left(\frac{1}{2} m v^2\right) e^{-\frac{m v^2}{2k_B T}} dv}{\int_{-\infty}^{+\infty} e^{-\frac{2k x^2}{2k_B T}} dv} + \frac{\int_{-\infty}^{+\infty} \left(\frac{1}{2} k x^2\right) e^{-\frac{k x^2}{2k_B T}} dx}{\int_{-\infty}^{+\infty} e^{-\frac{2k x^2}{2k_B T}} dx}$$

$$= \frac{\frac{1}{2}m\int_{-\infty}^{+\infty}e^{-\frac{mv^2}{2k_BT}}v^2 dv}{\int_{-\infty}^{+\infty}e^{-\frac{mv^2}{2k_BT}}dv} + \frac{\frac{1}{2}k\int_{-\infty}^{+\infty}e^{-\frac{kx^2}{2k_BT}}x^2 dx}{\int_{-\infty}^{+\infty}e^{-\frac{kx^2}{2k_BT}}dx}$$
$$= \frac{m\int_{0}^{\infty}e^{-\frac{mv^2}{2k_BT}}v^2 dv}{\sqrt{\frac{2\pi k_BT}{m}}} + \frac{k\int_{0}^{\infty}e^{-\frac{kx^2}{2k_BT}}x^2 dx}{\sqrt{\frac{2\pi k_BT}{k}}}$$

using the Gaussian integral.

Therefore, $\begin{aligned} \langle \varepsilon \rangle_{\text{vib}} &= \frac{m}{2} \sqrt{\frac{m}{2\pi k_B T}} \int_0^\infty e^{-\frac{mv^2}{2k_B T}} (v^2)^{\frac{3}{2}-1} d(v^2) \\ &+ \frac{k}{2} \sqrt{\frac{k}{2\pi k_B T}} \int_0^\infty e^{-\frac{kx^2}{2k_B T}} (x^2)^{\frac{3}{2}-1} d(x^2) \end{aligned}$ $= \frac{m}{2} \sqrt{\frac{m}{2\pi k_B T}} \frac{\left|\frac{3}{2}}{\left(\frac{m}{2k_B T}\right)^{\frac{3}{2}}} + \frac{k}{2} \sqrt{\frac{k}{2\pi k_B T}} \frac{\left|\frac{3}{2}}{\left(\frac{k}{2k_B T}\right)^{\frac{3}{2}}} \end{aligned}$

using the gamma function.

Therefore,

$$\left< \varepsilon \right>_{\rm vib} = \frac{1}{2} \, k_B T + \frac{1}{2} \, k_B T = k_B T$$

This shows that every vibrational motion has two modes, one kinetic and the other potential; each of them contributes $\frac{1}{2}k_BT$. Therefore, unlike the translational and the rotational component, each vibrational component contributes k_BT amount of energy, i.e. each vibrational motion (or each vibrational degree of freedom) contributes twice an amount of energy k_BT as that from a translational and rotational degree of freedom $\begin{pmatrix} 1 & \\ & \\ \end{pmatrix}^9$

$$\left(\frac{1}{2}k_BT\right).$$

2.17 HEAT CAPACITY OF IDEAL GASES

The molar heat capacity of a substance at constant volume is defined as

$$C_{v,m}\left(rac{\partial U_m}{\partial T}
ight)_v$$

where U_m is the molar internal energy. By applying the equipartition of energy principle, we shall first find an expression of U_m and then, differentiating with respect to T, we will evaluate $C_{v,m}$ values.

2.17.1 Monoatomic Molecules

The total degrees of freedom $f = 3 \times 1 = 3$ and it is totally the translational degrees of freedom; $f_t = 3$.

The average energy of a molecule (monoatomic) is then

$$\langle \varepsilon \rangle = f_t \left(\frac{1}{2} \, kT \right) = \frac{3}{2} \, kT$$
 per molecule

The molar energy is then

$$\langle U_m \rangle = N_0 \langle \varepsilon \rangle = \frac{3}{2} RT$$

 $C_{v,m} = \frac{\partial}{\partial T} \langle U_m \rangle = \frac{3}{2} R$

 \Rightarrow

and, considering ideal behaviour, the molar heat capacity at constant pressure

$$C_{P,m} = C_{v,m} + R = \frac{5}{2}R$$

⁹ In this section, we have represented Boltzmann constant by k_B because another k appears as the force constant; otherwise, the Bolzmann constant will be represented by the letter k

The ratio of the two heat capacities γ is then

$$=\frac{C_{P,m}}{C_{v,m}}=\frac{5}{3}=1.67$$

2.17.2 Diatomic Molecules

Atomicity n = 2; total number of degrees of freedom f is then $f = 3n = 3 \times 2 = 6$; the translational degrees of freedom $f_t = 3$; rotational degrees of freedom $f_r = 2$ and vibrational degree of freedom $f_v = 1$. The total average energy of a molecule is

$$\Rightarrow \qquad \langle \varepsilon \rangle = \{ \langle \varepsilon \rangle_{\operatorname{kin}(tr)} + \langle \varepsilon \rangle_{\operatorname{kin}(\operatorname{vib})} + \langle \varepsilon \rangle_{\operatorname{kin}(\operatorname{vib})} \} + \langle \varepsilon \rangle_{\operatorname{pot, vib}} \}$$

 $\langle \varepsilon \rangle = \langle \varepsilon \rangle_{\rm kin} + \langle \varepsilon \rangle_{\rm pot}$

$$\Rightarrow$$

$$= f_t \left(\frac{1}{2} kT\right) + f_r \left(\frac{1}{2} kT\right) + f_v \left(\frac{1}{2} kT\right) + f_v \left(\frac{1}{2} kT\right)$$

$$\Rightarrow \qquad \langle \varepsilon \rangle = \frac{7}{2} kT \text{ per molecule}$$

or
$$\langle U_m \rangle = \frac{7}{2} RT$$
 per mole

Therefore, $C_{v, m} = \frac{7}{2} R \text{ and } C_{P, m} = \frac{9}{2} R \text{ and, } \gamma = \frac{9}{7} = 1.286$

2.17.3 Triatomic Molecules (Linear)

Atomicity n = 3; $f = 3 \times 3 = 9$; $f_t = 3$; $f_r = 2$; $f_v = 4$ Following the same procedure

$$C_{v,\,m} = \frac{13}{2} R$$
; $C_{P,\,m} = \frac{15}{2} R$ and $\gamma = \frac{15}{13} = 1.154$

In general, for *n*-atomic non-linear molecule

$$f_t = 3; \ f_r = 3 \ and \ f_v = (3n - 6)$$

Therefore,

 \Rightarrow

$$\langle \varepsilon \rangle = 3 \left(\frac{1}{2} kT \right) + 3 \left(\frac{1}{2} kT \right) + (3n - 6) kT$$

 $\langle \varepsilon \rangle = 3 (n-1) kT$ per molecule

Therefore, $C_{v,m} = 3(n-1)R \text{ and } C_{P,m} = (3n-2)R \text{ and } \gamma = \frac{3n-2}{3n-3}$

Clearly, γ decreases as the atomicity *n* increase and this is due to the increase in the number of vibrational modes, and consequently, due to an increase into the vibrational contribution towards $C_{v, m}$. Now, let us look into experimental results.

If we analyse the case of monatomic inert gases, we find that the agreement between the theory and the experiment is excellent. The inert monoatomic molecules He, Ne, Ar, Kr and Xe have $C_{v, m}$ values $\frac{3}{2}R$ and $\gamma = 1.67$, which are also theoretically predicted.

However, for polyatomic molecules, the experimental $C_{v,m}$ values at ordinary temperature are substantially lower than the theoretically predicated values. The disagreement between the theoretical and experimental results becomes more clear when we examine the temperature variation of $C_{v,m}$ and γ (Figure 2.38).

Theory suggest that $C_{v,m}$ and hence γ values of all gases should be independent of temperature; but experimentally it is observed that, expecting for monatomic gases, the $C_{v,m}$ values of all gases increase with increasing temperature and attain the theoretical value at high enough temperature. For example, at 20 K the $C_{v,m}$ value of H₂ is found to be only $\frac{3}{2}R$ (Figure 2.39a), which is the theoretically predicted value for monoatomic gases. Correspondingly γ also changes markedly with change in temperature (Figure 2.39b). At 100°C, the experimental value of γ for H₂ is 1.404; O₂ has 1.399 and HI has 1.4; the results should have been 1.286.

These results might lead us to believe that the correct result is 1.4. But, when we look at I_2 , we are again disappointed; it has $\gamma = 1.3$, which is very close to 1.286.

The theory is therefore correct for one kind of molecules and wrong for the other; a horrible result. Take H_2 the value of γ decreases from 1.6 at 20 K to 1.3 at 2000 K.

All these facts were known to Maxwell, Boltzmann and Jeans, but they could not find out the way. *Jeans, once said, 'it seems that certain kinds of motion freeze-out, as the temperature is decreased'*. Now, if we assume that the vibrational motion is such that it exists at higher temperature but stops at a lower temperature then the experimental value of γ at 100°C

for H₂, O₂ and HI can be explained. The $C_{v,m}$ value is then $\left(\frac{3}{2}R+R\right)$, i.e. $\frac{5}{2}R$; $C_{P,m}$ is

then $\frac{7}{2}R$ and then, $\gamma = \frac{7}{5} = 1.4$. Similarly, we can explain the value of γ for H₂(1.66) at 20 K, if we can freeze-out the rotation even (Figure 2.39a).



Figure 2.39 Specific heat at constant volume of hydrogen versus absolute temperature.

In fact, these freezing of vibrational and rotational motions do happen; but classical mechanics cannot explain how these motions are freezed out as the temperature is lowered. Only after the development of quantum mechanics, the puzzle was solved.

According to the quantum principles, a bound system has a discrete sets of energy levels and, as a result it cannot exchange energy with the surroundings in a continuous manner. Note that according to classical mechanics, you can increase the energy of a one-dimensional harmonic oscillator continuously by a gradual increase in temperature; because the energy expression is kT. Moreover, the Boltzamann distribution reads:

$$\frac{p_1}{p_2} = \exp\left[\frac{-\Delta\varepsilon}{kT}\right]$$

where p_1 and p_2 are the probabilities of finding the system in the two states '2' and '1' with the energy gap $(\varepsilon_2 - \varepsilon_1) = \Delta \varepsilon$. Clearly, as $\varepsilon_2 > \varepsilon_1$, $p_2 < p_1$.

Let us now take a diatomic molecule and frame it like a one-dimensional harmonic oscillator; the vibrational energy levels are equispaced; the first being at the zero point energy $\frac{1}{2}hv$; the second level is at $\frac{3}{2}hv$, the third is at $\frac{5}{2}kT$, and so on and so forth $\left[\varepsilon_{\rm vib} = \left(v + \frac{1}{2}\right)hv; v = 0, 1, 2, 3, \ldots\right]$. For $H_2 hv = 8.8 \times 10^{-20}$ J. So, at 100°C, the probability

of finding a molecule in the first excited vibrational state (v = 1) relative to that in the ground state is

$$\frac{p_1}{p_0} = \exp\left[-\frac{hv}{kT}\right] = 3.7 \times 10^{-8}$$

That is, practically all the molecules are in the ground vibrational state.

If you slowly increase the temperature, the first and the onward levels will remain practically vacant, so long as T < hv. All the oscillators are therefore frozen and, do not contribute to the heat capacity; only the translational and rotational modes of motion will contribute. The explains the $C_{v,m}$ values of H_2 and O_2 and, also for HI, at 100°C. But what

happens to I_2 ? Iodine is so massive that its frequency of oscillation $v\left(=\frac{1}{2\pi}\sqrt{\frac{k}{m}}\right)$ is very

low, so that hv is much smaller than kT. For I_2 , $hv = 4.26 \times 10^{-21}$ J and, therefore, at 185°C the chance of finding the I_2 molecules in the first excited vibrational level relative to that in the ground vibrational level is

$$\frac{n_1}{n_0} = \exp\left[\frac{4.26 \times 10^{-21}}{(1.38 \times 10^{-23} \text{ Jk}^{-1}) (458 \text{ k})}\right] = 0.51$$

In essence, what we find is that due to the very small energy gap between the vibrational energy levels (~ 10^{-21} J) for I_2 , the excited vibrational levels (v = 1 and onwards) are also populated significantly, leading to some contribution towards $C_{v,m}$. This in turn decreases γ to 1.3 from 1.4, which would have been if there were no vibrational contribution. As we increase the temperature gradually, the population in the higher vibrational levels increases; this increases their contribution towards $C_{v,m}$ and consequently γ decreases further. When the temperature is sufficiently high, nearly all the levels are equally populated and the classical $\frac{1}{2} kT$ contribution is fully contributed. $C_{v,m}$ then assumes the theoretically predicted value. This is the reason that the theoretically predicted result of $C_{v,m}$ is often called the high temperature limiting value. Over this region of high temperature, γ also decreases to the predicted value 1.286 (for diatomic molecules).

The rotational levels are also quantised but the separation between two successive rotational levels is so small that almost always hv is exceeded by kT and, there is the full contribution from the rotational motion towards $C_{v, m}$. H₂ is the case for which this is not true at 20 K; the translational motions contribute only.

Example 2.45

Calculate the value of $\gamma \left(= \frac{\overline{C_{P,m}}}{C_{v,m}} \right)$ for a gaseous mixture consisting of $n_1 = 2$ moles of

oxygen and $n_2 = 3$ moles of carbon dioxide. The gases are assumed to be ideal.

Solution

From thermodynamic considerations, we write

$$dU = nC_{v,m} dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

 $dU = n C_{v,m} dT$; as $\left(\frac{\partial U}{\partial V}\right) = 0$ for ideal gases

or,
$$U = nC_{v,m} T$$
 (the neglecting constant of integration)

or

 \Rightarrow

 \Rightarrow

 \Rightarrow

 \Rightarrow

 \Rightarrow

 \Rightarrow

$$U = nR \frac{C_{v,m}}{R} T$$

$$\Rightarrow \qquad \qquad U = nR \, \frac{1}{\left(\frac{R}{C_{v,m}}\right)} T = \frac{nRT}{(\gamma - 1)}; \, \gamma = \frac{C_{P,m}}{C_{v,m}} \text{ and } C_{P,m} - C_{v,m} = R$$

The total internal energy U is then

 $U \operatorname{can} \operatorname{also} \operatorname{be} \operatorname{written} \operatorname{as}$

$$U = \frac{(n_1 + n_2) RT}{(\gamma - 1)}$$
... (B)

where γ is the ratio of the capacities for the mixture. Comparing Eqs (A) and (B); we find

$$\begin{aligned} \frac{(n_1 + n_2)}{(\gamma - 1)} &= \frac{n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1)}{(\gamma_1 - 1)(\gamma_2 - 1)} \\ \frac{(\gamma - 1)}{(n_1 + n_2)} &= \frac{(\gamma_1 - 1)(\gamma_2 - 1)}{n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1)} \\ \gamma &= 1 + \frac{(n_1 + n_2)(\gamma_1 - 1)(\gamma_2 - 1)}{n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1)} \\ \gamma &= \frac{n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1) + (n_1 + n_2)(\gamma_1 - 1)(\gamma_2 - 1)}{n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1)} \\ \gamma &= \frac{(n_1 - \gamma_2)}{n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1) + n_2(\gamma_1 - 1)} \\ \gamma &= \frac{(n_1 - \gamma_2)}{(n_1(\gamma_2 - 1) + n_2(\gamma_2 - 1) + n_2(\gamma_1 - 1))} \\ \gamma &= \frac{(n_1 + n_2)(\gamma_1 - 2 - n_1(\gamma_1 - n_2(\gamma_2))/[n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1)]}{(n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1))} \end{aligned}$$

$$\Rightarrow \qquad \gamma = (n_1 + n_2)\gamma_1\gamma_2 - n_1\gamma_1 - n_2\gamma_2) / [n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1)]$$

$$\Rightarrow \qquad \gamma = \frac{n_1\gamma_1(\gamma_2 - 1) + n_2\gamma_2(\gamma_1 - 1)}{n_1(\gamma_2 - 1) + n_2(\gamma_1 - 1)}$$

$$\Rightarrow \qquad \gamma = \frac{n_1 \gamma_1 (\gamma_2 - 1) + n_2 \gamma_2 (\gamma_1 - 1)}{n_1 (\gamma_2 - 1) + n_2 (\gamma_1 - 1)}$$

2.18 MOLECULAR COLLISIONS AND MEAN FREE PATH

Due to the random erratic motion, the molecules of a gas suffer continuous collisions among themselves and with the walls of the container. The latter one has already been taken up in the previous sections. In the section, we shall count the number of collisions among the molecules.

A molecular collision may be a two body (i.e. binary; two molecules collide) or many body (e.g. a ternary collision among three bodies, etc.). But since the probability that the centres of three or more molecules come at a particular point in space at a particular instant is very small, we consider only the binary collisions. The calculation of the binary molecular collisions is important because:

- 1. it helps calculating the rate of chemical reactions in the gas phase.
- 2. it helps calculating the mean free path of the molecules in a gas.

Moreover, do not forget that the collision between the molecules maintain the Maxwell's speed distribution in the steady state. A binary collision, however, should not be taken too much literally. There may not in fact be any real contact between the two molecules during a collision. Figure 2.40 shows the variation of intermolecular potential energy between two neutral molecules against their separation. It is a Lennard-Jones 6-12 potential. Later it

will be shown that the *net attractive force* varies as $\left(\frac{1}{r^6}\right)$ and the repulsive force as $\left(\frac{1}{r^{12}}\right)$,

r being the distance between two molecules; that is why it is called Lennard-Jones¹⁰ 6-12 potential.



rre 2.40(a) The two molecules A and B may be deflected from their original path before any real contact among them.

¹⁰ John E. Jones (a physicist) changed his surname to Lennard – Jones after marrying Kathleen Mary Lennard (1925)









As the two molecules approach each other, the potential energy starts falling off from a distance, say about 8 Å, due to attraction (Figure 2.40c), then forming a minimum, the potential energy curve rises up much steeply due to the repulsive effect. The closest approach between the two molecules σ can therefore be taken as the distance at which the interactive potential energy is zero (Fig 2.40c). Therefore, the rapidly growing repulsive force between two approaching molecules changes the direction of their flight even before any real contact (Figs. 2.40a and 2.40b). This separation σ is therefore an approximation to the sum of the radii of the two molecules.

In kinetic theory, this potential is approximated to the hard sphere potential model (Figure 2.41):



Figure 2.41 Hard sphere approximation for the variation of potential between two approaching molecules.

Potential Energy = 0 for $r \ge \sigma$ $= \infty$ for $r < \sigma$

We will therefore treat the molecules as hard spheres and the collisions as billiard-balllike collisions.

Let us take a mixture of two gases A and B. There are three kinds of collisions: A–A, B–B and A–B. We define

 $Z_{\rm (A)B} \Rightarrow$ Binary collision frequency of a single A molecule with the B molecules in one second.

 $Z_{\rm AB} \Rightarrow$ Number of binary collisions between A and B molecules per unit volume in one second.

Therefore, $Z_{(A)B}$ times the number of A molecules per unit volume n_A , is Z_{AB} ; i.e.

$$Z_{\rm AB} = Z_{\rm (A)B} n_{\rm A} \tag{2.86}$$

The calculation of $Z_{(A)B}$ at first sight seems to be a hopelessly complex task; for, you cannot trace the flight of a particular A molecule after one collision; the picture is completely random. However, the problem can be simplified if we could have thought of a picture in which the particular A molecule is moving through a uniform population of stagnant B molecules; obviously then, the A molecule is moving with the relative speed (relative with respect to the B molecules). Moreover, at each collision, the A molecule will change its line of flight; because the collision can take place at any angle from zero to 180 degrees (Figure 2.42). Therefore, if we let that $\langle v_{\rm rel} \rangle$ is the average speed of the A molecules (averaged over all possible directions) relative to the B molecules then, this A molecule can be assumed to be moving with this relative average speed $\langle v_{\rm rel} \rangle$ along a straight trajectory through the stagnant B molecules. Refer to Figure 2.43, a A molecule will suffer a collision with a B molecule when the distance between their centres is $(\sigma_A + \sigma_B)/2$ where σ_A and σ_B are the molecular diameters of the A and B molecules, respectively. A spherical volume of radius ($\sigma_A + \sigma_B$)/2 about the A molecule can be constructed, so that whenever the centre of any B molecule is, on or inside this volume, there will be a collision. In one second, this sphere of influence of this moving A molecule traces out a cylinder of length $\langle v_{
m rel}
angle$ and, of cross sectional are $\pi \left[\left(\sigma_{\rm A} + \sigma_{\rm B} \right) / 2 \right]^2$. This is called the collision cross-section. Therefore, the number of B molecules, whose centres are within this cylinder, will be equal to the number of collisions, this particular A molecule suffers with the B molecules in one second, i.e. to $Z_{(A)B}$ (Figure 2.44). The volume of the cylinder is $\pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \langle v_{rel}, \rangle$ and therefore

$$Z_{(A)B} = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \langle v_{\rm rel} \rangle n_B$$
(2.87)

and the total number of binary A-B collisions is [from Eqs. (2.86) and (2.87)].



Figure 2.42 Collisions may take place at all possible angles $\theta = 0$ to $\theta = 180^{\circ}$. The average angle of collision is then certainly $(0 + 180^{\circ})/2 = 90^{\circ}$.



Figure 2.43 The supposed picture of collion between a A and B molecule.



Figure 2.44 The possibilities of hitting the A by the B molecules

Now, it remains only find an expression for $\langle v_{\rm rel} \rangle$. As explained in Figure 2.42, from the triangle law of vector addition, the relative velocity a molecule with respect to a B molecule is $v_{\rm rel} = v_{\rm A} - v_{\rm B}$. But we want $\langle v_{\rm rel} \rangle$. For this, we have to average $v_{\rm rel}$ over all possible angles of collision: zero to 180°; i.e. over an average angle of approach 90°. Furthermore, since, collisions occur along all possible directions, we may call it the relative average speed:

$$\langle v_{\rm rel} \rangle^2 = \langle v_{\rm A} \rangle^2 + \langle v_{\rm B} \rangle^2 = \frac{8 RT}{\pi} \left(\frac{1}{M_{\rm A}} + \frac{1}{M_{\rm B}} \right)$$

$$\langle v_{\rm rel} \rangle = \sqrt{\frac{8 RT}{\pi \mu}}$$

$$(2.89)$$

where μ is reduced mass and M_A and M_B are, respectively, the molar masses of the two gases. The final expressions for the collision frequency $Z_{(A)B}$ and the collision number Z_{AB} are then

$$Z_{(A)B} = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8RT}{\pi\mu}} n_B$$
(2.90)

$$Z_{\rm AB} = \pi \left(\frac{\sigma_{\rm A} + \sigma_{\rm B}}{2}\right)^2 \sqrt{\frac{8RT}{\pi\mu}} n_{\rm A} n_{\rm B}$$
(2.91)

and

The collision frequency and the collision number for a pure gas, say A, are then

$$Z_{(A)A} = \pi \sigma^2 \sqrt{\frac{8RT}{\pi (M/2)}} \ n = \sqrt{2} \ \pi \sigma^2 \ \langle c \rangle n \tag{2.92}$$

and

$$Z_{\rm AA} = \frac{1}{\sqrt{2}} \pi \sigma^2 \langle c \rangle n^2 \tag{2.93}$$

In the latter case, we have to divide by 2 otherwise, each collision would have been counted twice

Example 2.46

Calculate the collision frequency and the collision number of oxygen molecules at 27°C and 1 atm. The collision diameter is 2.5 Å. Repeat the calculation at 2 atm and, at 10^{-6} mm Hg pressure, the temperature remaining the same. Also calculate the average time between two successive collisions.

Solution

The number of molecules per unit volume is

$$n = \frac{P}{kT} = \frac{PN_0}{RT} = \frac{(101325 \text{ kPa}) (6.022 \times 10^{23} \text{ mol}^{-1})}{(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(300 \text{ K})}$$
$$n = 2.45 \times 10^{25} \text{ m}^{-3}$$

The average speed of the molecules is then

$$\langle C \rangle = \sqrt{\frac{8RT}{\pi M}} \sqrt{\frac{8(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(300 \text{ K})}{3.14(0.032 \text{ kg mol}^{-1})}} = 445.6 \text{ ms}^{-1}$$

Therefore, the collision frequency is

$$\begin{split} Z_{\rm (A)A} &= \sqrt{2} \ \pi \ \sigma^2 \langle C \rangle \ n \\ &= \sqrt{2} (3.14) \ (2.5 \times 10^{-10} \ {\rm m}^2) \ (445.6 \ {\rm ms}^{-1}) \ (2.45 \times 10^{25} \ {\rm m}^3) \\ Z_{\rm (A)A} &= 3.03 \times 10^9 \ {\rm s}^{-1} \end{split}$$

or

The average time between two successive collisions is

$$\tau = \frac{1}{Z_{(A)A}} = 3.3 \times 10^{-10} \text{ sec}$$

and, the collision number is

$$Z_{\rm AA} = \frac{1}{2} Z_{(A)A} \cdot n = \frac{1}{2} (3.03 \times 10^9 \text{ s}^{-1}) (2.45 \times 10^{25} \text{ m}^{-3})$$

or

$$Z_{\rm AA} = 3.71 \times 10^{34} \text{ m}^{-3} \text{s}^{-1}$$

You can also use Eq. (2.93) directly to get Z_{AA} . From Eqs (2.92) and (2.93) we find or $Z_{(A)A} \sim \rho$ and $Z_{AA} \sim \rho^2$

Therefore,

$$Z_{(A)A}$$
 at 2 atm = $\frac{(2 \text{ atm})}{(1 \text{ atm})} Z_{(A)A}$ at 1 atm
 $Z_{(A)A}$ at 2 atm is 6.06 × 10⁹ s⁻¹

Similarly,

 \Rightarrow

$$Z_{AA}$$
 at 2 atm is
 Z_{AA} at 2 atm = $2^2 (Z_{AA}$ at 1 atm) = $1.48 \times 10^{35} \text{ m}^{-3} \text{ s}^{-1}$

Similarly

$$Z_{(A)A}(at \ 10^{-6} \ mm \ Hg) = \frac{(10^{-6} \ mm \ Hg)}{(760 \ mm \ Hg)} \times 3.03 \times 10^{-9} \ s^{-1}$$

or

and the average time of collisions is 0.25 s.

Comment The collision frequency is directly $\propto \rho$ of the gas but the collision number is directly $\propto \rho^2$. At extremely low pressure, the system becomes almost collision free.

 $Z_{(A)A}$ (at 10⁻⁶ mm Hg) = 4 s⁻¹

Example 2.47

Calculate the ratio of the wall collision frequency and the binary collision frequency of oxygen molecules at 1 atm and 27°C.

Solution

From the previous problem we have

$$\langle C \rangle = 445.6 \text{ ms}^{-1} \text{ and}, n = 2.45 \times 10^{25} \text{ m}^{-3}$$

The wall collision frequency

$$Z_{\text{Wall}} = \frac{1}{4} n \langle C \rangle = \frac{1}{4} (2.45 \times 10^{25} \,\text{m}^{-3}) (445.6 \,\text{ms}^{-1})$$

or

 $Z_{Wall} = 2.73 \times 10^{27} \text{ m}^{-2} \text{s}^{-1}$

The binary collision frequency is (from the previous problem)

$$Z_{(A)A} = 3.03 \times 10^9 \text{ s}^{-1}$$

The ratio

$$\frac{Z_{\text{Wall}}}{Z_{\text{(A)A}}} = \frac{2.73 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}}{3.03 \times 10^9 \text{ s}^{-1}} \approx 1 \times 10^{18} \text{ (numerically)}$$

Comment Wall collision frequency under ordinary conditions of temperature and pressure is as much as 10^{18} times more frequent than the collision frequency.

Example 2.48

The average composition of air is $x_{N_2} = 0.8$ and $x_{O_2} = 0.2$ as the mol-fractions of nitrogen and oxygen, respectively. Calculate at 1 atm and 27°C,

- (i) the number of collisions suffered by one nitrogen molecule with the oxygen molecules in one second.
- (ii) the number of collisions suffered by one oxygen molecule with the nitrogen molecules per second, and
- (iii) the number of binary collisions per cm³ per second between the nitrogen and oxygen molecules. $\sigma_{N_2} = 3.7 \text{ Å}$; $\sigma_{O_2} = 2.5 \text{ Å}$, and
- (iv) the total number of collisions suffered by a single nitrogen molecule in one second.

Solution

We first calculate the following:

The average speed of the nitrogen molecules

050.00

$$\langle c \rangle_{\rm N_2} = \sqrt{\frac{8(8.314 \,\mathrm{JK}^{-1} \,\mathrm{mol}^{-1}) \,(300 \,\mathrm{K})}{3.14(0.028 \,\mathrm{kg \ mol}^{-1})}} = 476.4 \,\mathrm{ms}^{-1}$$

and that of oxygen molecules

$$\langle c \rangle_{O_2} = \sqrt{\frac{8(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(300 \text{ K})}{3.14(0.032 \text{ kg mol}^{-1})}} = 445.6 \text{ ms}^{-1}$$

Total number of molecules per m³

$$n = \frac{P}{kT} = \frac{(101325 \text{ Pa})}{(1.38 \times 10^{-23} \text{ JK}^{-1}) (300 \text{ K})} = 2.45 \times 10^{25} \text{ m}^{-3}$$

Therefore, the number density of the N_2 molecules is

$$n_{\rm N_2} = x_{N_2} \cdot n = 1.96 \times 10^{+25} {\rm m}^{-3}$$

and, that of the O_2 molecules is

$$n_{\rm O_2} = x_{\rm O_2} \cdot n = 0.49 \times 10^{25} \text{ m}^{-3}$$

The reduced mass is

$$\mu = \frac{(0.028 \text{ kg mol}^{-1}) (0.032 \text{ kg mol}^{-1})}{(0.028 + 0.032) \text{ kg mol}^{-1}} = 0.015 \text{ kg mol}^{-1}$$

and

$$\langle v_{\rm rel} \rangle = \sqrt{\frac{8RT}{\pi\mu}} = \sqrt{\frac{8(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{3.14 (0.015 \text{ kg mol}^{-1})}} = 650.88 \text{ ms}^{-1}$$

(i) A single N_2 molecule suffers $Z_{(N_2)O_2}$ collisions with the O_2 molecules in one second [Eq.(2.90)].

$$\begin{split} &Z_{\rm (N_2)O_2} = \pi \left(\frac{\sigma_{\rm N_2} + \sigma_{\rm O_2}}{2}\right)^2 \langle v_{\rm rel} \rangle \, n_{\rm O_2} \\ &= 3.14 \left(\frac{(3.7 + 2.5) \times 10^{-10} \,\mathrm{m}}{2}\right)^2 \, (650.88 \,\mathrm{ms^{-1}}) (0.49 \times 10^{25} \,\mathrm{m^{-3}}) \end{split}$$

or,

$$Z_{(N_2)O_2} = 9.62 \times 10^8 \text{ s}^{-1}$$

Similarly, (ii)

$$Z_{\rm (O_2)\,N_2} = \pi \left(\frac{\sigma_{\rm N_2} + \sigma_{\rm O_2}}{2}\right)^2 \langle \mu_{\rm rel} \rangle \, n_{\rm N_2}$$

or

$$Z_{(O_2)N_2} = 3.14 \left(\frac{(3.7 + 2.5) \times 10^{-10} \text{ m}}{2}\right)^2 (650.88 \text{ ms}^{-1})(1.96 \times 10^{25} \text{ m}^{-3})$$

or

 $Z_{(N_2)O_2} = 3.85 \times 10^9 \text{ s}^{-1}$

(iii) Total number of binary collisions per unit volume per second

$$Z_{O_2, N_2} = Z_{(O_2) N_2} \times n_{O_2}$$

or

 \Rightarrow

$$\begin{split} Z_{\rm O_2,\,N_2} = & (3.85 \times 10^9 \, {\rm s}^{-1}) \, (0.49 \times 10^{25} \ {\rm m}^{-3}) \\ Z_{\rm O_2,N_2} = & 1.9 \times 10^{34} \ {\rm m}^{-3} {\rm s}^{-1} \end{split}$$

(iv) The result is

$$Z = Z_{(N_2)O_2} + Z_{(N_2)N_2}$$

$$\begin{split} Z_{\rm (N_2)N_2} &= \sqrt{2} \ \pi \ \sigma_{\rm N_2}^2 \ \langle c_{\rm N_2} \rangle \ n_{\rm N_2} \\ Z_{\rm (N_2)N_2} &= \sqrt{2} \ (3.14) (3.7 \times 10^{-10} \ {\rm m})^2 \sqrt{\frac{8 (8.314 \ {\rm JK^{-1} \ mol^{-1}}) (300 \ {\rm K})}{3.14 \ (0.028 \ {\rm kg \ mol^{-1}})}} \\ &\times 1.96 \times 10^{25} \ {\rm m^{-3}} \end{split}$$

or

or

$$Z_{
m (N_2)N_2}$$
 = $5.7 imes 10^9~{
m s}^{-1}$

 $Z = 1.53 \times 10^9 \text{ s}^{-1}$

From (i) $Z_{(N_2)O_2} = 9.62 \times 10^8 \text{ s}^{-1}$

Therefore,

2.19 MEAN FREE PATH: FIRST PARADOX OF KINETIC THEORY

According to the kinetic theory, the average speed of the molecules of a gas under ordinary condition is about 500 ms⁻¹, a tremendous speed. This implies that if a dense gaseous sample is placed at a corner of a closed room, the molecules would instantaneously diffuse out uniformly all over the space available. In fact, what is observed is that a considerable time is lapsed for the uniform distribution of the molecules in the room. Take another example, if you open the stopper of a bottle of perfume, and if no wind blows, then after a certain time lag the smell of the perfume is detected.

This slow rate of diffusion of the gas molecules was raised as a serious objection against the kinetic theory at its initial stage of development. Clausius solved the problem by recognising the fantastic number of molecules in a small volume (of the order of 10^{19} molecules per cm³), and the frequent binary collisions between them. Each collision

deflects a molecule from its otherwise straightforward path and, may even recoil it in the opposite direction. That is why the rate of diffusion is so slow.

The straight path, a molecule traverses between two successive collisions is called the free

path; it may have values from zero to infinity. The arithmetic mean of the free paths is called the mean free path (λ).

Refer to Figure 2.45, it shows the trajectory of a single molecule in one second; the breaks at the traject are due to collisions of a molecule with other molecules and, l_1 , l_2 , ... etc. are the free paths. Clearly, we must have

$$\langle C \rangle = l_1 + l_2 + l_3 + \dots = Z_{(A)A}\lambda$$

where λ is the mean free path and $Z_{(A)A}$ is the collision frequency of the molecules. Therefore

$$\lambda = \frac{\langle c \rangle}{Z_{(A)A}} = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$$
(2.94)

or

The mean free path of the molecules of a gas is therefore inversely proportional to the pressure and directly proportional to its kelvin temperature.

In a mixture of two different gases A and B,

$$\lambda_A = \frac{\langle C \rangle_A}{Z_{(A)A} + Z_{(A)B}} \quad \text{and} \quad \lambda_B = \frac{\langle C \rangle_B}{Z_{(B)B} + Z_{(B)A}}$$
(2.95)

Example 2.49

Calculate the mean free path of the oxygen molecules at 1 atm and at 10^{-6} mm Hg pressure. The temperature is 300 K and $\sigma = 2.5$ Å.

Solution

The number of molecules per unit volume

$$n = \frac{P}{kT} \frac{(1 \text{ atm})}{(1.38 \times 10^{-23} \text{ JK}^{-1}) (300 \text{ K})} \times \frac{(101,325 \text{ Pa})}{(1 \text{ atm})}$$
$$n = 2.45 \times 10^{25} \text{ m}^{-3}$$

or

Therefore, the mean free path is (at 1 atm)



Figure 2.45 Due to random elastic collision a molecule very

often deflects from its otherwise straight path.

$$\begin{split} \lambda &= \frac{1}{\sqrt{2} \ \pi \sigma^2 n} = \frac{1}{\sqrt{2} (3.14) \ (2.5 \times 10^{-10} \ \text{m})^2} \ (2.45 \times 10^{25} \ \text{m}^{-3})} \\ \lambda &= 1.47 \times 10^{-7} \ \text{m} = 1470 \ \text{\AA} \end{split}$$

or

At 1×10^{-6} mm Hg,

$$n = (2.45 \times 10^{25} \text{ m}^{-3}) \times \left(\frac{1 \times 10^{-6} \text{ mm Hg}}{760 \text{ mm Hg}}\right) = 3.2 \times 10^{16} \text{ m}^{-3}$$

and,

$$\lambda = 112.6 \text{ m}$$

Comment

At extremely low pressure, the mean free path becomes longer than the dimensions of the box. This explains the *collision free state* of the gas molecules under such a good vacuum condition. *Only the wall collisions occur under such condition*.

Under ordinary condition, about 10^{24} molecules are present per m³. Assuming uniform population density, the distance between two molecules is then $(1m)/\sqrt[3]{10^{24}}$, i.e. 1×10^{-8} m = 100 Å.

We, therefore, notice that under ordinary conditions of pressure and temperature:

- (i) The mean free path is larger than the separation between the molecules (cf. Example 2.47)
- (ii) The mean free path is much larger than the molecular diameter and
- (iii) The mean free path is smaller than the dimension of the box.

Example 2.50

A molecule traverses an average distance λ , the mean free path, between two successive collisions. Consider a plane AB of unit area. The total number of molecules striking this plane from one side is $\frac{1}{4} n \langle c \rangle$ (cf. [Eqs (2.20) and (2.47b)]. These molecules are coming from

all possible directions (Figure 2.46); but for each molecule, the distance of the point at which the molecule strikes the plane AB from the point of their last collision is λ . Show that the average

perpendicular distance of the plane from the point of their last collision is $\frac{2}{3}\lambda$.



Figure 2.46 Each molecule traverses a distance λ before striking the surface, but since they may come from different angles with normal to the surface, their perpendicular distance of the plane from the point of their last collision $\lambda \cos \theta$ is different for different directions.

Solution

In Section 2.2 [Eq. (2.19)], we have calculated the number of molecules striking a unit area with all possible speeds (from zero to infinity) but, from one side of the plane, at an angle θ and ϕ as

$$dn_{\theta,\phi} = \frac{n\langle c\rangle}{4\pi} \sin\theta \cos\theta \, d\theta \, d\phi$$

For these molecules, *the perpendicular distance* to the unit plane *AB*, since their last collision is ($\lambda \cos \theta$). Therefore, the average perpendicular distance is

$$\begin{split} \langle \lambda \cos \theta \rangle &= \frac{\int\limits_{\theta=0}^{\pi/2} \int\limits_{\phi=0}^{2\pi} \lambda \cos \theta \cdot dn_{\theta,\phi}}{\frac{1}{4} n \langle c \rangle} \\ &= \frac{4\lambda}{n \langle c \rangle} \int\limits_{\theta=0}^{\pi/2} \int\limits_{\phi=0}^{2\pi} \cos \theta \frac{n \langle c \rangle}{4\pi} \sin \theta \cos \theta \, d\theta \, d\phi \\ &= \frac{\lambda}{\pi} = \int\limits_{\theta=0}^{\pi/2} \cos^2 \theta \, \sin \theta \, d\theta \int\limits_{\theta}^{2\pi} d\phi \\ &= 2\lambda \int\limits_{\theta=0}^{\pi/2} \cos^2 \theta \, \sin \theta \, d\theta, \end{split}$$

and finally

$$\langle \lambda \cos \theta \rangle = \frac{2}{3} \lambda$$

This is an important result. The molecules strike a unit area from an average perpendicular distance of $\frac{2}{3}\lambda$.

Example 2.51

Prove the result in Example 2.50 from the Maxwell's distribution of molecular velocity.

Solution

Using Eq.(2.65b), we write the Maxwell's distribution equation as

$$dn_{c,\theta,\phi} = n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} c^2 dc \sin\theta d\theta d\phi$$

where $dn_{c, \theta, \phi}$ is the number of molecules per unit volume moving with speeds in the range C to C + dC and at direction determined by θ and ϕ (Figure 2.47). If we draw a slant cylinder of length C and of unit area, at the angles θ and ϕ , its volume is $c \cos \theta$, and, it contains ($C \cos \theta$) $dn_{c, \theta, \phi}$ molecules which will definitely hit the unit

area in one second. For each of these molecules, the distance covered before the hit is λ (along the θ and ϕ directions) and, therefore, the perpendicular distance from the unit area is ($\lambda \cos \theta$). The average of this distance is then

$$\langle \lambda \cos \theta \rangle = \frac{1}{\frac{1}{4} n \langle c \rangle} \int_{c=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} (\lambda \cos \theta) (C \cos \theta) dn_{c, \theta, \phi}$$

Do the integrals yourself and find that

$$\langle \lambda \cos \theta \rangle = \frac{2}{3} \lambda$$



Figure 2.47

2.20 VISCOSITY

2.20.1 Definition

You might have observed that under comparable conditions, honey flows much less readily than water; glycerol flows with even much more difficulty. Viscosity is a property of a fluid (gas and liquid) that measures its power to resist flow.

To understand what is viscosity and how it arises, we consider a fluid confined between

two plates, placed parallel to the x-y plane (Figure 2.48a); one at z = 0 and the other at z = h. The plane at z=0 is fixed. We now slide the z = h plane along the x-axis with velocity v_m . If we now consider the fluid as a stack of several parallel layers like the pages of a book, then the layer which is just adjacent to the z = h plane also moves with the velocity u_m . Due to the presence of internal friction between adjacent layers, the next lower layer will experience a dragging force and will also exert a forward dragging force on the next lower layer. In this way, a velocity (du)

gradient $\left(\frac{du}{dz}\right)$, normal to the direction of flow, will

be set up and, at the steady state each layer will move



with a constant velocity v, which is a function of z. The bottom layer which is in contact with z = 0 plane will remain stagnant.¹¹

If we now consider a plane at height z, then the frictional force acts on the immediate underneath layer in the forward direction and an equal frictional force (by the Newton's 3rd law) on the upper layer in the backward direction; both of the them acting parallel to the surface. This frictional force, or shearing force, acting between the interface of two layers having a relative velocity is called the viscous force. Experimentally, it has been observed that viscous force is directly proportional to the area of contact A, between the

two adjacent layers and to the velocity gradient $\left(\frac{dv}{dz}\right)$ that is

viscous force,
$$F = \eta A \frac{dv}{dz}$$
 (2.96)

where η is a proportionality constant, called the coefficient of viscosity or simply, the viscosity of the fluid. A faster moving layer thus tends to speed up a slowly moving layer and a slowly moving layer tends to slow down a faster moving layer. Equation (2.96) is referred to as the *Newton's equation of viscosity*. It is applicable for steady or laminar flow of incompressible and newtonian fluids. A laminar flow is one in which each small element of the fluid continues its own track of motion, without penetrating into the other, i.e. each layer slips past the adjacent layers (Figs. 2.48b and 2.48c). Incompressible fluid means that the density will remain fixed. A newtonian fluid is one for which η is independent of the velocity gradient $\frac{dv}{dz}$. Gases are certainly newtonian on their flow; liquids of small

molecular size are also newtonian. However, polymers and colloidal suspensions, in which the long chain molecules cannot be oriented along the planes, are non-newtonian.



¹¹ This is called *no slip condition*; the layer immediately adjacent to the lower plate (which is stagnant) will have a velocity v = 0; similarly the layer of the fluid just underneath the upper plate will move with the velocity v_m .

The coefficient of viscosity may therefore be defined as the viscous force required to maintain a unit velocity gradient between two adjacent layers of unit cross-section. In parallel CGS system, its unit is dyne sec cm⁻², commonly called 1 poise in honour of the physicist Poiseuille. In SI system the unit is Nsm⁻².

2.20.2a The Poiseuille Flow Equation

Let us consider the flow of an incompressible fluid through a long straight tube of uniform radius r and length L. The velocity of the flow is small so that the flow is laminar if it is a liquid and a steady state motion if it is a gas. The flow is along the axis of the tube and is due to the pressure difference $\Delta P = (P_1 - P_2)$; P_1 and P_2 are the pressures at the two ends $(P_1 > P_2)$, Figure 2.49. The layer of the fluid just adjacent to the wall of the cylinder is stagnant and, as the centre is approached the velocity of the cylindrical layers increase.



Figure 2.49 The steady, streamline flow of an incompressible fluid through a narrow tube of length *L* and radius *r*.

Let v be the velocity of the layer at a distance z from the centre. Then from Eq. (2.96), we write for the viscous force F as

$$F = -\eta \left(2\pi zL\right) \frac{dv}{dz} \tag{2.97}$$

a negative sign is put before the equation because the sign of $\frac{dv}{dz}$ is negative. This force

is acting along the direction opposite to that of the flow. To maintain the steady condition, this force must be equal to the driving force $\pi z^2 (P_1 - P_2)$. Equating these two forces, we get

$$\eta \left(2\pi zL\right)\frac{dv}{dz} = \pi z^2 \left(P_1 - P_2\right)$$

$$dv = -\frac{z}{2\eta L} \left(P_1 - P_2\right) dZ$$

.

and integrating between limits

$$\int_{0}^{v} dv = -\frac{(P_1 - P_2)}{2\eta L} \int_{r}^{z} Z \, dZ$$

$$v = \frac{(P_1 - P_2)}{4\eta L} (r^2 - z^2)$$
(2.98)

The velocity profile is then found to be parabolic (Figure 2.50) in nature.



Figure 2.50 The parabolic profile of the velocity of an incompressible fluid, flowing through a narrow tube in a steady state.

The total volume of the fluid flowing through the tube per unit time is then

$$\frac{dV}{dt} = \int_{0}^{r} (2\pi \ Z dZ) \ v$$

and using Eq. (2.98),

$$\frac{dV}{dt} = \int_{0}^{r} 2\pi Z \, \frac{(P_1 - P_2)}{4\pi L} (r^2 - z^2) \, dZ = \frac{\pi \, (P_1 - P_2)}{8\eta L} \, r^4$$

$$\eta = \frac{\pi \, (P_1 - P_2) \, r^4}{8 \, L \left(\frac{dV}{dt}\right)}$$
(2.99)

 \Rightarrow

This is the Poiseuille's equation. It must be remembered that the Eq. (2.99) applies only to incompressible fluid.

2.132

2.20.2b Viscosity of Gases

Gases are not incompressible; Eq. (2.99) therefore needs some modification for the compressible character of a gas since a liquid may be considered as almost incompressible, the volume as well as the mass flowing through any section of the tube per unit time is constant. But, since gases are compressible, although the mass flowing through any given section of tube may considered constant, the volume is not.

If *V* be the volume of the gas flowing across a section per unit time at a distance *x* from the entrance point of the tube, and ρ is density at the pressure *P*, then

$$\rho V = \text{constant}$$

Considering the gas to be ideal, we know $\rho \alpha P\left(:: \rho = \frac{MP}{RT}\right)$ we may write

PV = constant

We now consider a section of thickness dx at a distance x from the entrance point. Let the pressure difference across this section be dP; then by the Poiseuille Eq. (2.99) we may write

$$V = -\frac{\pi r^4}{8\eta} \frac{dP}{dx} \qquad (dP \text{ is negative })$$
$$PV = -\frac{\pi r^4}{8\eta} \frac{P dP}{dx}$$

If V_1 be the volume of the gas entering the tube at pressure P_1 then, by Boyle's law (T is kept fixed)

$$P_1 V_1 = -\frac{\pi r^4}{8\eta} \frac{P dP}{dx}$$

 $P_1 V_1 \int_0^1 dx = -\frac{\pi r^4}{8\eta} \int_{P_1}^{P_2} P dP$

and finally

 $P_1 V_1 = \frac{\pi r^4}{16\eta L} \left(P_1^2 - P_2^2 \right) \tag{2.100}$

Several different methods were employed to estimate η for gases; however, the most commonly used method is that of Rankine (see any standard text). The above equation may also be written as

$$\frac{n}{t} = \frac{\eta r^4 (P_1^2 - P_2^2)}{16 \eta L R T}$$
(2.101)

where *n* is the number of moles (ideal gas) flowing out in time *t*.

 \Rightarrow

 \Rightarrow

$$P_1V_1 = PV$$
2.20.3 Validity of Poiseuille's Equation

Equations (2.99) and (2.100) hold good when:

- (i) the flow is steady and streamline
- (ii) there is no radial flow
- (iii) the layer of the fluid in contact with the wall of the tube is stationary, i.e., there is no velocity of slip, and
- (iv) for gases, the mean free path of the molecules is less than the radius of the tube.

Example 2.52

In an experiment to measure the viscosity of O_2 at 0°C, the gas is allowed to pass through a narrow tube of radius 0.21 mm and length 2.5 m. The pressures at the inlet and outlet are 1.2 and 1 atm, respectively. The volume of the gas collected at the outlet is 24.36 mL per minute. Calculate the viscosity coefficient of the gas.

Solution

The number of moles of O_2 at the outlet is

$$n = \frac{PV}{RT} = \frac{(101325 \text{ Pa})(24.36 \times 10^{-6} \text{ m}^3)}{(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(273 \text{ K})}$$

or

 $n=1.087\times 10^{-3}\,\mathrm{mol}$

Therefore,

$$\frac{n}{t} = \frac{1.087 \times 10^{-3} \text{ mol}}{60 \text{ sec}} = 1.81 \times 10^{-5} \text{ mol s}^{-1}$$

From Eq. (2.103)

 $\eta = \frac{\pi r^4 (P_1^2 - P_2^2)}{16 \, RTL(n/t)}$

or

or

$$\eta = \frac{(3.14)(0.21 \times 10^{-3} \text{ m})^4(2.2 \times 0.2 \times 101325 \times 101325 \text{ P}_a{}^2)}{16 (8.314 \text{ JK}{}^{-1} \text{ mol}{}^{-1}) (273 \text{ K}) (2.5 \text{ m}) (1.81 \times 10^{-5} \text{ mol s}{}^{-1})}$$

$$\eta = 1.68 \times 10^{-5} \text{ Ns m}{}^{-2} (1.68 \times 10^{-4} \text{ poise})$$

2.20.4 Viscosity of Gases from Kinetic Theory

Kinetic theory offers an excellent explanation for the viscosity of a dilute gas and also furnishes a fairly simple method for estimating η .

Let us first see how viscosity arises during a steady flow of a gas. Consider a gas flowing parallel to the x-y plane along the *x*-axis with the mean velocity v (which is assumed to be very small compared to the mean thermal speed of the molecules); obviously, v is an increasing function of z. The motion of the molecules along the y- and z-directions

are random, i.e. $\langle c_y \rangle = 0 = \langle c_z \rangle$, but along the *x*-axis, their average component of velocity $\langle c_x \rangle = v$, which is the velocity of the mass motion of the gas.

Consider a plane parallel to the x-y plane at z = h. The molecules above this plane have somewhat greater *x*-component of velocity than the molecules below this plane. So, when the molecules cross this plane from above, they carry with themselves a certain *x*-component of momentum which is transferred to the gas below the plane. Similarly, when the molecules cross the z = h plane from below, some *x*-component of momentum is transferred to the gas above the plane. Since, the velocity gradient is along the *Z*-axis, there is always a net transfer of the *x*-component of momentum from the upper to the lower portion across the plane.

The result is that the layer of gas below the plane gains momentum and the gas layer above the plane loses momentum along the *x*-axis. The effect is therefore the same as if the upper layer exerts a forward drag on the lower layer and as a reaction force (Newton's third law) the lower layer exerts a viscous drag on the upper layer. The picture may be exemplified by citing two trains moving in the same direction with unequal speeds. As the faster train overtakes the slower train, workers on each train constantly pick up sand bags from their train and throw them onto the other train. Then there is a transfer of momentum between the trains so that the slower train tends to be accelerated and the faster train to be decelerated. We shall now derive an expression of η of a gas from this concept.

Refer to Figure 2.51, AB is a plane of unit area placed at z = h, parallel to the *x*-*y* plane. Let the velocity of mass motion of the gas at this height be *v*. The number of molecules striking this unit area in one second at the θ , ϕ direction is

$$dn_{\theta,\phi} = \frac{n}{4\pi} \left\langle c \right\rangle \sin\theta \cos\theta \, d\theta \, d\phi \tag{2.104}$$

where *n* is the number of molecules per unit volume and $\langle c \rangle$ is the average speed of the molecules.

Before striking this area, these molecules have suffered collisions with the other molecules a number of times but the distance of the plane AB from their point of last collision (along the z axis) is $\lambda \cos \theta$. Since the mass motion of the plane AB is v, the velocity of mass motion of the plane situated at the height $\lambda \cos \theta$ from AB is $\left(v + \lambda \cos \theta \frac{dv}{dz}\right)$; $\frac{dv}{dz}$ being the velocity gradient. Therefore, per unit time, each molecule in Eq. (2.104) transfers a momentum of $m\left(v + \lambda \cos \theta \frac{dv}{dz}\right)$ across the plane AB in the θ - ϕ direction (it is assumed that the molecular velocity is adjusted at every collision). Hence, the total momentum transferred across the plane AB from above and from all possible directions is



Figure 2.51 $dn_{\theta\phi}$ is the number of molecules present in the slant cylinder of length $\langle c \rangle$ oriented at angles θ and ϕ . Before striking the unit area *AB*, they have suffered their last collision at point *P*. So the distance *OP* = λ ; but the perpendicular distance *PQ* = $\lambda \cos \theta$. If the layer *AB* moves with velocity *v*,

the velocity of mass motion of the layer at a height PQ from the AB surface is $\left(v + \lambda \cos\theta \frac{dv}{dz}\right)$.

$$p \downarrow = \frac{n\langle c \rangle}{4\pi} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \sin\theta \,\cos\theta \,d\theta \,d\phi \bigg[m \bigg\{ v + \lambda \cos\theta \frac{dv}{dz} \bigg\}$$

or

or

$$p \downarrow = \frac{mn\langle c \rangle}{4\pi} \int_{0}^{\pi/2} \sin\theta \cos\theta \left(v + \lambda \cos\theta \frac{dv}{dz} \right) d\int_{0}^{2\pi} d\phi$$
$$p \downarrow = \frac{1}{2}mn\langle c \rangle \int_{0}^{\pi/2} \sin\theta \cos\theta \left(v + \lambda \cos\theta \frac{dv}{dt} \right) d\theta$$

Similarly, the total momentum transfer across the AB plane from below and from all possible directions per unit time is

$$p\uparrow = \frac{1}{2}mn\langle c\rangle \int_{0}^{\pi/2} \sin\theta\cos\theta \left(v - \lambda\cos\theta \frac{dv}{dz}\right)d\theta$$

The net momentum transferred across the unit AB plane per second is

$$\Delta p = p \downarrow - p \uparrow = \lambda \ mn \langle c \rangle \left(\frac{dv}{dz}\right) \int_{0}^{\pi/2} \sin\theta \cos^{2}\theta \ d\theta$$
$$\Delta p = \frac{1}{3} \ mn \langle c \rangle \ \lambda \left(\frac{dv}{dz}\right)$$

or

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This momentum change per second Δp is nothing but the shearing stress, which is $\eta \left(\frac{dv}{dz}\right)$. Equating these two results we get

$$\eta = \frac{1}{3} mn \langle c \rangle \lambda$$

$$\eta = \frac{1}{3} \rho \langle c \rangle \lambda$$
(2.105)

or

Equation (2.105) presents some interesting predictions: From Eq. (2.94), substituting the expression of λ , we find

$$\eta = \frac{m\langle c \rangle}{3\sqrt{2} \ \pi \sigma^2} \tag{2.106}$$

which suggests that the viscosity of a gas is independent of n and hence of the pressure of the gas. The result is remarkable and was not certainly intuitively expected. It means that the viscous drag on the plane AB at z = h (Figure 2.51) will remain the same if we increase the pressure say from 1 mm Hg to 100 atm. This apparent paradox is due to the fact that as the pressure is doubled, the number of molecules per unit volume gets doubled and, this doubles the number of molecules exchanged between the two layers. At the same time, on doubling the pressure, the mean free path is halved, and therefore, each molecule now conveys as much as only half the momentum as before. The net momentum transfer therefore remains the same. These predictions had in fact been confirmed experimentally by Maxwell himself (Figure 2.52). From this figure, it is also clear that this independence does not hold at *extremely low* and at *extremely high* pressure. The reason is as follows:



Figure 2.52 Pressure dependence of η of Ar at 300 K.

We have made two assumptions in deriving Eq. (2.105); it is assumed that

- (i) $\sigma \ll \lambda$, i.e. the mean free path is much longer than the molecular diameter and
- (ii) $\lambda \ll L$, i.e. the mean free path is much smaller than the smallest linear dimension L of the container.

At very low pressure condition (ii) fails and at very high pressure condition (i) fails. Hence the equation fails at very low and very high pressure. As the pressure is decreased λ increases until it becomes comparable to L, and thereafter, remains constant. On further reducing the pressure only the density ρ decrease which decreases η . The other way to understand this is if the gas is made so dilute that the condition $\lambda \ll L$ is violated, then the viscosity η must decrease, since in the limiting case when $n \rightarrow 0$ (perfect vacuum) the tangential force on the moving planes must clearly go to zero. On the other hand, the departure at very high pressure may be due to the fact that the mean free path becomes of the order of molecular diameter and then the transfer of momentum occurs not over the distance λ but over ($\lambda + \sigma \cos \theta$) where σ is the molecular diameter and θ is the angle between the free path and the normal to the *x*-*y* plane. The effect of each molecule is therefore additive and η rises almost proportionately with the pressure of the gas.



Figure 2.53 Due to the softness of the electron cloud there may be an overlap of the so-called hard spheres at high *T*; this increases the repulsive interaction between the two molecules.

Kinetic theory suggests that η should vary according to the square root of the absolute temperature, i.e. $\eta \propto T^{1/2}$. However, this prediction does not match very well with the experimental results. The viscosity is found to be increase somewhat more rapidly than \sqrt{T} . One reason may be that the molecules are not to be regarded as hard spheres, but to be conceived of being surrounded by a force of field which is repulsive in nature. As the temperature is increased, the velocity of the molecules increases too, and hence can penetrate these force fields (Figure 2.53). That is to say that the molecules have some degree of softness. The effective size of σ therefore decreases thereby increasing the value of λ and hence η more than the factor $T^{1/2}$. Another explanation put forward by Sutherland is to consider the weakly attracting rigid sphere model. The weak attractive force between the two molecules bends the trajectory (Figure 2.40(b)) of the two approaching molecules. The result is that some molecules would now collide which would have been missed in the absence of the forces. The collision frequency being increased, the mean free path λ is reduced, and η , which is proportional to λ , is reduced by the same proportion. According to this model, detailed calculation shows that

$$\eta \,\alpha \frac{\sqrt{\tau}}{\left(1 + b \,/\, T\right)} \tag{2.107}$$

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where *b* is a positive constant to be determined experimentally (ref., R. D. Present; *The Kinetic Theory of Gases*). Electric field has got no effect on the viscosity coefficient of a gas; but η values of paramagnetic gases, e.g. O₂, NO, etc. may be decreased by application of a magnetic field. The mean free path of these molecules decreases in the presence of a magnetic field.

Example 2.53

Calculate the viscosity coefficient of O_2 at 0°C and 1 atm from the kinetic theory expression. σ = 2.5 Å.

Solution

Using Eq. (2.106),

 $\eta = \frac{m\langle c\rangle}{3\sqrt{2}\ \pi\sigma^2}$

we first calculate $\langle c \rangle$

$$\langle c \rangle = \sqrt{\frac{8 RT}{\pi M}} = 425 \text{ ms}^{-1}$$

Therefore,

or

$$\eta = \frac{(0.032 / 6.022 \times 10^{23}) \text{ kg} (425 \text{ ms})}{3\sqrt{2} (3.14) (2.5 \times 10^{-10} \text{ m})^2}$$
$$\eta = 2.7 \times 10^{-5} \text{ Ns m}^{-2}$$

2.20.5 Alternative Method of for the Expression of η of an Ideal Gas

From Eqs (2.20) and (2.47b) we know that the number of molecules striking a unit area from all directions but from one side of the plane is $\frac{1}{4} n \langle c \rangle$.

From Examples 2.48 and 2.49, we also know that the *average perpendicular distance* a molecule traverses to hit a plane is $\frac{2}{2}\lambda$.

Therefore, the momentum delivered to a reference plane from the upper section, per unit area per second is

$$p \downarrow = m \left(\frac{1}{4} n \left< c \right> \right) \left[v + \frac{2}{3} \lambda \frac{dv}{dz} \right]$$

and that from the lower section is

$$p\uparrow = m\left(\frac{1}{4}n\left\langle c\right\rangle\right)\left[v-\frac{2}{3}\lambda\frac{dv}{dz}\right]$$

where v is the velocity of the plane of interest.

The net momentum delivered is then

$$\Delta p = p \downarrow - p \uparrow = \frac{1}{3}mn \langle c \rangle \lambda \frac{dv}{d}$$
 per second.

This is the viscous force; equating the Newton's equation to this, we find

$$\eta \frac{dv}{dz} = mn \langle c \rangle \lambda \frac{dv}{d}$$
$$\eta = \frac{1}{3}mn \langle c \rangle \lambda$$

or

the same as in Eq. (2.105).

PROBLEMS

- **2.1** Compare the gravitational forces between two CO_2 molecules (radius, $r = 1.62 \times 10^{-8}$ cm) with their translational kinetic energy at 27°C.
- [*Ans.*: P.F. = 1.1×10^{-51} J; $\langle \varepsilon \rangle_{tr} = 6.21 \times 10^{-22}$ J] **2.2** Calculate the temperature of a sample of 6 g of He gas whose energy is found to be 11.224 kJ. [*Ans.*: 600 K]
- **2.3** Modern vacuum pumps permit the pressure down to $P = 4 \times 10^{-15}$ atm to be reached at room temperature (300 K). Assuming the gas exhausted is N₂, find the number of its molecules per cm³. Also find the mean distance between the molecules at this pressure. [*Ans.*: $n = 1 \times 10^5$ cm⁻³; $\langle l \rangle = 0.0215$ cm]
- **2.4** The normal density of H_2 is 0.000089 gcm⁻³. Calculate the root mean square speed of O_2 at NTP. [Ans.: 4.6×10^4 cm s⁻¹]
- **2.5** Calculate the kinetic energy of 1 kg of O_2 at 227°C. [Ans.: 1.95×10^5 J]
- **2.6** At what temperature will the rms speed of O_2 be (3/2) times its value at NTP? [Ans.: 614.25 K]
- **2.7** Calculate the most probable, the mean, and the root mean square speed of the molecules of a gas, whose density under standard atmospheric pressure (1 atm) is equal to $\rho = 1 \text{ gL}^{-1}$. [*Ans.*: $C_{\text{mps}} = 0.45 \text{ km s}^{-1}$; $\langle c \rangle = 0.51 \text{ km s}^{-1}$; $C_{\text{rms}} = 0.55 \text{ km s}^{-1}$] **2.8** A 2 L flask contains two non-reacting gases *A* and *B* (the diameters are: $\sigma_A = 2\text{\AA}$;
- **2.8** A 2 L flask contains two non-reacting gases A and B (the diameters are: $\sigma_A = 2$ Å; $\sigma_B = 3$ Å) at a constant temperature 300 K, and at a total pressure of 1 atm. The number of moles of the gases are 2 moles of A and 3 moles of B. Calculate
 - (i) the collision frequency of an A molecule with the B molecules
 - (ii) the collision frequency of a B molecule with the A molecules
 - (iii) the collision number between the A molecules
 - (iv) the collision number between the B molecules, and
 - (v) the total number of binary collisions per cm³ per second (molar mass of A is 4 g mol^{-1} and that of B is 28 g mol^{-1})

$$[Ans.: (i) 2.4 \times 10^{11} \text{ s}^{-1}; (ii) 1.6 \times 10^{11} \text{ s}^{-1}; (iii) 4.06 \times 10^{31} \text{ cm}^{-3} \text{ s}^{-1}; (iv) 7.77 \times 10^{31} \text{ cm}^{-3} \text{ s}^{-1}; (v) 2.63 \times 10^{32} \text{ cm}^{-3} \text{ s}^{-1}]$$

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- **2.9** Two ideal gases *A* and *B* at pressures and volumes, respectively, P_A , P_B , V_A and V_B , such that $P_A V_A = P_B V_B$. Analyze the system. [*Ans.*: Two situations may arise:
 - (i) If $N_A = N_B$ then their temperatures are equal, i.e., $T_A = T_B$ N represents the total number of molecules of the respective gases, and
 - (ii) If $N_A > N_B$ then $T_A < T_B$]
- **2.10** Two flasks A and B have equal volumes. A is maintained at 300 K and B at 600 K. A contains H_2 gas and B contains an equal mass of CH_4 . Assuming ideal behaviour of both the gases, answer the following:
 - (i) Which flask contains greater number of molecules and, how many times as great?
 - (ii) In which flask is the pressure greater? How many times as great?
 - (iii) In which flask are the molecules moving faster? How many times as fast?
 - (iv) In which flask are the number of binary collisions greater? How many times as great? (Assume $2\sigma_{H_2} = \sigma_{CH_4}$)
 - (v) In which flask is the mean free path of the molecules greater? How many times as great? (Assume $2\sigma_{H_2} = \sigma_{CH_4}$)
 - (vi) In which flask is the viscosity more? How many times as more?

n

- (vii) In which is the kinetic energy per mole greater? How many times as great?
- (viii) In which flask is the total kinetic energy greater? How many times as great?

$$\begin{bmatrix} Ans.: (i) & \frac{n_{H_2}}{n_{CH_4}} = 8; \\ (ii) & \left\langle v_{H_2} \right\rangle = 2 \left\langle v_{CH_2} \right\rangle; \\ (iv) & Z_{H_2} = 32 Z_{CH_4}; \\ (v) & \lambda_{H_2} = \frac{1}{2} \lambda_{CH_4}; \\ (vi) & \frac{U_m (H_2)}{U_m (CH_2)} = \frac{1}{2} \\ (vii) & \frac{u_{H_2}}{u_{CH_2}} = 4] \end{bmatrix}$$

- **2.11** The viscosity of H₂ at 0°C is 8.41×10^{-15} poise; determine the mean free path of the molecules at this temperature and 1 atm pressure. [Ans.: $\lambda = 1.67 \times 10^{-5}$ cm]
- **2.12** One of the methods used to find the molecular diameters is through the measurements of the coefficient of viscosity. [*Ans.*: Let us discuss the method. Using the Eqs (2.94) and (2.105), which are:

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 n}$$
 and $\eta = \frac{1}{3} \rho \langle c \rangle \lambda$

To eliminate λ , we do as

$$\eta = \frac{1}{3} \rho \left\langle c \right\rangle \frac{1}{\sqrt{2}\pi \sigma^2 n}$$

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 \Rightarrow

 \Rightarrow

$$\sigma^{2} = \frac{r(r)}{3\sqrt{2}\pi\eta n} = \frac{r}{3\sqrt{2}\pi\eta n} \sqrt{\frac{r}{\pi M}}$$

$$\sigma^{2} = \frac{2\rho}{3\pi\eta n} \sqrt{\frac{RT}{\pi M}}$$
(a)

/

8 RT

At NTP (T = 273 K; P = 1 atm) the coefficient of viscosity of hydrogen has been found to be 8.41×10^{-5} poise. The number of molecules per unit volume is

$$n = \frac{\rho N_0}{RT} = \frac{(1 \text{ atm}) (6.022 \times 10^{23} \text{ mol}^{-1})}{(82.05 \text{ cm}^3 \text{ atm} \text{ K}^{-1} \text{ mol}^{-1}) (273 \text{ K})}$$

$$\Rightarrow \qquad n = 2.7 \times 10^{19} \text{ cm}^{-3} \text{ ; and } \rho = \frac{2}{22414} \text{ gcm}^{-3} = 8.9 \times 10^{-5} \text{ gcm}^{-3}.$$

ρ

 $\rho(c)$

ი

Using Eq. (a),

$$\sigma^{2} = \frac{2 \times 8.9 \times 10^{-5} \text{ g/cm}^{-5}}{3(3.14) (8.41 \times 10^{-6} \text{ g/cm}^{-1} \text{ s}^{-1}) (2.7 \times 10^{19} \text{ cm}^{-5})} \\ \times \sqrt{\frac{(8.314 \times 10^{7} \text{ erg } \text{ K}^{-1} \text{ mol}^{-1}) (273 \text{ K})}{3.14 \times 2 \text{ g mol}^{-1}}} \\ \Rightarrow \qquad \sigma^{2} = 0.0832 \times 10^{-19} \text{ cms} \times \sqrt{\frac{(8.314 \times 10^{7} \text{ g/cms}^{-2} \text{ cm}) (273)}{3.14 \times 2 \text{ g}}} \\ \Rightarrow \qquad \sigma^{2} = 0.0832 \times 10^{-19} \text{ cm s} (6 \times 10^{4} \text{ cm s}^{-1}) \\ \Rightarrow \qquad \sigma^{2} = 0.5 \times 10^{-15} \text{ cm}^{2} \\ \Rightarrow \qquad \sigma = 2.23 \times 10^{-8} \text{ cm}, \text{ i.e.}, \sigma = 2.23 \text{ Å} \end{bmatrix}$$

2.13Calculate the high temperature limiting value of the molar heat capacity at constant pressure for (i) C₂H₂ and (ii) NH₃. Also calculate the ratio the heat capacities γ .

[Ans.: (i)
$$C_{P,m} = \frac{21}{2} R$$
; $\gamma = 1.105$; (ii) $C_{P,m} = 11 R$; $\gamma = 1.22$]

2.14 The ratio of the heat capacities at constant pressure and constant volume of H_2 gas is 1.32 at 2000°C. Calculate the molar heat capacity (a) at constant pressure, (b) at constant volume. How much is the combined vibrational and rotational contribution to the heat capacity at 2000°C?

[Ans.: (a) 8.25 ; (b) 6.25 ; $C_{v,m} = 3.25$ cal K⁻¹ mol⁻¹]

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The Kinetic Theory of Gases

- **2.15** A 250°C, and 765 mm Hg pressure PCl_5 vapour is dissociated to the extent of 81% into PCl_3 and Cl_2 . What is the volume of the vessel in which 1.24 g of PCl_5 vapour was introduced at the specified temperature and pressure? [0.46 L]
- **2.16** When PCl₅ vapour is heated at 200°C and 1.22 atm pressure, it undergoes dissociation to the extent of 0.42. What is (a) the mole fraction, (b) partial pressure of PCl₅, PCl₃ and Cl₂?

[Ans.: (a)
$$x_{PCl_5} = 0.408$$
; $x_{PCl_3} = x_{Cl_2} = 0.296$;
(b) $P_{PCl_5} = 0.498$ atm; $P_{PCl_3} = P_{Cl_2} = 0.361$ atm]

2.17 Arrange in order of increase value: most probable speed of the molecules of a gas, rms speed and the average speed. Would you expect the difference between these three to increase, decrease, or remain the same with increasing temperature? [Ans.: $C_{\rm mps} < \langle C \rangle < C_{\rm rms}$; They will all increase accordingly at \sqrt{T} ; their difference

will increase with increasing temperature, because: $C_{\rm mps}$: $\langle C \rangle$: $C_{\rm rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$

= 1.414 : 1.596 : 1.732]

2.18 Assume that for argon and krypton the vapour densities at their respective normal boiling points are the same. This means that, at their respective normal boiling points, the molecular velocity in the argon vapour is greater than, or less than, or same or cannot tell, compared to the corresponding parameters in the krypton

vapour. [Ans.: They are all the same; because $C_{\rm rms} = \sqrt{\frac{3 RT}{M}} = \sqrt{\frac{3 P}{\rho}}$]

2.19 Calculate the mole fraction composition of a mixture of H_2 and O_2 gases (at STP) such that equal mass of each gas strikes a unit area of the container per second.

[Ans.: $x_{\rm H_2} = 0.8$; $x_{\rm O_2} = 0.2$]

2.20 Two containers of equal volume are separated by a fixed barrier with a pinhole of 10^{-4} cm² area as shown in the figure below. Initially, side A is vacuum, maintained at 0°C, and side B contains He at 1 atm pressure at 25°C. Initially, the pinhole was closed.



After the pinhole is opened, calculate:

(i) The initial rate of escape of He from B to A. Under this condition of P and T, the rate of striking of Xe gas (at. wt = 131) is 0.232 mole $cm^{-2} s^{-1}$.

(ii) Eventually a steady state is reached in which the effusion from A to B equal that of B to A. Calculate the ratio P_A/P_B at the steady state.

[Ans.: (i) $1.328 \times 10^{-4} \text{ mol s}^{-1}$; (ii) 0.957]

- **2.21** In a sample of gas, the molecules move over the entire speed range $(0 \rightarrow \infty)$. We now divide the total number of molecules into two groups : hot a cold. The cold group consists of 30% molecules and have an average speed 0.6 $\langle C \rangle$, and the hot group consists of 70% molecules and have an average speed 1.4 $\langle C \rangle$, where $\langle C \rangle$ is the average speed. Calculate the ratio of the surface collision frequencies of the hot to the cold group $Z_{\text{hot}}/Z_{\text{cold}}$. [Ans.: 5.44]
- **2.22** H_2 gas is taken at 2 atm and 100 K; separately O_2 gas is taken at 5 atm and 300 K. In which case there will be greater amount of mass of the two gases hitting a unit area per second? [Ans.: Mass of H_2 striking/mass of O_2 striking = 0.173]
- **2.23** Two separate bulbs are filled with neon and argon gas, respectively, Ar is at twice the kelvin temperature and hal of the density of the Ne. What is the ratio of their wall collision frequencies? (At. wt. of Ar = 0.04, Ne = 0.02 kg mol⁻¹)

 $[Ans.: Z_{Ne}/Z_{Ar} = 4]$

2.24 Give the ratio of the average speeds $\langle C \rangle_f / \langle C \rangle_i$ and of the wall collision frequencies Z_f/Z_i for the following changes in condition of an ideal gas: *T* is doubled at constant *P* and (b) *P* is doubled at constant *T*.

$$\left[(a) \frac{\langle C \rangle_f}{\langle C \rangle_i} = \sqrt{2}; (b) \frac{\langle C \rangle_f}{\langle C \rangle_i} = 1; (a) \left(\frac{Z_f}{Z_i} \right) = 0.707; (b) \left(\frac{Z_f}{Z_i} \right) = 2 \right]$$

- **2.25** A 2×10^{-3} m³ flask contains 0.015 kg of an ideal gas at 3×10^{5} Pa pressure. Calculate, how long should take for 2% of the gas to escape through a pinhole of 10^{-8} m² in area. [*Ans.:* 50 s]
- **2.26** Oxygen gas at STP has a most probable speed $C_{\rm mps}$ of 4×10^4 cms⁻¹, and a mean free path of 7.7×10^{-8} cm. Calculate the mean time between the collisions.
 - $[Ans.: 1.7 \times 10^{-12} \text{ s}]$
- **2.27** Express the Botzmann constant in units of eVK^{-1} . [Ans.: $8.625 \times 10^{-5} eVK^{-1}$]
- **2.28** How much is the average translational kinetic energy (in electron-volt) of O_2 molecules in air at room temperature (300 K)? Of the N_2 molecules?

[Ans.: 0.039 eV]

2.29 The speed of sound in an ideal gas is given by

$$v_{\text{sound}} = \sqrt{\frac{\gamma RT}{T}}, \text{ where } \gamma = \frac{\overline{C}_P}{\overline{C}_V}$$

Calculate the speed of sound in nitrogen at 300 K, and compare this with the rms speed of N₂ at the same temperature. [Ans.: $v_{\text{sound}} = 353 \text{ ms}^{-1}$; $v_{\text{rms}} = 517 \text{ ms}^{-1}$] Compare the most probable speed of a molecule that collides with a small surface

2.30 Compare the most probable speed of a molecule that collides with a small surf area with the most probable speed of a molecule in the bulk of the gas phase.

$$\left[Ans.:\frac{(v_{\rm mps})_{\rm surface}}{(v_{\rm mps})_{\rm bulk}} = \sqrt{\frac{3}{2}}\right]$$

3 CHAPTER

REAL GASES

3.1 INTRODUCTION

To define the state of a pure gaseous sample of a given mass, we require the specification of three parameters, viz., pressure, temperature and volume. These three parameters are not independent. The mathematical relation which interlink these parameters is called *the equation of state* and, in general, it can be written as f(P, V, T) = 0. It is so called because, if any two of these three parameters are known, then the third can be calculated if their interrelation, i.e., the equation of state is known. The simplest equation of state is that of an ideal gas: Pv - nRT = 0. This equation fails (except under certain limiting conditions) for the gases we encounter, i.e., the real (or non-ideal) gases. In this chapter our objectives will be

- $(i)\quad$ To analyse the experimental results regarding the behaviour of real gases
- (ii) To point out the reasons behind the departure of real gases from the ideal behaviour
- (iii) To construct equations of state for real gases, and
- $(iv) \quad \mbox{To test the validity of these equations of states}.$

3.2 THE WAY REAL GASES BEHAVE

Even Boyle himself knew very well that the equation Pv - nRT = 0 does not fit the experimental data except at very low pressure and at very high temperature $(P \rightarrow 0; T \rightarrow \infty)$.

The amazing observation by James Watt (1783) that, at sufficiently high temperature and pressure, the latent heat of vapourisation of water vanishes as the specific volumes of water and vapour become equal. This report may be marked as the beginning of an extensive search on the behaviour of gases, which in turn, had started the journey into finding a suitable equation of state for real gases.

Thomas Andrews (1863) first carried out a series of systematic experiments which threw much light into the actual behaviour of gases. For each fixed temperature, there is a definite volume of a given mass of gas corresponding to a fixed pressure. The locus of these points (P, V) at a fixed temperature is called an *isotherm*.

The isotherms obtained by Andrews for CO_2 are shown in Figure 3.1. Inspection shows that an isotherm at a low temperature consists of three well defined parts. Consider the isotherm at 243 K. Definitely, the behaviour is not ideal for otherwise, a rectangular hyperbola would have been obtained instead of the chair-like curve ABCD. The position CD however, is almost like a rectangular hyperbola and, it represents the ordinary gas behaviour. Starting from point D, the volume decreases considerably as the pressure is increased; this continues up to point C. Then there is a horizontal part BC; this indicates that the volume decreases considerably without any change in pressure. This is due to the liquefaction of the gas. Liquefaction begins at point C and ends up at B. In this portion the gas (more correctly vapour) is in equilibrium with the liquid. The almost vertical portion AB then corresponds to the liquid state, which also confirms the very low compressibility of the state. Starting with the liquid CO_2 and decreasing the pressure, at the fixed temperature, these changes go in the opposite direction. At point B, the first bubble of vapour is formed and, thereafter the pressure remains constant until the last drop of liquid is vapourised at point C; the volume of the vapour then increases with further decrease in pressure. The pressure corresponding to the portion BC is the saturated vapour pressure at the corresponding temperature (also called the *orthobaric vapour pressure*). The volume per gram of the liquid corresponding to the point B is the specific volume of the liquid and, that corresponding to point C is the specific volume of the vapour at the corresponding temperature.



Figure 3.1 Experimentally obtained isotherms of CO₂ by Andrews. The dashed curve is that for an ideal gas. The isotherm at 304.12 K (31.1°C) is at the critical temperature and is called the critical isotherm.

At a higher temperature, the isotherm follows the same trend; only the length of the horizontal part is shortened from either side.

The specific volume of the vapour therefore decreases and that of the liquid increases with increasing temperature. That is, with increase in temperature, the density of the vapour increases and, that of the liquid decreases. All these changes go on monotonously with increasing temperature until, at $31.1^{\circ}C$ (304.12 K), the specific volumes of the liquid and the vapour become equal; their densities are then also the same. The two states (vapour and liquid) thus become identical at this temperature; the horizontal portion merges to a point and, the curvature changes to positive from negative. This point P is therefore a point of inflexion and, was called by Andrews, the critical point, and corresponding temperature as the critical temperature $31.1^{\circ}C$ is therefore the critical temperature of CO_2 .

Above this temperature there is no horizontal part. This indicates that, above the critical temperature, no pressure, however high, will suffice to liquefy a gas. We now remark that the word 'gas' is coined when it is above its critical temperature and, vapour when it is below the critical temperature. The pressure, just required to liquefy a vapour at the critical temperature (T_c) is called the critical pressure P_c . The molar volume of the gas at T_c and P_c is called the critical volume V_c . This is not a unique behaviour of CO₂; all gases behave in the same way (Figure 3.2). The different regions of the *PV* isotherms of a gas, e.g., CO₂ are shown in Figure 3.3.



Figure 3.2 The *P*–*V* isotherms of isopentane.

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Figure 3.3 The PV vs P isotherms of CO₂.

3.3 CONTINUITY OF LIQUID AND VAPOUR STATES

Consider an isotherm, say ABCD, below the critical temperature of a gas (Figure 3.4). Since there are sharp discontinuities at the two points B and C, where the liquid and the vapour meet the horizontal line BC, we may think that there is a sharp line of demarcation between the liquid and the vapour state. In fact, this is not true. This can be shown by converting the vapour into the liquid or, the liquid into the vapour, without any visible appearance of a meniscus. To do this, the vapour is first taken at point P. It is now heated at a constant volume to the point Q, which is above the critical temperature. The vapour is now compressed at constant pressure, until the critical isotherm is crossed to point R; the system is next cooled to point S (below the critical temperature) at constant volume. The final state S represents the liquid state; but nowhere in the process there appeared any liquid-vapour meniscus. Andrews therefore correctly stated: "The vapour and the liquid states are only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption; the vapour and the liquid are therefore only distant stages of a long series of continuous physical changes."

To celebrate this idea of continuity, the term 'fluid' is coined to represent both the liquid and the vapour state. Below the critical temperature a fluid will be considered as liquid when the molar volume is less than the critical volume of the substance; otherwise it will be a vapour.



Figure 3.4 The continuity of states; the two phase equilibrium.

3.4 STATE OF MATTER AT CRITICAL POINT

When a liquid taken in a sealed tube is heated slowly (Cagniard de La Tour method) there reaches a limit at which the liquid meniscus disappears suddenly; the whole tube is then filled up with a flickering appearance, due to the mixing of the two phases which then merge to form a *homogeneous fluid*. This is the critical point. Similar observation was also made by Andrews. This smooth passage of liquid into vapour at the critical point and the homogeneity of of the entire system can be demonstrated by an experiment of the following type: an empty tube is first kept and balanced horizontally over a knife edge. An amount of the liquid (the amount must be sufficient so that it does not vapourise completely before T_c is reached) is then introduced, and the tube is maintained on the knife edge (Figure 3.5). The liquid is now slowly heated until, at the critical temperature the densities become equal and the tube again swings to the horizontal position.



Figure 3.5 Nadejdines' experiment (Source: An Advanced Treatise on Physical Chemistry; J.R. Partington)

The various properties observed at the critical point may be summarised as follows:

(i) $\left(\frac{\partial P}{\partial V}\right)_T$ is zero at the critical point; but it is negative on either side of the point.

Hence,
$$\left(\frac{\partial V}{\partial P}\right)_T = -\infty$$
 at the critical point. The isothermal compressibility is therefore,

 $\left[\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T\right], \text{ infinity at the critical point. It can be shown that the fluctuation}$

in the number density of particles is directly proportional to β . Since β is infinite at the critical point, there is a large density fluctuation at that point and this leads to a very large scattering of lights. This explains the flickery appearance of the substance at the critical point, which is known as the *critical point opalescence*.

(ii) Experiment shows that $\left(\frac{\partial P}{\partial T}\right)_V$ is a finite positive number at the critical point.

Therefore, since $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$, the coefficient of thermal expansion α is infinity at

the critical point.

<u>n</u>___

(iii)
$$C_P = C_V + \frac{\alpha^2 V_T}{\beta}$$
; therefore, C_P also tends to infinity at the critical temperature.

- (iv) The densities of the liquid and the vapour state are equal at the critical temperature; the meniscus therefore vanishes and the surface tension goes to zero at this point.
- (v) With rise in temperature, the latent heat of vapourisation decreases and vanishes at the critical point. This follows directly from the Clausius Clapeyron equation.

$$\Delta H = T \left(\frac{dP}{dT} \right) \times (V_{\text{vap}} - V_{\text{liq}}) \text{ as } V_{\text{vap}} \to V_{\text{liq}}, \Delta H \to 0$$

However, later works by Cailletet, Colardeau Callendar and many others, showed that the difference in the densities between the liquid and the vapour phases persists even up to few degrees above the critical point. This fact seemed acceptable for it explains the opalescence observed by many workers at the critical point.

3.5 DETERMINATION OF CRITICAL CONSTANTS

There are basically two methods for the determination of critical constants. The first is the Cagniard de La Tour's method of heating a liquid in a sealed tube and to locate the point where the liquid meniscus disappears. This method gives only the critical temperature, and is not free from errors. The second method is the Andrews method of constructing the isotherms at different temperatures and selecting the one at which the horizontal part just merges to a point. This method is useful for finding P_c and T_c exactly, but finding the exact location of V_c is not possible because a slight alteration in temperature will change the value of V_c significantly due to very high α -value of the system at the critical point. V_c can be determined with sufficient accuracy with the help of the so called rectilinear diameter method of Cailletet and Mathias.

3.6 LAW OF RECTILINEAR DIAMETER

According to this law, if ρ_I and ρ_V are the densities (orthobaric densities) of the liquid and the saturated vapour respectively, in equilibrium, then their mean value $\rho_m = (\rho_I + \rho_V)/2$, would be a linear function of temperature. That is

$$\rho_m = \frac{1}{2}(\rho_I + \rho_V) = \rho_0 + at \tag{3.1}$$

..

where a is a constant and ρ_0 is the value of ρ_m at 0°C. At first, the orthobaric densities are plotted versus temperature. The wings will be approximately parabolic in nature (Figure 3.6). Now, the points of the mean densities ρ_m are located; whose locus will be a straight line. By extrapolating the line to t_c , the critical density and hence, the critical volume is directly read off from the ordinate.



Figure 3.6 The demonstration of the law of rectilinear diameter.

3.7 AMAGAT'S ISOTHERM

Beside other inferences, the departure of real gases from ideal behaviour becomes also clear from Andrew's experiment. If the ideal gas equation is held true we should have obtained rectangular hyperbolic P-V isotherms. However, it is sometimes much easier to measure the deviation of a gas from the ideal behaviour with reference to a straight line. In this context, we define the compressibility factor of a gas Z, as the ratio of its actual molar volume to the ideal molar volume under a given set of temperature and pressure:

$$Z = \frac{V}{V_{id}} = \frac{PV}{RT}$$
(3.2)

According to Boyle, a plot of PV vs P for a given mass of gas at constant temperature should be a straight line parallel to the P-axis; i.e., a plot of Z versus P should be a straight horizontal line. Amagat carried out an extensive search on different gases and represented his results by a Z versus P plot at several different constant temperatures. The results on methane are shown in Figure 3.7. Different isotherms along with the critical one, the mixed phase region, the liquid region etc., are marked in the figures. At the inflexion point, we have now a vertical tangent $(\partial Z/\partial P)_T$ (Figure 3.7). The general trend is that above the critical point, each isotherm first decreases with increasing P(Z < 1); forms a minimum and then rises up, even above Z = 1, at high pressures. However, this trend follows up to a temperature, called the Boyle temperature, which is a characteristic parameter for each gas. This is the

temperature at which the initial slope of the Z versus P curve is zero, i.e., $\lim_{P \to 0} \left(\frac{\partial Z}{\partial P} \right)_T = 0$. So

at the Boyle temperature, there is an initial horizontal part and hence each gas obeys the ideal equation fairly accurately up to moderate pressures. Above the Boyle temperature, each isotherm slopes upward and shows no minimum (Figure 3.7(b)). The locus of the minima of the isothermals below the Boyle temperature is more or less parabolic in nature (Figure 3.7(c)). This is now well established that all gases give Z versus P isotherms of this type, but the scale varies so widely from gas to gas that when the critical temperature is very low, it may be exceedingly difficult to realise experimentally the lower isotherms. Thus for H₂, the critical temperature is 31 K, and the Boyle temperature is 116 K; for He, $T_c = 5$ K and $T_B = 23.8$ K; for N₂, $T_c = 127$ K and $T_B = 332$ K; for CO₂, $T_c = 304.1$ K and $T_B = 600$ K. A comparative Pv versus P isotherms for these gases are shown in Figure 3.8, at 300 K. Kammerling Onnes suggested an empirical relation.



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(d)

Figure 3.7 The Amagat's isotherm at different pressure regions, for methane



Figure 3.8 The Pv vs P isotherms of different gases at 300 K

3.9

 $Z = 1 + A_1 P + A_2 P^2 + A_3 P^3 + \cdots$ $Z = 1 + \frac{B_1}{V} + \frac{B_2}{V^2} + \frac{B_3}{V^3} + \cdots$ (3.3)

or

for the equation of the Z versus P isotherms. This is called the virial equation of state where A_1, A_2, A_3, \dots and B_1, B_2, B_3, \dots are called second, third and fourth virial coefficients respectively, and have decreasing order of magnitudes.

3.8 REASONS BEHIND THE DEPARTURE OF REAL GASES FROM IDEAL BEHAVIOUR

This can well be understood with reference to Amagat's isotherms (Figure 3.7). A gas can be liquefied by the application of a suitable pressure below the critical temperature. We know that in the liquid state the molecules are in a compact form with significant attractive forces among them, which held them tightly together, not as much as that in the solid state but, much more than that in the gaseous state. So, there must also be attractive forces among the molecules in the gas phase; but the molecules do not cluster due to increased thermal motion. The next point is that, you cannot compress a liquid as much as a gas. Definitely, it must be due to the strong short range repulsive forces among the molecules which resist them squashing into one another. You can also put it in another way: the molecules have finite volumes and cannot be compressed indefinitely. Now, consider an Amagat's isotherm below the Boyle temperature. At constant temperature, the PV value first decreases with the increasing pressure. This means that below the Boyle temperature and at low pressure, a gas is easier to compress compared to an idea gas (Z < 1). Obviously, this reflects the presence of attractive forces among the molecules which helps the compression. Then note that the slope of the curve decreases numerically with gradual increase in pressure. This means that there must be some other effect which becomes more and more prominent as the molecular separation decreases, and which opposes the effect of attractive force. Inevitably, this must be the repulsive force. The minimum in the isotherm is obtained when the rate of change of attractive force with respect to pressure equals the rate of change of repulsive force with respect to pressure. Thereafter, when the repulsive force strongly dominates the attractive force, Z becomes greater than unity and the gas becomes harder to compress than an ideal gas.

Hence, intermolecular attraction and repulsion are responsible for the deviation of gas behaviour from ideality. However, it is more convenient to speak of the effect of repulsive force among the molecules in terms of the finiteness of the size of the molecules.

Therefore, the equation of state PV = RT needs two corrections. During the last century, a large number of equation of states have been put forward by different workers; some of them are semi-empirical and other purely empirical. In the following section, we will take up some of them and discuss their triumphs and failures.

3.9 van der Waals EQUATION OF STATE

The van der Waals equation of state is given by (for 1 mole)

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

where *b* is the volume correction terms and a/V^2 is the pressure correction term, sometimes also called the internal pressure of the gas. Let us now see how the corrections are introduced.

3.9.1 Volume Correction

If we consider the molecules like the billiard balls (the hard sphere approximation) then they would definitely occupy some space during their translational motion and as a result, would collide the walls of the containing vessel more frequently than if they were point masses. This, in turn, would result in an increase in the pressure of the gas over the ideal value. This increase in the pressure can be accommodated in the equation. P = RT/V, by subtracting some positive quantity from the volume V, i.e., P = RT/(V - b).

The constant b can also be correlated to a molecular property as follows. Considering the molecules of a gas as hard spheres of diameter σ , the closest separation between the

centres of two molecules would be at their time of collision, and is equal to σ (Figure 3.9). So, if we consider а spherical space of volume $\frac{4}{3}\pi\sigma^3 = 8\left(\frac{4}{3}\right)\pi\left(\frac{\sigma}{2}\right)^3 = 8b_1$ (b_1 is the volume of a single molecule) round a single molecule then it is clear that this volume becomes excluded for this pair of molecules for their free movement. Therefore, the volume excluded per mole of gas is $b = 4N_0b_1$ (N_0 is the Avogadro's number). Recognising that, by the volume of a gas we mean the free space which is available for the free movement of the molecules, we find the volume of a mole of gas to be equal to the volume of the container V less this excluded volume b. Hence, the volume corrected equation of state is

$$P(V-b) = RT,$$

where $b = 4 \times N_0 \times (\text{volume of each molecule})$.

3.9.2 Pressure Correction

A molecule at the interior is pulled equally along all directions; but near the wall of the container it should experience a net pull towards the bulk. So, as a molecule approaches the wall its momentum is reduced gradually; the impulse of the blow on the wall is therefore



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Figure 3.9 The sphere of exclusion. The volume of the shaded region is unavailable for the free movement of the pair of molecules

reduced. The attractive force among the molecules therefore reduces the gas pressure below the ideal value. Now the pressure developed at the wall is directly proportional to the number of molecules striking per unit area of the wall per second. This number is proportional to the density of the gas. Now, consider a unit volume of gas just behind this unit area. The number of molecules in this volume is also proportional to the density. The cohesive force among the surface molecules and those in the unit volume, must therefore be proportional to the square of the density of the gas or inversely proportional to the square of the volume of the gas. The reduction in pressure below the ideal value is therefore given

by a/v^2 , where *a* is a constant. So we can write $P_{id} = P + \frac{a}{V^2}$, where *P*, is the pressure of the gas and P_{id} is the ideal pressure, instead of $P_{id}(v-b) = RT$, we now therefore write

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{3.5}$$

which is the van der Waals equation of state for 1 mol of gas. Writing this equation in the form as follows:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

We can recognise three different factors:

- (i) the thermal motion RT; it gives the main thrust;
- (ii) the repulsive force, or the finiteness in the size of the molecules increases the thrust and
- (iii) the attractive force, which reduces the thrust.
 To write the corresponding equation for n mole of a gas of volume V, we replace V by v/n and find,

$$\left(P + \frac{n^2 a}{v^2}\right)(v - nb) = nRT$$
(3.6)

as the van der Waals equation for n mole of gas.

3.10 DETERMINATION OF THE van der Waals CONSTANT 'a' AND 'b'

(i) Isothermal Method

From the van der Waals equation, we have

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$
$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

and

from these two equations, both the constants 'a' and 'b' can be determined from P and $\left(\frac{\partial P}{\partial V}\right)_{m}$ values obtained from the Andrew's isotherms.

(ii) Isochoric Method

From the van der Waals equation,

$$\left(\frac{\partial P}{\partial T}\right)_{V} = \frac{R}{V - b} \implies b = \left[V - \frac{R}{\left(\frac{\partial P}{\partial T}\right)_{V}}\right]$$
$$\left(\frac{\partial P}{\partial T}\right)_{V} = \frac{1}{T}\left(P + \frac{a}{V^{2}}\right) \implies a = V^{2}\left[T\left(\frac{\partial P}{\partial T}\right)_{V} - P\right]$$

and

Hence, 'a' and 'b' can be determined from known values of $\left(\frac{\partial P}{\partial T}\right)_V$, which can be obtained from constant volume gas thermometer.

(iii) From Critical Data

In the next section, we will show that the van der Waals constants 'a' and 'b' are related to P_c , V_c and T_c by the equations:

$$a = rac{27R^2}{64} rac{T_c^2}{P_c}$$
 and $b = rac{R}{8} rac{T_c}{P_c}$

Thus 'a' and 'b' can be obtained from the experimental values of P_c and T_c .

(iv) From Joule-Thomson Experiment

It can be shown that under ordinary condition of pressure, the inversion temperature of a gas, T_i is given by

$$T_i = \frac{2a}{Rb} \Rightarrow b = \frac{2a}{RT_i}$$

Hence, the constant 'b' can be evaluated from known values of T_i and 'a'.

3.11 NATURE OF van der Waals EQUATION

The equation, $P = RT/(V - b) - a/V^2$ is third degree in V; so it follows that for each value of P, V should have three values. Theory of equation therefore suggests that either all the three roots are real or one real and two imaginary. It has been found that above the critical temperature of a gas, only one root is real and below the critical temperature, all the three roots are real over a certain pressure region (see Figure 3.10).



Figure 3.10 Theoretical curves for CO₂ according to van der Waals' equation

It is further noted that:

- (i) Lt $P \rightarrow \infty$ as V approaches b
- (ii) In the Lt $P = 0, V \rightarrow \infty$ and
- (iii) any value of V less than 'b' is of no physical significance, for otherwise P becomes negative.

Hence, a straight line parallel to the P axis is an asymptote to the curve at V = b. The V-axis is also an asymptote to the curve. To determine the intermediate portions, we differentiate the equation:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$
(3.7)

For large values of T, the first term on the right hand side is only important in deciding the sign of the slope, and it is negative. Therefore, the high temperature isotherms have a concavity upwards. For intermediate values of T, both the terms in Eq. (3.7) are important. When $V \rightarrow b$, the first term is dominant and the curve slopes down with increase in volume. With further increase in V, a stage is reached at which the two terms in Eq. (3.7) become equal and the slope becomes zero; thereafter it becomes positive. For large values of V, the first term again predominates and the slope again changes to negative. To summarise:

close to V = b, the slope is negative; with gradual increase in V, the slope changes to zero, then positive and finally again negative. Thus, there must be one minimum and one maximum to each isotherm (below the critical temperature). This fact can also be seen by equating Eq. (3.7) to zero; which gives

$$T = \frac{2a(V-b)^2}{RV^3}$$
(3.8)

..

The equation is also cubic having either three real roots or one real and two imaginary roots. In case of three real roots (below the critical temperature), it can be shown that one root corresponds to a region V < b and has no physical significance.

For

$$V > b, (V - b) > 0$$

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

as

 $V \rightarrow b$; $(V - b) \rightarrow 0 + ; \frac{RT}{(V - b)} \rightarrow \infty$

As *V* goes to *b*, such that, (V - b) > 0

$$\frac{RT}{(V-b)}$$
 dominates $\frac{a}{V^2}$

 \Rightarrow

P > 0

Now assume that, $V < b \Rightarrow (V - b) < 0 \Rightarrow (b - V) > 0$

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

Since $\frac{RT}{(b-V)} + \frac{a}{V^2}$ is a positive quantity when (b-V) > 0.

Therefore, *P* is negative if (V - b) < 0 which is unacceptable, as $V \rightarrow b$, $P \rightarrow \infty$

The other two corresponds to one minimum and one maximum. These two optimum points approach each other with increasing temperature and coalesce into one another at the critical state.

Combining Eq. (3.8) with the van der Waals equation to eliminate T, we can write

$$P = \frac{a(V-2b)}{V^3} \tag{3.9}$$

This represents the locus of the maxima and the minima and is shown by the dotted line RdPbQ in Figure 3.10, where the theoretical isotherms are drawn from known values of 'a' and 'b' for a gas.

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3.12 DETERMINATION OF CRITICAL CONSTANTS FROM van der Waals EQUATION

Method 1

The isotherm, for which the maximum and the minimum has merged into one another and corresponds to the maximum of the parabolic curve RdPbQ [Eq. (3.9)], is the critical isothermal. The pressure and volume corresponding to the maximum of Eq. (3.9) are therefore the critical pressure P_c and critical volume V_c . To find out the critical constants, we therefore differentiate Eq. (3.9) and equate the result to zero.

$$P = \frac{a(V-2b)}{V^3}$$
$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{3a(V-2b)}{V^4} + \frac{a}{V^3}$$
$$\left(\frac{\partial P}{\partial V}\right)_T = 0$$

at the critical point,

This makes

$$\frac{a}{V_c^3} = \frac{3a(V_c - 2b)}{V_c^4}$$

 \Rightarrow

 \Rightarrow

$$V_c = 3b$$

Therefore, from Eq. (3.9)

$$P_c = \frac{a}{27b^2}$$

and from equation of van der Waals

$$T_c = \frac{8a}{27Rb}$$

Method 2

At the critical point, the curvature changes from negative to positive; and it is also an optimum to the P-V isotherm. The first condition requires that $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$ and the second condition requires $\left(\frac{\partial P}{\partial V}\right)_T = 0$ at the critical state.

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

$$\begin{pmatrix} \frac{\partial P}{\partial V} \end{pmatrix}_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \\ \left(\frac{\partial^2 P}{\partial V^2} \right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

and

Equating the above equations to zero at the critical point,

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}$$
 and $\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4}$

Dividing these two equations, we get, $V_c = 3b$; and using it in the first, we get, $T_c = 8a/27Rb.$

Using this T_c and V_c , we get, from the van der Waals equation, $P_c = \frac{a}{27h^2}$

Method 3

The van der Waals equation is cubic V, and has three roots. These roots are all equal at the critical point.

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

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$
(3.10)

 \Rightarrow

which can be written as $(V - V_c)^3 = 0$ or, $V^3 - 3V^2V_c + 3VV_c^2 - V_c^3 = 0$ where V_c is the root at the critical point. Comparing the coefficients of V, V^2 and the constant term, we get, (3.11)

$$3V_c = b + \frac{RT_c}{P_c}$$
$$3V_c^2 = \frac{a}{P_c}$$
$$V_c^3 = \frac{ab}{P}$$

and

From the last two equations, $V_c = 3b$; which when applied to the second, yields, $P_c = a/27b^2$. The first then yields $T_c = 8a/27 Rb$.

The critical coefficient of a van der Waals gas is then given by

$$\frac{RT_c}{P_c V_c} = \frac{8}{3} \tag{3.12}$$

3.12.1 Boyle Temperature

It has already been discussed in Sec. 3.7. From the van der Waals equation,

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

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

or

or

$$Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT} - \frac{a}{RTV} + \frac{ab}{RTV^2}$$

In the low pressure range the term ab/RTV^2 can be neglected,

 $Z = 1 + \frac{Pb}{RT} - \frac{aP}{R^2T^2} \quad (\text{using } PV = RT \text{ as an approximation})$ $\left(\frac{\partial Z}{\partial P}\right)_T = \frac{1}{RT} \left(b - \frac{a}{RT}\right)$ $\left(\frac{\partial Z}{\partial P}\right)_T = 0 \quad \Rightarrow \quad T_B = \frac{a}{Rb} \quad (3.13)$

Hence, for a van der Waals gas, the ratio of the Boyle temperature to the critical temperature

$$\frac{T_B}{T_c} = 3.375$$

So, we summarise the results for a van der Waals gas as

$$\frac{V_c}{b} = 3; \ \frac{T_B}{T_c} = 3.375; \ \frac{RT_c}{P_c V_c} = 2.67$$

3.13 HOW GOOD IS van der Waals EQUATION IN EXPLAINING THE ANDREW'S EXPERIMENTAL ISOTHERMS?

In Figure 3.11, the theoretical isotherms (bold lines) are drawn along with the experimental Andrew's curves (dotted lines). It is seen that at high temperature, the agreement between the theory and experiment is encouraging. But, below the critical temperature, particularly in the region where the liquid and the vapour coexist, there is a remarkable divergence between the theory and experiment. Let us consider the isotherm at 13.1°C. CD is the normal gas behaviour, and is along the experimental line. The liquid portion BA is again along the experimental line. We thus see that the van der Waals equation can also

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is

Now,



Figure 3.11 P-V isothermal of CO₂ (Dotted lines experimental; bold lines theoretical)

explain the behaviour of a liquid. But, while experiment gives a straight horizontal line BC, theory gives the curve ABabCD Figure 3.11. The theory therefore fails to explain this region of the experimental curve. However, this difference can be explained. If a liquid be taken in a cylinder and the pressure is released gradually under isothermal condition, then vapourisation would normally start at the correct pressure (corresponding to the point B). To ensure the process of vapourisation, presence of suitable nuclei is required. In the absence of any such nuclei, if the above process be conducted, the vapour will not be formed and the liquid will become superheated. This is indicated by the line Ba. This is a metastable state. Similarly, if the opposite process of liquefaction be conducted under mechanically shock free state and in absence of any dust particles, a metastable state of super cooled or supersaturated vapour, represented by the line Cb may be obtained. However, since these two metastable states are thermodynamically unstable towards mechanical shocks, presence of dust particles, etc., they cannot be experimentally realised. Superheating or the formation of supersaturated vapour can occur locally in very limited regions, but their net effect over any time period corresponds to the straight portion BC. In fact, the ~ shaped isotherm representing the continuous transition from liquid to vapour had been recognised by James Thomson in 1871 (before the publication of the van der Waals equation), and hence it is often called the James Thomson isotherm. Maxwell first pointed out that if a substance is subjected to a reversible isothermal change round the cycle BabCB, the net work is zero. This requires: area BaO = area ObC. The experimental horizontal part BDC therefore divides the James Thomson isotherm BaObCOB in such a position so as to cut off equal areas from above and below the horizontal part. The existence of negative pressures in some theoretical isotherms (Figure 3.12) also corresponds to the formation of metastable state which exists in tension. The van der Waals isotherms at the lower temperatures cross the v axis and, the part below the v axis corresponds with



Figure 3.12 Plots of isotherms of carbon dioxide from van der Waals equation

3.21

a negative pressure. Although this cannot exist for a gas, it may represent a metastable state for the liquids, which would then be in a state of tension. This isotherm, however, turns up again and re-crosses the *v*-axis in the direction of increasing pressure, so that it must have a minimum value of the tension, below which presumably the metastable state would breakdown into liquid and vapour (*An Advanced Treatise on Physical Chemistry*; J.R. Partington). (For a detail of what has been said above, the students are referred to '*A Treatise on Heat*; Saha and Srivastava').

3.14 HOW GOOD IS van der Waals EQUATION IN EXPLAINING THE AMAGAT'S ISOTHERM?

The nature of the Amagat's isotherm has already been discussed in Sec. 3.7. Now, let us see how good van der Waals equation can reflect these behaviours.

 $P = \frac{RT}{V-b} - \frac{a}{V^2}$ $PV = RT \frac{V}{V-b}$

or

$$V = RT \frac{V}{V-b} - \frac{a}{V}$$
$$= RT \left(\frac{1-b}{V}\right)^{-1} - \frac{a}{V}$$

 $\frac{PV}{RT} = Z = \left(\frac{1-b}{V}\right)^{-1} - \frac{a}{VRT}$

or

or

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots$$
(3.14)

which is of the form: $Z = 1 + \frac{B_1}{V} + \frac{B_2}{V^2} + \frac{B_3}{V^3} + \cdots$ the virial equation of state, initially

proposed by Kammerling and Onnes. To convert it into a power series of P, we write

$$Z = 1 + A_1 P + A_2 P^2 + A_3 P^3 + \cdots$$
(3.15)

where A_1, A_2 , etc., are also virial coefficients and are functions of temperature. Equating Eqs (3.14) and (3.15), and dividing by *P* throughout, we have

$$A_1 + A_2 P + A_3 P^2 + \dots = \left(b - \frac{a}{RT}\right) \frac{1}{PV} + \frac{b^2}{PV^2} + \frac{b^3}{PV^3} + \dots$$
$$= \left(b - \frac{a}{RT}\right) \frac{1}{PV} + \left(\frac{b}{PV}\right) P + \left(\frac{b}{PV}\right)^3 P^2 + \dots$$

which changes to, after introducing Z = PV/RT,

$$A_1 + A_2 P + A_3 P^2 + \dots = \frac{1}{ZRT} \left(b - \frac{a}{RT} \right) + \left(\frac{b}{RT} \right)^2 \frac{P}{Z^2} + \left(\frac{b}{RT} \right)^3 \frac{P^2}{Z^3} + \dots$$
(3.16)

Now, we know that in the limit $P \rightarrow 0, Z \rightarrow 1$; this limit gives

$$A_1 = \frac{1}{RT} \left(b - \frac{a}{RT} \right) \tag{3.17}$$

We thus get the first virial coefficient in the power series of P. Using this value of A_1 in Eq. (3.16), transferring it on the right hand side, then dividing throughout by P we then have,

$$A_{2} + A_{3}P + \dots = A_{1} \left(\frac{1}{Z} - 1\right) \frac{1}{P} + \left(\frac{b}{RT}\right)^{2} \frac{1}{Z^{2}} + \left(\frac{b}{RT}\right)^{3} \frac{P}{Z^{3}} + \dots$$
$$\Rightarrow \qquad A_{2} + A_{3}P + \dots = -A_{1} \left(\frac{Z - 1}{P}\right) \frac{1}{Z} + \left(\frac{b}{RT}\right)^{2} \frac{1}{Z^{2}} + \left(\frac{b}{RT}\right)^{3} \frac{P}{Z^{3}} + \dots$$

Now, from Eq. (3.15), we see that

$$\lim_{P \to 0} \frac{Z-1}{P} = A_1$$

Using this value, again with the limiting condition: $Z \rightarrow 1$ as $P \rightarrow 0$, we get

$$A_2 = \left(\frac{b}{RT}\right)^2 - A_1^2 \tag{3.18}$$

In this way, theoretically we can derive all the virial coefficients. The virial equation of state derived from van der Waals equation is therefore,

$$Z = 1 + \frac{1}{RT} \left(b - \frac{a}{RT} \right) P + \left[\left(\frac{b}{RT} \right)^2 - \left\{ \frac{1}{RT} \left(b - \frac{a}{RT} \right) \right\}^2 \right] P^2 + A_3 P^3 + \cdots$$

If the pressure is not too high, the higher order virials can be neglected and we get

$$Z = 1 + \frac{1}{RT} \left(b - \frac{a}{RT} \right) P \tag{3.19}$$

For gases, where a/RT > b, i.e., the attractive forces dominates the picture, the compressibility should first decrease with pressure with a slope $\frac{1}{RT} \left(b - \frac{a}{RT} \right)$ having zero

curvature. The decrease has in fact been experimentally verified; but a finite curvature of the experimental curve (Figure 3.13) reveals that 'a' and 'b' are not purely constants. However, for gases, where a/RT < b, i.e., the repulsive force is dominant, we get a steady increase in Z with P from the very beginning. For example, for H₂ and He, 'a' is almost zero; we therefore get a nearly straight line for Z versus P curve at ordinary temperature. Nevertheless H₂ would also show a minimum, but at extremely low temperature. Using the expression of the Boyle temperature $T_B = a/Rb$.

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Figure 3.13 The compressibility factor in the reduced form as a function of the reduced pressure at different θ values. The curves were calculated using the van der Waals equation of state.

We can write, at ordinary pressure

$$Z = 1 + \frac{b}{RT} \left(1 - \frac{T_B}{T} \right) P$$
$$\left(\frac{\partial Z}{\partial P} \right)_T = \frac{b}{RT} \left(1 - \frac{T_B}{T} \right)$$
(3.20)

 \Rightarrow

Hence, an Amagat's isotherm has a positive initial slope above Boyle temperature $(1 - T_B/T \text{ is positive})$ and has a negative initial slope below Boyle temperature. However, this point needs further clarification. Below T_B , at low pressure, the term 'b' can be neglected in comparison to V, and then the van der Waals equation changes to $\left(P + \frac{a}{V^2}\right)(V) = RT$ or

$$PV = RT - \frac{a}{V}$$
. Since with increasing pressure V decreases and $\frac{a}{V}$ increases, PV decreases

with increasing *P*. At a certain pressure *PV* is brought to a minimum but still remain less than *RT*. Thereafter, with increasing *P*, *PV* increases due to increased molecular repulsion and crosses the ideal line PV = RT. At fairly high pressure a/V^2 may be neglected and we can write

$$P(V-b) = RT$$

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(3.21)

or
$$PV = RT + bP$$

when PV rises up above the ideal line and increases with increasing P. This has in fact been experimentally verified.

We now set out to prove another characteristic of Amagat's isotherms.

Writing the van der Waals equation as

$$PV = RT\frac{V}{V-b} - \frac{a}{V}$$

and differentiating with respect to P at constant T

$$\left[\frac{\partial(PV)}{\partial P}\right]_{T} = \left[\frac{RT}{V-b} - \frac{RTV}{(V-b)^{2}} + \frac{a}{V^{2}}\right] \left(\frac{\partial V}{\partial P}\right)_{T}$$

We have seen that, below the Boyle temperature, each Amagat's isotherm shows a minimum. So, applying the condition of minimum, we get

$$\frac{RTV}{(V-b)^2} - \frac{RT}{(V-b)} = \frac{a}{V^2} \implies RT = \frac{a}{b} \left(\frac{V-b}{V}\right)^2$$
$$\left(P + \frac{a}{V^2}\right) = \frac{a}{b} \frac{(V-b)}{V^2}$$
$$PV^2 + a = \frac{aV}{b} - a$$
$$P^2V^2 - \frac{a}{b}PV + 2aP = 0$$
(3.

0

or

$$\Rightarrow \qquad PV^2 + a = \frac{aV}{b} - a$$

or

which is a parabolic path when PV is plotted vs. P at constant T. Thus, van der Waals equation requires that the locus of the minima of the Amagat's isotherms below the Boyle temperature should be parabolic. This has also been experimentally verified (cf - Figure 3.3).

3.15 VALIDITY OF van der Waals EQUATION OF STATE

The equation can be criticized on the following points:

- (i) van der Waals' curves do not fit well with the Andrew's curves below the critical temperature. The former suggests a minimum and a maximum, but which are not present in the experimental curve (obviously there is explanation for this discrepancy).
- (ii) The van der Waals constants 'a' and 'b' are supposed to be purely constants for a given gas. However, experimentally it has been found that both of them, specially a, vary significantly with temperature.

3.24

To explain the temperature dependence of 'a', we can assume that the variation in 'a' is due to change in number density of the molecules with change in temperature. From Boltzmann distribution, we have

$$n = n_0 \exp\left[-\frac{\varepsilon}{kT}\right]$$

where n is the number density of the molecules at the wall of the vessel in presence of cohesive forces and n_0 is the same in absence of cohesive forces. ε is the potential energy of the molecules arising out of this cohesive force. As temperature is increased, the exponent and hence the exponential factor increases, which decreases the difference between n and n_0 . This lowers the value of 'a'. To explain the temperature dependence of 'b', we have to give up the model of perfectly elastic hand spheres of the molecules. Actually, the molecules have some softness due to the existence of repulsive force field around them, and as the temperature is increased, due to their increased kinetic energy, each of them can penetrate the others repulsive field zone and the diameter of the excluded volume is lowered. This lowers the value of 'b'.

- (iii) The ratio V_c/b should be 3 according to the theory, but the actual value is close to 2.
- (iv) According to the equation, the critical coefficient RT_c/P_cV_c has a value of 2.67; but the experimental value varies from 3 to 5.
- (v) The ratio T_B/T_C is 3.65 for real gases and it is below 3.3 for other gases; while according to the van der Walls equation, it is 3.375.

3.16 REDUCED EQUATION OF STATE

The van der Waals constants 'a' and 'b' are different for different gases and hence the plots of PV versus P at constant temperatures are also different for different gases. Then, how would we compare different gases? One way to compare them is to compress or extend suitably the PV and P axes so as to make coincident all the isotherms along one trace. However, a slightly different way of doing the same thing is to express the equation of state in terms of the reduced variables, and then to plot the isotherms in terms of the reduced variables. We define the reduced variables as the ratio of the actual variable to its critical value, e.g.

the critical pressure, $\pi = \frac{P}{P_c}$ the critical volume $\phi = \frac{V}{V_c}$

and, the critical temperature, $\theta = \frac{T}{T_c}$
In terms of these reduced variables, π , ϕ and θ , the van der Waals equation changes to

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R\theta T_c$$

Using the values of P_c , T_c and V_c in terms of a and b, we finally have

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$$
 (3.22)

Equation (3.22) is called the reduced equation of state.

Characteristics and Importance

This equation of state is devoid of any characteristic constant, and even of R. So it is of universal applicability. Thus a plot of $\pi\phi$ versus π or $Z_r\left(=\frac{\pi\phi}{R\theta}\right)$ at a constant θ should be

the same for all gases (see Figure 3.13). It, therefore, follows that, if for any two substances any two of the three parameters π , ϕ , and θ , possess the same value, the third quantity must also be the same. This is called the law of corresponding states, and the substances are said to be in the corresponding states.

Validity

It can be shown classically that any equation of state having only two characteristic constants, one accounting the intermolecular attraction and the other accounting the intermolecular repulsion (the finiteness of the size of the molecules), such as the van der Waals 'a' and 'b', can always be converted into the corresponding equation of state. de Boer has proved that the law of corresponding state is also correct from the point of view of quantum theory if the potential energy of the substance can be expressed as a series of sums, all of which are inversely proportional to the distance between two molecules, and if the classical statistics is obeyed.

However, the law has not been found, experimentally to be rigorously true. For example, according to this principle, the critical coefficient RT_c/P_cV_c , should have been equal for all substances and should be equal to 2.67. In fact it has been observed to vary from 3 to 5. Nevertheless, the law has been found to be fairly accurate for small, non polar, spherical molecules; but for polar and oblate molecules the deviations from experiments are significant.

3.17 DIETERICI'S EQUATIONS OF STATE

In 1899, Dieterici modified the van der Waals equation by replacing the internal pressure term a/v^2 by $a/v^{5/3}$. His logic was as follows:

Let us imagine a molecule to be kept in a cube of side length d in which it just fits. The volume required to hold the molecule is then d^3 . If n be the total number of molecules in volume v, then the number of molecules per unit volume is n/v; this number times the volume required to hold one molecule, d^3 , is therefore, unity. That is $(n/v)d^3 = 1$ or $d = (n/v)^{-1/3}$. Now consider a slice of unit area and thickness d at the surface of the wall. The number of molecules in this volume slice is $(n/v)d = (n/v)^{2/3}$. Now consider a unit volume just behind the slice; the number of molecules contained in it is (n/v). The internal pressure must therefore be proportional to the product of the number of molecules in these two sections, i.e., to $(n/v)^{5/2}$. We therefore replace the factor a/v^2 by $a/v^{5/2}$, and write the Dieterici equation as

$$\left(P + \frac{a}{V^{5/3}}\right)(v-b) = RT \tag{3.23}$$

In the same year, Dieterici proposed a second equation of state. Here, the volume correction is exactly equal to that in van der Waals; the pressure correction term, however, is made in the following way. A molecule at the bulk is attracted by other molecules from all possible directions, and is therefore not acted upon by any net force. The pressure of the gas at the bulk is therefore equal to the ideal pressure, P_i . At the surface, the molecules are, however, attracted only from the rear side and therefore, the pressure felt at the wall of the container P, is less than P_i . Under isothermal condition, the work done by a mole of gas in coming from the bulk to the wall is therefore given by,

$$W = RT \ln \frac{P_i}{P_o}$$

 $\frac{a}{V} = RT \ln \frac{P_i}{P_o}$

 $P_i = P_o e^{a/RTV}$.

We now recognise that, larger the volume of the gas, greater will be their separation and lower will be their force of attraction, i.e., lower will be the magnitude of the work. We can therefore write, $W \propto \frac{1}{V}$ or $W = \frac{a}{V}$, where 'a' is a constant for a given gas. Therefore,

or

However, an alternative method is as follows:

A molecule at the bulk is acted upon by attractive force from all possible directions and hence is not acted upon by any net force. However, a molecule at the surface is acted upon by forces only from one side of it, and is therefore feels a net pull towards the bulk. The potential energy of the surface molecules is therefore higher than those in the bulk. Let this excess potential energy per mole be ΔE . Then, considering a unit volume at the bulk containing n_0 molecules, we can write

$$n = n_0 e^{-\frac{\Delta E}{RT}}$$

where *n* is the number of molecules out of n_0 , which can succeed in reaching the surface. The pressure *P* of the gas, where attractive forces are operating among the molecules is therefore proportional to *n*. Now, if the gas is ideal, ΔE is zero and all the n_0 molecules would come and strike the wall. The ideal pressure P_i , is therefore proportional to n_0 . We can therefore write

 $\frac{P_i}{P} = \frac{n_0}{n} = e^{\frac{\Delta E}{RT}}$ $P_i = P e^{\frac{\Delta E}{RT}}$

 $Pe^{\frac{\Delta E}{RT}}(V-b) = RT$

 $P(V-b) = RTe^{-\frac{\Delta E}{RT}}$

The correct equation of state is therefore

or

 \Rightarrow

 \Rightarrow

The excess potential energy of the surface molecules has been found to be inversely proportional to the volume of the system and therefore, we finally write,

$$P(V-b) = RTe^{-\frac{\alpha}{RTV}}$$
(3.24)

where 'a' is a constant for a given gas. Equation (3.24) is the Dieterici's equation of state for 1 mole. For *n* molecules, the equation of state is

$$P(v-nb) = nRTe^{-\frac{na}{RTV}}$$

You can check easily that the dimensions of van der Waals 'a' and the Dieterici's 'a' are same; the dimensions of the two 'b's are also the same. Nevertheless, for a given gas the two 'a's are different; the two 'b' values are also different. The Dieterici's equation of state has also three real roots below the critical temperature of a gas.

3.17.1 Critical Constants of Dieterici's Gas

Remembering that the critical state is a point of inflexion where the first derivative $\left(\frac{\partial P}{\partial V}\right)_T$, as well as the second derivative, $\left(\frac{\partial^2 P}{\partial V^2}\right)_T$ are zero, the critical constants can be evaluated by finding these two differentials and equation them to zero. The Dieterici Eq. (3.24) can also be written as

$$P = \frac{RT}{(V-b)} e^{-\frac{a}{RTV}}$$
$$P = \frac{RT}{(V-b)} \left[1 - \frac{a}{RTV} + \frac{1}{2} \left(\frac{a}{RTV}\right)^2 \cdots \right]$$

 \Rightarrow

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V-b)}$$
, neglecting the higher order terms.

At low and moderate pressures, $V - b \approx V$; therefore

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

the van der Waals form. To find the critical parameters, we proceed as follows:

$$P = \frac{RT}{(V-b)}e^{-\frac{a}{RTV}}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T} = -\frac{RT}{(V-b)^{2}}e^{-\frac{a}{RTV}} + \frac{RT}{(V-b)}\left(\frac{a}{RTV^{2}}\right)e^{-\frac{a}{RTV}}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T} = -\frac{P}{(V-b)} + \frac{aP}{RTV^{2}}$$
(3.25)

or

 \Rightarrow

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = -\frac{1}{(V-b)} \left(\frac{\partial P}{\partial V}\right)_T + \frac{P}{(V-b)^2} + \frac{a}{RTV^2} \left(\frac{\partial P}{\partial V}\right)_T - \frac{2aP}{RTV^3}$$

or

And,

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T \left[\frac{a}{RTV^2} - \frac{1}{(V-b)}\right] + P\left[\frac{1}{(V-b)^2} - \frac{2a}{RTV^3}\right]$$
(3.26)

At the critical point, both the differentials are zero.

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \Rightarrow \frac{1}{(V_c - b)} = \frac{a}{RT_c V_c^2} \tag{3.27}$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad \Rightarrow \frac{1}{\left(V_c - b\right)^2} = \frac{2a}{RT_c V_c^3}$$
(3.28)

Dividing the two equations we get

$$V_c = 2b$$

Then, from Eq. (3.27), we get

$$T_c = \frac{a}{4bR}$$

The critical pressure is then

$$P_c = \frac{RT_c}{(V_c - b)} e^{-\frac{a}{RT_c V_c}}$$

or
$$P_c = \frac{a}{4b^2}e^{-2}$$

and the critical coefficient is

$$Z_c = \frac{RT_c}{P_c V_c} = \frac{1}{2}e^2 = 3.695$$
(3.29)

To get the Boyle temperature T_B , we rewrite the Dieterici equation as

$$PV = \frac{RTV}{(V-b)}e^{-\frac{a}{RTV}}$$
$$\left[\frac{\partial(PV)}{\partial P}\right]_{T} = \left\{ \left(\frac{RT}{(V-b)} - \frac{RTV}{(V-b)^{2}}\right)e^{-\frac{a}{RTV}} + \frac{RTV}{(V-b)}\frac{a}{RTV^{2}}e^{-\frac{a}{RTV}}\right\} \left(\frac{\partial V}{\partial P}\right)_{T}$$

Since $\left(\frac{\partial V}{\partial P}\right)_T \neq 0$ and, at the Boyle temperature, the left-hand side of the above equation is zero, we find

$$\frac{RT_B}{(V-b)} - \frac{RT_BV}{(V-b)^2} + \frac{RT_BV}{(V-b)}\frac{a}{RT_BV^2} = 0$$
$$\frac{RT_BV}{(V-b)} \left[\frac{1}{V} - \frac{1}{V-b} + \frac{a}{RT_BV^2}\right] = 0$$

$$\Rightarrow \qquad \frac{a}{RT_{B}V^{2}} = \frac{1}{V-b} - \frac{1}{V} = \frac{b}{V(V-b)}$$

$$\Rightarrow \qquad \qquad RT_B = \frac{a(V-b)V}{bV^2}$$

$$\Rightarrow \qquad \qquad T_B = \frac{a}{Rb}$$

because, in the limit $P \rightarrow 0 (V - b) \approx V$.

Using the reduced variables, π , ϕ and θ , and using the expressions for V_c , T_c and P_c , you can easily arrive at the reduced equation of state, which is

$$\pi(2\phi - 1) = \theta \, e^{2-2/\theta\phi} \tag{3.30}$$

3.30

 \Rightarrow

 \Rightarrow

Status of the Dieterici's Equation of State

Comparison shows that the Dieterici's equation of state gives results which are more closer to the experimental results than those given by van der Waals. The T/T_c ratio predicted by Dieterici equation is however a bit more than the experimental value. Nevertheless, it has not been deemed worthy for use due to its difficult mathematical form.

3.18 BERTHELOT EQUATION OF STATE

The Berthelot equation of state is given as follows:

$$\left(P + \frac{a}{TV^2}\right)(V - b) = RT \tag{3.31}$$

By applying the criteria of the critical state, you can easily prove that

$$V_c = 3b, \ T_c^2 \frac{8a}{27Rb}$$
 and $P_c = \frac{RT_c}{8b}$

from which, you can also show that

$$a = 3P_c V_c^2 T_c, \ b = \frac{V_c}{3} \ \text{and} \ R = \frac{8}{3} \frac{P_c V_c}{T_c}$$

The values are no good than the van der Waals values. To modify the equation, Berthelot proposed that V_c should be equal to 4b instead of 3b. Replacing V_c by $(4/3)V_c$, we therefore have

$$a = \frac{16}{3} P_c V_c^2 T_c, \ b = \frac{V_c}{4} \quad \text{and} \quad R = \left(\frac{32}{9}\right) \left(\frac{P_c V_c}{T_c}\right)$$

and therefore

$$\frac{a}{R} = 6bT_c^2$$
 and $\frac{b}{R} = \frac{9}{128}\frac{T_c}{P_c}$

We now, transform the Berthelot's equation as

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

$$PV = RT \left(1 + \frac{Pb}{RT} - \frac{aP}{R^2T^3}\right) \qquad \left(\text{neglecting the } \frac{ab}{TV^2} \text{ term}\right)$$

or

Using the expression $\frac{a}{R} = 6bT_c^2$, the equation changes to $PV = RT\left[1 + \frac{Pb}{RT} \frac{-6bPT_c^2}{RT^3}\right]$

Physical Chemistry

$$PV = RT \left[1 + \frac{Pb}{RT} \left(1 - \frac{6T_c^2}{T^2} \right) \right]$$

and then using the expressions, $\frac{b}{R} = \frac{9}{128} \frac{T_c}{P_c}$, we finally get

$$PV = RT \left[1 + \frac{9}{128} \frac{PT_c}{TP_c} \left(1 - \frac{6T_c^2}{T^2} \right) \right]$$
(3.32)

There has been an extensive use of this equation, specially at low pressures, in finding out the heat capacity, enthalpy, free energy, etc., of real gases. To find the Boyle temperature, we find,

$$\left(\frac{\partial [PV]}{\partial P}\right)_{T} = \frac{9}{128} \frac{RT_{c}}{P_{c}} \left(1 - \frac{6T_{c}^{2}}{T_{B}^{2}}\right) = 0$$
$$\frac{T_{B}}{T_{c}} = 2.45$$

You can also check yourself that the reduced equation of state of Berthelot equation of state is

$$\pi\phi = \frac{32}{9}\theta + \frac{1}{4}\pi \left(1 - \frac{6}{\theta^2}\right)$$
(3.33)

3.19 SAHA–BASU EQUATION OF STATE

In all the subsequent modifications after the van der Waals equation of state (Dieterici, berthelot, and many others the change which were made, mainly have focussed into the effect of cohesive forces among the molecules; the effect of finiteness of the molecular volume, had, in general, been neglected. Satyendra Nath Basu and Megh Nath Saha highlighted this neglected part in constructing an equation of state. The readers are requested to go through the statistical concept of entropy before reading the following derivation.

Neglecting the influence of molecular forces, the probability that a single molecule out of N molecules. Which initially occupy a volume V_0 , will be found in a volume V is V/V_0 ; for the second molecule, the probability is $\frac{V-\beta}{V_0-\beta}$, where $\beta = 8 \times \text{volume of each molecule}$.

For the third, the probability is $\frac{V-2\beta}{V_0-2\beta}$, and so on. Hence the probability W that all the molecules will be contained in the volume V is

3.32

 \Rightarrow

$$\frac{v}{v_0} \cdot \frac{v-\beta}{v_0-\beta} \frac{V-2\beta}{V_0-2\beta} \cdots \frac{v-(N-1)\beta}{v_0-(N-1)\beta}$$

_

:..

:.

$$\frac{d\ln W}{dv} = \frac{1}{v} + \frac{1}{v - \beta} + \frac{1}{v - 2\beta} + \dots + \frac{1}{v - (N - 1)\beta}$$
(3.34)

The first fundamental thermodynamic equation of state

W =

.1 1... 117

dU = TdS - PdV, from which we may write

$$P = T\left(\frac{\partial S}{\partial v}\right) \tag{3.35}$$

where, U remains constant with change in volume. Again, from the Boltzmann theory,

 $S = k \ln W + \text{constant}$

$$\left(\frac{\partial S}{\partial v}\right)_{u} = k \frac{\partial \ln W}{\partial v}$$
(3.36)

Combining Eqs (3.35) and (3.36),

$$P = kT \frac{\partial \ln W}{\partial v}$$

Which, after using the result of Eq. (3.34), changes to,

$$P = kT \left[\frac{1}{v} + \frac{1}{v - \beta} + \frac{1}{v - 2\beta} + \dots + \frac{1}{v - (N - 1)\beta} \right]$$

= $kT \sum_{r=0}^{N-1} \frac{1}{v - r\beta} = \frac{kT}{v} \sum_{r=0}^{N-1} \frac{1}{1 - r\beta / v}$
= $\frac{NkT}{v} \frac{1}{N} \sum_{r=0}^{N-1} \left(\frac{1}{1 - \frac{r\beta N}{v} \frac{1}{N}} \right)$
= $\frac{NkT}{v} h \sum_{r=0}^{N-1} \frac{1}{\left(1 - \frac{2brh}{v}\right)}$ where $\beta N = 2b$ and $h = 1/N$

Since, by definition, we have

$$\lim_{h \to 0} h \sum_{r=0}^{N-1} f(a+rh) = \int_{a}^{b} f(x) \, dx$$

where Nh = b - a, or a + Nh = b, we can write

$$P = \frac{NkT}{v} \int_{0}^{1} \frac{dx}{1 - \frac{2bx}{v}}$$

Physical Chemistry

Because N is very large, and $rh = (N-1) \frac{1}{N} \approx 1$ at the upper limit and, $0 \times \frac{1}{N}$, i.e., zero at this lower limit. Integration gives:

$$P = \frac{NkT}{2b} \ln\left(1 - \frac{2b}{v}\right) \tag{3.37}$$

In order to account for the influences of cohesive forces, the right hand side of Eq. (3.37) is now multiplied by $e^{-a/RTV}$ (following Dieterici). The complete equation of state is therefore,

$$P = -\frac{RT}{2b} \ln\left(1 - \frac{2b}{v}\right) e^{-a/RTV}$$
(3.38)

which is the Saha-Basu equation of state for real gases. Writing the equation in the form

$$Pe^{-a/RTV} = -\frac{RT}{2b} \ln\left(1 - \frac{2b}{v}\right)$$
(3.38)

And expanding the log term on the right hand side,

$$Pe^{a/RTV} = -\frac{RT}{2b} \left[-\frac{2b}{V} - \frac{1}{2} \left(\frac{2b}{v} \right)^2 \cdots \right]$$

And, neglecting higher order terms,

$$P e^{a/RTV} = \frac{RT}{2b} \left[\frac{2b}{v} + \frac{2b^2}{v^2} \right]$$

where the series $\ln (1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \cdots$ has been used and, neglecting the higher order terms.

$$= RT\left(\frac{1}{v} + \frac{b}{v^{2}}\right)$$

$$= \frac{RT}{v}\left(1 + \frac{b}{v}\right) = \frac{RT}{v}\frac{1}{\left(1 + v/v\right)^{-1}} \approx \frac{RT}{v\left(1 - b/v\right)}$$

$$= \frac{RT}{v - b}$$
(3.39)

which is the Dietrici equation of state. Now, expanding the exponential term on the left hand side, and neglecting the higher order terms

$$P\left[1 + \frac{a}{RTV}\right], \frac{RT}{v - b} \Rightarrow \left(p + \frac{aP}{RTV}\right)(v - b) = RT$$
$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \text{ (using } RT \approx PV) \tag{3.40}$$

which is the van der Waals equation of state.

Starting from the equation of state

$$P = -\frac{RT}{2b} \ln\left(1 - \frac{2b}{v}\right) e^{-a/RTV}$$

$$\left(\frac{\partial P}{\partial v}\right)_{T} = -\frac{RT}{2b} \frac{1}{\left(1 - \frac{2b}{v}\right)} \left(\frac{2b}{v^{2}}\right) e^{-a/RTV} - \frac{RT}{2b} \ln\left(1 - \frac{2b}{v}\right) e^{-a/RTV} \left(\frac{a}{RTV^{2}}\right)$$

$$\left(\frac{\partial P}{\partial v}\right)_{T} = -\frac{RT}{v^{2}} \left(\frac{1}{1 - \frac{2b}{v}}\right) e^{-a/RTV} + \frac{aP}{RTV^{2}}$$
(3.41)

 \Rightarrow

$$\Rightarrow \qquad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT}{v^3 \left(1 - \frac{2b}{v^2}\right)} e^{-a/RTV} + \frac{RT}{v^2 \left(1 - \frac{2b}{v}\right)^2} \left(\frac{2b}{v^2}\right) e^{-a/RTV} \\ - \frac{RT}{v^2 \left(1 - \frac{2b}{V^2}\right)} e^{-a/RTV} \left(\frac{a}{RTV^2}\right) + \frac{a}{RTV^2} \left(\frac{\partial P}{\partial V}\right)_T - \frac{2aP}{RTV^3} \qquad (3.42)$$

Equating both the differentials $[{\rm Eqs}~(3.41)~{\rm and}~(3.42)]$ to zero at the critical point, we have

from Eq. (3.41)

$$\frac{R^2 T_C^2}{a \left(1 - \frac{2b}{v_C}\right)} e^{-a/R T_C V_C} = P_C$$
(3.43)

and, from Eq. (3.42)

$$\frac{R^2 T_C^2 e^{-a/RT_c V_c}}{\left(1 - \frac{2b}{v_c}\right)} \left[2 + \frac{2b}{V_c \left(1 - \frac{2b}{V_c}\right)} - \frac{a}{RT_c V_c}\right] = 2aP_c$$
(3.44)

Dividing Eq. (3.44) by (3.42) we get

$$\frac{2b}{\left(1-\frac{2b}{v_c}\right)} = \frac{a}{RT_c}$$

Physical Chemistry

or

 \Rightarrow

$$\frac{1}{\left(1-\frac{2b}{v_c}\right)} = \frac{a}{2b \ RT_c} \tag{3.45}$$

Using Eq. (3.45) in (3.43)

$$\frac{R^2 T_C^2}{a} \left(\frac{a}{2b R T_C}\right) e^{-\frac{a}{R T_C V_C}} = P_C$$

$$P_C = \frac{R T_C}{2b} e^{-a.R T_C V_C}$$
(3.46)

Equating Eq. (3.46) to the Eq. (3.38) at the critical state

 $\Rightarrow \qquad \ln\left(1-\frac{2b}{V_C}\right) = -1$

$$\Rightarrow \qquad \qquad \left(1 - \frac{2b}{V_C}\right) = -e^{-1}$$

$$\Rightarrow \qquad \qquad \frac{2b}{V_C} = \frac{(e-1)}{e}$$

or

 \Rightarrow

 $V_C = \frac{2eb}{(e-1)}$ or, $\frac{V_C}{b} = \frac{2e}{(e-1)} = 3.164$ (3.47)

 $-\frac{RT_C}{2b}\ln\left(1-\frac{2b}{V_C}\right)e^{-a/RT_CV_C} = \frac{RT_C}{2b}e^{-a/RT_CV_C}$

From Eq. (3.45)

$$\begin{split} \frac{1}{\left(1-\frac{2b}{V_C}\right)} &= \frac{a}{2b \; RT_C} \\ T_C &= \frac{a}{2bR} \left(1-\frac{2b}{V_C}\right) \\ &= \frac{a}{2bR} \left[1-\frac{2b(e-1)}{2eb}\right] \\ &= \frac{a}{2bR} \left[1-\frac{(e-1)}{e}\right] \end{split}$$

or,
$$T_C = \frac{a}{2ebR}$$
(3.48)

and finally, using Eq. (3.46)

$$P_C = \frac{RT_C}{2b} e^{-a/RT_C V_C} \tag{3.49}$$

3.37

$$\Rightarrow$$
 $P_C =$

The critical coefficient is then

$$\frac{RT_C}{P_C V_C} = e^{(e-2)} (e-1) - 3.524$$

BOYLE TEMPERATURE OF SAHA-BASU EQUATION 3.21

a

 $\overline{4b^2 e^e}$

Differentiating PV with respect to P at constant temperature from the equation

$$PV = -\frac{RT}{2b}V\ln\left(1-\frac{2b}{V}\right)e^{-a/RTV}$$

we have

 \Rightarrow

$$\begin{split} \left[\frac{\partial(PV)}{\partial P}\right]_{T} &= -\frac{RT}{2b} \left\{ \ln\left(1 - \frac{2b}{v}\right)e^{-a/RTV} + \frac{V}{\left(1 - \frac{2b}{V}\right)}\left(\frac{2b}{V^{2}}\right)e^{-a/RTV} + v\ln\left(1\frac{2b}{V}\right)\left(\frac{a}{RTV^{2}}\right)e^{-a/RTV} \right\} \left(\frac{\partial V}{\partial P}\right)_{T} \end{split}$$

At the Boyle temperature T_{B}

$$\operatorname{Lt}_{P \to 0} \left[\frac{\partial (PV)}{\partial / P} \right]_T = 0$$

$$\ln\left(1-\frac{2b}{V}\right) + \frac{V}{\left(1-\frac{2b}{V}\right)} \left(\frac{2b}{V^2}\right) + V \ln\left(1-\frac{2b}{V}\right) \frac{a}{RT_B V^2} = 0$$

because, $e^{-2/RT_BV} \neq 0$ and $\left(\frac{\partial V}{\partial P}\right)_T \neq 0$

=

Approximating the log terms as $L(1-x) \approx -x$, when x is very small, we have

$$-\frac{ab}{V} + \frac{2bV}{V^2 \left(1 - \frac{2b}{V}\right)} + \left(-\frac{2b}{V}\right) \frac{a}{RT_B V} = 0$$

$$\frac{a}{RT_B V^2} = \frac{V}{V^2 - 2bV} - \frac{1}{V} \approx \frac{2b}{V^2} \qquad (\because V^2 - 2bV \approx V^2)$$

$$\boxed{T_B = \frac{a}{2bR}} \qquad (3.49)$$

or,

or,

The ratio

$$\frac{T_B}{T_C} = e = 2.718 \tag{3.50}$$

3.22 REDUCED EQUATION OF STATE

Introducing the reduced variables as

reduced pressure $\pi = \frac{P}{P_C}$ reduced volume $\phi = \frac{V}{V_C}$

and reduced temperature $\theta = \frac{T}{T_C}$

where, $P_C = \frac{a}{4b^2 e^e}$; $T_C = \frac{a}{2ebR}$ and $V_C = \frac{2eb}{(e-1)}$

Equation,

$$P = -\frac{RT}{2b} \ln\left(1 - \frac{2b}{V}\right) e^{-a/RTV}$$

Changes to

$$\pi = -5.575 \ \theta \ln\left(1 - \frac{0.632}{\phi}\right) \ \exp\left(-\frac{1.718}{\theta\phi}\right) \tag{3.51}$$

which is the desired equation.

3.23 NATURE OF MOLECULAR FORCES

From the results of Joule-Kelvin experiment and the existence of cohesive force in liquids, it is clear that there are attractive and repulsive forces between the molecules. The general term *van der Waals forces* is coined to represent the interactions between closed-shell species. These interactions may be divided into several classes: *ion (monopole)-dipole*,

dipole-dipole, dipole-induced dipole and, *induced dipole-induced dipole*. Interactions may also result from *quadrupoles* but, they are of very small magnitudes.

3.24 ION-DIPOLE INTERACTION

From electrostatics we know that the force F between two point charges Q_1 and Q_2 , separated by a distance r is

$$F = \frac{Q_1 Q_2}{4\pi\varepsilon_0 R^2}$$

where ε_0 is the vacuum permittivity.



Figure 3.14 The interaction between an ion and a dipole

Another classical equation is

$$F = -\frac{\mathrm{d}V}{\mathrm{d}r}$$

where V is the potential energy of interaction. Integration gives

$$\int_{0}^{v} dV = -\frac{Q_1 Q_2}{4\pi\varepsilon_0} \int_{\infty}^{r} \frac{dr}{r^2}$$

$$V = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$
(3.52)

or,

As shown in Figure 3.14, a point charge $(+Q_2)$ is placed at the point *C* and, a dipole *AB* (with charges $+Q_1$ and $-Q_1$) of length *R*. The potential energy of interaction is then given by two pairwise additive terms:

$$V_{i,d} = \frac{1}{4\pi\varepsilon_0} \left[\frac{Q_1 Q_2}{AC} - \frac{Q_1 Q_2}{BC} \right]$$
(3.53)
$$(AC)^2 = (AO + ON)^2 + (CN)^2$$

Now,

as,

 $ON = r \cos \theta$ and $CN = r \sin \theta$

$$(AC)^{2} = \left(\frac{R}{2} + r\cos\theta\right)^{2} + (r\sin\theta)^{2}$$

or,
$$(AC)^2 = r^2 \left[\frac{R^2}{4r^2} + 1 + \frac{R}{r} \cos \theta \right]$$

or,

$$(AC)^{2} = r \left[1 + \frac{R}{r} \cos \theta + \frac{R^{2}}{4r^{2}} \right]^{1/2}$$

$$(BC)^{2} = (NB)^{2} + (CN)^{2}$$
(3.54)

Similarly,

or,

$$(BC)^{2} = (OB - ON)^{2} + (CN)^{2}$$

= $(OB)^{2} + (ON)^{2} - 2(OB)(ON) + (CN)^{2}$
= $\left(\frac{R}{2}\right)^{2} + (r\cos\theta)^{2} - 2\left(\frac{R}{2}\right)r\cos\theta - (r\sin\theta)^{2}$
= $r^{2}\left[1 + \frac{R^{2}}{4r^{2}} - \frac{R}{r}\cos\theta\right]$
 $(BC) = r\left[1 + \left(\frac{R^{2}}{4r^{2}} - \frac{R\cos\theta}{r}\right)\right]^{1/2}$ (3.55)

 \Rightarrow

Using Eqs (3.54) and (3.55) in Eq. (3.53),

$$\begin{split} v_{i,d} &= \frac{Q_1 Q_2}{4\pi \varepsilon_0} \Bigg[\frac{1}{r \Bigg[1 + \left(\frac{R}{r} \cos \theta + \frac{R^2}{4r^2} \right) \Bigg]^{1/2}} - \frac{1}{r \Bigg[1 + \left(\frac{R}{4r^2} - \frac{R \cos \theta}{r} \right) \Bigg]^{1/2}} \Bigg] \\ v_{i,d} &= \frac{Q_1 Q_2}{4\pi \varepsilon_0 r} \Bigg[\Bigg\{ 1 + \left(\frac{R}{r} \cos \theta + \frac{R^2}{4r^2} \right) \Bigg\}^{-1/2} - \Bigg\{ 1 + \left(\frac{R^2}{4r^2} - \frac{R \cos \theta}{r} \right) \Bigg\}^{-1/2} \Bigg] \end{split}$$

or,

Using the binomial expansion,

$$(1+x)^n = 1 + nx + \frac{n(n-1)}{2!}x^2 + \frac{n(b-1)(n-2)}{3!}x^3 + \dots \text{ for } |x| < 1$$

and hence,

$$(1+x)^{-1/2} = 1 - \frac{1}{2}x + \frac{3}{8}x^2 + \cdots$$
$$V_{i,d} = \frac{Q_1 Q_2}{4\pi \varepsilon_0 r} \left[\left\{ 1 - \frac{1}{2} \left(\frac{R}{r} \cos \theta + \frac{R^2}{4r} \right) + \frac{3}{8} \left(\frac{R}{r} \cos \theta + \frac{R^2}{4r^2} \right)^2 \right\} - \left\{ 1 - \frac{1}{2} \left(\frac{R^2}{4r^2} - \frac{R \cos \theta}{r} \right) + \frac{3}{8} \left(\frac{R^2}{4r^2} - \frac{R \cos \theta}{r} \right)^2 \right\} \right]$$

truncating the series after the second power of x on the approximation R << r. Simplification gives

$$\begin{aligned} V_{i,d} &= \frac{Q_1 Q_2}{4\pi\varepsilon_0 r} \left[-\frac{R\cos\theta}{r} + \frac{3}{8} \frac{R^3}{r^3}\cos\theta \right] \\ V_{i,d} &= -\frac{\mu_1 Q_2 \cos\theta}{(4\pi\varepsilon_0) Rr} \left[-\frac{R}{r} + \frac{3}{8} \frac{R^3}{r^3} \right] \end{aligned}$$

or,

or,

 $V_{i,d} = -\frac{\mu_1 Q_2 \cos \theta}{(4\pi\epsilon_0) r^2} \left[1 - \frac{3}{8} \frac{R^2}{r^2} \right]$

Since $R \ll r$, the equation is further approximated to

$$V_{i,d} = -\frac{\mu_1 Q_2 \cos \theta}{(4\pi\varepsilon_0)r^2}$$

The maximum interaction occurs when Q_1 is collinear with the axis of the dipole, i.e., when $\theta = 0$; the final result is then

$$V_{i,d} = -\frac{\mu_1 Q_2}{(4\pi\varepsilon_0)r^2} \tag{3.56}$$

..

The negative sign of the interaction energy $V_{i, d}$ means that, there is a net attraction.

Example 3.1

Calculate the energy of interaction between an H⁺ ion and a CH₃OH molecule (μ = 1.71 D) separated over a distance of 1 nm; the ion H⁺ is positioned along the bond axis of CH₃OH.

Solution

Using Eq. (3.56), we find the interaction energy as

$$\begin{split} V_{i-d} &= -\frac{\mu_1 \, Q_2}{(4\pi\varepsilon_0) r^2} \\ &= -\frac{(1.71 \, \mathrm{D}) \left(\frac{1.6 \times 10^{-29}}{4.8 \, \mathrm{D}} \, \mathrm{cm}\right) (1.6 \times 10^{19} \, \mathrm{C})}{4(3.14) (8.854 \times 10^{-12} \, \mathrm{J}^{-1} \, \mathrm{C}^2 \mathrm{m}^{-1}) \, (1 \times 10^9 \, \mathrm{m})^2} \\ &= -\, 8.2 \times 10^{-24} \, \mathrm{J} \text{ per unit, or} \\ &= -(8.2 \times 10^{-21} \, \mathrm{J}) \, (6.022 \times 10^{23} \, \mathrm{mol}^{-1}) \\ &= -4.94 \, \mathrm{kJ \ mol}^{-1} \end{split}$$

Unit Conversion

The conversion of units is done as follows:

If an electronic charge and a protonic charge are separated by a distance of 1 Å, the dipole moment of the unit is defined as

$$\mu = e \times r = (4.8 \times 10^{-10})(1 \times 10^{-8} \text{ cm}).$$

or

 $\mu = 4.8 \times 10^{-18} \mathrm{esu} \mathrm{cm}$

The (esu cm) is a very large units of dipole moment.

The unit Debye is then used as

$$1 \text{ D} = 1 \times 10^{-18} \text{ use cm}$$

The dipole moment of our unit is then

$$\mu = 4.8 \times 10^{-18} \text{ esu } \text{em} \left(\frac{1 \text{ D}}{1 \times 10^{-18}} \text{ esu } \text{em} \right)$$

or

The units of dipole moment in the SI system is

 $\mu = 4.8 \text{ D}$

$$\mu = e \times r = (1.6 \times 10^{-19} \text{ c}) (1 \times 10^{-10} \text{ m})$$

or

$$m = 1.6 \times 10^{-29} \text{ cm}$$

A useful conversion factor is then $\frac{1.6 \times 10^{-29} \text{ cm}}{4.8 \text{ D}}$, which is unity.

3.25 DIPOLE-DIPOLE INTERACTION (KEESOM FORCE)

Let us consider two polar molecules AB and CD with dipole moments μ_1 and μ_2 respectively, separated by a distance r, fixed in orientation and lying in one and the same plane as shown in Figure 3.15. In the gaseous and liquid state, the molecules can rotate and, the field of one dipole tends to orient the dipole of a neighbouring molecule. Moreover, the attractive forces dominate because it is of a longer range than the short range repulsive forces. The net result is then an attractive force.



Figure 3.15

Assuming that the dipoles have the same length R, for simplicity, the potential energy of interaction, according to the orientation in Figure 3.15,

$$\begin{aligned} V_{d-d} &= \frac{1}{4\pi\varepsilon_0} \left[\frac{2Q_1 Q_2}{r} - \frac{2Q_1 Q_2}{AD} - \frac{Q_1 Q_2}{BC} \right] \\ &= \frac{Q_1 Q_2}{4\pi\varepsilon_0} \left[\frac{2}{r} - \frac{1}{AD} - \frac{1}{BC} \right] \end{aligned} \tag{3.57}$$

Now,

$$(AD)^{2} = (AB + BO)^{2} + (OD)^{2}$$

= $(R + r \cos \theta)^{2} + r^{2} \sin^{2} \theta)$
 $(AD) = r \left[1 + \frac{R^{2}}{r^{2}} + \frac{2R}{r} \cos \theta \right]^{1/2}$ (3.58)

Similarly,

$$(BC)^{2} = (CN)^{2} + (NB)^{2} = (OD)^{2} + (NB)^{2}$$

= $r^{2} \sin^{2} \theta + (AB - AN)^{2}$
= $r^{2} \sin^{2} \theta + (R - r \cos \theta)^{2}$
 $(BC) = r \left[1 + \frac{R^{2}}{r^{2}} - \frac{2R}{r} \cos \theta \right]^{1/2}$ (3.59)

Using Eqs (3.58) and (3.59) in (3.57),

$$\begin{split} V_{d-d} &= \frac{Q_1 Q_2}{4\pi \varepsilon_0} \Bigg[\frac{2}{r} - \frac{1}{r \left[1 + \frac{R^2}{r^2} + \frac{2R}{r} \cos \theta \right]^{1/2}} - \frac{1}{r \left[1 + \frac{R^2}{r^2} - \frac{2R}{r} \cos \theta \right]^{1/2}} \Bigg] \\ V_{d-d} &= \frac{Q_1 Q_2}{(4\pi \varepsilon_0) r} \Bigg[2 - \left(1 + \frac{R^2}{r^2} + \frac{2R}{r} \cos \theta \right)^{-1/2} - \left(1 + \frac{R^2}{r^2} - \frac{2R}{r} \cos \theta \right)^{-1/2} \Bigg] \end{split}$$

Then using the binomial expansion as used earlier:

$$(1+x)^{-1/2} = 1 - \frac{1}{2}x + \frac{3}{8}x^2 + \cdots$$

and truncating the series after the second power of x (as $R/r \ll 1$) we have (after a few lines of algebra)

$$V_{d-d} = \frac{Q_1 Q_2 R^2}{4\pi \varepsilon_0 r^3} \left[(1 - 3\cos^2 \theta) = -\frac{3}{4} \frac{R^2}{r^2} \right]$$

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or
$$V_{d-d} = -\frac{\mu_1 \mu_2}{4\pi \varepsilon_0 r^3} (3\cos^2 \theta - 1); \ \mu_1 = Q_1 R; \ \mu_2 = Q_2 R$$
 (3.60)

...

where, again the approximation $R \ll r$ is used.

Now, an interesting point comes out: if all orientations between the dipoles are equally probable then the average V_{d-d} would be

$$\left\langle V_{d-d} \right\rangle = -\frac{\mu_1 \ \mu_2}{4\pi \ \varepsilon_0 \ r^3} \left\langle 3 \cos^2 \theta - 1 \right\rangle = \frac{\mu_1 \ \mu_2}{4\pi \ \varepsilon_0 \ r^3} \left\langle 1 - 3 \cos^2 \theta \right\rangle$$

but
$$\langle (1-3\cos^2\theta) \rangle = \frac{\int_{0}^{\pi} (1-3\cos^2\theta)\sin\theta \,d\theta}{\int_{0}^{\pi} \sin\theta \,d\theta}$$

 $= \frac{-\int_{1}^{-1} (1-3z^2) \,dz}{-\int_{1}^{-1} dz} = \frac{\int_{-1}^{-1} (1-3z^2) \,dz}{\int_{-1}^{1} dz} \cos\theta = z$
 $-\sin\theta \,d\theta = dz$
 $= \frac{1}{2} \int_{-1}^{1} (1-3z) \,dz$
 $= \frac{1}{2} \left[\left[z \right]_{0}^{1} - \frac{3}{3} \left[z^3 \right]_{0}^{1} \right] = 0$
 $= \frac{1}{2} [1-1] = 0$

that is, there is no net interaction. But, from statistical considerations it is concluded that certain orientations must be preferred and, the classical Boltzmann distribution is the key factor.

Equation (3.60) is then changed to

$$V_{d-d} = -\frac{\mu_1 \, \mu_2}{(4\pi \, \varepsilon_0) r^3} \, (3 \cos^2 \theta - 1) \, e^{-V/kT}$$

where V is given by Eq. (3.60). Assuming $V \ll kT$, we write

$$V_{d-d} = -\frac{\mu_1 \mu_2}{(4\pi\epsilon_0)r^3} (3\cos^2\theta - 1) \left(1 - \frac{V_{d-d}}{kT}\right)$$

and, the average V_{d-d} is

..

Now, $\left\langle (3\cos^2\theta - 1)^2 \right\rangle = \frac{\int_0^{\pi} (3\cos^2\theta - 1)^2 \sin\theta \, d\theta}{\int_0^{\pi} \sin\theta \, d\theta}$

or
$$\left\langle (3\cos^2\theta - 1)^2 \right\rangle = \frac{1}{2} \int_0^{\pi} (3\cos^2\theta - 1)^2 \sin\theta d\theta = \frac{4}{5}$$

and since $\langle (3\cos^2\theta - 1) \rangle = 0$, we find finally

$$\left\langle V_{d-d} \right\rangle = -\frac{4}{5} \frac{\mu_1^2 \ \mu_2^2}{\left(4\pi \ \varepsilon_0\right)^2 \ r^6 \ kT}$$

A more detailed analysis, for a general case, shows that the factor $\frac{4}{5}$ should be replaced by $\frac{2}{3}$. Hence we write

$$\left\langle V_{d-d} \right\rangle = -\frac{2}{3} \frac{\mu_1^2 \ \mu_2^2}{(4\pi \varepsilon_0)^2 \ kTr^6}$$
(3.61)

This kind of force is referred to as the *Keesom force* (W.H. Keesom, 1922). This is the so called *orientation effect*. Again we got a negative sign. This means that there is a net attractive potential.

Example 3.2

Calculate the Keesom interaction energy between two dipoles of the same moment (1 D) separated by 0.3 nm.

Solution

Using Eq. (3.69), the Keesom (dipole-dipole) interaction energy is

$$\left\langle V_{d-d} \right\rangle = -\frac{2}{3} \frac{\mu_1^2 \ \mu_2^2}{(4\pi \varepsilon_0)^2 \ kTr^6}$$

For simplicity, we first calculate the different terms separately:

$$\mu_1^2 \ \mu_2^2 = (I \ \not\!\!D)^2 \left(\frac{1.6 \times 10^{-29} \,\mathrm{cm}}{4.8 \ \not\!\!D}\right)^2 (1 \,\mathrm{D})^2 \left(\frac{1.6 \times 10^{-29} \,\mathrm{cm}}{4.8 \ \not\!\!D}\right)^2$$

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 \Rightarrow

$$\mu_1^2 \ \mu_2^2 = 0.0123 \times 10^{-116} \ c^4 \ m^4$$

and, and.

$$(4\pi\epsilon_0)^2 = (1.112 \times 10^{-10} \text{ J}^{-1} \text{ c}^2 \text{ m}^{-1})^2 = 1.237 \times 10^{-20} \text{ J}^{-2} \text{ c}^4 \text{ m}^{-2}$$

 $kT = (1.38 \times 10^{-23} \text{ JK}^{-1}) (300 \text{ K}) = 4.14 \times 10^{-21} \text{ J}$

and, $r^6 = (0.3 \times 10^{-9} \text{ m})^6 = 7.29 \times 10^{-58} \text{ m}^6$

Finally, accumulating the results together

$$\begin{split} \left\langle V_{d-d} \right\rangle &= -\frac{2}{3} \frac{0.0123 \times 10^{-116} \ \text{g}^{4} \ \text{pr}^{4}}{(1.237 \times 10^{-20} \ \text{J}^{-2} \ \text{g}^{4} \ \text{pr}^{-2}) (4.14 \times 10^{-21} \ \text{J}) (7.29 \times 10^{-58} \ \text{pr}^{6})} \\ \left\langle V_{d-d} \right\rangle &= -2.196 \times 10^{-21} \ \text{J} \ \text{per unit} \\ \left\langle V_{d-d} \right\rangle &= -(2.196 \times 10^{-21} \ \text{J}) (6.022 \times 10^{23} \ \text{mol}^{-1}) \end{split}$$

or

or $\langle V_{d-d} \rangle = -1.3 \text{ kJ mol}^{-1}$

It is noteworthy to look into the dependence of $V_{i,\,d}$ and $\left< V_{d-d} \right>$ on the factors r and T.

The dipole-dipole interaction will in general be less than the ion-dipole interaction.

2. The *inverse dependence of the dipole-dipole interaction upon temperature* means that the average dipole-dipole interaction energy decreases with increase in temperature. The tendency of the molecules towards orientation is randomized by the increased thermal motion of the molecules.

3.26 DIPOLE-INDUCED DIPOLE INTERACTION (DEBYE FORCE)

A polar molecule can induce a moment to an adjacent molecule. Then there is an additional interaction between the permanent dipole and the induced dipole. This is known as the induction effect, *the Debye force*. The magnitude of the resultant energy is given by

$$V_{d-id} = -\frac{2\alpha\mu^2}{\left(4\pi\varepsilon_0\right)^2 r^2} \tag{3.62}$$

The negative sign implies that the net interaction is again attractive (α is the polarizability of the molecule).

The forces described above have two serious difficulties:

- (i) All these interaction energies have been calculated for a pair of molecules, but they are not additive for all the molecules in a gas or liquid. In fact, since orientations of different possible molecular arrangements are there, the energies may cancel out; so there is no net attraction.
- (ii) All the forces described above *involve the permanent dipole moment of the molecules*. What is the story then for molecules like hydrogen, oxygen, carbon dioxide and, the inert gases; they all have no permanent dipole. In 1930, F. London solved this problem by a brilliant application of quantum mechanics.

3.27 INDUCED DIPOLE-INDUCED DIPOLE INTERACTION (LONDON DISPERSION FORCE)

From the Heisenberg uncertainty principle we know that all molecules must possess some energy even in their lowest states, i.e., the zero point energy. Now consider a non-polar molecule, such as argon. The positive nucleus is surrounded symmetrically by a cloud of negative charge, and, these two are undergoing some kind of vibration against one another. Therefore, although the time average of this charge distribution is spherically symmetrical, at any instant it will be somewhat distorted. Thus a snapshot taken of an argon atom would show a little dipole with a certain orientation. An instant later, the orientation would be different, and this continues; over a macroscopic period of time these instantaneous dipole moments would average to zero.

Do not think that these snapshot dipoles interact with those of other molecules to produce an attractive potential. This cannot happen since there will be repulsion just as often as attraction; there is no time for the instantaneous dipoles to line up with one another. Each instantaneous argon dipole induces an appropriately oriented dipole in the neighbouring atom in phase with themselves and, these moments interact with the original to produce an instantaneous attraction. Calculation shows that this *dispersion¹ interaction* leads to an interaction energy.

$$V_D = -\frac{3}{4} \frac{\alpha^2 h v}{(4\pi\epsilon_0)^2 r^6}$$
(3.63)

where h is the Planck constant and v is the characteristic frequency of the molecule. An important difference between the dispersion effect and the other mentioned previously is not only that the former is applicable to non-polar molecules but, it is additive for all pairs of molecules in the gas; this accounts for the cohesion between the molecules. Therefore, for any gas the interaction energy per pair of molecules is the sum of Eqs. (3.61), (3.62) and (3.63):

$$V_{\text{attr}} = -\frac{2}{\underbrace{3}_{\text{dipole}-\text{dipole}}^{\mu^2}} - \underbrace{\frac{2\alpha\mu^2}{(4\pi\varepsilon_0)^2 r^6}}_{\substack{\text{dipole}-\text{induced}\\ \text{dipole}}} - \underbrace{\frac{3}{4}_{\text{dipole}}^{\alpha^2 hv}}_{\substack{\text{dispersion}}}$$
(3.64)

Molecule	Dipole Moment (D)	Orientation Effect	Induction Effect	Dispersion Effect
$\rm H_2$	_	-	-	11.3
Ar	-	-	-	57
N_2	_	-	-	62
CH_4	_	-	-	117

Relative Magnitudes of Molecular Interaction Effects

(Contd.)

¹ The name dispersion is used because the oscillation producing the attractive force are also responsible for the dispersion of light by the molecules.

Cl_2	_	_	_	461
CO	0.12	0.0034	0.057	67
HCl	1.03	18.6	5.4	105
NH_3	1.5	84	10	93
H ₂ O	1.8	190	10	47

Source: A Text Book of Phys. Chemistry; S. Glasstone.

From the Eq. (3.64) and the table given, certain points come out:

- 1. For Non-polar molecules the London dispersion effect is the only contributor towards the van der Waals interaction between the molecules. It is also clear that this effect is more for a large molecule than that for a smaller one (smaller molecules are harder to be polarized than bigger one). For example, at room temperature I_2 is solid but F_2 is a gas. I_2 being much bigger in size than F_2 is easily polarizable, leading to a larger value of α , and hence, a greater dispersion force.
- 2. For polar molecules, the dispersion effect is also predominating. But for molecules with high dipole moments the orientation effect (the Keesom force) may predominate (e.g., NH_3 and H_2O).
- 3. The induction effect (the Debye force) is always very small.
- 4. All these three contributions [Eq. (3.64)] to the *potential energy of intermolecular* attraction display an r^{-6} dependence. Since these forces are of radial symmetry,

i.e., no preferred direction in space, we may use the classical equation $F = -\frac{dV}{dr}$ to argue that these attractive forces have an r^{-7} dependence. Equation may now be written as

$$V_{\text{attr}} = -\frac{A}{r^6} \tag{3.65}$$

where A stands for the sum of the three coefficients of r^{-6} in Eq. (3.64).

There are evidences to acknowledge that there are repulsive forces between the molecules as well. These forces account for the properties like the collision diameter, the effective size of the molecules, etc. This repulsive force arises due to the interaction of the electron clouds of the two approaching molecules; this is also being aided by the strong repulsion between the two approaching nuclei, probably, due to the Pauli exclusion principle of the two overlapping electron clouds. For a number of gases this repulsive interaction energy has been found to be as:

$$V_{\rm rep} = \frac{B}{r^{12}}$$
(3.66)

where *B* is a constant for a given gas. The *Repulsive force has an* r^{-13} *dependence*.

The mean interaction potential energy V, allowing molecular attraction and repulsion is therefore.

$$V = -\frac{A}{r^6} + \frac{B}{r^{12}}$$
(3.67)

where the first term represents the sum of the three attractive potentials Eq. (3.64) and the second terms represents the repulsive one.

When two molecules are widely apart, they do not interact; so their potential energy in interaction is zero. As they approach each other, an attraction first develops between the molecules and, increases as r is decreased.

However, at distances equal to or less than the collision diameter, the interaction potential energy rises steeply due to the strong repulsion between the two electron cloud and the nuclei of the two approaching molecules. The superposition of these two curves is of the form shown in Figure 3.16. There are also simpler potential functions: the *hard sphere* (Figure 3.17a) and the *square-well* (Figure 3.17b) models.



Figure 3.16 The intermolecular potential energy against the separation of two molecules. The so called Lennard-Jones 6-12 model.



Figure 3.17 The hard sphere model for the interaction potential. A discontinuity occurs at the hard sphere diameter $r = \sigma$. Since there is no minimum, this model cannot be used to find the equilibrium properties.

Starting form Eq. (3.67), i.e.,

$$V = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

and realising that at $r = \sigma$, V = 0 (Figure 3.16), we find

$$\frac{A}{\sigma^6} = \frac{B}{\sigma^{12}} \implies B = A\sigma^6 \tag{3.68}$$

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Using Eq. (3.68) in to (3.67), we find

$$V = A \left[\frac{\sigma^{6}}{r^{12}} - \frac{1}{r^{6}} \right]$$
(3.69)

Then, differentiating V with respect to r

$$\frac{dV}{dr} = A \left[-12 \,\sigma^6 r^{-13} + 6 \,r^{-7} \right]$$

at the minimum of the curve (Figure 3.16)

$$\frac{dV}{dr} = 0 \quad ; \quad r = r_{\min}$$

$$\Rightarrow \qquad 12 \sigma^6 r_{\min}^{-13} = 6 r_{\min}^{-7}$$

 $2 \sigma^6 r_{\min}^{-6} = 1$ or

or
$$r_{\min} = 2^{\frac{1}{6}} \sigma$$

or
$$r_{\min} = 2^6 \sigma$$

 \Rightarrow $r_{\min}^6 = 2 \sigma^6$

$$\Rightarrow$$
 $r_{\min}^{12} = 4 \sigma^{12}$

Starting from Eq. (3.69) again and, applying it at the minimum

$$V = A \left[\frac{\sigma^6}{r^{12}} - \frac{1}{r^6} \right]$$
$$\Rightarrow \qquad -\varepsilon_{\min} = A \left[\frac{\sigma^6}{r_{\min}^{12}} - \frac{1}{r_{\min}^{6}} \right]$$

and using Eq. (3.70)

$$\varepsilon_{\min} = -A \left[\frac{\sigma^6}{4 \sigma^{12}} - \frac{1}{2 \sigma^6} \right]$$

$$\varepsilon_{\min} = \frac{A\sigma^3}{4\sigma^{12}}.$$

 $A = 4 \sigma^6 \varepsilon_{\min}$

or,

(3.70)

and using, this in Eq. (3.69)

$$V = 4 \sigma^{6} \varepsilon_{\min} \left[\frac{\sigma^{6}}{r^{12}} - \frac{1}{r^{6}} \right]$$
$$V = 4 \varepsilon_{\min} \left[\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^{6}}{r^{6}} \right]$$

or

i.e.,
$$V = 4 \varepsilon_{\min} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$
(3.72)

which is known as the 6-12, *Lennard Jones potential*. The equation can also be transformed as

$$V = 4 \varepsilon_{\min} \left[\frac{1}{4} \frac{r_{\min}^{12}}{r^{12}} - \frac{1}{2} \frac{r_{\min}^{6}}{r^{6}} \right]$$
$$V = \varepsilon_{\min} \left[\left(\frac{r_{\min}}{r} \right)^{12} - 2 \left(\frac{r_{\min}}{r} \right)^{6} \right]$$
(3.73)

..

or

This Lennard-Jones 6-12 potential function has been found successful over a wide range of application. For argon and nitrogen ε_{\min} have been found to be 1.0 kJ mol⁻¹ and 3.7 kJ mol⁻¹. The larger value of nitrogen arises because, unlike Ar atoms, N₂ molecules have rotational and vibrational atoms modes of motion as well as of translation.

Moreover, the classical thermal energies at 300 K for Ar is $\left(\frac{3}{2}RT\right)$ 3.74 kJ mol⁻¹ and for N₂ is $\left(\frac{5}{2}RT\right)$ 6.24 kJ mol⁻¹.

It is then clear that *under ordinary condition of temperature*, the thermal energy of the molecules is much more than the intermolecular interactive potential energy. This strongly supports postulates of the kinetic theory.

Finally, the van der Waals contants 'a' and 'b' are certainly related to these attractive and repulsive potentials between the molecules. The 'a' terms is determined by the attractive potential and the 'b' term depends on both the attraction and repulsion between the molecules, because the collision diameter is finally determined from the competing effect of the attraction and repulsion potentials. For a very clear and detailed calculation to correlate the van der Waals constants a and b, the readers are referred to (1) *Phys. Chem.*: *A Molecular Approach*, by D. A. McQuarrie and J. D. Simon and (2) *Phys. Chem.*, G. W. Castellan.

Example 3.3

One mole of CO₂ gas was found to occupy a volume of 1.32 L at 48°C and pressure of 18.40 atm. Calculate the pressure that would have been expected (i) from the ideal gas equation; (ii) from the van Waals equation Given: a = 3.6 atm L² mole⁻²; $b = 4.28 \times 10^{-2}$ L mol⁻¹.

Solution

(i) Making use of the ideal gas equation

$$P = \frac{nRT}{V} = \frac{(1 \text{ mol})(0.082 \text{ L atm } \text{ K}^{-1} \text{ mol}^{-1})(321.15 \text{ K})}{(1.32 \text{ L})}$$

 \Rightarrow P = 19.95 atm.

(ii) From the van der Waals equation

$$P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

$$\Rightarrow P = \frac{(1 \text{ mol})(0.082 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1})(321.15 \text{K})}{1.32 \text{ L} - (1 \text{ mol})(4.28 \times 10^{-2} \text{ L mol}^{-1})} - \frac{(1 \text{ mol})^2(3.6 \text{ atm } \text{K}^2 \text{ mol}^{-2})}{(1.32 \text{ K})^2}$$

$$\Rightarrow P = \frac{26.33 \text{ } \text{! atm}}{1.277 \text{ } \text{! }} - 2.066 \text{ atm}$$
$$\Rightarrow P = 18.55 \text{ atm}$$

Comment: Note that, the pressure calculated from the van der Waals equation is less than that calculated from the ideal gas equation. Clearly this demonstrates that the attractive force among the molecules reduced the momentum poured on the wall of the vessel. Under this condition of P and T, the attractive force dominates the repulsive force.

Example 3.4

Two van der Waals gases *A* and *B* are taken in separate containers of equal volume, under identical conditions of *P* and *T*. the '*a*' and '*b*' values of the two gases are: for gas *A*, $a = 0.2048 \text{ Nm}^4 \text{ mol}^{-2}$; $b = 0.267 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$; for gas *B*, $a = 0.227 \text{ Nm}^4 \text{ mol}^{-2}$; $b = 0.0428 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$.

- (i) Which gas has the greater pressure correction term and, how many times as great?
- (ii) Which gas has the larger molecular size; how may times as great?
- (iii) Which gas has the higher value of T_c ? How many times as high?

Solution

(i) The pressure correction term is $\frac{a}{V^2}$; therefore

....

$$\frac{(a/V^2)_B}{(a/V^2)_A} = \frac{a_B}{a_A} = \frac{0.227 \text{ M m}^4 \text{ mol}^{-2}}{0.0248 \text{ M m}^4 \text{ mol}^{-2}} = 9.15$$

The gas B has the greater pressure correction term than the gas A, by a factor of 9.15. 4 2 . . 0.1

(ii)
$$b = 4 N_0 b_1$$
, where $b_1 = \frac{4}{3} \pi r^3$; r is the radius of the molecule. Therefore,

$$\frac{(b)_A}{(b)_B} = \frac{0.267 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}}{0.0428 \times 10^3 \text{ m}^3 \text{ mol}^{-1}} = 6.24$$

$$\Rightarrow \qquad \frac{(b)_A}{(b)_B} = \frac{4 N_0 \frac{4}{3} \pi r_A^3}{4 N_0 \frac{4}{3} \pi r_B^3} = \left(\frac{r_A}{r_B}\right)^3$$

$$\Rightarrow \qquad \frac{r_A}{(6.23)^{\frac{1}{3}}} = 1.84$$

Therefore, the diameter ($\sigma = 2r$) of the A molecules is 1.84 times that of the B molecules.

(iii)
$$T_c$$
 is given by the expression : $T_c = \frac{8a}{27 Rb}$

 r_{R}

$$\Rightarrow \qquad \frac{(T_c)_B}{(T_c)_A} = \left(\frac{a_B}{b_A}\right) \left(\frac{b_A}{a_A}\right) = \left(\frac{0.227 \text{ Nm}^4 \text{ mol}^{-2}}{0.042 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}}\right) \left(\frac{0.0267 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}}{0.0248 \text{ Nm}^4 \text{ mol}^{-2}}\right) \\ \Rightarrow \qquad \frac{(T_c)_B}{(T_c)_A} = 57.1$$

For the gas B, T_c is 57.1 times that of the gas A.

Example 3.5

 \Rightarrow

The experimental value of RT/V is 1.10 for 1 mole of a certain non-ideal gas. The gas is at 1 atm and its temperature is below the critical temperature. If the pressure is not halved, at constant temperature, it is to be expected that the new volume will be (i) more than twice; (ii) less than twice the original volume.

Solution

The compressibility factor Z is given by

$$Z = \frac{V}{V_{\text{ideal}}} = \frac{\rho V}{RT} = \frac{\rho}{\left(\frac{RT}{V}\right)} = \frac{1}{1.10} = 0.91 < 1$$

The compressibility factor will therefore increase with decrease in pressure. Hence the new volume will be more than twice the original volume. Look at the Amagad's isotherm; you will understand.

Example 3.6

Given the following data for a certain nonideal gas at 25°C:

$\frac{\rho}{P}$ (gL ⁻¹ atm ⁻¹)	10	11	10
P(atm)	1	10	20

The critical pressure of the gas must then be:

- (i) greater than 10 atm.
- (ii) greater than 20 atm.
- (iii) between 1 and 20 atm.
- (iv) between 1 and 10 atm.
- (v) Less than 20 atm.
- (vi) Cannot tell.

Solution

Since the density is given by $\rho = \frac{W}{V}$; then we have

$$\frac{\rho}{P} = \frac{W}{PV} = \frac{W}{RTZ}$$

Therefore, at a given temperature $\frac{\rho}{P}$ varies inversely as the compressibility factor. Therefore, a maximum in $\frac{\rho}{P}$ means a minimum in Z. In the plots of Z versus $\frac{\rho}{P_c}$, such minimum occurs only fro $T < T_c$ and $P > P_c$. We know that the minimum of Z occurs between 1 and 20 tam. Therefore P_c could be greater or less than 1 or 10 atm but must be less than 20 atm.

Example 3.7

At what temperature does the slope of *Z* versus *P* curve (at P = 0) have maximum value for a van der Waals gas? What is the value of the maximum slope?

Solution

The virial equation of state is

$$Z = 1 + A_1 P + A_2 P^2 + A_3 P^3 + \cdots$$
$$\left(\frac{\partial Z}{\partial P}\right) = A_1 + 2 A_2 P + 3 A_3 P^2 + \cdots$$

 \mathbf{i}

At the maximum, the left hand side is zero; this implies

1

$$\frac{1}{RT^{2}} \left(b - \frac{a}{RT} \right) = \frac{1}{RT} \times \frac{a}{RT^{2}}$$

$$\Rightarrow \qquad b - \frac{a}{RT} = \frac{a}{RT} \Rightarrow b = \frac{2a}{RT}$$

$$\Rightarrow \qquad \left[T = \frac{2a}{Rb} \right]$$
Slope = $\left(\frac{\partial Z}{\partial P} \right) = \frac{1}{RT} \left(b - \frac{a}{RT} \right)$

$$= \frac{Rb}{R 2a} \left(b - \frac{\cancel{A} \ \cancel{K} \ \cancel{b}}{\cancel{K} \cdot 2\cancel{a}} \right)$$

$$= \frac{b}{2a} \left(b - \frac{b}{2} \right) = \frac{b}{2a} \frac{b}{2}$$

$$\therefore \qquad \left[\text{maximum slope} = \frac{b^{2}}{4a} \right]$$

Example 3.8

The critical temperature and pressure for NO gas are 177 K and 64 atm, respectively, and for CCl_4 they are 550 K and 45 atm, respectively. Which gas

- (i) has the smaller value of the van der Waals constant *b*?
- (ii) the smaller value of the van der Waals constant *a*?
- (iii) has the larger critical volume, and
- (iv) is most nearly ideal in behaviour at 300 K and 10 atm?

Solution

Assuming that the gas obeys the van der Waals equation we know that:

$$V_{C}=3b\;;\;\;T_{C}=\frac{8a}{27Rb}\;;\;\;P_{C}=\frac{a}{27b^{2}}$$

..

(i)
$$\frac{T_C}{P_C} = \frac{8\not(27\ b^2)}{27\ Rb\ a} = \frac{8}{R}b$$

Therefore, smaller the ratio $\frac{T_C}{P_C}$, smaller will be 'b'.

For NO:
$$\frac{T_C}{P_C} = \frac{177}{64} = 2.77$$

For CCl₄
$$\frac{T_C}{P_C} = \frac{550}{45} = 12.22$$

Therefore NO gas has the smaller value of 'b'.

(ii) Divide T_C^2 by P_C ; we get

...

$$\begin{aligned} \frac{T_C^2}{P_C} &= \frac{(8a) (8 \not a) (27 \not b^2)}{(27 \not R \not b) (27 \not R \not b) \not a} = \frac{64 a}{27 \ R^2} \\ \left(\frac{T_C^2}{P_C}\right) &\alpha a \\ &\left(\frac{T_C^2}{P_C}\right)_{\rm NO} = \frac{(177)^2}{64} = 489.52 \\ &\left(\frac{T_C^2}{P_C}\right)_{\rm NO} = \frac{(550)^2}{45} = 6722.22 \end{aligned}$$

Therefore, NO gas has the smaller value of 'a'.

- (iii) As $V_C = 3b$, greater the value of b, larger will be V_C . From (a), we find CCl_4 has the larger b value. Therefore, CCl_4 gas will have the larger critical volume.
- (iv) Lower the critical temperature, more will be the behaviour at high temperature and pressure. Therefore, NO will behave more nearly ideally.

Test Problem 3.1

The van der Waals constants for HCl are a = 3.67 atm L² mol⁻² and b = 40.8 cm³ mol⁻¹. Find the critical constant of this substance.

Test Problem 3.2

A modified form of the van der Waals equation is

$$\left(P+\frac{n^2\alpha}{TV^2}\right)(V-n\beta)=nRT$$

where all the terms have their usual significance; α and β are constants. Deduced the expressions for α , β and R in terms of the critical constants.

PROBLEMS

3.1 One mole of ether occupies 741 cm³ at 300°C. Calculate the pressure (i) assuming ideal gas ; (ii) from the van der Waals equation. Given: a = 17.4 atm L² mol⁻²; $b = 13.4 \times 10^{-2}$ L mol⁻¹.

(the experimental pressure is 48.4 atm) [Ans.: (i) 63.5 atm; (ii) 45.78 atm]

3.2 Gases A, B, C and D obey the van der Waals equation with 'a' and 'b' values as given (SI):

	A	В	С	D
a	0.6	0.6	0.2	0.005
$10^3 b$	0.025	0.15	0.10	0.02

- (i) Which gas has the highest critical temperature?
- (ii) Which gas has the largest molecules?
- (iii) Which gas exhibits the most nearly ideal behaviour at STP?

 $[Ans.: (i) \operatorname{Gas} A; (ii) \operatorname{Gas} B; (iii) \operatorname{Gas} D]$

3.3 A nonideal gas is at its critical temperature and at a pressure 10% greater than its critical pressure. Doubling the pressure of the gas at constant temperature should (i) more than (ii) less than half its volume?

[Ans.: (ii) less than half]

3.4 Three two-dimensional plots, an isotherm, an isobar and, an isochor are given below for H_2O . State the ordinate and abscissa for each of them Explanation must be given.



[Ans.: (a) Isobar; T Vs V; (b) Isochor; P Vs T; (c) Isothem; P Vs V

- **3.5** The values of T_C and P_C for N₂ are 126 K and 34 atm; for C₂H₆ they are 305 K and 48 atm, respectively.
 - (i) Which gas has the smaller van der Waals constant b?
 - (ii) Which has the smaller a value ?
 - (iii) Which has the larger V_C value and
 - (iv) Which should show the most nearly ideal behaviour at 25°C and 10 atm?

[Ans.: (i) N₂; (ii) N₂; (iii) C₂H₆; (iii) N₂]

3.6 At 0°C and 100 atm the compressibility factor of O_2 is 0.927. Calculate the weight of O_2 necessary to fill a gas cylinder of 100 L under the given condition.

[Ans.: 15.24 kg]

4 CHAPTER

The Physics and Chemistry of Interface

4.1 INTRODUCTION

A solid melts into liquid and the liquid boils into vapour; the liquid state is therefore an intermediate between the solid and the vapour. In fact, the liquid state has a number of properties common to both solid and vapour phases. Liquids and solids are sometimes collectively called the condensed phases. At NTP, the molar volume of a dilute gas is about 22.4 litres, whereas that for solids and liquids is of the order of a few tens or hundreds of a cm³; the condensed phase is about thousand times more dense than the gaseous state. This means that the separation between the molecules in the vapour phase is 10 times more than that in the condensed phase. There is in general, a very little change in the density, specific gravity across the melting point, but change over orders across the boiling point; the heat of fusion is also small compared to the heat of vapourisation. This suggests that the liquid and the solid phases are closely related to each other compared to the vapour phase. In the solid, the particles do have only the vibrational motion; in the vapour state, the particles have all the three kinds of motion; in the liquid state, the molecules are not as chaotic as in the vapour/gas, and at the same time, not as orderly as that in the solid. In the solid we have both the short range and long range order in the arrangements of the molecules; in the vapour, no ordering is there; in the liquid, although long range order does not exist, a few short range order in arranging the molecules could be found.

There is another characteristic feature of the condensed phase; liquids and solids have boundaries. A number of interesting properties arise for such a two-phase system, e.g. a liquid in equilibrium with its vapour across the liquid/vapour interface or boundary, or a solid in equilibrium with its vapour. In this chapter, we will study some of these properties of the interfaces.

4.2 SURFACE TENSION

Dry leaves are often found remaining afloat on the surface of a body of water; small insects are sometimes observed crawling over water surfaces. If you look carefully you would not find any portion of the leaf or the leg of the insect submerged under water and are therefore not buoyed up according to the Archimedes' principle, but if you submerge these articles into water they will sink (according to the Archimedes' principle). So how they remain afloat? This is actually due to the surface tension of water-air interface. Hold a razor blade, its surface being kept parallel to the surface of water in a glass, and keep it carefully over it; it will remain afloat. But if you submerge it, it will sink. How then does the blade remain afloat? The floating object depresses the liquid layer slightly, and therefore its underneath surface gets stretched; this stretched surface then exerts a restoring force, whose vertical component holds the weight of the object.

Consider a body of water in equilibrium with its vapour. The number of molecules per unit volume is greater in the liquid than on the vapour side. Therefore, the molecules at the water-vapour interface feel a net attraction towards the bulk of the liquid, and the interface behaves as a stretched membrane, in the sense that any attempt to increase its area will require some work to be done on it (this is because, increasing area needs some molecules to be brought from the bulk to the surface against this inward force) (Figure 4.1). Surface tension γ , is then defined as the work required to increase the interfacial area by unity at constant P and T. If the area is increased by dA, the work required is therefore

$$dW = \gamma dA$$
 at const. *P* and *T* (4.1)

The free energy change associated with a change in surface area can be written as

$$dG = VdP - SdT + \gamma dA \tag{4.2}$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{P,T} = G^{\sigma} \tag{4.3}$$

The surface tension γ can therefore be defined as the surface free energy G^{σ} per unit area at constant P and T. According to this definition, the dimensions of γ is mt⁻². The units are erg cm⁻² and Jm⁻² in cgs and SI systems, respectively. Equation (4.2) also shows that the attainment of the configuration of minimum possible area assures the state of minimum free energy at constant P and T. Small droplets of water assume spherical shape, because the sphere has the minimum area to volume ratio.

A slightly different, but mathematically equivalent definition of γ is now laid here. Take a thin wire bent into the shape of three sides of a rectangle and fitted with a wire as the fourth side (Figure 4.2). By dipping the loop into a solution of a detergent, form a film in the loop. The film will tend to draw the sliding wire; to just stop it to contract, we apply a



$$\rightarrow$$

force F on the wire outward, and keep it in equilibrium. Under condition of equilibrium, the wire is now pulled outward over a distance dx. As Figure 4.2 explains the work required at constant P and T;

$$dW = Fdx = \frac{F}{2l}2l \cdot dx = \frac{F}{2l}dA \qquad (4.4)$$

(the factor '2' is included to consider interfaces from either side, front and rear). Comparison of Eq. (4.4) with (4.1) suggests that

$$\gamma = \frac{F}{2l}$$

This gives us the second definition of surface tension; the surface tension may then be defined as the force acting

normally to a unit line segment, along the surface of the liquid. In view of this definition, the unit of surface tension is dyn cm⁻¹ and Nm⁻¹ in CGS and SI systems, respectively. That, really there exists a force along the surface acting normally to any line segment can be illustrated by the example given in Figure 4.3.

(4.5)



Figure 4.3 A thread longer than the diameter of the circular frame is tied at two opposite ends; after forming a soap film it is found that the thread convolutes itself over the film. However, when one side of the film is punctured, the thread stretches itself towards the present film.

Example 4.1

The surface tension of Hg at 20° C is 0.485 Nm⁻¹. If two spherical globules of Hg, each of radius 1 cm stick together to form one globule, then calculate the change in the surface free energy.

Solution

Let the radius of the final globule be r. Assuming no loss of Hg,

$$2 \times \frac{4}{3}\pi (1 \text{ cm})^3 = \frac{4}{3}\pi r^3$$



Figure 4.2 The film formed tends to draw the wire inward.
$$\Rightarrow$$
 $r = 1.26 \text{ cm}$

The change in the surface area, $\Delta A = 4\pi (1.26 \text{ cm})^2 - 2(4\pi) (1 \text{ cm})^2 = -5.15 \times 10^{-4} \text{ m}^2$ The surface free energy change is therefore:

$$\Delta G_{P,T} = \gamma \Delta A = (0.485 \text{ Nm}^{-1}) (-5.15 \times 10^{-4} \text{ m}^2)$$

$$= -2.5 \times 10^{-4} \text{ J}$$

Comment: The decrease in the surface free energy, at constant P and T, shows that the process is spontaneous.

Test Problem 4.1

By how much the potential energy of each of the above drops would increase if it is broken up into 125 tiny equal sized drops?

4.3 CONTACT ANGLE AND WETTING

Surface tension always exists where there is a discontinuity, the material being different on the two sides of the surface. Thus mercury in contact with air has a certain surface tension, but in contact with water it has a different surface tension. More clearly, it can be said that the surface tension is not the property of the phases on either side of the boundary, rather it is a property of the interface. Hence, it may or may not be possible to attain equilibrium with three substances along a line.

Consider a liquid L, in equilibrium with its vapour V, be placed over a solid surface as shown in Figure 4.4.



Figure 4.4 A liquid spreading over a solid surface.

If the vector sum of the three surface tensions, which are tangential to the surfaces at the point of common contact is zero, then the arrangement is stable.

In this stable arrangement, the contact angle θ between the given liquid and the solid is defined as the angle made by the tangent drawn from the point of contact of the liquid with the solid, along the liquid surface, with the solid surface inside the liquid.

4.4

The Physics and Chemistry of Interface

$$\gamma_{SV} = \gamma_{LS} + \gamma_{LV} \cos \theta$$

4.5

 \Rightarrow

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{LS}}{\gamma_{LV}} \tag{4.5}$$

Therefore, the angle of contact between a given pair of liquid and solid depends on the three interfacial tensions, γ_{LS} , γ_{SV} and γ_{LV} . Although the absolute magnitude of θ depends on all the three tensions, whether θ will be acute or obtuse that depends on γ_{SV} and γ_{LS} .

If $\gamma_{SV} > \gamma_{LS} \Rightarrow \cos \theta > 0 \Rightarrow \theta < 90^{\circ}$; acute contact angle

If $\gamma_{SV} < \gamma_{LS} \Rightarrow \cos \theta < 0 \Rightarrow \theta > 90^{\circ}$; obtuse contact angle

In the first case, we say that the liquid wets the solid, and in the second case, the liquid does not wet the solid. The contact angle for water on glass at 25°C is approximately 18°, while that for mercury on glass is 140°. Hence, water spreads over glass while mercury will gather into a droplet (Figs 4.5a and 4.5b).



Figure 4.5 The wetting and non-wetting of a liquid over a solid surface.

4.4 WORK OF ADHESION AND WORK OF COHESION

Referring to Figure 4.6a, when the interface between the two phases α and β is decreased by 1 unit and simultaneously producing two new interfaces $\alpha - v$ and $\beta - v$, by 1 unit each, then the work required for the process at constant *T* and *P* is called the work of adhesion W_{ad} .

$$W_{ad} = \gamma_{\alpha v} + \gamma_{\beta v} - \gamma_{\alpha \beta} \tag{4.6}$$



Figure 4.6(a) This process of separation between the two phases α and β defines W_{ad} .



Figure 4.6(b) Separating a column of liquid into two sections, without any lateral contraction

Referring to Figure 4.6b, the work of cohesion of a liquid α is defined as the work required to pull a column of unit cross-section of the liquid α without any lateral contraction, to produce two new interfaces of $\alpha - v$ at constant *P* and *T*, each of unit cross-sectional area.

$$W_{C(\alpha)} = 2\gamma_{\alpha\nu} \tag{4.7}$$

Applying Eq. (4.6) to the liquid-solid interface and, Eq. (4.7) to the liquid, we find

 $W_{LS} = \gamma_{LV} + \gamma_{SV} - \gamma_{LS}$ (adhesional work between the *L* and *S*)

and

 $W_{C(L)} = 2\gamma_{LV}$ (cohesional work of the liquid)

and using Eq. (4.5),

or

$$\begin{split} W_{LS} &= \gamma_{LV} + \gamma_{LS} + \gamma_{LV} \cos \theta + \gamma_{LS} \\ W_{LS} &= \gamma_{LV} (1 + \cos \theta) \end{split}$$

or

$$W_{LS} = \frac{1}{2} W_C (1 + \cos \theta)$$

or

$$\cos \theta = \frac{W_{LS} - \frac{1}{2}W_C}{\frac{1}{2}W_C}$$
(4.8)

This is the Dupré equation. This shows that when $W_{LS} > \frac{1}{2} W_C$, i.e. the attraction between the solid and the liquid molecules is more than half of that between the liquid molecules, θ will be acute, i.e. wetting takes place. Furthermore, if $\theta = 0$, i.e. complete wetting,

 $W_{LS} = W_{C(L)}$. This implies that when the work of adhesion between the liquid and the solid becomes equal to the work of cohesion of the liquid, then the liquid spreads indefinitely on the surface of the solid. Similarly, if $\theta = 180^\circ$, $W_{LS} = 0$.

Example 4.2

Under what condition two liquids mix spontaneously?

Solution

Let the liquids are *A* and *B*. The work of adhesion between the two liquids is

$$W_{AB} = \gamma_{AV} + \gamma_{BV} - \gamma_{AB}$$

and, the work of cohesion of the two liquids

$$W_{C(A)} = 2\gamma_{AV} \text{ and } W_{C(B)} = 2\gamma_{BV}$$

$$W_{A(B)} = \frac{1}{2}(W_{C(A)} + W_{C(B)}) - \gamma_{AB}$$

Therefore, lower the interfacial tension γ_{AB} between the liquids higher is the work of adhesion between them, i.e. stronger, and more similar is the force of attraction between the molecules of the two kinds. Finally, when the interface A/B vanishes, i.e. when the two liquids mix spontaneously, $\gamma_{AB} = 0$ which makes

$$W_{AB} = \frac{1}{2} (W_{C(A)} + W_{C(B)})$$

4.5 CONDITION OF SPREADING OF ONE LIQUID OVER ANOTHER

Let, a liquid β be placed over another liquid α in which it has no solubility (Figure 4.7). At constant *T* and *P*, the change in the surface free energy is given by:

$$dG = \left(\frac{\partial G}{\partial A_{\alpha}}\right) dA_{\alpha} + \left(\frac{\partial G}{\partial A_{\beta}}\right) dA_{\beta} + \left(\frac{\partial G}{\partial A_{\alpha\beta}}\right) dA_{\alpha\beta}$$
$$= \gamma_{\alpha} dA_{\alpha} + \gamma_{\beta} dA_{\beta} + \gamma_{\alpha\beta} dA_{\alpha\beta}$$

where dA_{α} , dA_{β} and $dA_{\alpha\beta}$ are the changes in the area of the α -v, β -vap and α - β interfaces, respectively.



Figure 4.7 The spreading of one liquid over the other

Now, if the liquid β is to spread over the liquid α then dA_{β} and $dA_{\alpha\beta}$ are positive and dA_{α} is negative and moreover,

$$dA_{\beta} = dA_{\alpha\beta} = -dA_{\alpha}$$

Therefore, we have,

$$\begin{split} dG &= (-\gamma_{\alpha} + \gamma_{\beta} + \gamma_{\alpha\beta}) dA_{\beta} \\ \left(\frac{\partial G}{\partial A_{\beta}} \right)_{P,T} &= -\gamma_{\alpha} + \gamma_{\beta} + \gamma_{\alpha\beta} \end{split}$$

or

For spontaneous spreading, $\left(\frac{\partial G}{\partial A_{\beta}}\right)_{P,T}$ must be negative; we then define the spreading

coefficient of β over α as,

C

$$S_{\beta/\alpha} = -\left(\frac{\partial G}{\partial A_{\beta}}\right)_{P,T}$$
(4.9a)

or

$$S_{\beta/\alpha} = \gamma_{\alpha} - \gamma_{\beta} - \gamma_{\alpha\beta}$$
(4.9b)

So that, when $S_{\beta/\alpha}$ is positive, the free energy change is negative and it makes the spreading spontaneous.

Table 4.1 gives some data of spreading coefficient of different liquids on water at 20°C. This shows that, when added in little amount, isoamylalcohol, benzene, toluene, etc. will spread over water but bromoform, methylene iodide will remain as a lens.

Liquid B	$m{S}_{eta\!/\mathrm{H_2O}}$
Isoamyl alcohol	44.0
<i>n</i> -octyl alcohol	35.7
Heptaldehyde	32.2
Oleic acid	24.6
Benzene	8.8
Toluene	6.8
Isopentane	9.4
Nitrobenzene	3.8
Hexane	3.4
Heptane	0.2
Ethylene dibromide	-3.2
Carbon disulfide	-8.2
Iodobenzene	-8.7
Bromoform	-9.6
Methylene Iodide	-26.5

TABLE 4.1 Spreading coefficients of liquids on water at 20°C, S_{β/H_2O} (in CGS)

4.8

Initially, benzene spreads over water but eventually form a lens, why?

$$\gamma_{C_6H_6} = 28.9, \gamma_{H_2O} = 72 \text{ and } \gamma_{C_6H_6/H_2O} = 35 (\text{in erg cm}^{-2})$$

When benzene is added in little amount over water,

 $S_{C_{eHe}/H_{2}O} = 72 - 28.9 - 35 = 8.1 \text{ erg cm}^{-2}$

After the initial spreading, mutual saturation begins. First, the benzene layer gets saturated with water and this changes $\gamma_{C_6H_6}$ to 28.8 erg cm⁻². Then the underneath water layer gets saturated with benzene, and this change γ_{H_2O} to 62 erg cm⁻². The spreading coefficient also changes accordingly as

$$S_{\rm C_{eHe}/H_{2}O} = (72 - 28.8 - 35) = 8 \text{ erg cm}^{-2}$$

and finally,

$$S_{C_6H_6/H_2O} = 62 - 28.8 - 35 = -2 \text{ erg cm}^{-2}$$

As the final spreading coefficient becomes negative, the initially spread out film collects to a lens.

4.6 LIQUID MENISCUS INSIDE A CAPILLARY IS GENERALLY

Capillary means hair-like; a very narrow tube. Let us see what happens to the liquid level inside the capillary when the latter is dipped into the former.



Figure 4.8 The nature of liquid meniscus inside a capillary

In Figure 4.8, a capillary is dipped vertically down into a liquid. Consider a liquid molecule at the interface and adjacent to the glass surface. This molecule will be attracted by the solid particles of the glass, due to the force of adhesion. Let us denote this force of adhesion by the vector F_a , which certainly acts normal to the glass surface. The liquid molecule is also attracted by its own kind due to the force of cohesion, from all possible sides. Let this force acting on the molecule be F_C ; this vector acts at an angle 45° to the glass surface and directs towards the bulk of the liquid. The liquid molecule is therefore acted on by the two

forces, F_A and F_C , the resultant of which can be found by the law of parallelogram. The following three cases may come up.

Case I

If the resultant vector R is to be along the glass surface (Figure 4.8a), then

$$\sin 45^\circ = \frac{1}{\sqrt{2}} = \frac{F_A}{F_C}$$
$$F_C = \sqrt{2} F_A$$

or

 \Rightarrow

Case II

If the resultant is outwardly directed then (Figure 4.8b)

$$\label{eq:F_A_based} \begin{split} \frac{F_A}{F_C} &= \sin\theta(\theta>45^\circ)>\frac{1}{\sqrt{2}}\\ F_C<\sqrt{2}F_A \end{split}$$

Case III

If the resultant is directed inwards, i.e. inside the liquid then (Figure 4.8c)

$$\label{eq:F_A} \begin{split} \frac{F_A}{F_C} &= \sin\theta (\theta < 45^\circ) < \frac{1}{\sqrt{2}} \\ F_C &> \sqrt{2} F_A \end{split}$$

 \Rightarrow

Now, what happens to the molecule considered and to every molecule present over the circumference in contact with the glass. A liquid can not withstand a permanent shearing stress and therefore, it will try to get rid of their stress, the resultant vector R, by adjusting its surface so that R tends to act normally to the surface. Therefore in the first case, the liquid level will remain flat; in the case II, the liquid level will try to curl up, making the surface concave upwards and, in case III, it will curl down, making the surface inside the capillary convex upwards.

4.7 EXCESS PRESSURE ACROSS A CURVED SURFACE

If, across an interface, the pressures are the same on both sides, the surface will be planar. If the pressure on one side increases, the surface becomes concave on that side. Suppose that AB is a piece of cylindrical surface of radius r, the length of the cylinder taken at right angles to the plane of this paper being 1 unit (Figure 4.9). If the pressure below AB is, P, greater than that above AB then the force on the strip $rd\theta$ is $\Pr d\theta$ and resolving this parallel to OC, it is $\Pr \cos \theta d\theta$. The whole resolved force on AB acting parallel to OC is then

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Figure 4.9 Excess pressure across a curved surface.

Now, if γ be the surface tension, then resolved parallel to *OC*, the entire force vertically downward, is $\gamma \sin \theta + \gamma \sin \theta = 2\gamma \sin \theta$. Hence, for equilibrium of the section *AB*,

$$2\gamma \sin \theta = 2 \operatorname{Pr} \sin \theta$$
$$P = \frac{\gamma}{r}$$

 \Rightarrow

It should be noted that the curvature of the surface at right angles to the plane of this paper is zero, and does not contribute to *P*. If, however, there is a curvature of radius r_2 in this direction, then there would be a pressure difference, on account of this, of γ/r_2 . Calling the first radius of curvature as r_1 , we may then write, for the total pressure difference,

$$P = \gamma \left[\frac{1}{r_1} + \frac{1}{r_2} \right] \tag{4.10}$$

which is the Laplace-Young relation.

For a spherical surface, $r_1 = r_2$, and $P = 2\gamma/r$. Equation (4.10) is applicable to a liquid drop or a bubble inside a liquid, where there is only one interface. For a soap bubble, there are two interfaces, each of which contributes $2\gamma/r$, and hence the excess pressure inside a soap bubble is $4\gamma/r$. For a cylindrical drop, let one radius of curvature is r; the second radius of curvature is \propto ; the excess pressure inside a cylindrical drop is therefore γ/r .

Take two equal sized glass slides. Put a few drops of water over one, and then keep the second slide over the first; the water is in between the two slides. It is a common experience that, a minimum force is required to pull the two glass slides. The reason is as follows: as

Figure 4.10 given below shows water wetting the glass surface circularly and forms a concave outward surface, in between the slides. The excess pressure inside the water is then,

$$P = \gamma \left[\frac{1}{r} + \left(-\frac{2}{d} \right) \right] = -\frac{2\gamma}{d} \qquad (\because r \gg d)$$

where d is the distance between the two slides.

It is therefore seen that, as P is negative, the excess pressure acts from outside and holds the two slides tightly.





4.7.1 An Alternative Derivation of Laplace-Young Relation

As Figure 4.11 shows, consider a small section of an arbitrary curved surface with two radii of curvatures R_1 and R_2 . If the surface be moved outwards by a small displacement dz, the change in area will be

$$dA = d(xy) = xdy + ydx$$

The work required to increase the surface area by this amount is

$$dW = \gamma dA = \gamma [xdy + ydx]$$

If P be the excess pressure inside, then this work can also be written as

$$dW = P(xy)dZ$$

and therefore, equating these two expressions, we have

$$P(xy)dZ = \gamma[xdy + ydx]$$
(4.11)

From the consideration of similar triangles

$$\frac{x + dx}{R_1 + dZ} = \frac{x}{R_1} \implies dx = \frac{x dZ}{R_1}$$
$$\frac{y + dy}{R_2 + dZ} = \frac{y}{R_2} \implies dy = \frac{y dZ}{R_2}$$

and

Using these relations in Eq. (4.11), we get

$$P(xy)dZ = \gamma \left[\frac{xydZ}{R_1} + \frac{yxdZ}{R_2}\right]$$



Figure 4.11 Two different radii of curvatures are taken to find the excess pressure across the curved surface.

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or

$$P = \gamma \left[\frac{1}{R_1} + \frac{1}{R_2} \right]$$

Example 4.3

Consider two soap bubbles of radii $r_1 = 1$ cm and $r_2 = 4$ cm. What is the excess pressure inside each bubble if the soap solution has a surface tension = 40 dyn cm⁻¹. If the two bubbles collide and stick together, then what is the radius of the film between them, and on which side is the centre of curvature of the film?

..

Solution

 \Rightarrow

Excess pressure inside the smaller bubble is $(P = 4\gamma/r)$,

$$P = \frac{4 \times 40 \text{ dyne cm}^{-1}}{1 \text{ cm}} = 160 \text{ dyne cm}^{-2}$$

and that inside the bigger bubble is

$$P = \frac{4 \times 40}{4} = 40 \text{ dyne cm}^{-2}$$

As Figure 4.12 shows, the greater pressure inside the smaller bubble will blow the film outwards inside the bigger bubble until

160 dyne cm⁻² =
$$4\frac{\gamma}{R}$$
 + 40 dyne cm⁻²
 R = 1.33 cm



Figure 4.12 The sticking of two bubbles of different radius of curvature.

4.8 CAPILLARY RISE AND CAPILLARY DEPRESSION

We have seen that the liquid surface inside a capillary is either a concave (when $\theta < 90^{\circ}$) or convex (when $\theta > 90^{\circ}$) one, and there is also a pressure difference across the curved surface. The column of liquid inside a capillary therefore acts as a manometer, registers the pressure difference and either rises up ($\theta < 90^{\circ}$) or is depressed down ($\theta > 90^{\circ}$). Consider Figure 4.13, where a capillary made of glass.

is dipped into water partially.

The pressures at the points 1, 2 and 3 are equal $(P_1 = P_2 = P_3)$ because all of them are the same atmospheric pressure. The liquid level outside the capillary may be considered planar and therefore $P_1 = P_4$ and $P_3 = P_6$. So, $P_1 = P_2 = P_3 = P_4 = P_5 = P_6$; but, as the water level inside the capillary is concave upwards, $P_2 > P_5$, the difference is $2\gamma/r$, where r is the radius of the curved surface. Therefore $P_4 = P_6 > P_5$; inside water, the pressure outside



Figure 4.13

the capillary is more than inside, and this results into a spontaneous flow of water into the capillary. The water level therefore rises up along the tube until the hydrostatic pressure developed balances the pressure difference $P_2 - P_5$. Now, you try yourself to understand why the Hg level inside a glass capillary is depressed.

Consider a capillary of very small radius R, so that it forms a liquid meniscus which is a section of a sphere (radius r). If the contact angle is θ , then $\cos \theta = R/r$, the excess pressure across the meniscus is $\frac{2\gamma}{r} = \frac{2\gamma \cos \theta}{R}$ (Figure 4.14). If the capillary rise is h, and ρ and ρ_0 are the densities of the liquid and the surrounding fluid, respectively, then the hydrostatic pressure developed is $h(\rho - \rho_0)g$. As explained above, equilibrium will be reached when

$$\frac{2\gamma\cos\theta}{R} = h(\rho - \rho_0)g$$
$$\gamma = \frac{h(\rho - \rho_0)gR}{2\cos\theta}$$
(4.12)

In many cases, the density ρ_0 of the surrounding fluid, e.g. if Figure 4.14 it is a vapour, can be neglected in comparison with ρ , and Eq. (4.12) can be written as



I.14 The relation between the surface tension and the capillary rise.

$$\gamma = \frac{h\rho gR}{2\cos\theta} = \frac{h\rho gr}{2} \tag{4.13}$$

$$\Rightarrow$$

where *R* is the radius of the capillary and *r* is the radius of curvature of the curved surface. If θ is very small then $R \approx r$. Also note that if $\theta > 90^{\circ}$ then $\cos \theta$ will be negative, which implies that now there will be depression.

What happens when a capillary of insufficient length is dipped into water?

From Eq. (4.13),

$$rh = \frac{2\gamma}{\rho g} = \text{constant}$$

When a capillary longer than h is dipped into water, it is only the h, in the above, that changes (as the level of water rises up) to make $r \times h = \text{constant}$. But, if the capillary is shorter than this final value of h, let it be H, then r is now the variable and changes by spreading of water over the wall of capillary at the top so that, its new value, say R times H, is now equal to rh; so, there will be no fountain!

4.9 MEASUREMENT OF SURFACE TENSION

Different methods are available for the measurement of γ , of which only a few will be discussed here.

4.9.1 Capillary Rise Method

This method uses Eq. (4.13); a capillary is dipped partially and vertically into the liquid; the height of the liquid level inside the capillary is measured with a travelling microscope. The radius R of the capillary can also be measured easily. For finer results, the 'h' in

Eq. (4.13) should be added to $\frac{1}{3}R$.

4.9.2 Maximum Bubble Pressure Method

If a bubble is formed at the end of a tube of radius R immersed in the test liquid to a depth h, the pressure required is given by

$$P = h\rho g + \frac{2\gamma}{r} \tag{4.14}$$

where r is the radius of the bubble (Figure 4.15). In the above equation, the first term on the right hand side is the pressure required to overcome the hydrostatic pressure and the second term is due to the excess pressure inside the bubble. It is clear from Eq. (4.10), that

the bubble can sustain a maximum excess pressure of $\frac{2\gamma}{R}$. So, when the bubble begins to form, r > R, and the bubble grows in size, i.e. r decreases, and when it reaches R, the radius of the tube, P becomes maximum, and then r starts increasing.

So we write

$$P_{\max} = h\rho g + \frac{2\gamma}{R}$$

The pressure beyond which the bubble breaks away is measured and the surface tension is determined from the above equations.





4.9.3 Drop Weight Method

When a drop is formed at the tip of a capillary by delivering the liquid through it, a critical size is reached at which the surface tension cannot hold the drop anymore, and the drop falls. A rough sequence of the shapes during the formation of the drop is shown in Figure 4.16. Approximately, we can write

$$W_{\text{ideal}} = 2\pi r \gamma \tag{4.15}$$

Figure 4.16 High speed photographs during the formation of a drop.

where W_{ideal} is the weight of the drop which should fall and r is the radius of the capillary. But as explained in Figure 4.16, the drop leaves behind a considerable portion of the liquid and therefore the actual weight is

$$W = W_{\text{ideal}} \phi \tag{4.16}$$

4.16

where ϕ is a correction factor depending on $\frac{r}{v^{1/3}}$, where v is the volume of the drop. A table for a list of the values of ϕ had been prepared by Harkins and Brown.

Equation (4.16) is chiefly used in comparing surface tensions of different liquids. If m_1 and m_2 are the masses of the drops of two liquids 1 and 2 falling from the same capillary, then.

$$\frac{m_1}{m_2} = \frac{r_1 \phi_1}{r_2 \phi_2}$$

If the volumes of the drops of the two liquids are not very different then $\phi_1/\phi_2 = 1$; then we have

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} = \frac{v_1 \rho_1}{v_2 \rho_2}$$
 Using Eq. (4.15)

where *v*'s and ρ 's are the volumes of each drop and the densities of the liquids respectively. The stalagmometer, a pipette like tube ending in a capillary (Figure 4.17) is used for this purpose. The number of drops (formed slowly and completely before its detachment) falling from the end is counted in passing the liquid level between two marks on the stalagmometer. Let n_1 and n_2 be the number of drops for the liquids 1 and 2, respectively, in draining out *V* volume of each liquid. Then $V = n_1 v_1$ and $V = n_2 v_2$, and so we write,

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 \rho_1}{n_1 \rho_2}$$

So, if the surface tension of one liquid is known then that for the other can be determined from the above equation.

4.9.4 du Noüy Tensiometer

This method is developed by du Noüy, and is one of the many detachment methods used for convenience and accurate measurement of surface tension of liquids. Here, the force required to pull up a perfectly horizontal ring, of a previously cleaned and dried platinum from the surface of the test liquid, is measured. As a first approximation, it is assumed that the minimum force required to pull it up is equal to the weight of the ring plus that just required to overcome the inward pull on the periphery of the ring by the liquid due to surface tension.



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Force =
$$W_{\text{ring}} + 2(2\pi R\gamma)$$
 (4.17)

where $W_{\rm ring}$ is the weight of the ring and R is its radius. The multiplier 2 is necessary to account both the inner and outer periphery of the ring. Once again, for finer data, a correction factor ϕ called the Harkins and Jordan factor is necessary to account for the thickness and size of the ring and the density of the liquid (Figure 4.18).



Figure 4.18 The du Noüy method of measuring surface tension of a liquid.

4.10 VAPOUR PRESSURE OF CURVED SURFACE: KELVIN EQUATION

Another interesting manifestation of surface tension is the enhanced vapour pressure of curved surfaces. Let P be the vapour pressure over a convex drop of radius r and P_0 be the vapour pressure of a flat surface (of the same liquid). If we transfer, reversibly and isothermally, xg of the liquid (molar mass M) from the flat to the convex drop then the associated free energy change is $\frac{dx}{M}RT\ln\frac{P}{P_0}$. If this transfer has increased the area of the drop by dA then $dA = d(4\pi r^2) = 8\pi r dr$. The free energy change therefore can also be written as $\gamma dA = 8\pi r \gamma dr$. So, we have

$$\frac{dx}{M}RT\ln\frac{P}{P_0} = 8\pi r\gamma dr \tag{4.18}$$

Since the mass of the drop $x = \frac{4}{3}\pi r^3 \rho$, where ρ is density,

$$dx = 4\pi r^2 \rho dr \tag{4.19}$$

Using Eq. (4.19) in Eq. (4.18), we get,

$$\ln\frac{P}{P_0} = \frac{2V_m\gamma}{rRT} = \frac{2\gamma M}{\rho rRT}$$
(4.20)

where V_m is the molar volume of the liquid ($V_m = M/\rho$). Equation (4.20) is known as the Kelvin equation. Although it is derived here for a convex drop, it is in general applicable to any convex surface with radius of curvature r. For concave surface, there will be a minus sign on the right because the transfer of the liquid now decreases the area by dA.

4.18

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Example 4.4

Calculate the vapour pressure of a tiny water droplet of radius 10^{-4} and 10^{-7} cm at 25°C. $\gamma_{\text{water}} = 72$ dyne cm⁻¹.

Solution

$$\frac{P}{P_0} = \exp\left\{\frac{2\gamma V_m}{rRT}\right\}$$

For
$$r = 10^{-4}$$
 cm, $\frac{P}{P_0} = \exp\left\{\frac{2 \times 72 \text{ dyn cm}^{-1} \times 18 \text{ cm}^3 \text{mol}^{-1}}{10^{-4} \text{ cm} \times 8.314 \times 10^7 \text{ ergK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}\right\} = 1.001$

Similarly, for
$$r = 10^{-7}$$
 cm, $\frac{P}{P_0} = 2.85$

4.11 SUPER SATURATION OF VAPOUR AND SUPER HEATING OF LIQUIDS: THEORY OF NUCLEATION

We know that a liquid will be in equilibrium with its vapour, at a fixed temperature, at the saturated vapour pressure. So it is expected that, if the pressure of the vapour be increased slightly over this saturation value, spontaneous condensation will take place. Experiments, however, showed us that in the absence of any foreign surfaces, condensation does not take place if the vapour pressure is not increased beyond orders of magnitude of the saturated vapour pressure P_0 . The vapour phase is then (when the saturation vapour pressure is exceeded but, the liquid did not appear) said to be super-saturated, a metastable phase, i.e. thermodynamically unstable, but exists due to some kinetic reasons.

Similarly, a liquid may be cooled below its freezing point without the appearance of the solid phase. For example, Fahrenheit (1714) had observed that a sample of very pure water could be cooled down to -40° C at 1 atm without any ice-formation. Such liquids are called super-cooled liquids. These are also thermodynamically unstable, and exists due to some kinetic reasons.

We can understand this super-saturation and super-cooling with the help of the Kelvin equation [Eq. (4.20)]. From Eq. (4.20), the vapour pressure of liquid drops of radius r may be written as

$$P_{\rm drop} = P_0 e^{\frac{2V_m \gamma}{rRT}}$$
(4.21)

and the vapour pressure inside a cavity in a liquid as:

$$P_{\text{cavity}} = P_0 e^{-\frac{2V_m \gamma}{rRT}}$$
(4.22)

where P_0 is the saturated vapour pressure of the liquid of molar volume V_m . In the previous problem, we calculated the vapour pressure of tiny water droplets. It is 1.001 P_0 when the radius is 10^{-4} cm, and almost $3P_0$ when $r = 10^{-7}$ cm. The effect is therefore not too pronounced if the radius is not too small; the vapour pressure of a tiny drop of water of radius 10^{-7} cm is *three times* its saturated vapour pressure. This drop contains at most 140 molecules in it, and so we cannot rely on this magic number 3; nevertheless, we can use it to understand the super-saturation.

Moist warm water vapour, from seas and rivers, rises up into higher altitudes of cooler region and at some altitude, becomes thermodynamically unstable with respect to the liquid, and we might expect it to form rain. The sequence of steps in the formation of rain is; first a few molecules form a cluster (called germs) which then grows bigger by accretion and then come to a size of recognizable droplet (called nuclei) which can then coalesce to form the liquid bulk. Now, when the tiny clusters of molecules are formed they have a very small radii and therefore have a much higher vapour pressure than P_0 , and therefore not allowed due to the increased tendency of the tiny droplets to vapourize. We then say that, the vapour is super-saturated.

Let us consider the formation of a cluster:

$$nA(\operatorname{vap}, P) \to A_n$$

The free energy change of the process is cluster of n molecules of radius r; a small liquid drop

$$\Delta G = n \frac{R}{N_0} T \ln \frac{P_0}{P} + 4\pi r^2 \gamma$$
 (4.23)

where P_0 is the saturated vapour pressure of the liquid, P is the vapour pressure, N_0 is the Avogadro's number and γ is the surface tension of the liquid. The number of molecules n, in the drop of radius r is

$$n = \frac{\left(\frac{4}{3}\pi r^3\right)\rho N_0}{M} \Rightarrow \frac{n}{N_0} = \frac{4}{3}\pi r^3 \frac{\rho}{M}$$

therefore, Eq. (4.23) can be written as

$$\Delta G = -\frac{4}{3}\pi r^3 \frac{\rho}{M} RT \ln \frac{P}{P_0} + 4\pi r^2 \gamma$$

$$\Delta G = -\frac{4}{3}\pi r^3 \frac{\rho}{M} RT \ln x + 4\pi r^2 \gamma \qquad (4.24)$$

or

where $x = P/P_0 > 1$. Equation (4.24) clearly shows that a plot of ΔG versus r, first increases and then forming a maximum at some critical size r_c , decreases (Figure 4.19). It is therefore, the excess surface free energy of the droplet that makes its formation difficult.



Figure 4.19 The variation of 4G for the formation of a droplet with its size.

Differentiating ΔG with respect to *r*, we get

$$\left[\frac{\partial(\Delta G)}{\partial r}\right] = -4\pi r^2 \frac{\rho}{M} RT \ln x + 8\pi r\gamma$$

at the maximum, $r = r_c$, and $\left[\frac{\partial(\Delta G)}{\partial r}\right] = 0$

$$\Rightarrow \qquad RT\ln x = \frac{2\gamma M}{r\rho} \tag{4.25}$$

which is nothing other than the Kelvin equation. This shows that for each value of $x \left(=\frac{P}{P_0}\right)$, there is a critical r_c which is given by

$$r_c = \frac{2\gamma M}{(\rho RT \ln x)} \tag{4.26}$$

beyond which the drops will observe a decrease in the free energy with increase in their size, and hence will grow up spontaneously. The question that still remains is: how are the initial tiny drops formed which will eventually move on to r_c and then from the rain spontaneously? In this process, we need the presence of minute dust particles. These foreign particles provide surfaces, on which the clusters can nucleate and form the rain. That is why, fine KI solid is sprayed into a dense cloud to form a rain show. Exactly, the same thing happens in the *Wilson Cloud Chamber*. Here, the super-saturation is done by cooling it through adiabatic expansion. Now the passage of elementary charged particles (α or β) ionises the molecules, on which the vapour can condense. The trajectory is then mapped as a line of flight of the condensed water.

Exactly, in the same way, superheating of a liquid can be explained. If a very pure water be heated in a clean beaker, the cavity which is first formed, has a very low vapour pressure inside it [see Eq. (4.22)] and therefore collapses immediately; the temperature therefore rises above the boiling point without the formation of the vapour and, the liquid becomes superheated. To ensure a smooth boiling broken glass or porcelain pieces must be added to provide surface for the cavity to form.

4.12 SOLUBILITY AND PARTICLE SIZE

Let us consider a substance in equilibrium between the solid and its saturated solution (Figure 4.20). The condition of equilibrium is

$$\mu_s = \mu_l \tag{4.27}$$

where μ_s and μ_i are the chemical potentials of the substance in the solid and liquid phases respectively. Since the solid phase is pure, μ_s can be written as:

$$\mu_s = \mu_s^o + \gamma \overline{S} \tag{4.28}$$

where μ_s^o is the standard chemical potential of the substance in the solid phase, γ is the surface tension at the solid crystal surface and \overline{S} is the molar area of the solid. If one mole of the solid is assumed to consist of *n* small cubes of side length *x* then,

The molar volume $\overline{V} = n x^3$ or $n = \frac{\overline{V}}{x_3}$. The molar area, $\overline{S} = n(6x^2) = \frac{\overline{V}}{x^3} \times 6x^2 = \frac{6\overline{V}}{x}$;

therefore we write Eq. (4.28) as

$$\mu_s = \mu_s^o + \frac{6\gamma V}{x} \tag{4.29}$$

If the solution is considered ideal and C be the solubility then

$$\mu_s = \mu_l^o + RThC \tag{4.30}$$

From Eqs (4.27), (4.29) and (4.30), we get

$$\mu_s^o + \frac{6\gamma V}{x} = \mu_l^o + RT\ln C \tag{4.31}$$

Let C_0 be the solubility of a giant sized crystal, i.e. with $x \to \infty;$ then we write Eq. (4.31) as

$$\mu_s^o + 0 = \mu_l^o + RT \ln C_0 \tag{4.32}$$



Figure 4.20 A saturated solution in equilibrium with undissolved solid.

and subtracting Eq. (4.32) from Eq. (4.31), we get

$$C = C_0 e^{\frac{6\gamma \bar{V}}{xRT}}$$
(4.33)

an equation, exactly similar in form, to the Kelvin equation [Eq. (4.20)]. This shows that as the particle size decreases, the solubility C increases even more than the vapour pressure of a similar sized liquid drop (because γ for some solids are five to six times that of liquids). This in turn, means that what is saturated with respect to fine solid particles is supersaturated for bigger particles. This is why, when freshly precipitated solution is kept standing in the hot condition over a period of time, the finer particles gradually grow in size.

4.13 SURFACE TENSION AND TEMPERATURE

In Section 4.1 of this chapter, we have seen that the surface tensions may be defined as the surface free energy per unit area of the surface, G^{σ} , measured at constant *T* and *P*.

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P} = G^{\sigma},$$

differentiating the equation with respect to temperature at constant pressure we get

$$\left(\frac{\partial\gamma}{\partial T}\right)_{P} = \left(\frac{\partial G^{\sigma}}{\partial T}\right)_{P}$$
(4.34)

Now, if we write $\left(\frac{\partial G^{\sigma}}{\partial T}\right)_{p} = -S^{\sigma}$, then S^{σ} can be interpreted as the surface entropy per

unit area of the surface (S^{σ} is always positive by the third law of thermodynamics). Equation (4.34) can therefore be written as

$$\left(\frac{\partial\gamma}{\partial T}\right)_{P} = -S^{\sigma} \tag{4.35}$$

which predicts that, the surface tension decreases with increasing temperature. This prediction has in fact been experimentally verified with different kinds of surfaces, and over wide temperature ranges (Figure 4.21). The physical interpretation of this variation is as follows: as the temperature is increased, the increased thermal motions of the molecules of the liquid seem to make the cohesive forces among the molecules less significant, and now less work is to be done in bringing the molecules from the bulk to the surface.



Figure 4.21 Variation of γ for different liquids with temperature.

An important relationship between surface tension and temperature may be deduced as follows; let v be the specific volume of a liquid; its molar volume is then vM, where M is the molar mass of the liquid. If the liquid is assumed to be spherical then the molar surface area is proportional to $(vM)^{2/3}$. So the molar surface energy is $\gamma(vM)^{2/3}$. Experimentally, this molar surface energy has been found to vary almost linearly with temperature; so we write:

$$\frac{d}{dt} \left[\gamma(vM)^{2/3} \right] = -k \tag{4.36}$$

where k is a constant; the negative sign indicates that γ decreases with increase in temperature *t*. Integrating this equation between limits and remembering that the surface tension vanishes at the critical temperature of the liquid, we get,

$$\int_{0}^{\gamma V} d\left[\gamma(vM)^{2/3}\right] = -k \int_{t_c}^{t} dt$$
$$\gamma(vM)^{2/3} = k(t_c - t)$$

or

Since the interface gets diffused at a few degrees (normally 6) below t_c , the above equation is modified as

$$\gamma(vM)^{2/3} = k(t_c - t - 6) \tag{4.37a}$$

Equation (4.37a) is known as the Ramsay–Shield–Eötvös relation. The value of k can be evaluated by writing Eq. (4.37a) at two different temperature t_1 and t_2 where the specific volumes and the surface tensions are v_1 , γ_1 and v_2 , γ_2 , respectively, and then, taking the difference:

$$k = \frac{\gamma_2 (v_2 M)^{2/3} - \gamma_1 (v_1 M)^{2/3}}{t_1 - t_2}$$
(4.38)

The value of k has been found to be 2.1 for a number of normal liquids, e.g. carbon tetrachloride, chloroform, benzene, nitrobenzene, ether, ester, etc. For certain liquids, e.g. H_2O , alcohols, carboxylic acids etc. the value of k has not only been found to be less than 2.1, it also changes with temperature. It is proposed that, in these liquids, a few molecules form a cluster due to hydrogen bonding and the effective molar mass is then xM not M, where x is the average number of molecules in the clusters. Equation (4.37a) therefore, should now be written as

$$\gamma(vxM)^{2/3} = k(t_c - t - 6) \tag{4.37b}$$

If the observed value of k for these liquids be k', then

$$k' = \frac{k}{x^{2/3}}$$
 or $x = \left(\frac{k}{k'}\right)^{3/2} = \left(\frac{2.1}{k'}\right)^{3/2}$ (4.39)

from which the factor of association x, can be evaluated. Another empirical equation due to Guggenheim is

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$$\gamma = \gamma_0 \left(1 - \frac{T}{T_C} \right)^n \tag{4.40}$$

where γ_0 is an empirical parameter characteristic of the liquid and *n* is very close to 11/9 for many liquids.

4.14 THERMODYNAMICS OF SURFACES

Let us consider a system consisting of the phases α and β with the interfacial region σ (Figure 4.22). Although the thickness of the interface due to the short range molecular

forces is not more than a few molecular diameters, the exact value depends on the positions of the boundary planes AA' and BB'. We draw these planes subject to the conditions: (i) all the properties are uniform in the α -phase right upto AA' and also those of the β -phase upto BB' (ii) within the interfacial region, all the properties vary continuously from the pure phase α at AA' to the pure phase β at BB'. For example, the concentration of a component *i* c_i , being one of the properties of the system, when plotted versus the length of the system (assuming it to be a cylindrical of uniform cross-section) gives a plot as shown in Figure 4.23.



4.25

Figure 4.22 Two phases α and β are separated by thickness σ .



Figure 4.23 The placement of the 2-D dividing plane.

There are thermodynamic treatments for this interfacial region of definite thickness, but here, we will discuss the more simpler treatment of Gibbs in which the interface is modelled

as 2a-dimensional plane (which has no volume). Now, the question is, where to place this 2-dimensional dividing plane? Before finding out the position of this place, let us make ourselves clear about two facts. The first is, when we replace the actual 3-dimensional interface by a 2-dimensional plane, we understand that then the two phases α and β are homogeneous right upto this plane. To understand the second point, let us keep the plane at OO'. The total number of moles of component i, n_i , present in this system, is equal to the area under the solid curve from Z = 0 to Z = B, times the area of cross-section of the cylinder A. But in our model-system of 2-dimensional interface, the number of moles of component i in phase α , n_i^{α} is the area of the rectangle abdc times A, area and that in the phase β , n_i^{β} is the area of the rectangle defg times A. If we now take the subtraction $n_i - (n_i^{\alpha} + n_i^{\beta})$, then what we get is the number of moles of component i present at the 2-d interface n_i^{σ} . Thus

$$n_i^{\sigma} = n_i - (n_i^{\alpha} + n_i^{\beta}) \tag{4.41}$$

and this is equal to the algebraic sum of the two shaded areas with proper sign. When this n_i^{σ} is divided by the area of the dividing plane A, what we get $\Gamma_i = n_i^{\sigma}/A$, is called the surface excess of the component *i*. Clearly, the surface excess of a component may be positive, negative as well as zero; it all depends on the position of the dividing plane. Now let us come to the point of the placement of the dividing plane. Usually it is placed at a position for which the surface excess of one specified component, usually the solvent, is zero. And after fixing the position of the plane, the surface excess of the other components is evaluated using Eq. (4.41) and with respect to the fixed plane. If the surface excess of a solute, so obtained, is found positive, the solute molecules are said to be adsorbed at the interface; on the other hand, if it is found negative, then the solute molecules are said to be negatively adsorbed at the surface. In the first case, there is an enrichment of the solute molecules at the interface while in the latter the solute molecules tend to depopulate the interface and populate the bulk phase. Na⁺ and K⁺-salts of long chain fatty acids and alcohols in aqueous solution are examples of the first kind, while electrolytes are examples of the second kind. Defining the concept of adsorption (adsorption is the enrichment of a component at the interface compared with the bulk region) quantitatively as the surface excess, a thermodynamic relation can be derived between the extent of adsorption and the change in surface tension of the solution with concentration. This is the famous Gibbs adsorption equation.

4.15 GIBBS ADSORPTION ISOTHERM

For the system in Figs 4.22 and 4.23 under condition of equilibrium, the first fundamental equation is:

$$dU = TdS - PdV + \gamma dA + \Sigma \mu_i dn_i \tag{4.42}$$

where γ is the surface tension, μ_1 is the chemical potential of the component *i*, which is same everywhere and n_i is the number of moles of component *i*.

Equation (4.42), written for the α -phase only, takes the form,

$$dU_{\alpha} = TdS_{\alpha} - P_{\alpha}dV_{\alpha} + \Sigma\mu_i dn_i^{\ \alpha}$$
(4.43)

and that for the β phase is

$$dU_{\beta} = TdS_{\beta} - P_{\beta}dV_{\beta} + \Sigma \mu_i dn_i^{\beta}$$
(4.44)

In the above equations, U, U_{α} and U_{β} are the internal energy of the whole system, of the α -phase and of the β -phase, respectively. Similar is the notation for S, V, P and n_i . Adding Eqs (4.43) and (4.44) and subtracting it from Eq. (4.42), we get

$$d[U - U_{\alpha} - U_{\beta}] = T_d[S - (S_{\alpha} + S_{\beta})] - PdV + P_{\alpha}dV_{\alpha} + P_{\beta}dV_{\beta} + \gamma dA + \Sigma \mu_i d[n_i - (n_i^{\alpha} + n_i^{\beta})]$$

If we define the internal energy, U^{σ} and entropy, S^{σ} of the interface as

$$U^{\sigma} = U - (U^{\alpha} - U^{\beta})$$
 and $S^{\sigma} = S - (S_{\alpha} + S_{\beta})$

then the above equation changes to

$$dU^{\sigma} = TdS^{\sigma} - PdV + P_{\alpha}dV_{\alpha} + P_{\beta}dV_{\beta} + \gamma dA + \Sigma \mu_{i}dn_{i}^{\sigma}$$

where n_i^{σ} is the number of moles of component *i* at the interface. If now the interface is considered to be planar then $P = P_{\alpha} = P_{\beta}$ which gives,

$$du^{\sigma} = TdS^{\sigma} + \gamma dA + \Sigma \mu_{i} dn_{i}^{\sigma}$$

[:: $V = V_{\alpha} + V_{\beta}$; the 2 dimensional interface has no volume] (4.45)

Integrating the above equation while holding *T*, γ and μ_i fixed we get,

$$u^{\sigma} = TS^{\sigma} + \gamma A + \Sigma \mu_i n_i^{\sigma}$$

which on complete differentiation gives

$$du^{\sigma} = TdS^{\sigma} + \gamma dA + \Sigma \mu_i dn_i^{\sigma} + S^{\sigma} dT + Ad\gamma + \Sigma n_i^{\sigma} d\mu_i$$
(4.46)

and finally comparing Eqs (4.45) and (4.46), we get,

 $S^{\sigma}dT + Ad\gamma + \Sigma n_i^{\sigma}d\mu_i = 0$

and under isothermal condition,

$$Ad\gamma + \Sigma n_i^{\sigma} d\mu_i = 0 \tag{4.47}$$

The above equation for a two-component solution in equilibrium with its vapour (one kind of solute in a solvent) is,

 $Ad\gamma + n_1^{\sigma}d\mu_i + n_2^{\sigma}d\mu_2 = 0$ [suffix 1 is used for the solvent, and 2 for the solute]

As discussed earlier, n_1^{σ} and n_2^{σ} depend on the position of the 2-dimensional dividing plane, and hence are not experimentally measurable quantities. As already mentioned the adsorption of the solute is measured relative to the solvent, as if, there is no adsorption of the solvent molecules at the 2-D interface. The dividing surface is now chosen to be situated such $n_1^{\sigma} = 0$, the above equation then reads

$$Ad\gamma + n_{2(1)}^{\sigma}(1) d\mu_2 = 0$$

where $n_{2(1)}^{\sigma}$ is the relative number of moles of the solute at the interface with respect to the solvent (this quantity can be shown to be independent of the exact location of the boundary) and is an experimentally measurable quantity. The relative surface excess of the solute is defined as

$$\Gamma_{2(1)} = \frac{n_{2(1)}^{\sigma}}{A}$$

which is now expressed as

$$\Gamma_{2(1)} = -\frac{d\gamma}{d\mu_2} \tag{4.48}$$

If the activity of the solute in the solution be a, then,

$$d\mu_2 = RTd \ln a$$

and using this in the above equation, we get

$$\Gamma_{2(1)} = -\frac{1}{RT} \frac{d\gamma}{d\ln a} = -\frac{a}{RT} \frac{d\gamma}{da}$$
(4.49)

which, in dilute solution can be written as

$$\Gamma_{2(1)} = -\frac{c}{RT}\frac{d\gamma}{dc} \tag{4.50}$$

where C is the molar concentration of the solute. Equations (4.47)–(4.50) are the various forms of the Gibbs adsorption isotherm, and which has been experimentally verified.

Equation (4.50) suggests that $\Gamma_{2(1)}$ is positive if the surface tension of the solution decreases with increase in concentration and vice-versa. On the basis of the variation of γ versus C, solutes are generally classified among three categories. In type I, Figure 4.24, the surface

tension increases slowly with increase in concentration. Examples are aqueous solution of electrolytes. The ions, by virtue of the ion-dipole forces, pull the water molecules inside the bulk of the liquid and greater work is to be done in bringing them at the surface. The surface tension therefore increases with increase in concentration; and consequently these species and negatively adsorbed at the interface.

Type II solutes include most organic compounds that have some degree of solubility in water. These molecules, e.g. phenol, have a polar group and a non-polar hydrophobic part. The polar group is involved in interaction with the water dipoles and is attracted inside water and projecting the hydrophobic polar group (Figure 4.25) outwards. Due



Figure 4.24 Variation of γ for different substances with concentration.

to an increase in their concentration at the interface, the surface tension decreases. The surface excess of these solutes is therefore positive.

Finally, there is the type III solutes; these are Na⁺ or K⁺ salts of long chain (number of C atoms in the chain > 5) fatty acids and alcohols; the surface tension of these solutions decreases very rapidly and almost linearly with concentration and thereafter remains almost constant. For these solutes, $\frac{d\gamma}{dC}$ is large negative and the surface excess is very high. These solutes, which decrease the surface tension considerably by strongly adsorbing at the

interface are called *surface active reagent*.

4.16 SURFACE FILMS ON LIQUIDS

There are a number of compounds (type III solutes) having a long hydrophobic chain,

terminated with a polar head like -COOH, -OH group or their Na⁺, K⁺ salts. These compounds are either solids or liquids with high boiling points: consequently, their vapour pressure is also a few mm of Hg. On adding such a substance to water, the molecules spread over the water surface; their polar heads peep into the water leaving the long hydrophobic chain afloat over the water surface. On increasing the concentration, a monomolecular film may be produced which corresponds to a compact packing of the molecules, all erected vertically, projecting the hydrophobic tail upwards (Figure 4.26). This is justified by Figure 4.27, where $T_{2(1)}$ for an aqueous solution of sodium dodecyl sulphate is plotted versus concentration. The saturation of $\Gamma_{2(1)}$ reveals the formation of monomolecular film.

Such a surface film is studied in the PLAWM (Pockels Langmuir-Adam-Wilson-McBain) through.

A thin rubber membrane attached to a float separates the clean water from its solution. The portion of the rubber membrane inside water is so convoluted that it can buckle easily to give an equalisation to any difference of hydrostatic pressure on the either side. Let γ_0 be the surface tension of pure water and γ be that of the solution. Since $\gamma_0 > \gamma$, a force, $\gamma_0 - \gamma$, which is purely a surface tension in origin, acts per unit length of the float (Figure 4.28). This force per unit length is defined as surface pressure π .



Figure 4.26 Hydrophobic molecules in aqueous solution at the Pockels point.





Figure 4.25 These substances are populated at the interface.



Figure 4.27 The measurement of a monomolecular film.



Figure 4.28 The PLAWM trough.

$$\pi = \gamma_0 - \gamma \tag{4.51}$$

Exactly in the same manner, as we have explained the pressure of a gas due to the impacts of the molecules on the wall of the container, the surface pressure can also be explained as due to the bombardment of the solutes on the float during their motion restricted over the interface. This force on the float can be measured by a torsion wire attached to it. The experiment involves the determination of the surface pressure with decreasing area of the solution by moving the rubber membrane to the left. An experimental plot of π versus area is shown in Figure 4.29. As the area decreases, the adsorption $\Gamma_{2(1)}$ increases; this increases the surface pressure. As the area is decreased beyond a certain point, called the Pockels point, the surface pressure begins to increase very sharply. At this point, the molecules are almost in contact with each other and strongly resist further compression. Langmuir found that this area divided by the number of molecules present in the film for all long chain fatty acids CH_3 (CH_2)_n COOH, (n = 14, 16 - 26) is independent of the value of n and is roughly 21 Å². The cross-sections of these molecules are therefore equal. Figure 4.30 gives another interesting feature. The cross-section of the isostearic acid is slightly more than that of stearic acid. This is due to the presence of the bulky tertiary carbon atom at the end of the chain. It is also seen that the monomolecular film of tri-p-cresyl phosphate is much more compressible than those of stearic and isostearic acids. This is probably due to their structural features (Figure 4.31).



Figure 4.29 The variation of surface pressure with the area.



Figure 4.30



Figure 4.31 Tri-p-cresyl phosphate.

4.17 EQUATION OF STATE OF A TWO-DIMENSIONAL IDEAL GAS

For solutes of type III, it is clear from Figure 4.24 that in the low concentration range (before the formation of the monomolecular film), the surface tension bears almost a linear relation with concentration:

Let us write,
$$\gamma = \gamma_0 - bc$$
 (4.52)

where γ and γ_0 are the surface tensions of the solution at concentration *C* and, of the pure water, respectively, and *b* is a characteristic constant.

$$\frac{d\gamma}{dc} = -b \tag{4.53}$$

The surface pressure,

$$\pi = \gamma_0 - \gamma = bc \tag{4.54}$$

Therefore from the Gibbs adsorption isotherm,

$$\Gamma_{2(1)} = -\frac{c}{RT} \frac{d\gamma}{dc} = \frac{bc}{RT} = \frac{\pi}{RT}; \Rightarrow \frac{n_{2(1)}}{A} = \frac{\pi}{RT}$$

$$\pi A = n_{2(1)}RT \text{ or } \pi = \Gamma_{2(1)}RT$$

$$(4.55)$$

or

which is exactly similar in form with the ideal gas equation PV = nRt or P = CRT. As explained earlier, the existence of this 2-dimensional pressure and the 2-dimensional concentration and, the similarity of Eq. (4.55) with the equation of state of a ideal gas prompts us to say that a surface film is an analogue of a 2-dimensional ideal gas (!). Equation (4.55) is therefore called the equation of state of 2-dimensional ideal gas. Moreover, again like the gas behaviour, Eq. (4.55) is obeyed only in the limiting condition of low Γ (the surface excess). Furthermore, the curves of π versus A (at fixed temperature) in Figure 4.30 show that they are very similar to the Andrew's isotherm of P versus V of a gas. A 2-dimensional van der Waals equation

$$\left(\pi + \frac{a}{A^2}\right)(A - b) = RT \tag{4.56}$$

may therefore be proposed empirically and tested.

Example 4.5

4.8 mL of glycerol trioleate [olive oil, $(C_{17}H_{33}COO)_3 C_3H_5$] is found to form a monomolecular film of area 2030 m². Calculate the thickness of the film and the cross-section of each molecule. Also calculate $T_{2(1)}$ for the film (given, density of glycerol trioleate is 0.9 gm ml⁻¹.

Solution

Molar mass of the oil = 884 g mol^{-1}

 $\therefore \qquad 4.8 \text{ mL} = 2.95 \times 10^{21} \text{ molecules} (4.89 \times 10^{-3} \text{ mol})$

If the thickness of the film be h, then (2030 m²) $h = 4.8 \text{ cm}^3 \Rightarrow h = 23.6 \text{ Å}$

:. Cross-section of each molecule = $\frac{2030 \text{ m}^2}{2.95 \times 10^{19}} = 68.80 \text{ }\dot{\text{A}}^2$

and $\Gamma_{2(1)} = \frac{4.89 \times 10^{-3}}{2030 \text{ m}^2}$ mole = 2.4×10^{-10} mol cm⁻²

Example 4.6

The surface tensions of 0.05 M and 0.127 M solutions of a surfactant are 67.7 and 60.1 dyne cm⁻¹, respectively at 20°C. Assuming this lowering of the surface tension with concentration as a linear calculate the surface excess of the surfactant at a concentration of 0.053 M at this temperature. Also find out π and its equivalent 3-dimensional pressure (assume that the diameter of the molecule is 4 Å).

Α

Solution

Assuming the variation of surface tension with concentration as linear,

$$\begin{aligned} \frac{d\gamma}{dc} &= \frac{\gamma_2 - \gamma_1}{c_2 - c_1} = \frac{-7.6 \text{ dyn cm}^{-1}}{0.077 \text{ M}} = -98.7 \text{ dyn cm}^{-1} \text{ M}^{-1} \\ \therefore \qquad & \Gamma_{2(1)} = -\frac{c}{RT} \frac{d\gamma}{dc} \\ &= -\frac{(0.053 \text{ M})}{(8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}) (293 \text{ K})} [-98.7 \text{ dyn cm}^{-1} \text{ M}^{-1}] \\ &= 2.15 \times 10^{-10} \text{ mol cm}^{-2} \\ \therefore \qquad & \pi = \Gamma_{2(1)} RT = (2.15 \times 10^{-10} \text{ mol cm}^{-2}) (8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}) (293 \text{ K}) \\ &= 5.24 \text{ dyn cm}^{-1} \end{aligned}$$

The equivalent 3-dimensional pressure is obtained by dividing π with the thickness of the molecule (4 × 10⁻⁸ cm)

:.
$$P = \frac{\pi}{h} = \frac{5.24 \text{ dyn cm}^{-1}}{4 \times 10^{-8} \text{ cm}} = 1.31 \times 10^8 \text{ dyn cm}^{-2} \approx 130 \text{ atm}$$

This calculation shows that the lateral compression in the film is alarming at the molecular level.

4.18 GAS ADSORPTION AT SOLID SURFACES

In the preceding chapters, we studied the adsorption of solute molecules from liquid solutions at the liquid-vapour interface. In this section, we will study the adsorption of gas molecules (adsorbate) on the surface of a solid (adsorbent). Intense research in this field is now undergoing for the technological development with minimum possible pollution, starting from electrical lamps to three-way automobile catalytic converter.

When a molecule approaches a solid surface it experiences a net attractive potential energy which is exactly similar to that between two molecules; but at close separation it is attracted by a number of closely-spaced solid atoms. However, there is a point at which the net attractive potential is the most negative, and the molecule is then said to be arrested on the surface, i.e. adsorbed. During this adsorption process,

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$$A(g) + - \stackrel{|}{S} - \longrightarrow - \stackrel{|}{S} -$$

where A is a molecule in the gas phase, $-S^-$ is a vacant surface atom and $-S^-$ is the adsorbed state) which is spontaneous ($\Delta G < 0$ at constant T and P), the molecule A

certainly loses it translational and rotational degrees of freedom; and the entropy change of adsorption is therefore negative. The heat of adsorption $\Delta H_{\rm ad}$, which is equal to $\Delta G_{\rm ad} + T\Delta S_{\rm ad}$, is therefore negative. In general, adsorption is therefore an exothermic process. An exception is the adsorption of H₂ on glass, for which $\Delta H_{\rm ad}$ is positive. One possible explanation is: after adsorption, H₂ dissociates and the adsorbed H atoms gain some translational mobility over the surface. This makes $\Delta S_{\rm ad}$ positive, which in turn makes $\Delta H_{\rm ad}$ slightly positive.

4.18.1 Physisorption and Chemisorption

Adsorption in the gas phase is classified either as physisorption or chemisorption. If the weak, long range and non specific intermolecular van der Waals forces (which are responsible for the condensation of a vapour into liquid) are responsible for holding the molecules on the surface, then it is called physisorption. Physisorption is therefore only important for gases below their critical temperature, i.e. for vapours. On the other hand, in chemisorption, the molecules are held over the surface by relatively strong chemical bonds (which are very specific and short range forces) with the surface atoms and may occur at both above and below the critical temperature.

Physisorption is therefore nonspecific but chemisorption is highly specific. For example, N_2 can be *physisorbed* on any surface, provided the temperature is below its critical temperature; but N_2 can be *chemisorbed* on Fe, W, Ti, etc., but not on Ag, Ni, Cu, etc. Solid gold can chemisorb O_2 , C_2H_2 , CO but not H_2 , CO_2 or N_2 .

The heat of physisorption ΔH_{phys} , is usually less (<35 kJ mol⁻¹) and is of the order of the heat of condensation of the vapour. On the other hand, the heat of chemisorption is usually much higher (40 – 400 kJ mol⁻¹).

Since during physisorption, there is only a redistribution of the electron density in the adsorbate and adsorbent, separately, a physisorbed molecule retains its identity. A physisorbed gas may be desorbed by lowering the pressure and increasing the temperature. On the other hand, since during chemisorption, there is an exchange of electron density between the molecules and the surface atoms, the molecule may dissociate and change its identity in the chemisorbed state. For example, when a system of O_2 gas adsorbed over charcoal is heated, the gas comes out as a mixture of CO and CO_2 .

The chemisorbed layer is only one molecule in thickness whereas a physisorbed layer is multimolecule in thickness. However, physisorption may take place on the top of a chemisorbed layer.

The equilibrium of the physisorption is attained very fast whereas the rate of chemisorption may be slow and can be increased by increasing the temperature. This fact indicates the presence of an activation energy for chemisorption. In fact, it may happen that, a molecule first enters into the physisorbed state and then slowly moves into the chemisorbed state. Figure 4.32 illustrates some special cases, where the potential energy is plotted as a function of the distance of the molecule from the surface.



Figure 4.32(a) The molecule AB is first physically adsorbed at point X and then quickly passes on to the state where dissociation and subsequent adsorption of the atoms A and B takes place (point Y).

In Figure 4.32(a), the molecule AB is first physically adsorbed (point X) and then quickly moves into a state, in which the atoms A and B are chemisorbed. This is called *dissociative* chemisorption. Here, both the physisorption and chemisorption are fast processes. In Figure 4.32(b), again the molecule AB is physisorbed and subsequently passes over quickly into the *non-dissociative chemisorbed state*. Again, the rate of both the processes are very fast. In Figure 4.32(c), there is a potential barrier between the physisorbed AB molecule (point X) and the chemisorbed atoms A and B (point Y). At low temperature, physisorption takes place and it is fast. Chemsorption cannot take place at this low temperature because the physisorbed AB molecules can not acquire the energy to surmount the barrier from the low thermal energy kT. However, when the temperature is increased, the thermal energy increases and the physisorbed molecules can now shake themselves off, cross the barrier and move into the *dissociative chemisorbed state*. This passage is therefore an activated process and its rate increases with increase in temperature. So, while physisorption is always fast, chemisorption may be a slow as well as a fast process. These cases can also be understood with reference to Figure 4.33. Figure 4.33(a), where there is no barrier to adsorption, is representing the cases in Figure 4.32(a) and 4.32(b). The molecules which strike the surface with high kinetic energy, even after a loss, bounce back to the gas phase. As the temperature decreases, the average kinetic energy decreases and now they can be trapped in the well. In Figure 4.33(b), there is a barrier to adsorption and is a representative of the case in Figure 4.32(c). At very low temperature, the molecules are only physically adsorbed. On increasing the temperature, some of the molecules now cross the barrier and get trapped in the chemisorbed state. Here also, if a molecule strikes the surface with very high kinetic energy, it just bounces off the surface. An example of the case in Figure 4.32(c) is H₂ and Ni. Figure 4.34 shows the temperature dependence of the extent of adsorption. AB is the locus of the normal decrease in the extent of physisorption with increase in temperature; this happens in the low temperature range. As the temperature is increased, there is a non equilibrium transition from the physisorbed state (called the precursor state of chemisorption) to the chemisorbed state, where again the extent of adsorption decreases with increase in temperature. On cooling, CB is not retraced but some combination of BC and CC' is observed.



Figure 4.32(b) The molecule AB is first physically adsorbed (point X) and is then chemically adsorbed (nondissociate) at point Y. This is a fast process.

Figure 4.32(c) The passage from physisorption to chemisortption is slow due tho the requirement of the activation energy Y.



Distance from the surface

Figure 4.33(a) Chemisorption may be a fast as well as a slow process.



Figure 4.34

4.18.2 Adsorption Isotherm

Adsorption studies are done over atomically clean surfaces. However, under ordinary conditions, the surface of a solid remains adsorbed by the different gases of the atmosphere. Therefore to produce an atomically clean surface, the surface may be heated at ultra high vacuum (pressure not exceeding 5×10^{-10} torr) or a crystal may be cleaved under high vacuum.

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It is always assumed that, the molecules in the gas phase over the solid are in dynamic equilibrium with those in the adsorbed layer. The amount or the volume of the gas adsorbed at a fixed temperature varies with pressure of the overlying gas. An adsorption isotherm is an equation which gives this variation at a fixed temperature.

4.18.3 Freundlich Adsorption Isotherm

It is one of the earliest adsorption isotherms proposed on purely empirical ground:

$$v = kP^n \tag{4.57}$$

where v is the volume of the gas adsorbed at the equilibrium pressure P, and k and n are constants (0 < n < 1). This shows that the amount of adsorption increases with P, but not as rapidly as P. Taking logarithm on Eq. (4.57)

$$\log v = \log k + n \log P \tag{4.58}$$

A plot of $\log v$ versus $\log P$ is therefore expected to be a straight line with intercept $\log k$ and slope n. The values of k and n can therefore be obtained from such a slope (if the equation is found correct!). The Freundlich adsorption isotherm has however been found invalid at too high and too low pressures. This isotherm can also be applied to the adsorption of solutes from solution. Here, the equilibrium concentration C replaces P and the mass of the solute adsorbed per gram of the adsorbent m replaces v:

$$m = kC^n \tag{4.59}$$

4.18.4 Langmuir Adsorption Isotherm

In 1918, Langmuir used the kinetic theory to arrive at an equation of adsorption isotherm. He assumed that:

- (i) A solid surface is uniform and has a certain number of equivalent sites each of which may be occupied by only one molecule of the adsorbate.
- (ii) Once adsorbed, the molecules are localised (that is, the activation energy hindering migration to an adjacent site is much greater than the thermal energy kT).
- (iii) The heat of adsorption per site remains constant irrespective of the fraction of the sites covered. This means that the adsorbed molecules do not interact laterally with each other.
- (iv) Adsorbing molecules are continually colliding the surface. If they impact on a vacant adsorption site, it may be adsorbed but if it happens to collide a filled site, it bounces back into the gas phase.

 (v) A dynamic equilibrium exists between the molecules in the overlying gas and those in the adsorbed layer at a fixed temperature and pressure.

A non-dissociative adsorption of a molecule can therefore be represented as

$$A(g) + - \stackrel{|}{S} - \stackrel{k_a}{\underset{k_d}{\longleftarrow}} - \stackrel{A}{S} -$$
Α

where A is a molecule in the gas phase, $-\dot{S}$ - is a vacant surface site, $-\dot{S}$ - is the adsorbed molecule and, k_a and k_d are the rate constants for the adsorption and desorption steps, respectively. Let N be the total number of sites and say θ be the fraction of these sites occupied at some instant when the pressure in the gas phase is *P*. The number of vacant and filled sites at this instant are therefore, $(1 - \theta) N$ and $N\theta$, respectively. The rate of adsorption v_a is directly proportional to the rate of striking of the molecules on the surface and to the number of vacant sites. The first of these two factors depends on the pressure of the gas at a fixed temperature. Therefore, the rate of adsorption is give by:

$$v_a = k_a P(1 - \theta)N \tag{4.60}$$

The rate of desorption v_d depends (at a fixed temperature) on the number of occupied sites $N\theta$. So,

$$v_d = k_d \, N\theta \tag{4.61}$$

At equilibrium, these two rates are equal;

$$k_a P(1 - \theta)N = k_d N\theta$$

or

or

$$\frac{1-\theta}{\theta} = \frac{1}{KP}, \text{ where } K = \frac{k_a}{k_d}, \text{ the equilibrium constant of the adsorption,}$$
$$\theta = \frac{KP}{KP}$$
(4.62)

This θ is called the surface coverage.

1 + KP

Surface coverage,
$$\theta = \frac{\text{no. of sites filled up at equilibrium}}{\text{total number of sites present on the surface}}$$

Equation (4.62) is the Langmuir adsorption isotherm which gives the variation of the surface coverage with pressure.

In the limit
$$P \to 0, \theta = \frac{KP}{1 + KP} = 0$$

In the limit $KP \ll 1$, when the pressure is very low, $\theta = \frac{KP}{1 + \text{very small no.}} \approx KP$

In the limit *KP* >> 1, when the pressure is very high, $\theta = \frac{KP}{1 + KP} \approx 1$



Figure 4.35 Plots of θ vs ρ at temperatures 300 K, 400 K and 500 K for CO on charcoal.

These features are shown in Figure 4.35. Initially θ increases linearly with pressure; at intermediate pressures, the linearity is broken, but θ goes on increasing and finally approaches unity asymptotically at very high pressure. The Langmuir adsorption isotherm can also be written as

$$\frac{1}{\theta} = 1 + \frac{1}{KP} \tag{4.63a}$$

and which can be experimentally verified by plotting $1/\theta$ versus 1/P. Adsorption of different gases on different solids will have different slopes, but their intercepts are all expected to be unity. This has experimentally been confirmed for a number of cases (Figure 4.36). More generally, the adsorption study is made by measuring the volume of the gas adsorbed. If v be the volume of the gas adsorbed when the surface coverage is θ and v_m be the volume of the gas adsorbed when the surface coverage is θ and v_m be the volume of the gas adsorbed when the figure 4.36). More generally for a number of the gas adsorbed when the surface coverage is θ and v_m be the volume of the gas adsorbed when the surface coverage is θ and v_m be the volume of the gas adsorbed when infinitely high pressure is applied, i.e. when $\theta = 1$, and a complete monolayer formed then

$$\theta = \frac{v}{v_m} = \frac{KP}{1 + KP} \tag{4.63b}$$

and the Langmuir adsorption isotherm can be put in the form

$$\frac{P}{v} = \frac{1}{v_m K} + \frac{P}{v_m} \tag{4.64}$$

An experimental verification of this equation is possible by plotting P/v vs. P. A straight line with positive slope and intercept is obtained (Figure 4.37). From the inverse of the slope, $v_{m\nu}$ the volume required to form a complete monolayer can be evaluated from which the surface area of the solid can be estimated.



Figure 4.36 Plots of $1/\theta$ versus $1/\rho$ for O₂ and CO on silica.



Figure 4.37 A verification of the Langmuir adsorption isotherm.

4.18.4.1 Determination of the Surface Area of a Solid from Langmuir Adsorption Isotherm

A plot as given in Figure 4.37 is first made. From its slope, v_m is evaluated and then reduced to NTP. The number of molecules present in v_m (in ml at NTP) volume of the gas is $\frac{V_m(\text{in ml at NTP}) N_0}{22414}$, where N_0 is the Avogadro number. If the cross-section of each molecule, A, is known, a priori, then the surface area per gram of the solid is

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 $S = \frac{v_m (\text{in ml at NTP}) N_0 \text{ A}}{22414(\text{m})}; \text{ m is the mass of the solid used. This specific surface area}$

S is one of the fundamental parameters used in choosing the appropriate surface in heterogeneous catalysis.

4.18.4.2 Isosteric Heat of Adsorption

It has already been mentioned that adsorption is an exothermic process. The heat of adsorption is usually measured calorimetrically by determining the amount of heat evolved when a certain amount of gas is allowed to adsorb on a clean surface. When this measurement is made at different surface coverages and the heat of adsorption so obtained, plotted versus θ , a cure as shown in Figure 4.38 is observed. The figure clearly shows that ΔH_{ad} is not actually independent of the surface coverage (so the third postulate of Langmuir is not correct). One reason is that as the surface coverage increases, the closely packed adsorbed molecules may laterally interact with each other and change the heat of adsorption. In order to take into account the effect of this lateral interaction, the *isosteric heat of adsorption*, which is the enthalpy of adsorption at a fixed surface coverage θ , is defined as:



Figure 4.38 The heat of adsorption varies with the surface coverage

Since the equilibrium constant of adsorption K changes with temperature different curves of θ versus P is obtained at different temperatures (Figure 4.39). This temperature dependence of K can be used in determining the isosteric heat of adsorption. From Eq. (4.62), we can write,

$$K = \frac{\theta}{1 - \theta} \frac{1}{P}$$

taking logarithm on both sides,

$$\ln K = \ln \frac{\theta}{1-\theta} - \ln P$$

and differentiating with respect to temperature at constant θ ,

$$\left(\frac{\partial \ln K}{\partial T}\right)_{\theta} = -\left(\frac{\partial \ln P}{\partial T}\right)_{\theta}$$

and combining with Eq. (4.65), we get,

$$\left(\frac{\partial \ln P}{\partial T} \right)_{\theta} = -\frac{\Delta H_{ad}}{RT^2}$$

$$\left[\frac{\partial \ln P}{\partial \left(\frac{1}{T} \right)} \right]_{\theta} = \frac{\Delta H_{ad}}{R}$$

$$(4.66)$$

or

As shown in Figure 4.39, from the isotherms at different temperatures, $\ln P$ data are plotted versus 1/T corresponding to a fixed θ ; the plot will be a straight line (Figure 4.40) whose slope is $\Delta H_{\rm ad}/R$. The measurement of the slope of this plot enables us to calculate the isosteric heat of adsorption. The free energy of adsorption $\Delta G_{\rm ad}$, can be calculated directly from the value of K (obtained by dividing the slope of the line in Figure 4.37 by its intercept) and, this value can be combined with isosteric heat of adsorption to evaluate the entropy of adsorption.



Figure 4.39 Determination of isosteric heat of adsorption, $T_1 > T_2 > T_3 > T_4$. P_1 , P_2 and P_3 are the pressures for a fixed at θ temperatures T_3 , T_2 and T_1 .

4.44



Figure 4.40 Plot of ln P versus 1/T the (from the data of Figure 4.39)

4.18.4.3 Langmuir Adsorption Isotherm for a Dissociative Adsorption

As explained earlier, if a diatomic molecule undergoes fragmentation into the atoms during adsorption then the form of the Langmuir adsorption isotherm would be slightly different. The process is now represented as:

$$\mathbf{A}_{2}(\mathbf{g}) + - \underbrace{\mathbf{S}}_{|} - \underbrace{\mathbf{S}}_{|} - \underbrace{\mathbf{k}_{a}}_{k_{d}} - \underbrace{\mathbf{S}}_{|} - \underbrace{\mathbf{S}}_{|} - \underbrace{\mathbf{S}}_{|}$$

The rate of adsorption is again proportional to the pressure of the overlying gas, but now, when two sites are required for adsorption, the rate is second order in $N(1 - \theta)$; therefore,

$$v_a = k_a P N^2 (1 - \theta)^2$$
(4.67)

..

Similarly, two adsorption sites are required for desorption and therefore, the rate of desorption

$$v_d = k_d N^2 \theta^2 \tag{4.68}$$

At equilibrium,

$$\begin{aligned} v_a &= v_d \\ k_a \, P N^2 (1-\theta)^2 &= k_d \, N^2 \theta^2 \\ \theta &= \frac{\sqrt{KP}}{1+\sqrt{KP}} \end{aligned}$$

or

The variation of θ with pressure is again almost similar to that in the non-dissociative case (Figure 4.35) but the dependence is now much weaker.

Example 4.7

When two different molecules A and B compete for the same sites of a surface, derive expressions for the surface coverages θ_A and θ_B of the two kinds.

Solution

Let the partial pressure of the gas A be P_A and that of the gas B be P_B . Let θ_A and θ_B are the fractions of the total sites adsorbed by A and B molecules, respectively, at equilibrium. Then the condition of equilibrium of the gas A is given as:

$$k_{dA} \ N\theta_A = k_{aA} \ P_A N(1 - \theta_A - \theta_B) \tag{I}$$

and that of gas B is

$$k_{dB} \ N\theta_B = k_{aB} \ P_B N(1 - \theta_A - \theta_B) \tag{II}$$

Solving these two simultaneous equations for θ_A and θ_B , we find

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \text{ and } \theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B}$$
$$K_A = \frac{k_{aA}}{k_{dA}} \text{ and } K_B = \frac{k_{aB}}{k_{dB}}$$

where

One of the restrictions in using Langmuir adsorption isotherm is that it does not allow for the possibility that the adsorbed film thickness may be more than one molecule. There are ample examples where multilayer formation takes place, and then the enthalpy of adsorption in the first layer will be certainly different from the enthalpy of adsorption in the higher stacks (the strength of adsorbent-adsorbate bond is certainly different from the adsorbate-adsorbate bonds). Langmuir adsorption isotherm is best in analysing the data of chemisorbed systems where the adsorbed layer can not go beyond one molecule. In fact, there are five different kinds of adsorption isotherm (Figure 4.41). The type-I can only be explained by the Langmuir adsorption isotherm. This type is typically observed in chemisorption. Type-II is very common, particularly in physisorption, where multilayer formation takes place. Type-III curves are relatively rare and apparently correspond to situations where the heat of adsorption is either equal or less than the heat of condensation of the vapour. Examples of type-III are: adsorptions of N_2 on ice, adsorption of H_2O on graphitized carbons or polyethylene. In both the types (II and III), the curve approaches the line at P^0 , asymptotically. The behaviour in types IV and V is indicative of the process of capillary condensation and may exhibit hysteresis effect. Again, by introducing some simplifying assumptions, Brunauer, Emmett and Teller (BET) modified the Langmuir adsorption isotherm. The assumptions are:

- (i) The surface contains some definite number of equivalent sites of uniform energy.
- (ii) Stacking of molecular layers can take place on the first layer. That is, second layer adsorption can take place on the top of the first, third on the top of the second: fourth on the top third and so on.
- (iii) A dynamic equilibrium exists between the molecules of any two successive layers.
- (iv) The heat of adsorption in the first layer is ΔH_{ad} , which depends on the nature of the adsorbate and the adsorbent, but that in the 2nd, 3rd, 4th, etc. layers are all equal, and is equal to the heat of condensation of the vapour.



Figure 4.41 The five kinds of isotherm. P⁰ is the saturated vapour pressure. The type VI kind is a very recent type observed for noble gas adsorption on well defined uniform solids such as highly oriented pyrolytic graphite.

Derivation of BET Adsorption Isotherm 4.18.5.1

Consider the equilibrium between adsorption and desorption in the first layer:

$$A(g) + S \rightleftharpoons AS$$

If k_{a1} and k_{d1} are the rate constants for the adsorption and desorption processes and θ_0 and θ_1 are the fractions of the surface sites lying vacant and, filled up by one molecule layer, respectively, then

 $k_{a1} \, P(\theta_0) = k_{d1} \; \theta_1,$ where P is the pressure of the overlying gas

$$\frac{k_{a1}}{k_{d1}} = \frac{\theta_1}{\theta_o P} \Longrightarrow K_1 = \frac{\theta_1}{P\theta_0}$$
(4.69)

or

If this was the only story then, Eq. (4.69) would be

 $K_1 = \frac{\theta}{P(1-\theta)}$

 $\theta = \frac{K_1 P}{(1 + K_1 P)}$

where θ is the surface coverage. Rearrangement of this equation gives:

$$\frac{(1-\theta)}{\theta} = \frac{1}{K_1 P}$$
$$\frac{1}{\theta} = \frac{(1+K_1 P)}{K_1 P}$$

or

 \Rightarrow

the Langmuir adsorption isotherm [(Eq. 4.63(b)].

 K_1 is the equilibrium constant of adsorption in the first layer. Now, consider the formation of the second layer:

$$A(g) + AS \rightleftharpoons A_2S$$

Exactly, as before we find

$$K_2 = \frac{\theta_2}{\theta_1 P} \tag{4.70}$$

where θ_2 is the fraction of the surface sites which are covered with an adsorbed layer of two molecules in thickness, and K_2 is the corresponding equilibrium constant. Going on building stacks one above the other we write:

--

$$\begin{array}{lll} \mathbf{A}(\mathbf{g}) + \mathbf{A}_{2}\mathbf{S} \rightleftharpoons \mathbf{A}_{3}\mathbf{S} & : & K_{3} = \theta_{3}/\theta_{2}P \\ \mathbf{A} & + \mathbf{A}_{3}\mathbf{S} \rightleftharpoons \mathbf{A}_{4}\mathbf{S} & : & K_{4} = \theta_{4}/\theta_{3}P \\ \vdots & \vdots & \vdots \\ \mathbf{A} & + \mathbf{A}_{n-1}\mathbf{S} \rightleftharpoons \mathbf{A}_{n}\mathbf{S} : & K_{n} = \theta_{n}/\theta_{n-1}P \end{array}$$

$$(4.71)$$

4.48

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where θ_n is the fraction of the surface sites covered by an adsorbed layer of *n*-molecules in thickness.

From the fourth postulate, we find that the equilibrium constant K_2 , K_3 , ..., K_n are all equal (this is justified because the force with which a molecule is held on the third layer is not different from that which holds a molecule in the fourth layer; they are all adsorbate forces) and equal to that of the condensation of the vapour; that is:

$$K_2 = K_3 = \ldots = K_n = K$$

where *K* is the equilibrium constant of the process:

$$\operatorname{vap}(P^0) \rightleftharpoons \operatorname{Liquid}; K = \frac{1}{P^0}; P^0 \text{ is the saturated vapour pressure}$$
(4.72)

From Eqs (4.70) and (4.71), we find

$$\theta_2 = \theta_1 KP, \ \theta_3 = \theta_2 KP = \theta_1 (KP)^2; \ \theta_4 = \theta_1 (KP)^3$$

and hence in general

$$\theta_n = \theta_1 (KP)^{n-1} \tag{4.73}$$

..

The sum of θ_0 and all the θ_n 's is unity, i.e.

or
$$1 = \theta_0 + \Sigma \theta_n$$
$$1 = \theta_0 + \{\theta_1 + \theta_1 (KP) + \theta_1 (KP)^2 + ...\}$$

or
$$1 = \theta_0 + \theta_1 \{1 + (KP) + (KP)^2 + ...\}$$

or
$$1 = \frac{\theta_1}{K_1 P} + \frac{\theta_1}{1 - KP} = \theta_1 \frac{1 - KP + K_1 P}{K_1 P (1 - KP)}$$

$$\theta_1 = \frac{CKP (1 - KP)}{[1 + (C - 1)KP]} [\text{where } C = K_1 / K]$$
(4.74)

where $C = K_1/K$. Let N_m be the total number of surface sites present over the surface, and N be the total number of molecules adsorbed on the surface, then

$$N = N_m \left[1.\theta_1 + 2\theta_2 + 3\theta_3 + \cdots \right]$$
$$\frac{N}{N_m} = \theta_1 \left[1 + 2KP + 3(KP)^2 + \cdots \right] \text{ using Eq. (4.73)}$$

or

or

$$= \frac{\theta_1}{(1 - KP)^2}$$
$$= \frac{CKP(1 - KP)}{[1 + (C - 1)KP](1 - KP]^2}$$

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or

$$N/N_m = CKP/[1 + (C - 1) KP] [1 - KP]$$
(4.75)

If v be the total volume of the gas adsorbed over the solid and v_m be the volume of the gas required to form a complete monolayer then

$$\frac{N}{N_m} = \frac{v}{v_m}$$

with which Eq. (4.75) changes to

$$\frac{v}{v_m} = \frac{CKP}{[1 + (C - 1)KP][1 - KP]}$$

and using Eq. (4.72),

$$\frac{v}{v_m} = \frac{C(P/P^0)}{[1 + (C - 1)P/P^0][1 - P/P^0]}$$

$$v = \frac{v_m CP}{(P^0 - P)[1 + (C - 1)P/P^0]}$$
(4.76)

or

which is the BET adsorption isotherm. This equation clearly shows that $V \rightarrow \alpha$ as $P \rightarrow P^0$ (this is observed in types II and III curves). An immediate explanation is that as the saturated vapour pressure is approached, the adsorbed layer seems to change into the liquefied state of the vapour, which would otherwise occur at P^0 in absence of any surface. Equation (4.76) can also be written as

$$\frac{P}{v(P^0 - P)} = \frac{1}{v_m C} + \frac{(C - 1)}{v_m C} \frac{P}{P^0}$$
(4.77)

which demands that a plot of $\frac{P}{v(P^0 - P)}$ versus P/P^0 will be a straight line with slope

 $\frac{(C-1)}{v_m C}$ and intercept $\frac{1}{v_m C}$. Taking the inverse of the sum of the slope and intercept, we can get the value of v_m . In many cases, this expectation has been found correct, and therefore, as we have done earlier, for such surfaces, the specific surface area of the solid can be estimated if the cross section of each molecule is known, a priori.

The adjustable parameter *C*, as it is called, can be correlated to the heat of adsorption in the first layer ΔH_{ad} , and the heat of condensation ΔH_C as follows:

$$C = \frac{K_1}{K} = \frac{e^{-\frac{\Delta G_1^\circ}{RT}}}{e^{-\frac{\Delta G_C^\circ}{RT}}} = \frac{e^{-\frac{\Delta H_{ad}^\circ}{RT}} \cdot e^{\frac{\Delta S_1^\circ}{R}}}{e^{-\frac{\Delta H_C^\circ}{RT}} \cdot e^{\frac{\Delta S_C^\circ}{R}}}$$

4.50

where ΔG° , ΔH° and ΔS° are the standard free energy, enthalpy and entropy of adsorption. With suffix 1, they refer to the first layer, and with suffix *C*, they refer to the next successive layers, or the process of condensation. Without much error, it can be argued that wherever a molecule is adsorbed, it always loses the entropy to the same extent irrespective of, in which layer it is trapped, i.e. $\Delta S_{1}^{\circ} \approx \Delta S_{C}^{\circ}$. The above equation therefore changes to

$$C \approx \exp\left\{-\frac{(\Delta H_{ad}^{\circ} - \Delta H_{C}^{\circ})}{RT}\right\}$$
(4.78)

4.18.5.2 Explanation of the Five Kinds of Adsorption Isotherms by BET Equation

Type I We know that the curve of this type represents a purely chemisorbed state where the thickness of the adsorbed layer is only one-molecule. This happens at a pressure much lower than the saturated vapour pressure ($P^{\circ} >> P$). Furthermore, the enthalpy of adsorption in the first layer is also much greater than the entahlpy of condensation, i.e. C >> 1. Moreover, since we have seen that the Langmuir adsorption isotherm can explain this kind of curve, it is possible to derive the Langmuir equation from the BET under this condition of C >> 1 and $P^{\circ} >> P$. We do it as follows: $P^{\circ} >> P \Rightarrow P^{\circ} - P \approx P^{\circ}$ and as $C >> 1 \Rightarrow C - 1 \approx C$ With these results, Eq. (4.77) changes to

$$\frac{P}{vP^{\circ}} = \frac{1}{v_mC} + \frac{1}{v_m}\frac{P}{P^{\circ}} \implies \frac{P}{v} = \frac{P^{\circ}}{v_mC} + \frac{P}{v_m} \implies \frac{P}{v} = \frac{1}{v_mK_1} + \frac{P}{v_m}$$

which is the Langmuir equation.

- **Type II** When *C* is greater than unity which is possible if $\Delta H_{ad} > \Delta H_C$, the curves of Type II are obtained. Adsorption, here takes place, preferentially on the first layer; and after almost complete formation of the monolayer, which is indicated by the knee of the curve, multilayer formation takes place.
- **Type III** If $\Delta H_{ad} < \Delta H_C$, *C* will be less then unity. Under this condition, curves of Type III are observed. Here, multilayer formation takes place from the very beginning.

Type IV and Type V

These curves are, as such, very difficult to explain from the BET equation. However, the similarity of Types II and III with the first part of IV and V, respectively, suggests that $\Delta H_{ad} > \Delta H_C$ for Type IV and $\Delta H_{ad} < \Delta H_C$ for Type V. But, in contrast to the steep increase in adsorption for types II and III as P° is approached, there is a saturation in Types IV and V well before P° is reached. This is due to the condensation of the vapour within capillaries (which may be present in the solid just under its skin) of pore size not exceeding 5 nm. Recall from the Kelvin equation that the vapour condenses at a pressure much lower than the saturated vapour pressure inside a capillary if the liquid wets the surface.

4.19 RATE OF SURFACE ADSORPTION

The surface of a solid has about 10^{15} atoms per square centimetre, and the Langmuir equation assumed that each of these atoms, i.e. a surface site, can hold-on one adsorbate molecule. Now, if a molecule strikes the surface, it is not that it will be immediately adsorbed. If the energy of the striking molecule could be dissipated as heat, the molecule will be adsorbed; otherwise, the molecule will translate over the surface until a vibration knocks it off the surface to the overlying gas again. The sticking probability S, is defined as the fraction of the total number of strikes on the surface that leads to a successful adsorption.

$$S = \frac{\text{rate of adsorption of molecules on the surface}}{\text{rate of striking of molecules on the surface}}$$
(4.79)

The denominator can be calculated using the kinetic theory of gas and the numerator can be calculated using various techniques, e.g. by measuring the rate of decrease of pressure of the gas with time. According to Langmuir adsorption isotherm,

$$S = \frac{k_a \ N(1-\theta)}{Z_W} = S_0 \ (1-\theta)$$
(4.80)

where k_a is the rate constant of adsorption, N is the total number of sites present on the surface and Z_W is the striking rate of the molecules on the surface; the parameter $k_a N/Z_W$ is finally replaced by S_0 , the sticking probability at $\theta = 0$.

Example 4.8

Calculate the maximum rate of adsorption of oxygen molecules over a clean metal surface at 298 K and at a pressure 10^{-6} Torr. Assume that there are 10^{15} atoms per cm² of the surface.

Solution

Maximum rate of adsorption means striking probability S = 1.

Form the result in kinetic theory, $Z_W = \frac{1}{4} n \langle c \rangle$

$$\begin{split} Z_W &= \frac{1}{4} \Biggl(\frac{10^{-6}}{760} \text{ atm} \Biggr) \Biggl(\frac{6.023 \times 10^{23} \text{ mol}^{-1}}{82.05 \text{ (cm}^3 \text{ atm } \text{K}^{-1} \text{ mol}^{-1})} \Biggr) \times \sqrt{\frac{8 \times (8.314 \times 10^7 \text{ erg } \text{K}^{-1} \text{ mol}^{-1}) \text{ (298 K)}}{3.14 \times 32 \text{ g mol}^{-1}}} \\ &= 3.6 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1} \end{split}$$

Therefore the maximum rate of adsorption

$$v_a = \frac{3.6 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}}{10^{15} \text{ cm}^{-2}} = 0.36 \text{ sites per sec.}$$

Therefore in one second, 36 percent of the surface will be covered by the monolayer.

This express the exposure of a surface towards the gas, the surface scientists have defined the unit: $1 \text{ Langmuir} = 10^{-6} \text{ Torr s}$. The above problem shows that, the exposure of surface to 1 Langmuir leads to 36 percent of surface coverage. The exposure of the surface to two Langmuir (i.e., a 2 second exposure at a pressure of 10^{-6} Torr or one second exposure at a pressure of 2×10^{-6} Torr) would then result in 72 percent surface coverage. In the above calculation, we have considered the sticking probability to be unit; in fact it is less than one. So the maximum rate of adsorption is less than the above value. For example, if the sticking probability is 0.8, then the maximum rate of adsorption would be 36×0.8 = 28.8 percent surface coverage at one Langmuir. Moreover, as Eq. (4.80) suggests, the sticking probability decreases linearly with the surface coverage, and therefore, in the above example $(28.8 \times 2 = 57.6 \text{ percent surface coverage needs more than two Langmuir,}$ i.e. longer than 2 seconds at 10^{-6} Torr pressure. Figure 4.42 shows the variation of sticking probability with surface coverage. It is found that S does not fall linearly with θ ; sometimes it falls off too sharply and sometimes too slowly. The former is generally observed in dissociative chemisorption, where the adsorption of one molecule fills up two vacant sites. The slow variation of S with θ can be explained as follows: Langmuir assumed that when a molecule strikes a filled site, it rebounds back into the gas phase. But in fact, the molecule could be physically adsorbed on the chemisorbed layer, spend some time moving over the surface until either it finds a vacant site and gets adsorbed or really kicked off the surface.



Figure 4.42 The variation of S with θ .

Example 4.9

Calculate the rate of adsorption of hydrogen (assume dissociative chemisorption) at a pressure of 10^{-9} Torr and 300 K on the (110) plane of a body-centred cubic lattice. The unit cell has a side length of 316 pm and the sticking probability is 0.6.

Solution

The rate of striking of the molecules on the surface at $1\times 10^{-9}\, \text{Torr}$ and 300 K is

$$Z_{W} = \frac{1}{4} n \langle C \rangle = \frac{1}{4} \frac{P N_{0}}{RT} \sqrt{\frac{8RT}{\pi M}}$$
$$= 1.43 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$$

The (110) plane of the unit cell of the body centred lattice contains $1 + 1/4 \times 4 = 2$ atoms. The area of this plane is $\sqrt{2}a^2$ which is $\sqrt{2} (316 \times 10^{-12} \text{ m})^2 = 1.412 \times 10^{-15} \text{ cm}^2$

Therefore, the number of sites (i.e. atoms) per unit area of 110 plane is

$$\frac{\text{number of atoms}}{\text{area}} = \frac{2}{1.412 \times 10^{-15}} = 1.416 \times 10^{15} \text{ sites cm}^{-2}$$

Assuming the striking probability to be unity, the rate of adsorption is then

$$v_a = \frac{1.43 \times 10^{12} \text{ cm}^{-2} \text{s}^{-1}}{1.416 \times 10^{15} \text{ cm}^{-2}} \approx 1 \times 10^{-3} \text{ s}^{-1} \left(= \frac{\text{rate of hit per unit area}}{\text{no. of sites per unit area}} \right)$$

Now remember that the striking probability is not unity, it is 0.6. So the rate will be lower,

$$v_a = 0.6 \times 1 \times 10^{-3} \text{ s}^{-1} = 6 \times 10^{-4} \text{ s}^{-1}$$

and finally, since the adsorption is dissociative, each molecule on adsorption occupies two vacant sites. So, the rate of formation of the monolayers in one second is 1.2×10^{-3} s⁻¹.

4.20 RATE OF DESORPTION AND RESIDENCE TIME

The rate constant of desorption k_d , has a special significance. If an adsorbed molecule is to bounce off the surface, it has to have an energy greater than or equal to the depth of the potential well of the adsorbed state, i.e. $-\Delta H_{\rm ad}$. Let us call this energy $E_{\rm act}$. The desorption therefore needs an activation energy, and the temperature dependence can be expected to be Arrhenius type:

$$k_d = A \ e^{-\frac{E_{\text{act}}}{RT}} = A \ e^{\frac{\Delta H_{\text{ad}}}{RT}}$$
(4.81)

where A is a constant. Assuming the desorption process to be first order, the average life time of a molecule in the adsorbed state is therefore

$$\tau = \frac{1}{k_d} = \tau_0 \ e^{-\frac{\Delta H_{ad}}{RT}} \tag{4.82}$$

where τ_0 is some constant (mind that, ΔH_{ad} contains its own sign). This average life time of a molecule in the adsorbed state is called the residence time τ . It is also clear from the above equation that the residence time in the chemisorbed state is much longer than that in the physisorbed state, and, in any case, the residence time decreases with increase in the temperature.

Example 4.10

Calculate the residence time of CO on palladium surface when it is (a) physically adsorbed and (ii) chemically adsorbed at 300 K. Given $\Delta H_{\rm phy} = 25$ kJ mol⁻¹ and $\Delta H_{\rm chem} = -146$ kJ mol⁻¹. The value of τ_0 is 1 ps for the physisorbed state and 100 ps in the chemisorbed state.

Solution

When it is physically adsorbed the residence time is given by:

$$\begin{split} \tau &= (1 \text{ ps}) \exp \left\{ 25000/8.314 \times 300 \right\} \\ &= 2.3 \times 10^{-8} \text{ s} \end{split}$$

when it is chemically adsorbed,

$$\tau = (100 \text{ ps}) \exp \{146000/8.314 \times 300\}$$

$$= 2.6 \times 10^{15} \text{ s}$$

4.21 TEMPERATURE PROGRAMMED DESORPTION (TPD)

Today, a number of different surface sensitive spectroscopic techniques are available to make the study of surface science more clear at the atomic and molecular level. Temperature programmed desorption (TPD) is one of such techniques. In the TPD, a gradual change in temperature is applied to the system and the rate of desorption is measured as a function of temperature. The final analysis of the data depends on the kinetics of desorption. In the following we give an outline of this novel experiment assuming a *first order* desorption rate.

The temperature of the sample of a solid covered with the adsorbed layer is increased by heating the sample in such a manner that the temperature T bears a linear relation with time t.

$$T = T_0 + \beta t \tag{4.83}$$

where T_0 is the initial temperature and β is the constant rate at which the temperature is increased with time. There is also a provision of measuring this temperature continuously (a thermocouple junction is normally used). Finally, there is also a detector (the most modern laboratories have a quadrupole mass spectrometer for this purpose) to monitor the rate of desorption of the molecules from the surface. The thermocouple output (X) and the mass spectrometer output data (Y) are then fed into an X–Y recorder (Figure 4.43). The mass spectrometer data basically give the rate of desorption and apparently it may seem that this rate would increase in an Arrhenius manner with the increase in temperature. However, the actual result is that the count first increases and then forming a maximum decrease. This is due to the following reason. The rate of desorption (assuming a first order rate law) is given by:



Figure 4.43 Spectrum of a TDP experiment.

With increase in temperature, k_d increases exponentially but the surface coverage decreases (because adsorption is exothermic); so the net variation is convolutions of these tow factors (Figure 4.44).

Using Eq. (4.82), the above equation can be written as:

$$-\frac{d[SA]}{dt} = \tau_0^{-1}[SA] e^{\frac{\Delta H_{\rm ad}}{RT}} (\Delta H_{\rm ad} \text{ contains its own sign})$$
(4.84)



Thermocouple output (*x*)

Figure 4.44 A TDP spectrum.

Now
$$\frac{d}{dt} = \frac{dT}{dt} \frac{d}{dT}$$

or

$$dt \quad dt \quad dT$$
$$\frac{d}{dt} = \beta \frac{d}{dT} \quad [(\text{from Eq.} (4.83)]$$

Therefore from Eq. (4.84),

$$\frac{d[SA]}{dT} = -\frac{\tau_0^{-1}}{\beta} [SA] e^{\frac{\Delta H_{ad}}{RT}}$$
(4.85)

As we have already mentioned, the rate desorption, i.e. $-\frac{d[AS]}{dT}$, shows a maximum, when plotted versus *T*. Differentiating Eq. (4.84), with respect to temperature *T*, we get

$$\frac{d}{dT}\left(-\frac{d}{dt}\left[AS\right]\right) = \tau_0^{-1} e^{\frac{\Delta H_{ad}}{RT}} \left[-\frac{\left[SA\right] \Delta H_{ad}}{RT^2} + \frac{d\left[AS\right]}{dt}\right]$$

and using Eq. (4.85),

$$\frac{d}{dT}\left(-\frac{d\left[AS\right]}{dt}\right) = \tau_0^{-1} e^{\frac{\Delta H_{ad}}{RT}} \left[-[AS]\frac{\Delta H_{ad}}{RT^2} \frac{\tau_0^{-1}}{\beta} [AS] e^{\frac{\Delta H_{ad}}{RT}}\right]$$

..

. .

at the maximum, where $T = T_{max}$, the left hand side of the above equation is zero. This gives us:

$$\frac{\Delta H_{\rm ad}}{RT_m^2} = -\frac{\tau_0^{-1}}{\beta} e^{\frac{\Delta H_{\rm ad}}{RT_m}}$$

or

$$\frac{E_{\text{act}}}{R \tau_0^{-1}} = \frac{T_m^2}{\beta} e^{\frac{\Delta E_{\text{act}}}{R T_m}} [\because E_{\text{act}} = -\Delta H_{ad}]$$

or

$$\ln \frac{E_{\rm act}}{R \tau_0^{-1}} = 2 \ln T_m - \ln \beta - \frac{E_{\rm act}}{R T_m}$$

$$2\ln T_m - \ln \beta = \frac{E_{\text{act}}}{RT_m} + \ln \frac{E_{\text{act}}}{R\tau_0^{-1}}$$
(4.86)

The experiment is repeated at several different fixed rates of increase in temperature with time β , and the corresponding T_{\max} is noted. Then from a plot of $(2 \ln T_{\max} - \ln \beta)$ versus $(1/T_{\max})$, which is expected to be linear, E_{act} and hence $\Delta H_{\text{ads}} H_{\text{ad}}$, is evaluated from the slope. The parameter τ_0 can also be evaluated from the slope and intercept of the plot.

PROBLEMS

4.1 Calculate the minimum work required to expand the surface of water from 10 to 15 cm^2 at 27°C. At this temperature, the surface tension of water is 72 dyn cm⁻¹.

[Ans.: (360 erg)]

- **4.2** One cm³ of Hg, initially in the spherical shape is broken down into 125 tiny droplets
of equal size. Calculate the Gibbs free energy change of the process. The surface
tension of Hg at 25°C is 0.484 Nm^{-1} .[Ans.: $9.36 \times 10^{-4} \text{ J}$]
- **4.3** A glass capillary of internal diameter 0.5 mm is dipped into water vertically. If the surface tension of water be 72 dyn cm⁻¹ then calculate the capillary rise ($\theta = 14^{\circ}$ and $\rho_{water} = 1 \text{ g cm}^{-3}$. [Ans.: 5.7 cm]
- **4.4** Repeat problem 3 by assuming $\theta = 0$ and compare the results. [Ans.: 5.87 cm]
- **4.5** For Hg-air interface on glass, $\theta = 140^{\circ}$. Calculate the depression of Hg inside a capillary of internal radius 2 mm at 20°C; ρ Hg = 13.6 g cm⁻³ and γ = 490 dyn cm⁻¹. [*Ans.:* -0.28 cm]
- **4.6** At 25°C, methanol has $\gamma = 22$ dyn cm⁻¹, $\rho = 0.7914$ g cm⁻³. If a capillary of internal diameter 0.6 mm be dipped into methanol obliquely making an angle of 30° with the liquid surface then calculate the length of the capillary through which methanol rises up. [*Ans.:* 3.8 cm]
- **4.7** Two glass sheets, kept parallel to each other at 0.2 mm separation, are dipped into water vertically. Neglecting the effects at the edge, calculate the height through which water rises up.

$$\gamma = 72 \text{ dyn cm}^{-1}$$
, $\rho_{\text{water}} = 0.987 \text{ g cm}^{-3}$ and $\theta = 14^{\circ}$. [Ans.: 14.4 cm]

4.58

- 4.8 Consider Problem 4.4; after the water rises up along the capillary, a glass rod of diameter 0.4 mm is put into the capillary axially. Now calculate the capillary rise between the inner surface of the capillary and the glass rod. Use the same data as in Problem 4.4. [Ans.: 32.62 cm]
- **4.9** What happens to the level of water inside a capillary of 0.4 mm diameter when another capillary of diameter 0.6 mm is dipped into the same bulk of water? At 20°C, $\rho_W = 0.9942 \text{ g cm}^{-3}$ and $\gamma = 72 \text{ dyn cm}^{-1}$. [Ans.: $\Delta h = 2.46 \text{ cm}$]
- **4.10** Two bubbles of radii 1 and 4 cm are connected by a hollow tube. Will the arrangement be stable? If not, what happens? $\begin{bmatrix} Ans.: R = \frac{4}{3} \text{ cm} \end{bmatrix}$
- **4.11** At 20°C, the surface tension at the interface between *n*-butylalcohol and water is 1.8 dyn cm⁻¹. The densities of *n*-butylalcohol and water are 0.81 and 0.990 g cm⁻³ respectively. Assuming $\theta = 0$, calculate the capillary rise for an internal diameter 0.5 mm, inserted vertically into this two phase water-*n*-butylalcohol system. [Ans.: 0.815 cm]
- **4.12** A capillary of radius 0.5 mm is dipped into water so that its tip is at 1 m under the water-air interface. What is the maximum pressure required to form a cavity of radius equal to that of the capillary? = 72 dyn cm⁻¹, $\rho = 1$ g cm⁻³.

[Ans.: 0.0996 atm]

4.13 Under 1 atm external pressure and isothermally at 25°C, two bubbles of a soap solution of radii r_1 and r_2 stick together, with a film between them of radius r.

Express *r* in terms of
$$r_1$$
 and $r_2\left(\frac{1}{r} = \frac{1}{r_1} - \frac{1}{r_2}\right)$.

- **4.14** At 20°C, the interfacial tension between diethylene glycol and water is 57 dyn cm⁻¹. If for water–vapour and diethylene glycol—vapour interfaces, γ are 72 and 31 dyn cm⁻¹, respectively, then calculate:
 - $(i)\;\;$ the work of adhesion between diethylene glycol and water.

 $[Ans.: 46 \text{ erg cm}^{-2}]$

(ii) the work of cohesion of the two liquids.

 $[Ans.: 62 \text{ erg cm}^{-2}; 144 \text{ erg cm}^{-2}]$

- (iii) the spreading coefficient of diethylene glycol on water. $[Ans.: -16 \text{ erg cm}^{-2}]$
- **4.15** Show that $\left(\frac{\partial \gamma}{\partial P}\right)_{A,T}^{T} = \left(\frac{\partial V}{\partial A}\right)_{P,T}^{T}$

A-area, V-volume, γ -surface tension.

4.16 Eighty four drops of water are formed from a stalagmometer, while 92 drops of another liquid are formed from the same stalagmometer. If the densities of water and the liquid are 0.9987 and 0.6632 g cm⁻³, respectively, and if $\gamma_{\text{water}} = 72$ dyn cm⁻¹, then calculate the surface tension of the liquid.

 $[Ans.: 43.65 \text{ dyn cm}^{-1}]$

- **4.17** Liquid benzene has a surface tension of 28.88 dyn cm⁻¹ at 20°C, which decreases to 23.61 at 61°C. The densities at these two temperatures are 0.8787 and 0.8330 g cm⁻³, respectively. Calculate the Ramsay Shield Eötvös constant and the critical temperature of benzene. [Ans.: 2.14]
- **4.18** Calculate the net force required to pull up a ring of diameter 5 cm from just under the surface of water if $\gamma = 72$ dyn cm⁻¹.

[Ans.: mg + 2260.8 dyn; m is the mass of the ring]

- **4.19** Calculate the vapour pressure of a spherical droplet of water of radius 1000 Å at 20°C. The saturated vapour pressure of water at this temperature is 2.3 kPa and its density is 0.9982 g cm⁻³ and $\gamma = 72$ dyn cm⁻¹. [*Ans.*: 2.325 kPa) or (17 mm Hg]
- **4.20** What is the vapour pressure of water inside a cavity of radius 0.1 mm produced inside a bulk of water at 20°C. Use the other required data from Problem 4.19.

[Ans.: 2.3 kPa]

- **4.21** At 20°C, the vapour pressure of bulk water is 2.3 kPa. The surface tension is 72 dyn cm⁻¹ and density is 0.9982 g cm⁻³. Calculate the vapour pressure of tiny water droplets of radius 10^{-7} cm. What is the critical size of the droplet beyond which condensation will take place spontaneously? [Ans.: 6.68 kPa; 10.66 Å]
- **4.22** If the solubility of the course crystals of AgI be 1×10^{-8} M at 25°C then calculate the same for finer crystals (assumed to be of cubical shape) of edge length 100 Å. At this temperature, $\gamma = 0.6$ Nm⁻¹ and $\rho = 5$ g cm⁻³. [Ans.: 9.21 × 10⁻⁶ M]
- **4.23** The surface tension of a 0.05 M aqueous solution of sodium dodecyl sulfate is 54.5 dyn cm⁻¹ whereas that of pure water is 72 dyn cm⁻¹ at 20°C. Calculate the surface excess of a 0.03 M solution, assuming that a plot of γ versus C is linear. Also calculate the surface pressure at this concentration.
- $[Ans.: 4.2 \times 10^{-10} \text{ mol m}^{-2}, 0.733 \text{ atm}]$ 4.24 Stearic acid CH₃(CH₂)₁₆ COOH, has a density of 0.94 g cm⁻³. 10 mg of the acid forms monomoleculer film of area 4.452 × 10⁴ cm². Calculate the cross-sectional area and length of the hydrocarbon chain. [Ans.: 21 Å; 23.8 Å]
- 4.25 The adsorption of a diatomic gas on a solid surface is described by the Langmuir adsorption isotherm with $K = 10 \text{ atm}^{-1}$. Calculate the surface coverage at 1 atm. Calculate the pressure at which the surface coverage is 25% and 75% considering (i) non-dissociative, and (ii) dissociative process. Compare the results.

[Ans.: (i) 0.33 atm for 25% and 0.3 atm for 75%

(ii) 0.111 atm for 25% and 0.9 atm for 75%]

4.26 At 300 K, a certain solid adsorbs 0.572 mg of CO when the equilibrium pressure is 0.4 atm. At the same temperature, the adsorption increases to 0.75 mg when the equilibrium pressure is 0.6 atm considering the Langmuir adsorption isotherm (non dissociative) to apply, calculate the equilibrium constant of the adsorption and the surface coverages at these two pressures.

[Ans.: $K = 1.016 \text{ atm}^{-1}$; $\theta_1 = 0.289$; $\theta_2 = 0.379$]

- **4.27** At 200 K, a solid adsorbs 50 ml (measured at NTP) of N_2 when the equilibrium pressure is 30 mm Hg. The pressure required to adsorb the same volume of gas (again measured at NTP) is now found to be 74 mm Hg at 250 K. Calculate the isosteric heat of adsorption. [Ans.: -7.51 kJ mol⁻¹]
- **4.28** The pressure of O_2 required to give a particular coverage of adsorbed oxygen atoms on the silver surface at 700 K was 1 m bar. At 800 K, a pressure of 36 m bar was required to establish the same surface coverage. Estimate the isosteric heat of adsorption. [Ans.: -166.28 kJ mol⁻¹]
- **4.29** The volume of N_2 gas (measured at NTP) adsorbed on 1 g of charcoal is 45 mL at 10 Torr pressure, and 60.2 mL at 30 torr pressure. Calculate the volume required to form a complete monolayer. Also find out the surface area of charcoal if the diameter of a nitrogen molecule is 0.4 mm
- [Ans.: $v_m = 72.46 \text{ mL}$; $2.45 \times 10^6 \text{ cm}^2 \text{ g}^{-1}$] **4.30** The data below are for the chemisorption of N₂ on charcoal at 25°C. Test graphically the applicability of the Freundlich and Langmuir adsorption isotherms.

Also check the validity of BET isotherm. Calculate the V_m from the Langmuir and BET plot and compare them.

4.31 It is known that O_3 is adsorbed on the surface of charcoal and the process can be described by the Langmuir adsorption isotherm. How will you proceed to establish that the adsorption is nondissociative or dissociative as

(i)
$$O_3(g) + - \stackrel{|}{S} - \stackrel{|}{S} - \stackrel{|}{s} - \stackrel{|}{s} - \stackrel{|}{S} - \stackrel{|}{s}$$

OR

(ii)
$$O_3(g) + -S - S - S \xrightarrow{O} - S - S - S$$

- **4.32** Express one Langmuir in units of Pascals instead of torr. [Ans.: 1.33×10^{-4} PaS]
- **4.33** Solid nickel is face centred cubic with a unit cell of side length 350 pm. Calculate the rate of adsorption of H_2 on the (100), (110) and (111) planes, when exposed to 0.1 Langmuir at 25°C. Assume the stiking probability to be 60%, 70% and 80% of the planes (100), (110) and (111), respectively.

[Ans.: For 100-plane: $7.06 \times 10^{-2} \text{ s}^{-1}$; for 110-plane: 0.35 s^{-1} ; for 111-plane: 0.245 s^{-1}]

- **4.34** The average life time of an adsorbed oxygen atom over tungsten is 0.4 s at 2500 K and 3.5 s at 2300 K. Find the activation energy for desorption. Do you think this adsorption to be physical or chemical?
- [Ans.: -518.46 kJ mol⁻¹; Chemisorption] **4.35** The enthalpy of adsorption of H atom over a solid surface is 15 kJ mol⁻¹ when it is physically adsorbed, and 150 kJ mol⁻¹ when it is chemically adsorbed. Calculate the half life time of an adsorbed H-atom in the two states of adsorption at 300 K, if $\tau_0 = 0.2$ Ps. and 20 Ps for physisorbed and chemisorbed rituals, respectively. How long, on an average, the atoms spend over the surface at 600 K?

[Ans.: 56.7 Ps; 1.82×10^{15} s]

4.36 In a TPD study, the maximum rate of desorption of CO from Pb surface occurs at 650 K when the heating rate is 15 K s⁻¹. Calculate the activation energy of desorption if $\tau_0 = 1.4$ Ps.

Solution to Problem 4.36

According to the problem, T_m = 650 K; β = 15 K s^{-1} and, τ_0 = 1.4 \times 10^{-12} s. Using Eq. (4.86),

$$2\ln(650) - \ln(15) = \frac{E_{act}}{R(650)} + \ln\frac{E_{act}}{R(1.4 \times 10^{-12})^{-1}}$$

$$12.95 - 2.71 = \frac{E_{\rm act}}{5.4} + \ln \frac{E_{\rm act}}{5.94 \times 10^0}$$

where E_{act} is in kJ mol⁻¹ therefore,

 $10.24 = 0.185 E_{act} - 22.5 + \ln E_{act}$

 $\Rightarrow \qquad 0.185 E_{\rm act} + \ln E_{\rm act} - 12.26 = 0$

This equation is to be solved numerically.

There are different numerical methods to solve equations. The *Newton–Raphson method of iteration* is a very commonly used method because of its simplicity and speed.

Newton-Raphson Method of Iteration

In this method, for solving equations, y = f(x) = 0, where it is assured that, f has a continuous derivative f'. The fundamental idea is that, we approximate the graph of f by suitable tangents. Then using an approximate value x_0 obtained from the graph of f, we let x_1 be the point of intersection on the *x*-axis, by the tangent to the curve of f at x_0 (Figure 4.45), then

$$\tan \beta = \frac{f(x_0)}{(x_0 - x_1)}$$
 or $x_1 = x_0 - \frac{f(x_0)}{\tan \beta}$





$$\Rightarrow \qquad x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}$$

In the second step, we write

$$x_2 = x_1 - \frac{f(x_1)}{f'(x_1)};$$

in the third step, $x_3 = x_2 - \frac{f(x_2)}{f'(x_2)}$; and so on, until we get a constant value of x_n .

We construct the function as

 $f = 0.185 \, E_{\rm act} + \ln E_{\rm act} - 12.26 = 0$ using x for $E_{\rm act},$ the equation is

 $f = 0.185x + \ln x - 12.26 = 0 \tag{4.87}$

and
$$f' = 0.185 + \frac{1}{x}$$
 (4.88)

First Step: n = 0; and let $x_0 = 150$ as our first choice. Therefore,

$$\begin{split} f(x_0) &= (0.185) \ (150) + \ln \ (150) - 12.26 \\ f(x_0) &= 20.5 \end{split}$$

or

using Eq. (4.88)

$$f'(x_0) = 0.185 + \frac{1}{150} = 0.1917$$

..

Therefore,

Then,

re, $x_1 = x_0 - \frac{f(x_0)}{f'(x_0)} = 150 - \frac{20.5}{0.1917} = 43.06$

 $f(x_1) = 0.185 \ (43.06) + \ln \ (43.06) - 12.26$

 $f(x_1) = -0.5313$

and

or

$$f'(x_1) = 0.185 + \frac{1}{43.06} = 0.208$$

Therefore,
$$x_2 = x_1 - \frac{f(x_1)}{f'(x_1)} = 43.06 + \frac{0.5313}{0.208} = 45.6$$

Then, $f(x_2) = 0.185(45.6) + \ln (45.6) - 12.26 = -0.004$

and
$$f'(x_2) = 0.185 + \frac{1}{45.6} = 0.207$$

Therefore,

 $x_3 = x_2 - \frac{f(x_2)}{f'(x_2)}$

or

$$x_3 = 45.6 + \frac{0.004}{0.207}$$

or $x_3 = 45.6 + 0.019 = 45.62$

almost the same as x_2 . This is the final result: x = 45.6.

5 CHEMICAL KINETICS

5.1 INTRODUCTION

Chemical kinetics is the study of reaction rates and, thereby, focusing on the pathways through which reactions proceed. A reacting system is not certainly at the equilibrium position, and therefore, its study is *not thermodynamic* but, *kinetic in nature* i.e. *the time parameter* comes into play *as a variable*. When an arbitrary mixture of N_2 , H_2 and NH_3 is taken in a closed vessel of constant volume V at a fixed temperature, the direction in which the reaction will take place and, to what extent to attain the equilibrium position are the concerns of *thermodynamic study*. But, the rate at which the process takes place is the concern of chemical kinetics. This is important because, it may be that the yield of NH_3 is favourable but, the rate is so poor that the process is not economically good. In that case, we have to find out now the rate of production of NH_3 could be increased by changing the temperature, changing the concentration of a particular component or, by introducing a suitable catalyst, etc. These informations come from the study of reaction rates; finally, the reaction pathways are also illuminated.



Figure 5.1 Variation of the concentrations of N_2 , H_2 and NH_3 . The tangents at t = 0 give 0the initial rate of production and consumption of the components.

5.2 ADVANCEMENT OF A REACTION: RATE OF REACTION

5.2.1 Rate of Change of Concentration of the Reacting Species

Let us consider a homogeneous gas phase reaction

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

It is clear that, as the time marches on, the concentrations of N_2 and H_2 decreases and, that of the product NH_3 increases (Figure 5.1). The rate of change of the concentration of the three species are

$$-\frac{dC_{\rm N_2}}{dt}; -\frac{dC_{\rm H_2}}{dt} \text{ and } \frac{dC_{\rm NH_3}}{dt}$$
(5.1)

These three differential rates may be obtained from the slopes of the concentration-time profiles (Figure 5.1). But, from the stoichiometry of the reaction, we may write

$$-\frac{dC_{\rm N_2}}{dt} = \frac{1}{3} \left(-\frac{dC_{\rm H_2}}{dt} \right) = \frac{1}{2} \left(\frac{dC_{\rm NH_3}}{dt} \right)$$
(5.2)

The rates of consumption and production of the different reacting species are different. Their units are, however, mol $L^{-1} s^{-1}$ or, atm min⁻¹ or likewise.

Example 5.1

The rate of formation of NH₃ at a fixed temperature (600 K) is found to be 1.5×10^{-3} mol dm⁻³ min⁻¹. Calculate this rate in terms of (i) molecule cm⁻³ s⁻¹; (ii) mol m⁻³ min⁻¹; (iii) atm min⁻¹; (iv) Torr s⁻¹ and (v) rate of decrease of H₂ concentration.

Solution

$$\frac{dC_{\rm NH_3}}{dt} = 1.5 \times 10^{-3} \text{ mol } dm^{-3} \text{ min}^{-1}$$
(i) $\frac{dC_{\rm NH_3}}{dt} = 1.5 \times 10^{-3} \text{ mol } dm^{-3} \text{ min}^{-1} \left(\frac{6.022 \times 10^{23} \text{ molecule}}{1 \text{ mol}}\right)$
 $\times \left(\frac{1 \text{ dm}^3}{1000 \text{ cm}^3}\right) \left(\frac{1 \text{ min}}{60 \text{ s}}\right)$
 $dC_{\rm NH}$

$$\Rightarrow \qquad \frac{dC_{\rm NH_3}}{dt} = 1.506 \times 10^{16} \text{ molecule cm}^{-3} \text{ s}^{-1}$$

(ii)
$$\frac{dC_{\rm NH_3}}{dt} = (1.5 \times 10^{-3} \text{ mol } \text{dm}^{-3} \text{ min}^{-1}) \left(\frac{10^3 \text{ dm}^3}{1 \text{ m}^3}\right) = 1.5 \text{ mol } \text{m}^{-3} \text{ min}^{-1}$$

Chemical Kinetics

(iii) Assuming that the component gases behave ideally, we may write for the partial pressure of NH_3 as

$$P_{\rm NH_3} = C_{\rm NH_3} RT$$

Therefore,
$$\frac{d}{dt} C_{\text{NH}_3} = \frac{1}{RT} \frac{d}{dt} (P_{\text{NH}_3}) = 1.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$$

 $\Rightarrow \qquad \frac{dP_{\text{NH}_3}}{dt} = RT(1.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1})$
 $= (0.082 \text{ dm}^{-3} \text{ atm } \text{ K}^{-1} \text{ mol}^{-1}) (600 \text{ K}^{-1}) (1.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1})$
 $= 7.38 \times 10^{-2} \text{ atm min}^{-1}$
(iv) $\qquad \frac{d P_{\text{NH}_3}}{dt} = 7.38 \times 10^{-2} \text{ atm min}^{-1} \left(\frac{760 \text{ Torr}}{1 \text{ atm}}\right) \left(\frac{1 \text{ min}}{60 \text{ s}}\right)$

$$\Rightarrow \qquad rac{d \, P_{\mathrm{NH}_3}}{dt} = 0.9348 \ \mathrm{Torr} \ \mathrm{s}^{-1}$$

(v)
$$-\frac{d}{dt}(C_{\text{H}_2}) = \frac{3}{2} \frac{dC_{\text{NH}_3}}{dt}$$
 [using Eq. (5.2)]

$$\Rightarrow$$

$$\frac{dC_{\rm H_2}}{dt} = 1.5 \times 1.5 \text{ mol m}^{-3} \text{ min}^{-1} = 2.25 \text{ mol m}^{-3} \text{ min}^{-1}$$

5.2.2 Advancement of a Reaction

Consider a chemical reaction, represented stoichiometrically as

$$\alpha A + \beta B \longrightarrow \gamma C + \delta D$$

where A and B are the reactants and, C and D are the products. The stoichiometric coefficients are then, $-\alpha$, $-\beta$, γ and δ , respectively. By one mole of this reaction ($\xi = 1 \text{ mol}$), we mean that the indicated number of moles of the reactants (as given in the stoichiometric representation of the reaction) reacts to produce the indicated number of moles of the products. Therefore, if the above reaction is said to be advanced to $\xi = 1 \text{ mol}$, then, the changes in the number of moles of the reacting species are

$$\Delta n_A = -\alpha \Delta \xi = -\alpha (1 \text{ mol}) = -\alpha \text{ mol, and similarly}$$

$$\Delta n_B = -\beta \Delta \xi = -\beta (1 \text{ mol}) = -\beta \text{ mol,}$$

$$\Delta n_C = +\gamma \Delta \xi = \gamma (1 \text{ mol}) = \gamma \text{ mol and}$$

$$\Delta n_D = +\delta \Delta \xi = \delta (1 \text{ mol}) = \delta \text{ mol,}$$

Now, during the course of the reaction, if the reaction be advanced from ξ to $(d + \xi)$ over the time period $t \rightarrow t + dt$ then the changes in the number of moles of the reacting components over this time period are

$$dn_A = -\alpha d\xi$$
; $dn_B = -\beta d\xi$; $dn_C = \gamma d\xi$; $dn_D = \delta d\xi$

The rates of change of the number of moles of the components with time are then

$$\frac{dn_A}{dt} = -\alpha \frac{d\xi}{dt}; \frac{dn_B}{dt} = -\beta \frac{d\xi}{dt}; \frac{dn_C}{dt} = \gamma \frac{d\xi}{dt} \text{ and } \frac{dn_D}{dt} = \delta \frac{d\xi}{dt}$$
(5.3)

$$\Rightarrow$$

 $\frac{d\xi}{dt} = -\frac{1}{\alpha} \frac{dn_A}{dt} = -\frac{1}{\beta} \frac{dn_B}{dt} = \frac{1}{\gamma} \frac{dn_C}{dt} = \frac{1}{\delta} \frac{dn_D}{dt}$ (5.4)

We now define the rate of the reaction as the rate of change of the advancement with time per unit volume of the reaction mixture. At constant volume V, we may write, the rate of the reaction (v) as

$$v = \frac{1}{V}\frac{d\xi}{dt} = -\frac{1}{\alpha}\frac{d(n_A/V)}{dt} = -\frac{1}{\beta}\frac{d(n_B/V)}{dt} = \frac{1}{\gamma}\frac{d(n_C/V)}{dt} = \frac{1}{\delta}\frac{d(n_D/V)}{dt}$$
$$v = \frac{1}{V}\frac{d\xi}{dt} = -\frac{1}{\alpha}\frac{dC_A}{dt} = -\frac{1}{\beta}\frac{dC_B}{dt} = \frac{1}{\gamma}\frac{dC_C}{dt} = \frac{1}{\delta}\frac{dC_D}{dt}$$
(5.5)

or

Example 5.2

Gaseous N_2O_5 decomposes at 600 K as

$$2 \operatorname{N}_2\operatorname{O}_5(g) \longrightarrow 4 \operatorname{NO}_2(g) + \operatorname{O}_2(g)$$

The rate of the reaction is found to be 4×10^{-6} mol dm⁻³ s⁻¹. Calculate the values of

$$rac{dC_{
m N_2O_5}}{dt}$$
, $rac{dC_{
m NO_2}}{dt}$ and $rac{dC_{
m O_2}}{dt}$

Solution From Eq. (5.5), we find the rate of the reaction as

10

$$v = -\frac{1}{2} \frac{dC_{N_2O_5}}{dt} = \frac{1}{4} \frac{dC_{NO_2}}{dt} = \frac{dC_{O_2}}{dt} = 4 \times 10^{-6} \text{ mol } \text{dm}^{-3} \text{ s}^{-1}$$

Therefore,

$$\frac{dC_{N_2O_5}}{dt} = -2v = -2(4 \times 10^{-6} \text{ mol } \text{dm}^{-3} \text{ s}^{-1})$$

- --

$$\frac{dC_{\rm N_2O_5}}{dt} = -8 \times 10^{-6} \text{ mol } \rm{dm}^{-3} \text{ s}^{-1}$$

or

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Similarly,

$$\frac{dC_{\rm NO_2}}{dt}$$
 = 4v = 1.6 × 10⁻⁵ mol dm⁻³ s⁻¹

and,

$\frac{dC_{\rm O_2}}{dt} = 4 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

Example 5.3

Calculate the rate of advancement of the reaction with time for the reaction in Example 5.2 at an instant if the rate at that instant is found to be 4×10^{-6} mol dm⁻³ s⁻¹. The volume of the reaction mixture is 3 L.

Solution Using Eq. (5.5), we write

$$\frac{d\xi}{dt} = v \cdot V = (4 \times 10^{-6} \text{ mol } \text{dm}^{-3} \text{ s}^{-1}) (3 \text{ dm}^{3}) \quad (\because 1 \text{ dm}^{3} = 1 \text{ L})$$
$$\frac{d\xi}{dt} = 1.2 \times 10^{-5} \text{ mol } \text{s}^{-1}$$

or

Example 5.4

Equation (5.5) gives the expression of the rate of a reaction carried out at a constant volume and temperature. Find the rate expression if the volume is allowed to change during the course of the reaction.

Solution The number of moles of a reactant A is $n_A = C_A V$, where C_A is the molar concentration of the reactant A and, V is the volume of the reaction mixture. On differentiating, we get

$$dn_A = C_A dV + V dC_A$$

The rate of the reaction v is then [cf. Eq. (5.5)]

$$\begin{split} v &= -\frac{1}{\alpha} \frac{1}{V} \frac{dn_A}{dt} = -\frac{1}{\alpha V} \bigg[C_A \frac{dV}{dt} + V \frac{dC_A}{dt} \bigg] \\ v &= -\frac{1}{\alpha V} C_A \frac{dV}{dt} - \frac{1}{\alpha} \frac{dC_A}{dt} \end{split}$$

 \Rightarrow

Note that the above expression changes to Eq. (5.5), if V is held fixed.

5.3 RATE LAW AND ORDER OF A REACTION

The *rate law* is an *experimentally obtained equation*, which shows how the rate of the reaction depends on the concentration terms of the reactive species. Very often, but not

5.5

always, the rate law of a reaction

$$\alpha A + \beta B \longrightarrow \gamma C + \delta D$$

has been found to be of the form

$$v = k C_A^a C_B^b \dots aga{5.6}$$

where, C_A , C_B ,... are the concentration of the species A, B,... etc. The proportionality constant k is called the rate constant of the reaction or, the specific reaction rate. k depends on both the temperature and pressure; but, the pressure dependence is usually very small, and is neglected.

On the basis of the above rate law [Eq. (5.6)], the reaction is said to have the order 'a' with respect to the component *A*, 'b' with respect to *B*, ... etc. The overall order of the reaction 'n' is then; $n = a + b + \cdots$. Note that, the concept of order is reserved only for those reactions for which the rate law contains the concentration terms (or, the partial pressures) in a multiplicative form as given in Eq. (5.6). Some empirical rate laws are

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 $v = k P_{\text{NH}_3}^{\frac{1}{n}}$ (n > 1) at intermediate pressure v = k (at high enough pressure)

The order of reaction (2) cannot be defined. However, the order of a very similar reaction (1) can be defined; it is first order with respect to each of H_2 and I_2 , and hence, overall second order. The overall order of the reaction (4) is three; second order with respect of NO, and first order with respect to O_2 . From Examples 3, 5 and 6, we find that there is no correspondence between the stoichiometry and the order of a reaction. Moreover, the order of a reaction may be fractional. Example 8 shows that, although the order of the overall reaction cannot be defined, at very low concentration of H_2O_2 , and, if k_1 is very small, the overall reaction is overall third order (considering only the second term).

Example 9 shows that the order of a reaction with respect to a particular component, here the Hg^{2+} ion, may be negative and, both the concentrations of the reactant and product may appear in the rate law. Finally, Example 10 shows that the order of a reaction may change due to a change in the reaction condition.

5.4 ELEMENTARY REACTION AND MOLECULARITY

A reaction is not as simple as that written on paper, e.g. there is a much belief that the gas phase decomposition of N_2O_5 into NO_2 as O_2 occurs as follows:

- (a) $N_2O_5 \rightarrow NO_2 + NO_3$
- (b) $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$
- (c) NO + NO₃ \rightarrow 2 NO₂

However, step (a) has to take place twice per occurrence of the steps (b) and (c). These steps, through the sequence of which the reactants are converted into the final products, are called the elementary steps. A reaction, in which there is only one elementary step, is called an elementary reaction. Most of the reactions are not elementary, as they consist of a number of elementary steps; these are called complex reactions.

The species involved in an elementary step of a reaction may be a molecule, a free radical, an atom or an ion. The number of species which takes an active role in leading an elementary step is called the molecularity of that elementary step. The concept of molecularity is restricted only to the elementary step and should not be used to describe an overall reaction and, should not be confused with the order of the reaction. For example, the nucleophilic substitution reaction of R_2 CHBr in aqueous medium.

$$R_2CHBr + OH^- \rightarrow R_2CHOH + Br$$

has been found to be first order in the alkyl halide, i.e.

$$v = k C_{R_2 CHB_1}$$

The mechanism is believed to be:

$$R_{2}CHBr \xrightarrow{slow} R_{2} \overset{+}{CH} \xrightarrow{H_{2}O} R_{2} \overset{+}{CH} \xrightarrow{H_{2}O} R_{2} \overset{+}{CH}(OH_{2}) \xrightarrow{-H^{+}} R_{2}CHOH$$

There are therefore three elementary steps with molecularity 1, 2 and 1, respectively, (note that Br does not take any active role in the second elementary step). So, the concept of molecularity is used to describe an elementary step but, the order, which is an experimental parameter is used to describe the overall reaction. Nevertheless, it is noteworthy that, *the order of an elementary step and its molecularity are all the same*. For example, the rate of the first step may be written as $k_1C_{R_2CHB_r}$ that of the second step as

 $k_2 C_{R_2 CH}^{+} C_{H_2O}$ and that of the third as $k_3 C_{R_2 CH(OH_2)}^{+}$. Therefore, for an elementary step the order can be written according to its stoichiometry.

5.5 PSEUDO ORDER

Sometime it is found that the concentration of a particular component remains constant or almost constant during a particular run of a reaction. In that case, that concentration term is included in the rate constant k, and the reaction is then said to have pseudo- n^{th} order, where n is the sum of the exponents of the remaining concentration terms. For example, in the hydrolysis of sucrose, catalysed by H⁺ ions.

The rate law has the form

$$v = k^{\prime\prime} C_{H_2O}^n C_{H^+} C_{sucrose}$$

Since the reaction is carried out in aqueous medium, in which C_{H_2O} is much greater than that of sucrose, it may be supposed that C_{H_2O} remains virtually constant and therefore, the rate law may be written as

$$v = k' C_{H^+} C_{sucrose}$$
; $k'' C_{H_2O}^n = k'$

Moreover, in a particular run, the concentration of the catalyst H^+ does not change; so including C_{H^+} within k' we write the rate law as

$$v = k C_{\text{sucrose}}$$
; $k = k' C_{\text{H}^{4}}$

The reaction is therefore referred to as a pseudo first order reaction.

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5.6 ORDER WITH RESPECT TO CONCENTRATION (THE TRUE ORDER): ORDER WITH RESPECT TO TIME

It has already been mentioned that the order of a reaction is determined experimentally. There are two different approaches: (1) The differential method, and (2) The method of integration. In the following section we first consider the differential method. The method of integration will be treated later separately.

5.6.1 Differential Method

This was first suggested by van't Hoff (1884). The concentration-time profile of a reactant is first made. If the reaction is of n^{th} order with respect to a particular reactant then,

$$v = -\frac{dC}{dt} = kC^{n}$$

log $v = \log k + n \log C$ (5.7)

 \Rightarrow

We, then measure v at several different concentrations C (v is measured from the slopes of the concentration-time curve. The final plot is made by plotting log v versus log C. A straight line is expected according to the Eq. (5.7). The slope of this plot gives the order n. This procedure is done in two different ways. In this first method, the concentration-time profile is made with several different initial concentrations (Figure 5.2).



Figure 5.2 The concentration-time curve with different initial concentrations. The slope of the curve at t = 0 is the initial rate.

Then, the tangents are drawn for each curve at t = 0; this gives the initial rates. These rates are then used in Eq. (5.7) and, a plot of log v versus log C (C being the initial

concentration for each set) is made. A straight line is expected whose slope gives the order n_C (Figure 5.3).^{*} Analytical methods may also be used. In the second method, a single run is made with a given initial concentration, and from the concentration-time profile (Figure 5.4) so obtained, a plot of log v versus log C made; again a straight line is expected (Figure 5.5), the slope of which is the order with respect to time n_t (because the slopes are taken at different instants during the course of a single run).



Figure 5.3 The plot of log v versus log C; all v's are measured at t = 0. The slope gives the true order.

Figure 5.4 The slopes at different instants give the rate of the reaction at the corresponding instants of time.



Figure 5.5 The slope gives the order with respect to time.

^{*} This is referred to as the order with respect to concentration or, the true order n_{C}

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Since the true order n_C is obtained from the data of the initial (t = 0) slopes, it is devoid of any complication which may arise during the course of the reaction. These two orders, n_C and n_t are sometimes found to be different.

If n_C is found to be more than n_t ($n_C > n_t$), then it means that the rate falls off more less rapidly with time then that it should have been. Auto-catalytic process may be one of the reasons. On the other hand, if n_C is found to be less than n_t ($n_C < n_t$), then it means that the reaction rate falls off more rapidly with time than that it should have been. Inhibition may be one of the reasons.

The differential method may also be applied in another tricky way. This is explained in the following section.

5.6.1.1 The Method of Isolation

This method is particularly important when two or more reactant concentration terms appear in the rate law. The main objective is to fix one or another concentration so as *isolate* (or, *remove*) the dependence of the rate on each species in turn. This is usually done by using a large excess of the first reactant, and then with the second reactant, and so on.

Consider the reaction

$$2 \text{ NO} + \text{H}_2 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$$

Suppose that in the first run, we use a large excess concentration of NO such as $P_{\text{NO}}^0 = 800$ Torr and $P_{\text{H}_2}^0 = 20$ Torr.

The rate law then becomes

$$v = k p_{\rm NO}^{\alpha} p_{\rm H_2}^{\beta} = k' p_{\rm H_2}^{\beta} (k' = k p_{\rm NO}^{\alpha})$$

because $P_{\rm NO}$ remains almost constant with respect to $P_{\rm H_2}$.

 β is then evaluated by the method discussed earlier. We then reverse the situation by using a large excess of H₂ such as $P_{H_2}^0 = 800$ Torr and $P_{NO}^0 = 20$ Torr. The rate law then becomes

$$v = k p_{\rm NO}^{\alpha} p_{\rm H_2}^{\beta} = k'' p_{\rm NO}^{\alpha} (k'' = k p_{\rm H_2}^{\beta})$$

 α is then finally determined.

There is another witty method to find the order of a reaction whose rate depends upon two or more concentration terms. We exemplify this by the following problem.

Example 5.5

Under certain condition, the reaction $H_2 + Br_2 \rightarrow 2HBr$ obeys the rate law of the form

$$\frac{d}{dt}C_{\rm HBr} = k C_{\rm H_2}^{\ a} C_{\rm Br_2}^{\ b} C_{\rm HBr}^{\ c}$$
(3)

At a certain fixed temperature *T*, the reaction rate is found to be *R* when $C_{\text{HBr}} = 2 \text{ M}$ and, C_{H_2} and C_{Br_2} are both 0.1 M. The rate varies with concentration as follows:

Con			
$C_{ m H_2}$	$C_{ m Br_2}$	$C_{ m HBr}$	Rate
0.1	0.1	2	R
0.1	0.4	2	8 R
0.2	0.4	2	16 R
0.1	0.2	3	1.88 R

Find *a*, *b* and *c*.

Solution

Using the first two entries

$$R = (0.1)^a (0.1)^b (2)^c \tag{1}$$

$$8 R = (0.1)^a (0.4)^b (2)^c \tag{2}$$

Dividing Eq. (2) by Eq. (1), we get $8 = 4^{b}$

 \Rightarrow

$$3 \ln 2 = 2 b \ln 2$$

$$b = \frac{3(\ln 2)}{2(\ln 2)} = 1.5$$

Dividing the 3rd entry by the 2nd.

 $\frac{16 R}{8 R} = \frac{k (0.2)^a (0.4)^b (2)^c}{k (0.1)^a (0.4)^b (2)^c}$ $2 = 2^{a}$ \Rightarrow a = 1 \Rightarrow

Finally, dividing 4th entry by the 1st entry

$$\frac{1.88R}{R} = \frac{k(0.1)(0.2)^{\frac{3}{2}}(3)^c}{k(0.1)(0.1)^{\frac{3}{2}}(2)^c}$$
$$1.88 = 2^{\frac{3}{2}}(1.5)^c$$

c = -1

or

 \Rightarrow

The orders are then 1, $\frac{3}{2}$ and -1 with respect to H₂, Br₂ and HBr, respectively.

or

Example 5.6

.

The rate law for the reaction $2 \text{ NO} + \text{H}_2 \longrightarrow \text{N}_2 + 2 \text{ H}_2\text{O}$ is determined by measuring the initial rate. If the initial pressure of NO is 400 Torr, the rate is found to be 1.35 Torr s⁻¹ and 0.92 Torr s⁻¹ for initial pressures of H₂ of 290 and 200 Torr, respectively. If the initial H₂ pressure is 400 Torr, then the rate is 1.5 and 1.04 Torr s⁻¹ for initial NO pressure of 360

and 300 Torr, respectively. Show what *a* and *b* are in the rate law: $-\frac{dP_{\text{NO}}}{dt} = kP_{\text{NO}}^{a}P_{\text{H}_{2}}^{b}$, and calculate the rate constant *k*.

Solution

Using the rate law

 $v = k C_{\rm NO}^{a} C_{\rm H_2}^{b}$

 $\frac{1.35}{0.92} = \frac{k(400)^a (290)^b}{k(400)^2 (200)^b}$

we write

 \Rightarrow

 \Rightarrow

 $1.467 = 1.45^{b}$ b = 1

Similarly, $\frac{1.5}{1.04} = \frac{k(360)^a (400)^b}{k(300)^a (400)^b}$

 $\Rightarrow \qquad 1.44 = (1.2)^a$

 \Rightarrow a = 2

The rate constant is then obtained as

1.35 Torr s⁻¹ = $k (400 \text{ Torr})^2 (290 \text{ Torr})$ = $4.64 \times 10^7 k \text{ Torr}^3$ $k = 2.9 \times 10^{-8} \text{ Torr}^{-2} \text{ s}^{-1}$

5.6.2 Method of Integration: Integrated Rate Laws

In this method, the differential rate laws are first integrated, and the experimentally obtained concentration data with time are tested for the integrated rate equations for different orders.

The primary objective is therefore to get the concentrations of the reacting components as a function of time. Today, a number of software packages are available to solve even the most complex differential rate laws. In the following we give some simple cases, where the solutions can be found analytically. In all these cases, it is supposed that

- (i) the reaction is carried out at a fixed temperature, and
- (ii) the reaction is carried out at constant volume.

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5.6.2.1 First Order Reaction

Suppose the reaction

$$\alpha A \longrightarrow \text{Product (s)}$$

is first order with respect to the reactant *A*; the differential rate law is:

$$-\frac{1}{\alpha}\frac{dC_A}{dt} = k'C_A \tag{5.8a}$$

$$-\frac{dC_A}{dt} = (k'\alpha)C_A$$
$$-\frac{dC_A}{dt} = kC_A$$
(5.8b)

here, k' is the rate constant of the reaction and, k is the rate constant of the disappearance of A. If C_A^0 be the initial concentration of A and C_A be the concentration at time t, then integration between limits gives

$$\int_{C_{A}^{0}}^{C_{A}} \frac{dC_{A}}{C_{A}} = -k \int_{0}^{t} dt$$

$$C_{A} = C_{A}^{0} e^{-kt}; \ln C_{A} = \ln C_{A}^{0} - kt; \ln \frac{C_{A}^{0}}{C_{A}} = kt$$
(5.9)

The concentration of the reactant in a first order reaction decreases exponentially with time; the reaction goes to completion after infinite time. Moreover, greater the value of k, faster is the decay rate (Figure 5.6).

A more convenient plot is that of $\ln\left(\frac{C_A}{C_A^0}\right)$ versus *t*. A straight line is expected with a negative slope of -k (Figure 5.7).

or

or

 \Rightarrow



Figure 5.6 The first order decay of the concentration of the reactant with time. As the rate constant k increases, the decay becomes more faster. For a, b, c and d, the rate constants are a: 0.125 s⁻¹; b: 0.250 s⁻¹; c: 0.05 s⁻¹ and d: 0.1 s⁻¹.



Figure 5.7 The logarithmic version of the plots in Figure 5.6.

Example 5.7

A first order reaction is 20% complete in 50 minutes at 300 K. Calculate the time required to finish 99.99% reaction.

Solution

Using Eq. (5.9),

$$k = rac{1}{t} \ln rac{C_A^0}{C_A} = rac{1}{(50 ext{ min})} \ln rac{C_A^0}{(0.8 C_A^0)} = 4.46 imes 10^{-3} ext{ min}^{-1}$$

Therefore t for 99.99% reaction is

$$t_{0.9999} = \frac{1}{k} \ln \frac{C_A^0}{0.0001 C_A^0} = \frac{9.21}{(4.46 \times 10^{-3} \text{ min}^{-1})} = 2065 \text{ min}^{-1}$$

The half life time $t_{0.5}$ of a reaction is defined as the time span after which the reactant concentration C_R goes down to half its initial concentration C_R^0 ; i.e. at $t = t_{0.5}$ $C_R = \frac{1}{2}C_R^0$. Using Eq. (5.9), we find

$$t_{0.5} = \frac{1}{k} \ln \frac{C_R^0}{\left(\frac{1}{2} C_R^0\right)} = \frac{1}{k} \ln 2 = \frac{0.693}{k}$$
(5.10)

The half life time of a first order reaction is therefore independent of the initial concentration of reactant. This means that after every span of $t_{1/2}$, the concentration of the reactant becomes half of its initial concentration. This is exemplified in Figures 5.8(a) and 5.8(b).



Figure 5.8(a) The variation of concentration of the reactant with time for a first order process in two formats.



Figure 5.8(b) It shows the significance of half life time.

The first order rate constant has the unit of time⁻¹, and therefore, the value of the rate constant is independent of the scale of the concentration chosen. Moreover, the first order rate constant k has two interesting significances

(1) From Eq. (5.9), we write

$$egin{aligned} C_A &= C_A^0 \; e^{-kt} \; \Rightarrow \; dC_A &= -k C_A^0 \; e^{-kt} \; dt &= -k C_A \; dt \ & \displaystyle rac{-\left(rac{dC_A}{C_A}
ight)}{dt} &= k \end{aligned}$$

 \Rightarrow

i.e. the fractional decrease in the reactant concentration per unit time is a constant, and is equal to the rate constant of the reaction. Let us see an example.

Example 5.8

It takes 10 minutes for a certain first-order reaction, $R \rightarrow P$, to go 20% towards completion. What are *k* and $t_{0.5}$ and, how long should it take for 75% reaction?

Solution Using Eq. (5.9)

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$$k = rac{1}{t} \ln rac{C_A^{\ 0}}{C_A} = rac{1}{(10 ext{ min})} \ln rac{C_A^{\ 0}}{0.8 ext{ } C_A^{\ 0}} = 0.0223 ext{ min}^{-1}$$

...

Then using Eq. (5.10)

$$t_{0.5} = \frac{0.693}{0.0223} \min = 31.07 \min$$

Using the first order rate law

-

$$t_{75\%} = \frac{1}{k} \ln \frac{C_A^0}{(0.25 \, C_A^0)}$$

0

r
$$t_{75\%} = \frac{1}{k} \ln 4 = 2 \frac{\ln 2}{k} = 2 t_{0.5} = 62.14 \text{ min}$$

1 0

 $t_{75\%} = 2 \ t_{0.5}$ Note that

Comment: There is nothing special for a first order reaction, about the half-life time. The time required for the reactant concentration to drop down to the fraction f of its initial concentration is

$$t_f = \frac{1}{k} \ln \frac{C_R^0}{f C_R^0} = -\frac{\ln f}{k}$$

which is independent of the initial concentration of the reactant.

The average life time of the reactants is (2)

$$\begin{aligned} t_{\rm av} &= \frac{-1}{C_R^0} \int_0^\infty t \, dC_R^{*} = \frac{-1}{C_R^0} \int_0^\infty t \, d(C_R^0 \, e^{-kt}) \\ \Rightarrow & t_{\rm av} = -\int_0^\infty t d(e^{-kt}) = -\left[t \, e^{-kt}\right]_0^\infty + \int_0^\infty e^{-kt} \, dt \\ &= \frac{-1}{k} \left| e^{-kt} \right|_0^\infty = \frac{1}{k} \end{aligned}$$

It is noteworthy that, this $t_{\rm av}$ is the time span after which the reactant concentration becomes $\left(\frac{1}{e}\right)^{\text{th}}$ of its initial concentration:

$$kt = \ln\left(\frac{C_R^0}{C_R}\right) = \ln e = 1$$

5.18

The negative sign is included to make t_{av} positive as dC_R is itself negative.

 \Rightarrow

$$t_{\frac{1}{e}} = \frac{1}{k} = t_{av}$$

Example 5.9

At 100°C, the gaseous reaction $A \longrightarrow 2B + C$ is observed to be first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of the system is 176 Torr, and after a long time it is 270 Torr. From these data, find

..

- (a) the initial pressure of A;
- (b) the pressure of A at the end of 10 minutes;
- (c) the rate constant of the reaction and,
- (d) The half life time of A.

Solution

The reacting system is analysed as:

$$3P_A^0 = 270 \text{ Torr} \implies P_A^0 = 90 \text{ Torr}$$

and $P_A^0 + 2p = 176 \text{ Torr}$

 \Rightarrow p = 43 Torr

The pressure of A at the end of 10 minutes is then

$$p_A = P_A^0 - p = (90 - 43)$$
 Torr = 47 Torr

The rate constant is then calculated as:

$$k = \frac{1}{t} \ln \frac{P_A^0}{P_A} = \frac{1}{(10 \text{ min})} \ln \frac{(90 \text{ Torr})}{(47 \text{ Torr})} = 0.065 \text{ min}^{-1}$$

The half life time is then

$$t_{0.5} = \frac{0.693}{k} = \frac{0.693}{(0.065 \text{ min}^{-1})} = 10.66 \text{ min}$$

5.6.2.2 Integrated Rate Law of a First Order Reaction at Constant Pressure Consider a first order reaction

$$A \longrightarrow vB$$

(5.11)

Let us start with n_A^0 mole of the reactant *A*. If the reaction be advanced by ξ mole at time *t* then, the number of mole of *A* at time *t* is $n_A = n_A^0(1 - \xi)$, and the number of mole of *B* at time *t* is $n_B = vn_A^0 \xi$. The total number of mole at time *t* is then, $n = n_A + n_B$

$$n = n_A^0 (1 - \xi) + v n_A^0 \xi$$

$$n = n_A^0 + (v - 1) n_A^0 \xi$$
(5.12)

or

Since the reaction is conducted at constant pressure condition, constant *T* condition is to be understood always, the volume changes proportionately with the number of mole in the reaction vessel. If V_0 and *V* are the volumes, respectively, at t = 0 and at time *t*, then,

 $PV = n_A^0 [1 + (v - 1)\xi] RT$ (5.13)

and

$$PV_0 = n_A^0 RT \tag{5.14}$$

Dividing Eq. (5.13) by (5.14), we get

 $V = V_0 [1 + (v - 1)\xi]$ (5.15)

For a first order process we may write

$$n_A = n_A^0 e^{-kt}$$

 $\frac{n_A}{V} = \frac{n_A^0}{V} e^{-kt}$

k is the rate constant of the reaction. Dividing the above equation by V, we find

 $C_A = \frac{n_A^0}{V_0[1 + (v - 1)\xi]} e^{-kt}$

 $C_A = \frac{C_A^0}{[1 + (y - 1)\xi]} e^{-kt}$

 \Rightarrow

$$\Rightarrow \qquad \qquad \frac{C_A^0}{C_A} = [1 + (\nu - 1)\xi]e^{kt}$$

$$\Rightarrow \qquad \qquad \frac{C_A^{\ 0}}{C_A} = e^{kt} + (v-1)\xi e^{kt}$$

Using the relation $n_A = n_A^0(1 - \xi)$, we find

$$\xi = 1 - \frac{n_A}{n_A^0} = (1 - e^{-kt})$$
, and substituting in the above equation, the result is
$$\frac{C_A^0}{C_A} = e^{kt} + (v - 1) (1 - e^{-kt}) e^{kt}$$

 $= e^{kt} + (v - 1)e^{kt} - (v - 1)$ $= e^{kt} + ve^{kt} - e^{kt} - (v - 1)$

or

 \Rightarrow

which is the integrated rate equation for a first order reaction, carried out at constant pressure conditions.

For v = 2, Eq (5.16) changes to

 $\frac{C_A^0}{C_A} = v e^{kt} - (v - 1)$

$$\frac{C_A^0}{C_A} = 2e^{kt} - 1 \tag{5.17}$$

which is completely different from that, if the reaction is conducted at constant volume [cf. Eq. (5.9)].

The Compounded Interest on a Loan Taken from a Bank: A First-Order Process

Let us do it with a problem.

A family buys a micro-oven for ₹8500, paying ₹2500 down, so that P_0 , the initial principal on their loan is ₹6000. Let *P* be the monthly payment and *i* be the interest rate in % per month. Derive an equation relating P_0 , *P*, *i* and *n*, where *n* is the number of payments to pay off the loan.

The first premium *P* paid after the first month goes to $P(1 + i)^{n-1}$ at the end; the second premium goes to $P(1 + i)^{n-2}$; the third premium goes to $P(1 + i)^{n-3}$, ..., and the last premium to $P(1 + i)^0$. This is exemplified in the following scale

0 1 2 3 4 5 n

The net amount paid P_T is therefore

$$\begin{split} P_T &= P(1+i)^{n-1} + P(1+i)^{n-2} + \dots + P(1+i)^0 \\ P_T &= P[(1+i)^{n-1} + P(1+i)^{n-2} + \dots + 1] \end{split}$$

This is a G.P. series; the sum is therefore

$$P_T = \frac{P(1+i)^{n-1}[1-(1+i)^{-n}]}{1-(1+i)^{-1}}$$
(i)

(5.16)

On the other hand, the initial principal P_0 has grown up to $P_T = P_0(1+i)^n$ at the end of the time span. We therefore write

$$P_0(1+i)^n = \frac{P(1+i)^{n-1}[1-(1+i)^{-n}]}{1-(1+i)^{-1}} = \frac{P(1+i)^{n-1}[1-(1+i)^{-n}]}{1-\frac{1}{1+i}}$$

$$=\frac{P(1+i)^{n-1}[1-(1+i)^{-n}]}{\frac{i}{(1+i)}}$$

$$\Rightarrow \qquad P_0(1+i)^n = \frac{P(1+i)^{n-1}[1-(1+i)^{-n}]}{i}$$

 $\Rightarrow \qquad \qquad P_0 = \frac{P[1-(1+i)^{-n}]}{i}$

It is simply a first order process.

5.6.2.3 Second Order Reaction

Second order reactions are of two types:

- (a) second order with respect to a particular reactant and,
- (b) first order with respect to two reactants.

(a) Considering the First, Let the Reaction be

$$2R \longrightarrow P$$

The differential rate law is

$$v = -\frac{1}{2}\frac{dC_R}{dt} = k'C_R^2$$

$$\Rightarrow \qquad -\frac{dC_R}{dt} = kC_R^2$$

where k' is the rate constant of the reaction and k is the rate constant for the rate of disappearance of the reactant R. Integrating between limits

(k = 2k')

$$-\int_{C_{R}^{0}}^{C_{R}} \frac{dC_{R}}{C_{R}^{2}} = k \int_{0}^{t} dt$$
$$\frac{1}{C_{R}} = \frac{1}{C_{R}^{0}} + kt$$
(5.18)

5.22

 \Rightarrow

The equation may be tested by plotting $\frac{1}{C_R}$ versus *t*; a straight line is obtained with slope k and intercept $\left(\frac{1}{C_R^0}\right)$. This is shown in Figure 5.9. The half life time is evaluated as [using Eq. (5.18)]



Figure 5.9 An expected plot of $(1/C_R)$ versus t for a second order reaction involving a single reactant or two reactants of equal initial concentrations.

$$\frac{1}{(C_R^0/2)} = \frac{1}{C_R^0} + kt_{0.5}$$
$$t_{0.5} = \frac{1}{kC_R^0}$$
(5.19)

 \Rightarrow

The half life time of a second order reaction is therefore inversely proportional to the initial concentration of the reactant. This is in contrast to a first order reaction. For a second order reaction $t_{0.5}$ is doubled after the first 50% reaction, further doubled after the second 50% reaction, i.e. from 50 to 75% and so on. But for a first order reaction $t_{0.5}$ remains the same (Figure 5.10). A second order reaction therefore gets more slower than a first-order decay with the passage of time. In fact, with the same rate constant, the decay of the reactant concentration becomes more and more slower as the order increases. The units of the second order rate constant are that of conc⁻¹ time⁻¹, e.g. mol⁻¹ Ls⁻¹, molecule⁻¹ cc min⁻¹, atm⁻¹ s⁻¹ and so on.



Figure 5.10 A comparison between the decay of the reactant in a first order process and a second order process.

Example 5.10

At 330°C acrolein and 1,3-butadiene undergo Diels-Alder reaction to form tetrahydrobenzaldehyde, and the reaction goes essentially to completion. The two reactants are taken in equimolar amounts. Initially, the total pressure of the reaction mixture was 480 Torr. The total pressure of the reaction mixture was then measured at different time intervals. The data recorded is shown in the following table.



Time (s)	0	63	181	384	542	745	925	1145	1374	1627	1988
Total	240	476.52	470.4	460.26	453.22	444.08	437.63	429.39	421.82	414.22	404.20
Pressure											
(Torr)											

Confirm that the reaction follows a second-order kinetic process and, find out the rate constant of the reaction.

Solution

Since the two reactants are taken at equimolar amounts, their initial partial pressures are equal, i.e. for each reactant the initial partial pressure is (480 Torr)/2 = 240 Torr. Using Eq. (5.18), we write

$$\frac{1}{P_R} = \frac{1}{P_R^0} + kt$$
(5.20)

where P_R is the partial pressure of each reactant at time *t*, and $P_R^0 = 240$ Torr

If x be the partial pressure of the product at time t, then the partial pressures of the reactants are $(P_R^0 - x)$ each. The total pressure of the reaction mixture is then:

$$P_{T} = (P_{R}^{0} - x) + (P_{R}^{0} - x) + x$$

$$P_{T} = 2P_{R}^{0} - x$$

$$x = 2P_{R}^{0} - P_{T}$$
(5.21)

or, \Rightarrow

The partial pressure of each reactant P_R is then

or,

 $P_{R} = (P_{R}^{0} = x)$ $P_{R} = [P_{R}^{0} - (2P_{R}^{0} - P_{T})]$ $P_{R} = (P_{T} - P_{R}^{0})$ (5.22)

or,

Using this equation we then calculate P_R and $(1/P_R)$ at different time intervals; the result is:

t(s)	0	63	181	384	542	745	925	1145	1374	1627	1988
P _R (Torr)	240	236.52	230.4	220.26	213.22	204.08	197.63	189.39	181.82	174.22	164.20
$\frac{1}{P_R}$ (Torr ⁻¹)		4.228 × 10 ⁻³	4.34 × 10 ⁻³	4.54×10^{-3}	4.69×10^{-3}	4.9 × 10 ⁻³	5.06×10^{-3}	5.28×10^{-3}	5.5×10^{-3}	5.7×10^{-3}	6.09×10^{-3}

We now make a plot of $1/P_R$ versus *t*; it is shown in Figure 5.11. The smooth fitting of the data on a straight line, as being demanded by Eq. (5.20), confirms that the reaction follows a second-order kinetics. Moreover, from the intercept we find



Figure 5.11 The plot of $1/P_R$ versus t [Eq. (5.20)].

$$\frac{1}{P_R^0} \times 10^3 = 83.5 \times 0.05 = 4.175$$

 $P_R^{\ 0} = 239.5 \approx 240 \text{ Torr}$

exactly the same as that given in the problem. The slope of the straight line is then evaluated

Slope =
$$\frac{\left(\frac{1}{P_R}\right) \times 10^3}{t \times 10^{-2}} = \frac{\left(\frac{1}{P_R}\right) \times 10^5}{t} = \frac{35 \times 0.05}{93.5 \times 0.2} = 0.09358$$

 $k = \frac{\frac{1}{P_R}}{t} = 9.4 \times 10^{-7} \text{ Torr}^{-1} \text{ s}^{-1}$

The rate constant of the reaction.

 \Rightarrow

 \Rightarrow

(b) We now consider the second type of the second order reaction, where two different reactants A and B are involved

$$A + B \longrightarrow P$$

If the initial concentrations of A and B are equal, then, the rate process can be analysed as discussed in the previous section. Here we concern when the initial concentrations of A, C_A^0 and B, C_B^0 are different, and the reaction is first order with respect to each reactant, i.e. the rate law is

$$v = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k C_A C_B$$
(5.23)

Where v is the rate of the reaction at time t when the concentrations of A and B are C_A and C_B , respectively. From the stoichiometry of the reaction we may write

$$C_A^{\ 0} - C_A = C_B^{\ 0} - C_B \tag{5.24}$$

Equation (5.23) then becomes [using Eq. (5.24)]

$$-\frac{dC_{A}}{dt} = kC_{A}(C_{B}^{0} - C_{A}^{0} + C_{A})$$
$$-dC_{A}\left[\frac{1}{C_{A}(C_{B}^{0} - C_{A}^{0} + C_{A})}\right] = kdt$$
(5.25)

Then using the method of partial fractions we write

$$\frac{1}{C_A(C_B^0 - C_A^0 + C_A)} = \frac{p}{C_A} + \frac{Q}{(C_B^0 - C_A^0 + C_A)}$$

$$1 = P(C_B^0 - C_A^0 + C_A) + QC_A$$
(5.26)

 \Rightarrow

 \Rightarrow

$$1 = P(C_B^0 - C_A^0) + (P+Q)C_A$$

P+Q = 0; or P = -Q, and

 \Rightarrow

$$P + Q = 0$$
; or $P = -$
 $P(C_A^0 - C_B^0) = 1$

Therefore,

$$P = \frac{1}{(C_B^0 - C_A^0)} \text{ and } Q = -\frac{1}{(C_B^0 - C_A^0)}$$

Using these results in Eq. (5.25) with Eq. (5.26), we have

$$-\frac{1}{(C_B^0 - C_A^0)}\frac{dC_A}{C_A} + \frac{1}{(C_B^0 - C_A^0)}\frac{d(C_B^0 - C_A^0 + C_A)}{(C_B^0 - C_A^0 + C_A)} = kdt$$

Physical Chemistry

Integrating between limits:

$$= \frac{1}{(C_B^0 - C_A^0)} \int_{C_A^0}^{C_A} \frac{dC_A}{C_A} + \frac{1}{(C_B^0 - C_A^0)} \int_{C_A^0}^{C_A} \frac{d(C_B^0 - C_A^0 + C_A)}{(C_B^0 - C_A^0 + C_A)} = k \int_0^t dt$$

$$= \frac{1}{(C_B^0 - C_A^0)} \left[\ln \frac{C_A^0}{C_A} + \ln \frac{(C_B^0 - C_A^0 + C_A)}{C_B^0} \right] = kt$$

$$\frac{1}{(C_B^0 - C_A^0)} \ln \frac{C_A^0 (C_B^0 - C_A^0 + C_A)}{C_A C_B^0} = kt$$

 $\frac{1}{(C_B^0 - C_A^0)} \ln \frac{C_A^0 C_B}{C_A C_B^0} = kt \quad \text{[using (Eq. 5.24)]}$ (5.27)

or

 \Rightarrow

which is the final form of the integrated rate law. In terms of the variable x, representing the decrease in the concentration of the components, i.e.

$$C_A^0 - C_A = x = C_B^0 - C_B$$

The above Eq. (5.27) may be rewritten as

$$\frac{1}{(b-a)}\ln\frac{a(b-x)}{b(a-x)} = kt \quad (a \neq b)$$

$$\frac{1}{(a-b)}\ln\frac{b(a-x)}{a(b-x)} = kt \quad (a \neq b)$$
(5.28)

or

Where $C_A^{\ 0} = a$ and $C_B^{\ 0} = b$ are used for simplicity

Example 5.11

Equation (5.28) is an indeterminate for a = b. Nevertheless, show as $b \rightarrow a$, Eq. (5.28) that switches on to Eq. (5.18).

Solution

Equation (5.28) may be written as

$$\frac{1}{(a-b)} \left[\ln \frac{b}{a} + \ln \frac{(a-x)}{(b-x)} \right] = kt$$
$$\frac{1}{(a-b)} \left[\ln \left\{ 1 - \frac{(a-b)}{a} \right\} + \ln \left\{ 1 + \frac{(a-b)}{(b-x)} \right\} \right] = kt$$

 \Rightarrow

In the limit $b \rightarrow a$, (a - b) is a very small number; we then approximate the above equation using:

 $\ln(1+x) \approx x$ for very small x, i.e. $x \ll 1$,

$$\frac{1}{(a-b)} \left[-\frac{(a-b)}{a} + \frac{(a-b)}{(a-x)} \right] = kt$$
$$\frac{1}{a-x} = \frac{1}{a} + kt$$
$$\frac{1}{C_R} = \frac{1}{C_R^0} + kt$$

or

 \Rightarrow

Example 5.12

Formulate the integrated rate law of a second order reaction between two reactants A and B (the reaction being first order with respect to each of A and B) when the reaction is stoichiometry

$$aA + bB \longrightarrow$$
Products

0

...

Solution

 $aA + bB \longrightarrow$ Products $C_A^{\ 0} \qquad C_B^{\ 0}$

at t = 0

 $(C_A^0 - x) \quad (C_B^0 \frac{b}{a}x)$ at time t

The rate of the reaction is then

$$v = -\frac{1}{a} \frac{dC_A}{dt} = kC_A C_B$$

$$C_A = C_A^0 - x \; ; \; \Rightarrow \; \frac{-dC_A}{dt} = \frac{dx}{dt}$$
(5.29)

The rate law is therefore,

$$\frac{dx}{dt} = ak \left(C_A^0 - x\right) \left(C_B^0 - \frac{b}{a}x\right)$$
$$\frac{dx}{\left(C_A^0 - x\right) \left(C_B^0 - \frac{b}{a}x\right)} = ak dt$$

 \Rightarrow

..

Physical Chemistry

Using the method of partial fraction and integrating with the lower limit as: x = 0 at t = 0, we find

$$\frac{1}{(bC_A^0 - aC_B^0)} \ln \frac{C_B^0 (C_A^0 - x)}{C_A^0 \left(C_B^0 - \frac{b}{a}x\right)} = kt$$
$$\frac{1}{(bC_A^0 - aC_B^0)} \ln \frac{C_B^0 C_A}{C_A^0 C_B} = kt$$
(5.30)

 \Rightarrow

It may be checked that if a = b = 1, then the above Eq. (5.30) changes to Eq. (5.27), derived earlier.

Two special cases may appear:

(I) If $C_A^0 \ll C_B^0$, then very small amount/concentration of *B* is consumed compared to *A*, during the course of the reaction; C_B is then essentially the constant C_B^0 . Under this condition, Eq. (5.29) changes as

$$-\frac{dC_A}{dt} = (ak C_B^0)C_A = k_{app} C_A$$
(5.31)

The reaction then behaves as a first-order kinetic process. This is a *pseudo-first-order* rate law.

(II) If $bC_A^0 = aC_B^0$, Eq. (5.30) again becomes indeterminate. Since $bC_A^0 = aC_B^0$, it follows

that $bC_A = aC_B$ at all times, and Eq. (5.29) changes to

$$-\frac{dC_A}{dt} = akC_A\left(\frac{b}{a}C_A\right) = bkC_A^2 = (\text{const})C_A^2$$

a form similar to that of a second order reaction of the type: $2A \rightarrow$ Products (s).

Example 5.13

The rate law for the reaction $A + B \longrightarrow$ Product (s) is

$$-\frac{dC_A}{dt} = kC_A C_B$$

with $k = 0.02 \text{ M}^{-1} \text{ min}^{-1}$. What percent of A has reacted after 15 minutes if

(a)
$$C_A^0 = 0.1$$
 M and $C_B^0 = 0.3$ M
(b) $C_A^0 = C_B^0 = 0.1$ M and,

(c) $C_A^{\ 0} = 0.001 \text{ M}$ and $C_B^{\ 0} = 0.3 \text{ M}$?

5.30

Solution

(a) Since $C_A^0 \neq C_B^0$, we use Eq. (5.27);

$$\frac{1}{(C_A^0 - C_B^0)} \ln \frac{C_A^0 C_B}{C_A C_B^0} = kt$$

using the data we get

$$\frac{1}{(0.3-0.1)M} \ln \frac{(0.1) C_B}{(0.3) C_A} = (0.02 M^{-1} \min^{-1}) (15 \min)$$

$$\Rightarrow \qquad \qquad \frac{1}{0.2}\ln\frac{3C_A}{C_B} = -0.3$$

$$\Rightarrow \qquad \qquad \ln \frac{3C_A}{C_B} = -0.06$$

$$\Rightarrow \qquad \qquad \frac{3C_A}{C_B} = \exp(-0.06)$$

or
$$\frac{C_A}{C_B} = 0.3139$$

Now,
$$\frac{C_A}{C_B} = \frac{(0.1 - x)}{(0.3 - x)}$$

where x is the concentration of the two reactants reacted at time t = 15 minutes. Equating the two results for $\frac{C_A}{C_B}$, we find $x = 8.45 \times 10^{-3}$ M. With respect to A, the reaction has therefore approached by

$$\frac{(8.45 \times 10^{-3} \,\text{M})}{(0.1 \,\text{M})} \times 100 = 8.45\%$$

(b) Since, $C_A^{\ 0} = C_B^{\ 0} = 0.1 \text{ M}$, we now use Eq. (5.18)

$$\frac{1}{C_A} = \frac{1}{(0.1 \text{ M})} + (0.02 \text{ M}^{-1} \text{ mm}^{-1}) (15 \text{ mm})$$
$$\frac{1}{C_A} = 10.3 \text{ M}^{-1}$$

or $C_A = 0.09709 \text{ M}$

 \Rightarrow

The percent of A(and B) reacted is then

$$\frac{(0.1 - 0.09709)M}{0.1M} \times 100 = 2.91\%$$

(c) Since C_B^0 is $\left(\frac{0.3}{0.001}\right)$, 300 times C_A^0 , this is a pseudo-first-order process. Using

Eq. (5.31), we find, after integration,

$$\ln \frac{C_A}{C_A^0} = -(kC_B^0)t = -(0.02 \ \text{M}^{-1} \ \text{min}^{-1})(0.3 \ \text{M})(15 \ \text{min})$$

$$\Rightarrow \qquad \qquad \ln \frac{C_A}{C_A^0} = -0.09$$

$$\Rightarrow \qquad \qquad \frac{C_A}{C_A^0} = 0.9139$$

The percent reaction is therefore

$$\left(1-\frac{C_A}{C_A^0}\right)100=8.61$$

Example 5.14

Consider a second order reaction, first-order with respect to the analyte A, and first-order with respect to the reagent R:

$$A+R \longrightarrow P$$

The rate law is

$$v = kC_A C_R$$

If $C_R \gg C_A$, so that the change in the concentration of R is very little, compared to C_A , during the course of the reaction, we can write $kC_R = k' = \text{constant}$, we then get a pseudo-first-order rate law

$$v = k'C_A$$

For a given run if $C_R = 100 C_A$, find the relative error from the assumption that k' is constant when the reaction is 40% complete.

Solution

According to the problem

$$C_R^{\ 0} = 100 \ C_A^{\ 0}$$

5.32

after 40% reaction

$$C_A = (C_A^0 - 0.4C_A^0) = 0.6C_A^0$$
 and $C_R = C_R^0 - 0.4C_A^0$
 $C_R = (100 C_A^0 - 0.4 C_A^0) = 99.6 C_A^0$

or

Assuming pseudo-first-order kinetics

$$v = kC_R^0 C_A = k(100 C_A^0) (0.6 C_A^0) = 60 k(C_A^0)^2 \qquad \dots (i)$$

The true rate is

$$v = k(99.6 C_A^0) (0.6 C_A^0) = 59.76 k(C_A^0)^2$$
 ...(ii)

The relative error is then (60 - 59.76)/59.76

= + 0.004, i.e. + 0.4%

5.6.2.4 Zeroth Order Reaction

A reaction is referred to as a zeroth-order reaction when *the rate of the reaction has no dependence on any concentration term of the reactant*(s). Now, when the reaction proceeds as the time marches on, definitely the reactant concentration(s) must change with time.

Therefore, no dependence on any concentration term means no dependence on time. Therefore, for a zeroth order reaction

 $A \rightarrow product(s)$

the rate v is

$$-\frac{dC_A}{dt} = k \tag{5.32}$$

On integration between limits:

$$\int_{C_A}^{C_A} dC_A = -k \int_0^t dt$$

$$C_A = C_A^0 - kt$$
(5.33)

where C_A is the reactant concentration at time *t* and C_A^0 is the initial concentration. A plot of C_A versus *t* would then be a straight line with a negative slope of (-k), (Figure 5.12).

These reactions should more properly be called *pseudo-zero-order* reactions because there must be some mechanistic pathway through which the reaction proceeds in such a way that the overall rate becomes independent of any concentration term. This may be explained as follows:

(a) During a photochemical reaction, the initial step is the photo excitation, where each reactant molecule absorbs a single photon from the incident radiation. The intensity of the incident radiation measures the number of photons per unit

5.33

volume per unit time. If I_{abs} be the intensity of the absorbed radiation and I_0 be the intensity of the incident beam then, according to the Beer's law

$$I_{abs} = I_0 (1 - e^{-\alpha cl})$$
(5.34)

where α is the absorption coefficient, *C* is the molar concentration of the absorbing solute particles and, *l* is the path length. The rate of the photochemical reaction will be

$$v = \phi I_{\rm abs} \tag{5.35}$$

where ϕ is an efficiency factor, called the quantum yield of the reaction. Now, in the limit of very high concentration of the reactant molecules, the factor $e^{-\alpha cl}$ may be neglected and, Eq. (5.34) then gives us: $I_{\rm abs} = I_0$ and Eq. (5.35) changes as

$$\nu = \phi I_0 \tag{5.36}$$

a rate law which is of zeroth order. Thus, although the rate is independent of the reactant concentration, it does depend on the I_{abs} . Probably, sufficient number of absorbing molecules are present in comparison to I_0 .

But, if the concentration is lowered, Eq. (5.34) will change as

$$I_{\rm abs} = I_0 \left[1 - \left\{ 1 - \alpha cl + \frac{\alpha^2 C^2 l^2}{2!} - \cdots \right\} \right]$$
$$I_{\rm abs} = I_0(\alpha l)C \tag{5.37}$$

 \Rightarrow

the rate law then switches on to a first order process.

(b) There are ample examples of zeroth order reactions in heterogeneous catalysis. For such a reaction like

$$A(g) + - \stackrel{|}{S} - \stackrel{|}{\longrightarrow} - \stackrel{|}{S} - \longrightarrow Product(s) + - \stackrel{|}{S} -$$

۸

where A(g) is a reactant molecule in the gas phase, S is a vacant surface atom on the solid

catalyst used and $-\overset{A}{\overset{}_{S}}$ is the adsorbed state of the reactant molecule. These adsorbed

molecules shake-off to form the product(s). If θ be the fraction of the surface sites occupied at an equilibrium pressure P, then the rate of the reaction would be

$$v = k' A \theta \tag{5.38}$$

where A is the effective surface area and k' is a rate constant. For the simplest case, it can be shown that (the Langmuir equation)

$$\theta = \frac{KP}{(1+KP)} \tag{5.39}$$

where K is the adsorption-desorption equilibrium constant, and P is the pressure of the overlying gas. The rate then becomes

$$v = \frac{k'A \ KP}{(1+KP)} \tag{5.40}$$

a rate law whose order cannot be defined. However, two limiting conditions may be considered. At very low pressure, $(1 + KP) \approx 1$ and we have

$$v = k'AKP = k_1P \tag{5.41}$$

a first order kinetics. On the other hand, at very high pressure $(1 + KP) \approx KP$; we then have

$$v = k'A = k_2 \tag{5.42}$$

which a zeroth order rate law. Thus, the order of the reaction changes from 1 to zero as the pressure is gradually increased. The reason is that, at very low pressure there is an affluence of surface sites for the reactant molecules to get adsorbed; hence, the rate increases proportionately with pressure [Eq. (5.41)]. As the pressure is gradually increased, this proportionality is broken; the rate slows down. At sufficiently high pressure, θ becomes almost unity; all the surface sites are now occupied, and we get the maximum rate.

Further increase in the pressure is then of no use; the reaction then goes as zeroth-order. It is noteworthy that a zeroth order reaction unlike first and second order, goes to 100% completion within a finite time of [using Eq. (5.33)]

$$t_{100\%} = \frac{C_A^0}{k} \qquad (\because C_A = 0) \tag{5.43}$$

This is also confirmed from Figure 5.12; the straight line will intersect the time axis at $t_{100\%}$. The half life time $t_{0.5}$ is then



Figure 5.12 A zero order rate plot for a reaction where $[A]_0 = 0.75$ M and k = 0.012 mol/1.

5.6.2.5 Third Order Reaction with Three Reactants

Let the stoichiometry of the reaction be

- ---

$$A + B + C \longrightarrow \text{Product(s)}$$

and the reaction is of third-order; first-order with respect to each of A, B and C, i.e. the rate law is

$$-\frac{dC_A}{dt} = k C_A C_B C_C \tag{5.45}$$

Since

 $C_{A}^{0} - C_{A} = C_{B}^{0} - C_{B} = C_{C}^{0} - C_{C}$, we find

$$C_B = C_B^0 - C_A^0 + C_A$$
 and $C_C = C_C^0 - C_A^0 + C_A$

Therefore,

$$-\frac{dC_A}{dt} = k C_A (C_B^0 - C_A^0 + C_A) (C_C^0 - C_A^0 + C_A)$$

and integrating by partial fractions, we find

$$\frac{1}{(C_A^0 - C_B^0) \ (C_B^0 - C_C^0) \ (C_C^0 - C_A^0)} \ln \left[\left(\frac{C_A}{C_A^0} \right)^{(C_B^0 - C_C^0)} \left(\frac{C_B}{C_B^0} \right)^{(C_C^0 - C_A^0)} \left(\frac{C_C}{C_C^0} \right)^{(C_A^0 - C_B^0)} \right] = kt \quad (5.46)$$

Third Order Reaction with Two Reactants 5.6.2.6

Let the stoichiometry be

 $2A + B \longrightarrow \text{Product}(s)$

the rate law is then

$$-\frac{dC_A}{dt} = k C_A^2 C_B$$

Here,

$$C_A^0 - C_A = 2(C_B^0 - C_B)$$
 and $C_B = C_B^0 - \frac{C_A^0}{2} + \frac{C_A}{2};$

R

then

 $-\frac{aC_A}{dt} = kC_A^2 \left(C_B^0 - \frac{C_A}{2} + \frac{C_A}{2} \right)$ The form of the partial fractions is then

$$1 \qquad P \quad Q$$

$$\frac{1}{C_A^2 (C_B^0 - \frac{C_A^0}{2} + \frac{C_A}{2})} = \frac{1}{C_A^2} + \frac{C_A}{C_A} + \frac{1}{C_A} + \frac{1}{C_B^0 - \frac{C_A^0}{2} + \frac{C_A}{2}}$$

Evaluating constants P, Q and R, the final integrated rate law comes out as

$$\frac{2}{(2C_B^0 - C_A^0)} \left(\frac{1}{C_A} - \frac{1}{C_A^0} \right) + \frac{2}{(2C_B^0 - C_A^0)^2} \ln \frac{C_B^0 C_A}{C_A^0 C_B} = kt; (2C_B^0 \neq C_A^0)$$
(5.47)

Examples of this kind of reaction are reactions between NO and O_2 , Cl_2 or Br_2 .

5.6.2.7 Third Order Reaction with a Single Reactant

 $3A \longrightarrow \text{Products}(s)$

The rate law is

$$-\frac{dC_A}{dt} = kC_A^3$$

Integrating between limits

$$\int_{C_A}^{C_A} C_A^{-3} dC_A = -k \int_0^t dt$$

$$\left(\frac{1}{C_A^2} - \frac{1}{(C_A^0)^2}\right) = 2kt$$
(5.48)

 \Rightarrow

A plot of $\frac{1}{C_A^2}$ versus time should be linear and have a slope of 2k. After the first half life

 $t_{0.5}, C_A = \frac{1}{2} C_A^{\ 0}$. Using Eq. (5.48) we then get

$$2 k t_{0.5} = \frac{4}{(C_A^0)^2} - \frac{1}{(C_A^0)^2} = \frac{3}{(C_A^0)^2}$$
$$t_{0.5} = \frac{3}{2 k (C_A^0)^2}$$
(5.49)

or

Example 5.15

For the reaction

$$2\operatorname{Fe}\operatorname{Cl}_3 + \operatorname{Sn}\operatorname{Cl}_2 \longrightarrow 2\operatorname{Fe}\operatorname{Cl}_2 + \operatorname{Sn}\operatorname{Cl}_4$$

in aqueous medium the following data were obtained at 25°C.

$t(\min)$	1	3	7	11	40
y(M)	0.01434	0.02664	0.03612	0.04102	0.05058

where y is the amount of FeCl₃ reacted in M. The initial concentrations of SnCl₂ and FeCl₃ were 0.03125 M and 0.0625 M, respectively. Show that the reaction is third-order and, calculate the average rate constant.

Solution

at t = 0

The reaction is of the type given in Section 5.8.6; but, we cannot use the corresponding integrated rate law given in Eq. (5.47). This is because, $2C_B^0 = C_A^0$ for our problem [2(0.03125) = 0.0625]; the equation becomes indeterminate. It should now be represented by Eq. (5.48). Let the reaction be represented as

> $\operatorname{FeCl}_3 + \operatorname{FeCl}_3 + \operatorname{SnCl}_2 \longrightarrow 2\operatorname{FeCl}_2 + \operatorname{SnCl}_4$ 0.3125 0.03125 0.03125

The integrated rate law, Eq. (5.48), is then used to calculate k at different time intervals. In our calculation we then use $C_R^0 = 0.03125$ M.

Let the amount of $SnCl_2$ reacted at time *t* be *x*. At t = 1 min

$$x = \frac{y}{2} = \frac{0.01434 \text{ M}}{2} = 0.00717 \text{ M},$$

$$C_R = C_R^{0} - x = (0.03125 - 0.00717) \,\mathrm{M} = 0.02408 \,\mathrm{M}$$

$$\Rightarrow \qquad \frac{1}{C_R^2} = 1724.59, \text{ and therefore}$$

$$k = \frac{1}{2(1\min)} [1724.59 - 1024] \text{ M}^{-2} = 350.3 \text{ M}^{-2} \min^{-1}$$

At
$$t = 3 \min$$
 $C_R = \left(0.03125 - \frac{0.02664}{2}\right) M = 0.01793 M$

$$\Rightarrow \frac{1}{C_R^2} = 3110.57$$

$$k = \frac{1}{6 \min} [3110.57 - 1024] \,\mathrm{M}^{-2} = 347.8 \,\mathrm{M}^{-2} \,\mathrm{min}^{-1}$$

At t = 7 min; proceeding along same manner $k = 337.4 \text{ M}^{-2} \text{ min}^{-1}$

 $k = 347.5 \text{ M}^{-2} \text{ min}^{-1}$ $t = 11 \min;$ At $k = 339.1 \text{ M}^{-2} \text{ min}^{-1}$ and at t = 40 min:

The values of k obtained are of the same order in magnitudes; the reaction is therefore a third-order process with the average rate constant $344.4 \text{ M}^{-2} \text{ min}^{-1}$.

5.6.2.8 A General n-th Order Reaction

Finally, we consider an n-th order reaction involving a single reactant, or different reactants of equal concentration

$$nR \longrightarrow$$
 Product (s) or $R_1 + R_2 + \cdots \longrightarrow$ Product (s)

Let C_R^0 be the concentration of the reactant initially (t = 0), and C_R be the reactant concentration at time t; the rate law is then

$$v = -\frac{dC_R}{dt} = kC_R^n$$

which on integration between limits gives

$$k = \frac{1}{t(n-1)} \left[\frac{1}{C_R^{n-1}} - \frac{1}{C_R^{0^{n-1}}} \right] \qquad (n \neq 1)$$
(5.50)

The half life time $t_{0.5}$ for such a process is then

$$t_{0.5} = \frac{1}{(n-1)kC_R^{0^{n-1}}} [2^{n-1} - 1] \qquad (n \neq 1)$$
(5.51)

Now, let us see, for what values of *n*, the reaction may go to 100% completion, 100% completion means, $C_R = 0$. Rearranging Eq. (5.50) as

$$t = \frac{C_R^{0^{(1-n)}}}{k(n-1)} \left[\left(\frac{C_R}{C_R^0} \right)^{1-n} - 1 \right]$$

$$t_{100\%} = -\frac{C_R^{0^{(1-n)}}}{k(n-1)}$$
(5.52)

From Eq. (5.52) it is clear that, for $t_{100\%}$ to be a finite and positive (n-1) must be negative. The required condition is then

$$\begin{array}{c} n-1 < 0 \\ \Rightarrow & n < 1 \end{array}$$
 (5.53)

Previously we found that zeroth order reactions also go to completion. Therefore, reactions with order $n(0 \le n < 1)$ will go to 100% completion within a finite time.

Example 5.16

The catalysed decomposition of H_2O_2 in aqueous solution is followed by removing equal volume samples at various time intervals and titrating them with $KMnO_4$ to determine the undecomposed H_2O_2 . The results obtained are

 \Rightarrow

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Time (min)	5	10	20	30	50
KMnO ₄ (mL)	37.1	29.8	19.6	12.3	5

Find the order of the reaction, and the value of the rate constant. Also estimate the volume of KMnO₄ required for the titration of the sample at t = 0.

Solution

This kind of problem is generally solved by the method of trial-and-error. A particular order is suspected and then checked whether the given data gives a concurrent value of k. Intuition suggests that the reaction is first-order:

$$\mathrm{H}_{2}\mathrm{O}_{2} \xrightarrow{k} \mathrm{H}_{2}\mathrm{O} + \frac{1}{2}\mathrm{O}_{2}$$

The integrated rate law is

$$k = \frac{1}{t} \ln \frac{C_R^0}{C_R}$$

where C_R^0 is the initial concentration of the reactant and C_R is its concentration at time t. There is no data given to find C_R^0 , because, the volume of KMnO₄ consumed at time t refers to the amount of the undecomposed H₂O₂ at that time t^* . We therefore rewrite the above equation as

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{C_{R1}}{C_{R2}}$$

where C_{R1} and C_{R2} are the concentrations of the undecoposed H_2O_2 at time intervals t_1 and t_2 , respectively. Using the data we find

(i) for $t = 5 \min$ and $t_2 = 10 \min$

$$k = \frac{1}{(10-5)\min} \ln \frac{(37.1 \text{ mL})}{(29.8 \text{ mL})} = 0.0438 \min^{-1}$$

(ii) for $t = 10 \min \text{ and } t_2 = 20 \min$

$$k = \frac{1}{10 \min} \ln \frac{29.8}{19.6} = 0.0419 \min^{-1}$$

(iii) for $t_1 = 20$ min and $t_2 = 30$ min

$$k = \frac{1}{10 \min} \ln \frac{19.6}{12.3} = 0.0466 \min^{-1}$$

There is no data at t = 0.

(iv) for $t_1 = 30$ min and $t_2 = 50$ min

$$k = \frac{1}{20 \min} \ln \frac{12.3}{5} = 0.0450 \min^{-1}$$

Within the limit of experimental error, the constancy of the values of k confirms that the reaction follows a first-order kinetics with an average rate constant of 0.044 min⁻¹.

..

Once the value of the rate constant is obtained, we may now write

$$k = \frac{1}{t} \ln \frac{V_0}{V_t}$$

 \Rightarrow

$$V_0 = V_t e^{kt}$$

Using the data for t = 5 min; $V_t = 37.1 \text{ mL}$, we find

$$V_0 = (37.1 \text{ mL}) \left[e^{(0.044 \text{ min}^{-1}.5 \text{ min})} \right]$$

or,

$$V_0 = 46.2 \text{ mL}$$

Example 5.17

In the vapour phase, ethylene oxide decomposes into methane and carbon monoxide at 415°C. The pressure of the reaction vessel with time is given below.

t (min)	0	5	7	9	12	18
p (Torr)	116.1	122.56	125.72	128.74	133.23	141.37

Show that the reaction follows a first-order kinetics and, calculate the rate constant.

Solution

The reaction is



As shown above, the initial pressure is $P_0 = 116.51$ Torr.

At time t, the total pressure P_T is

 $P_T = (P_0 - P) + P + P = P_0 + P$

From the given data we the find

- at $t = 5 \min_{0} P_0 + P = 122.56$ Torr;
- \Rightarrow P = 6.05 Torr; i.e. $P_0 P = 110.46$ Torr

5.41

using the integrated first order rate law

$$k = \frac{1}{t} \ln \frac{P_o}{P_0 - P} = \frac{1}{(5 \text{ min})} \ln \frac{116.51 \text{ (Terr)}}{110.46 \text{ (Terr)}} = 1.07 \times 10^{-2} \text{ min}^{-1}$$

at $t = 7 \min_{0} P_0 + P = 125.72$ Torr;

 \Rightarrow P = 9.21 Torr; i.e. $P_0 - P = 107.3$ Torr

Therefore,
$$k = \frac{1}{(7 \text{ min})} \ln \frac{116.51 \text{ (Torr)}}{107.3 \text{ (Torr)}} = 1.18 \times 10^{-2} \text{ min}^{-1}$$

at
$$t = 9 \min, P_0 + P = 128.74$$
 Torr;
 $\Rightarrow P = 12.23$ Torr; i.e. $P_0 - P = 104.28$ Torr
1 116 51 (Terr)

Therefore,
$$k = \frac{1}{(9 \text{ min})} \ln \frac{116.51 \text{ (Torr})}{104.28 \text{ (Torr})} = 1.23 \times 10^{-2} \text{ min}^{-1}$$

at $t = 12 \min_{0} P_0 + P = 133.23$ Torr;

$$\Rightarrow$$
 $P = 16.72$ Torr ; i.e. $P_0 - P = 99.79$ Torr

Therefore,
$$k = \frac{1}{(12 \text{ min})} \ln \frac{116.51 \text{ (Torr)}}{99.79 \text{ (Torr)}} = 1.29 \times 10^{-2} \text{ min}^{-1}$$

at
$$t = 18 \min_{n} P_{o} + P = 141.37$$
 Torr;

$$\Rightarrow$$
 $P = 24.86$ Torr; i.e. $P_0 - P = 91.65$ Torr

Therefore $k = \frac{1}{(18 \text{ min})} \ln \frac{116.51 \text{ (Torr)}}{91.65 \text{ (Torr)}} = 1.33 \times 10^{-2} \text{ min}^{-1}$

The almost constant value of *k* confirms that the reaction follows a first order kinetics with an average rate constant of $1.22 \times 10^{-2} \text{ min}^{-1}$.

Example 5.18

At 25°C methylacetate is saponified by mixing the ester and NaOH (aq), both at the concentration 0.01 M finally. Small aliquots of the reaction mixture are then titrated at different time intervals with a standardised HCl solution. The data obtained are:

Time (min)	3	5	7	10	15	21	25
Conc. of base (M)	0.00740	0.00634	0.00550	0.00464	0.00363	0.00288	0.00254

Find the order of the reaction and determine the rate constant of the reaction.

Solution

 \Rightarrow

Saponification is a second-order process, first-order with respect to each of the ester and OH^- ion. For equal initial concentration of both the reactants, we will use Eq. (5.18)

$$\frac{1}{C_R} = \frac{1}{C_R^0} + kt$$

$$k = \frac{(C_R^0 - C_R)}{t C_R^0 C_R}$$
(i)

 C_R^{0} is the initial concentration of each reactant, i.e. $C_R^{0} = 0.01$ M, and C_R is the concentration at time *t*. Since we are titrating the aliquot with a standard HCl, the titre values given in the 2nd period represent the amount of unreacted NaOH (and the ester) at that time, i.e. C_R . We now check the Eq. (i) with the given data ($C_R^{0} = 0.01$ M):

1. $t = 3 \min; C_R = 0.00740 M; \implies (C_R^0 - C_R) = 0.0026 \text{ M}$ $\implies k = \frac{(0.0026 \text{ M})}{(0.01 \text{ M}) (3 \min) (0.00740 \text{ M})} = 11.7 \text{ M}^{-1} \min^{-1}$

2.
$$t = 5 \min; C_R = 0.00634 \text{ M}; \implies (C_R^0 - C_R) = 0.0037 \text{ M}$$

$$\Rightarrow \qquad k = \frac{(0.0037 \text{ M})}{(0.01 \text{ M})(5 \text{ min})(0.00634 \text{ M})} = 11.67 \text{ M}^{-1} \text{ min}^{-1}$$

3.
$$t = 7 \min; C_R = 0.0055 \text{ M}; \implies (C_R^0 - C_R) = 0.0045 \text{ M}$$

$$\Rightarrow \qquad k = \frac{(0.0045 \text{ M})}{(0.01 \text{ M}) (7 \text{ min}) (0.0055 \text{ M})} = 11.69 \text{ M}^{-1} \text{ min}^{-1}$$

4.
$$t = 10 \text{ min}; C_R = 0.00464 \text{ M}; \implies (C_R^0 - C_R) = 0.0054 \text{ M}$$

$$\Rightarrow \qquad k = \frac{(0.0054 \text{ M})}{(0.01 \text{ M}) (10 \text{ min}) (0.00464 \text{ M})} = 11.64 \text{ M}^{-1} \text{ min}^{-1}$$

5.
$$t = 15 \text{ min}; C_R = 0.00363 \text{ M}; \implies (C_R^0 - C_R) = 0.0064 \text{ M}$$

$$\Rightarrow \qquad k = \frac{(0.0064 \text{ M})}{(0.01 \text{ M}) (15 \text{ min}) (0.00363 \text{ M})} = 11.75 \text{ M}^{-1} \text{ min}^{-1}$$

6.
$$t = 21 \text{ min}; C_R = 0.00288 \text{ M}; \implies (C_R^0 - C_R) = 0.0071 \text{ M}$$

$$\Rightarrow \qquad k = \frac{(0.0071 \text{ M})}{(0.01 \text{ M}) (21 \text{ min}) (0.00288 \text{ M})} = 11.74 \text{ M}^{-1} \text{ min}^{-1}$$

7.
$$t = 25 \text{ min}; C_R = 0.00254 \text{ M}; \implies (C_R^0 - C_R) = 0.0075 \text{ M}$$

$$\Rightarrow \qquad k = \frac{(0.0075 \text{ M})}{(0.01 \text{ M})(25 \text{ min})(0.00254 \text{ M})} = 11.81 \text{ M}^{-1} \text{ min}^{-1}$$

The constancy in the values of k proves that the reaction follows the second-order kinetics. The average rate constant is then $k = 11.72 \text{ M}^{-1} \text{min}^{-1}$.

Example 5.19

The hydrolysis of 1-chloro-1-methylcycloundecane in 80% ethanol has been studied. The extent of hydrolysis was measured by titrating the acid formed at different time intervals with a solution of NaOH. The data reported are

time/h	0	1	3	5	9	12	~
vol. of NaOH reqd (mL)	0.035	0.295	0.715	1.055	1.505	1.725	2.197

(a) What is the order of the reaction?

- (b) Calculate the rate constant, and
- (c) How much of the reactant is left unhydrolyzed after 8 hours?

Solution

In acid medium, hydrolysis is generally first-order. Let us check it with the given data. The volume of NaOH required at t = 0 should have been zero; but the little volume required may be due to the acidic character of the alcohol. Therefore, every data for the consumed NaOH volume should be subtracted from 0.035. At infinite time the reaction is complete; therefore if a is the initial concentration of the reactant and x be the hydrolyzed time t, then $a \propto (2.197 - 0.035) \text{ mL}$, $\Rightarrow a \propto 2.162 \text{ mL}$

at t = 1h, $x \propto (0.295 - 0.035)$ mL, $\Rightarrow x \propto 0.26$ mL and $(a - x) \propto 1.902$ mL

therefore, using the equation $k = \frac{1}{t} \ln \frac{a}{(a-x)}$; (the proportionality constants cancel out)

$$\Rightarrow \qquad k = \frac{1}{(1 \, \text{h})} \ln \frac{(2.162 \, \text{mL})}{(1.902 \, \text{mL})} = 0.128 \, \text{h}^{-1}$$

at
$$t = 3 \text{ h}; \ x \propto (0.715 - 0.035) \text{ mL} \propto 0.68 \text{ mL}$$

and, $(a - x) \propto 1.482 \text{ mL}$

therefore,
$$k = \frac{1}{(3h)} \ln \frac{(2.162 \text{ mL})}{(1.482 \text{ mL})} = 0.126 \text{ h}^{-1}$$

at $t = 5 \text{ h} \ x \propto (1.055 - 0.035) \propto 1.02 \text{ mL}$

5.44

 $\therefore \qquad (a-x) = 1.142 \text{ mL}$ $\Rightarrow \qquad k = \frac{1}{(5 \text{ h})} \ln \frac{(2.162 \text{ mL})}{(1.142 \text{ mL})} = 0.128 \text{ h}^{-1}$

at
$$t = 9 \text{ h}; x \propto (1.055 - 0.035) \text{ mL} \propto 1.47 \text{ mL}$$

$$\therefore$$
 $(a-x) \propto 0.692 \text{ mL}$

$$\Rightarrow \qquad k = \frac{1}{(9 \,\mathrm{h})} \ln \frac{(2.162 \,\mathrm{mL})}{(0.692 \,\mathrm{mL})} = 0.127 \,\mathrm{h}^{-1}$$

at
$$t = 12 \text{ h} \ x \propto (1.725 - 0.035) \text{ mL} \propto 1.69 \text{ mL}$$

and $(a - x) \propto 0.472 \text{ mL}$

$$\Rightarrow \qquad k = \frac{1}{(12 \,\mathrm{h})} \ln \frac{(2.162 \,\mathrm{mL})}{(0.472 \,\mathrm{mL})} = 0.127 \,\mathrm{h}^{-1}$$

The constancy in the values of *k* suggests that the reaction is of first-order with an average rate constant of k = 0.127 h⁻¹. The fraction remaining unhydroyzed after 8 hours is then

$$\frac{C_R}{C_R^0} = e^{-kt} = e^{-(0.127 \text{ M}^{-1}) (8 \text{ M})} = 0.362$$

Example 5.20

Equimolar quantities of *A* and *B* are added to a litre of a suitable solvent. At the end of 500s, half of *A* has reacted according to the reaction $A + B \rightarrow P$. How much of *A* will be reacted at the end of 800s if the reaction is

- (a) zeroth-order with respect to both A and B
- (b) first-order with respect to A and zeroth-order with respect to B
- (c) first-order with respect to both A and B

Solution

(a) The rate law is:

$$-\frac{dC_A}{dt} = k \implies C_A = C_A^0 - kt$$

Therefore,

$$k = rac{{C_A^{\ 0} - C_A}}{t} = rac{{C_A^{\ 0} - 0.5 C_A^{\ 0}}}{500 \, {
m s}} = rac{{C_A^{\ 0} }}{1000} \, {
m s}^{-1}$$

Therefore, at 800s

$$C_A = C_A^0 - kt = C_A^0 - 10^{-3}C_A^0(800) = 0.2C_A^0$$

i.e. 80% of A will be consumed.

(b) The rate law is

$$\frac{dC_A}{dt} = kC_A$$

using the integrated rate law

$$k = {0.693 \over 500} \, {
m s}^{-1}$$

 $C_A = 0.33 C_A^{0}$

Therefore, at 800s

$$C_A = C_A^{\ 0} \ e^{-\left(\frac{0.693}{500} \, \text{s}^{-1}\right)(800 \, \text{s})}$$

 \Rightarrow

i.e. 67% of A will be consumed.

(c) The integrated rate law is

$$\frac{1}{C_A} = \frac{1}{C_A^0} + kt \implies k = \frac{(C_A^0 - C_A)}{t C_A^0 C_A} = \frac{0.5 C_A^0}{(500 \,\mathrm{s}) C_A^0 (0.5 C_A^0)} = \frac{1}{500 C_A^0} \,\mathrm{s}^{-1}$$

Therefore, at 800s

$$\frac{1}{C_A} = \frac{1}{C_A^0} + \frac{8}{5C_A^0} = \frac{13}{5C_A^0}$$

$$\Rightarrow \qquad C_A = \frac{5}{13}C_A^0 = 0.385 C_A^0, \text{ i.e. } 61.5\% \text{ of } A \text{ will be consumed.}$$

Example 5.21

Sucrose (cane-sugar) is dextrorotatory, its specific rotation being + 66.5° (25°C). On hydrolysis with dilute acids, sucrose yields an equimolar mixture of D(+) glucose and D(-) fructose

Since D(-) fructose has a greater specific rotation than D(+) glucose, the resulting mixture gradually changes from dextrorotatory to laevorotatory with time. For this reason, the hydrolysis of cane-sugar is known as the inversion of cane-sugar. In an experiment the polarimetric readings are

t/min	0	30	90	330	~
Angle of rotation, \propto	46.75	41.00	30.75	2.75	-18.75

Show that the reaction follows a first-order kinetics and, estimate the rate constant.

5.46

Solution

We shall use the equation

$$k = \frac{1}{t} \ln \frac{a}{(a-x)}$$

where a is the initial concentration of the sugar, and x is the portion hydrolyzed at time t.

Over the entire course of the reaction from t = 0 to $t \to \infty$, the total sugar has reacted; so we write

$$(\alpha_0 - \alpha_\infty) \alpha a$$

and, since x is the concentration of sugar reacted at time t

 $(\alpha_0 - \alpha_t) \alpha x$

 \Rightarrow

$$(\alpha_t - \alpha_{\infty}) \alpha (a - x)$$

The expression of the rate constant then can be written as

$$k = \frac{1}{t} \ln \frac{(\alpha_0 - \alpha_\infty)}{(\alpha_0 - \alpha_\infty)}$$

We now use the data at different time intervals to find k.

At $t = 30 \text{ min}, \quad k = \frac{1}{(30 \text{ min})} \ln \frac{(46.75 + 18.75)}{(41.00 + 18.75)} = 3.06 \times 10^{-3} \text{ min}^{-1}$

at $t = 90 \text{ min}, \quad k = \frac{1}{(90 \text{ min})} \ln \frac{65.5}{(30.75 + 18.75)} = 3.11 \times 10^{-3} \text{ min}^{-1}$

at
$$t = 330 \text{ min}, \quad k = \frac{1}{(330 \text{ min})} \ln \frac{65.5}{(2.75 + 18.75)} = 3.38 \times 10^{-3} \text{ min}^{-1}$$

The constancy in the values of *k* confirms that the reaction follows a first order kinetics for a given catalyst concentration, and the average rate constant is $3.18 \times 10^{-3} \text{ min}^{-1}$.

Example 5.22

At a fixed temperature 30°C, a mixture is prepared by adding 10 mL 2 volume H_2O_2 , 10 mL 12 N H_2SO_4 acid, 2 mL of a freshly prepared starch solution and the volume is made up to 200 mL by distilled water. 50 mL of 4% (w/v) KI is then added to the reaction mixture, and, a stop-watch is immediately started. This moment refers to t = 0 for the reaction. The colour of the mixture turns blue. A small volume of sodium thiosulphate (0.1 N) is then added as fast as possible to the reaction mixture. The time of appearance of the blue colour is recorded. Another small volume of the thio-solution is then added, so
that the colour goes off; the time of the second appearance of the blue colour is recorded. In this way, the time of appearance of the blue colour of the reaction mixture is noted after gradual addition of small volume of the thio-solution. The results are given in the table below.

Vol. of thio added (mL)	6.2	10.2	15.1	17.8	20.3
Time (s)	64	117	193	246	298

In a separate flask, the same composition, except the starch solution, is taken and kept in the dark for 15 minutes. The iodine liberated is then titrated with the same thio-solution with starch as an indicator. The volume required is found to be 40.4 mL. Calculate the pseudo-first-order rate constant of the reaction.

Solution

According to discussion, $V_0 = 40.4$ mL.

at
$$t = 64$$
s: $k = \frac{1}{(64 \,\mathrm{s})} \ln \frac{40.4}{(40.4 - 6.2)} = 2.6 \times 10^{-3} \,\mathrm{min}^{-1}$

at
$$t = 117$$
s: $k = \frac{1}{(117 \text{ s})} \ln \frac{40.4}{(40.4 - 10.2)} = 2.5 \times 10^{-3} \text{ min}^{-1}$

at
$$t = 193$$
 s: $k = \frac{1}{(193 \text{ s})} \ln \frac{40.4}{(40.4 - 15.1)} = 2.4 \times 10^{-3} \text{ min}^{-1}$

at
$$t = 246$$
 s: $k = \frac{1}{(246 \text{ s})} \ln \frac{40.4}{(40.4 - 17.8)} = 2.4 \times 10^{-3} \text{ min}^{-1}$

at
$$t = 298$$
 s: $k = \frac{1}{(298 \text{ s})} \ln \frac{40.4}{(40.4 - 20.3)} = 2.3 \times 10^{-3} \text{ min}^{-1}$

The constancy of the values of k for the given sets of data confirms that the reaction is a pseudo-first-order reaction with respect to H_2O_2 , with an average rate constant $2.4 \times 10^{-3} \text{ min}^{-1}$. The students are advised to plot $\ln \frac{V_0}{(V_0 - V_t)}$ versus t on their own from the given data of this problem, and then, to find k from the slope. The straight line should meet the origin.

5.7 COMPLEX REACTION

Most of the reactions occurring in nature or in the laboratory *are not one step act*; as if, two reactant molecules collide and give the final product(s) in a single step. There is a mechanistic pathway, a series of steps, through which the reaction occurs. These

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Chemical Kinetics
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are called the elementary steps. Such reactions are called *complex reactions*. There basic kinds of complex reactions are

- (1) Parallel Reaction
- (2) Consecutive Reaction and
- (3) Opposing Reaction

5.7.1 Parallel Reaction

From our elementary chemistry we know that, when phenol is nitrated, we get two products: *o*-nitrophenol and *p*-nitrophenol. This means that, during the reaction some phenol molecules give the *ortho*-product and the rest give the *p*-product. We say that the reaction is a *parallel reaction*.

Suppose a reactant R undergoes a parallel reaction to give three products P_1 , P_2 and P_3 at different rates and with different rate constants k_1 , k_2 and k_3 .

The reaction scheme is then



For the simplest case, we consider that all the three routes are of first-order with rate constant k_1 , k_2 , and k_3 . If the initial concentration, i.e. at t = 0, of the reactant R be C_R^0 and C_1 , C_2 and C_3 are the concentration of the three products P_1 , P_2 and P_3 at time t, when R concentration is C_R , we may write

$$C_R^0 = C_R + C_1 + C_2 + C_3 \tag{5.54}$$

The rate of disappearance of R is the sum of the rates of the three processes,

$$-\frac{dC_R}{dt} = k_1 C_R + k_2 C_R + k_3 C_R = (k_1 + k_2 + k_3) C_R$$

Integration with limits give

$$C_R = C_R^0 e^{-(k_1 + k_2 + k_3)t}$$
(5.55)

The rate of formation of the product P_1 is

$$\frac{dC_1}{dt} = k_1 C_R = k_1 C_R^0 e^{-(k_1 + k_2 + k_3)t}$$
$$dC_1 = k_1 C_R^0 e^{-(k_1 + k_2 + k_3)t} dt$$

 \Rightarrow

and on integration

$$C_1 = -\frac{k_1 C_R^0}{(k_1 + k_2 + k_3)} e^{-(k_1 + k_2 + k_3)} + z$$

The integration constant z is evaluated as at $t = 0, C_1 = 0$. This gives us

$$t = \frac{k_1 C_R^0}{(k_1 + k_2 + k_3)}$$

$$C_1 = \frac{k_1 C_R^0}{(k_1 + k_2 + k_3)} \left[1 - e^{-(k_1 + k_2 + k_3)t} \right]$$
(5.56)

and, similarly we find

$$C_{2} = \frac{k_{2}C_{R}^{0}}{(k_{1} + k_{2} + k_{3})} \left[1 - e^{-(k_{1} + k_{2} + k_{3})t} \right]$$
(5.57)

$$C_{3} = \frac{k_{3}C_{R}^{0}}{(k_{1} + k_{2} + k_{3})} \Big[1 - e^{-(k_{1} + k_{2} + k_{3})t} \Big]$$
(5.58)

The concentration-time profile of the reactant and the three products P_1 , P_2 and P_3 is shown in Figure 5.13. To construct the figure, we have used : $C_R^0 = 1$ M and $k_1 = 0.03 \text{ min}^{-1}$; $k_2 = 0.03 \text{ min}^{-1}$ and $k_3 = 0.01 \text{ min}^{-1}$.



Figure 5.13 Variation of the concentration of the reactant and the products with time.

It is also noteworthy to find that at any time *t*

$$\frac{C_2}{C_1} = \frac{k_2}{k_1}$$
 and $\frac{C_3}{C_2} = \frac{k_3}{k_2}$ or, $\frac{C_3}{C_1} = \frac{k_3}{k_1}$

or $C_1: C_2: C_3 = k_1: k_2: k_3$

(5.59)

The products are in constant ratio to one another, which is independent of time and the initial concentration of the reactant. Furthermore, you can also check that at any time t

$$C_R + C_1 + C_2 + C_3 = C_R^0 (5.60)$$

From Eq. (5.55), the average life time of may be expressed as

$$t_{0.5} = \frac{0.693}{(k_1 + k_2 + k_3)} \tag{5.61}$$

..

5.7.1.1 Investigation of the Reaction $H_2O_2 + 2HI \longrightarrow I_2 + 2H_2O_2$

This reaction is kinetically of second order—not, as might be expected, third order. The mechanism is probably an initial, rate determining step

$$H_2O_2 + I^- \longrightarrow H_2O + IO^- \text{ (slow)}$$

followed by a rapid reaction

$$IO^{-} + 2H^{+} + I' \longrightarrow H_2O + I_2 \text{ (fast)}$$

The latter presumably also occurs by steps, not by a simultaneous collision among four ions. The rate of the reaction is then

$$v = k'C_{I} C_{H_2O_2}$$
(i)

The order of the reaction with respect to H_2O_2 can be studied conveniently by choosing conditions such that there is a constant excess of I⁻ (or HI). The rate law (i) then follows a *pseudo-first-order kinetics:*

$$v = k C_{\text{H}_2\text{O}_2} \quad (k = k' C_{\text{T}})$$
 (ii)

Experimentally, this is achieved by continually adding small volumes of sodium thiosulphate solution to remove the iodine as soon as it is liberated, and to regenerate I^- ions according to the reaction

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

By using a large volume of solution and adding small amount of concentrated thiosulphate solution, one can neglect the small increase in the volume of the solution, and making $C_{\rm I^-}$ as a constant. At a fixed temperature the rate of the reaction then depends only on $C_{\rm H_2O_2}$. The course of the reaction can readily be followed by timing the appearance of iodine with its blue colour (indicated by a small value of starch solution added to the reaction mixture at the start) after a small known volume V_t of thiosulphate solution has been added. Another addition of thiosulphate is immediately made, the moment the blue colour appears. In this way, the set of V_t values is recorded versus time. Since 1 mole of $\rm H_2O_2$ is destroyed for every mole of $\rm I_2$ liberated, the V_t values provide the $C_{\rm H_2O_2}$ reacted at

different instants of time t. If V_0 be the volume of thiosulphate required to react with the total I_2 produced by the reaction mixture (it is to be found separately) then the first order rate law may be written as

$$\ln \frac{V_0}{(V_0 - V_t)} = kt$$

A plot of $\ln\left(\frac{V_0}{V_0 - V_t}\right)$ versus *t* may now be made to find *k*.

Example 5.23

Potassiun-argon dating is used in geology and archeology rocks. Potassium–40 decays by two different paths:



The overall half life for the decay of potassium–40 is 1.3×10^9 years. Estimate the age of sedimentary rocks with an Ar – 40 to K – 40 ratio of 0.0102.

Solution

Using Eq. (5.61), the overall half life time of $^{40}_{19}$ K is

$$\begin{split} t_{0.5} &= \frac{0.693}{(k_1 + k_2)} \\ (k_1 + k_2) &= \frac{0.693}{1.3 \times 10^9 \, y} = 5.33 \times 10^{-10} \, y^{-1} \end{split}$$

 \Rightarrow

 \Rightarrow

Starting with $n_k(0)$ mole of K (at t = 0), number of moles of ${}^{40}_{19}$ K left at time t is

$$n_{\rm K}(t) = n_{\rm K}(0) \exp\left(-5.33 \times 10^{-10} t\right)$$
 (5.62)

Therefore, the number of moles ${}^{40}_{19}$ K decayed $n_{d.K}(t)$ at time *t* is

$$n_{d,K}(t) = n_{K}(0) - n_{K}(t)$$

$$n_{d,K}(t) = n_{K}(0) - n_{K}(0) e^{-5.33 \times 10^{-10}t}$$
(5.63)

$$n_{d,K}(t) = n_{K}(0) \left[1 - e^{-5.33 \times 10^{-10}t}\right]$$
(5.64)

5.53

Number of moles of ${}^{40}_{18}$ Ar produced is then (at time t)

$$n_{\rm Ar}(t) = 0.107 \, n_{\rm K}(0) [1 - e^{-5.33 \times 10^{-10} t}]$$
(5.65)

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Therefore, according to the problem

$$\frac{n_{\rm Ar}(t)}{n_{\rm K}(t)} = \frac{0.107 \ n_{\rm K}(0) \left[1 - e^{-5.33 \times 10^{-10} t}\right]}{n_{\rm K}(0) \ e^{-5.33 \times 10^{-10} t}}$$

 \Rightarrow

or

$$0.0102 = 0.107 \left[e^{5.33 \times 10^{-10} t} - 1 \right]$$

and solving for t we get

$$t = 1.71 \times 10^8 y.$$

The rock is about 1.71×10^8 years old.

5.7.2 Consecutive Reaction and Steady State Approximation

Consider the (4n + 2) series of $\frac{238}{92}$ U

$$\underset{92}{\overset{238}{_{92}}} U \xrightarrow{-\alpha} \underset{90}{\overset{234}{_{91}}} Th \xrightarrow{\beta} \underset{91}{\overset{234}{_{91}}} Pa \xrightarrow{-\beta} \underset{92}{\overset{234}{_{92}}} U \longrightarrow$$

10

finally ending up to $\frac{206}{82}$ Pb.

This is a *consecutive process*. We take the simplest consecutive reaction where the reactant R produces an intermediate I, which in turn, produces the final product P; both the steps being first-order with rate constants k_1 and k_2 .

$$R \xrightarrow{k_1} I \xrightarrow{k_2} P$$

at t = 0 $C_R^0 = 0$ 0

at t C_R C_I C_P

The concentrations of the species initially, and at time t are shown above. In any kinetic study the most important thing is the *concentration-time profile* of the reacting species. We first do it for R.

The rate of decrease in the reactant concentration at time t is

$$\frac{-dC_R}{dt} = k_1 C_R \quad \Rightarrow \quad C_R = C_R^0 e^{-k_1 t}$$
(5.66)

The reactant concentration C_R is therefore decreased exponentially; the usual first order decay.

The rate of accumulation of the intermediate I at time t is

$$\frac{dC_I}{dt} = k_1 C_R - k_2 C_I \tag{5.67a}$$

and using Eq. (5.66), the rate law is

$$\frac{dC_I}{dt} + k_2 C_I = k_1 C_R^0 e^{-k_1 t}$$
(5.67b)

This is an imperfect differential. We therefore multiply Eq. (5.67b) by the integrating factor $e^{k_2 t}$ to make it perfect.

$$e^{k_{2}t} \left(\frac{dC_{I}}{dt} + k_{2}C_{I}\right) = k_{1}C_{R}^{0} e^{-(k_{1} - k_{2})t}$$
$$d(C_{I} e^{k_{2}t}) = k_{1}C_{R}^{0} e^{-(k_{1} - k_{2})t} dt$$

 \Rightarrow

 \Rightarrow

 \Rightarrow

then integrating between limits

$$\begin{split} & \int_{0}^{C_{I}} d(C_{I} e^{k_{2}t}) = k_{1} C_{R}^{0} \int_{0}^{t} e^{-(k_{1} - k_{2})t} dt \\ & C_{I} e^{k_{2}t} = \frac{-k_{1} C_{R}^{0}}{(k_{1} - k_{2})} \left[e^{-(k_{1} - k_{2})t} - 1 \right] \\ & C_{I} e^{k_{2}t} = \frac{k_{1} C_{R}^{0}}{(k_{1} - k_{2})} \left[1 - e^{-(k_{1} - k_{2})t} \right] \end{split}$$

and finally,

$$C_{I} = \frac{k_{1}C_{R}^{0}}{(k_{1} - k_{2})} \left[e^{-k_{2}t} - e^{-k_{1}t} \right]$$
(5.68)

The concentration-time profile for the product P is then obtained from the equation

$$C_P = C_R^0 - C_R - C_I$$

which is

$$C_P = C_R^0 \left[1 - \frac{k_1}{(k_1 - k_2)} e^{-k_2 t} - \frac{k_2}{(k_2 - k_1)} e^{-k_1 t} \right]$$
(5.69)

The concentration-time profiles of *R*, *I* and *P* [Eqs. (5.66), (5.68) and (5.69)] are now shown in Figure 5.14, with $C_R^0 = 1$ M, $k_2 = 0.2 \text{ min}^{-1}$ and $k_1 = 0.1 \text{ min}^{-1}$. Such a case is generally

unusual because the intermediate is more reactive then the reactant. However, the location of maximum of the C_I vs t curve is of interest. The intermediate concentration-time profile is given by Eq. (5.68)

$$C_{I} = \frac{k_{1}C_{R}^{0}}{(k_{1} - k_{2})} \left[e^{-k_{2}t} - e^{-k_{1}t} \right]$$

^

$$\Rightarrow$$

 \Rightarrow

$$\frac{dC_I}{dt} = \frac{k_1 C_R^0}{(k_1 - k_2)} \left[-k_2 e^{-k_2 t} + k_1 e^{-k_1 t} \right]$$



Figure 5.14 A consecutive reaction where $C_R^0 = 1.00 \text{ M}$, $k_1 = 0.200 \text{ min}^{-1}$ and $k_2 = 0.100 \text{ min}^{-1}$.

at the maximum, $\frac{dC_I}{dt} = 0$; this gives us

$$t_{\max} = \frac{(\ln k_1 - \ln k_2)}{(k_1 - k_2)} \tag{5.70}$$

 t_{max} is the time at which C_I goes to its maximum. The concentration of C_I at its maximum is then [using Eq. (5.68)]

$$\begin{split} (C_I)_{\max} &= \frac{k_1 C_R^0}{(k_1 - k_2)} \Bigg[e^{-k_2 \frac{\ln\left(\frac{k_1}{k_2}\right)}{(k_1 - k_2)}} - e^{-k_1 \frac{\ln\left(\frac{k_1}{k_2}\right)}{(k_1 - k_2)}} \Bigg] \\ &= \frac{k_1 C_R^0}{(k_1 - k_2)} \Bigg[e^{-\frac{k_2}{(k_1 - k_2)} \ln\left(\frac{k_1}{k_2}\right)} - e^{-\frac{k_1}{(k_1 - k_2)} \ln\left(\frac{k_1}{k_2}\right)} \Bigg] \end{split}$$

 $k_2 e^{-k_2 t_{\max}} = k_1 e^{-k_1 t_{\max}}$

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$$= \frac{k_1 C_R^0}{(k_1 - k_2)} \left[e^{\ln\left(\frac{k_1}{k_2}\right)^{-\frac{k_2}{k_1 - k_2}}} - e^{\ln\left(\frac{k_1}{k_2}\right)^{-\frac{k_1}{k_1 - k_2}}} \right]$$

$$= \frac{k_1 C_R^0}{(k_1 - k_2)} \left[\left(\frac{k_1}{k_2}\right)^{-\frac{k_2}{k_1 - k_2}} - \left(\frac{k_1}{k_2}\right)^{-\frac{k_1}{k_1 - k_2}} \right]$$

$$\Rightarrow \qquad (C_I)_{\max} = \frac{k_1 C_R^0}{(k_1 - k_2)} \left[\left(\frac{k_1}{k_2}\right)^{\frac{k_2}{(k_2 - k_1)}} - \left(\frac{k_1}{k_2}\right)^{\frac{k_1}{(k_2 - k_1)}} \right]$$

$$= \frac{k_1 C_R^0}{(k_1 - k_2)} \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2 - k_1}} \left[1 - \left(\frac{k_1}{k_2}\right)^{-1} \right]$$

$$= \frac{k_1 C_R^0}{(k_1 - k_2)} \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{(k_2 - k_1)}} \frac{(k_1 - k_2)}{k_1}, \text{ and finally}$$

$$(C_I)_{\max} = C_R^0 \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{(k_2 - k_1)}} \tag{5.71}$$

It is to be noted carefully that, as k_2 increases for a given value of k_1 , both the t_{\max} and $(C_I)_{\max}$ decrease. This is shown in Figures 5.15(a) and (b).



Figure 5.15(a) A consecutive reaction where $C_R^0 = 1.00 \text{ M}$, $k_1 = 0.100 \text{ min}^{-1}$ and $k_2 = 0.200 \text{ min}^{-1}$.



Figure 5.15(b) A consecutive reaction where $C_R^0 = 1.00 \text{ M}$, $k_1 = 0.100 \text{ min}^{-1}$, and $k_2 = 1.00 \text{ min}^{-1}$.

5.7.2.1 The Parent-Daughter Relation

At the outset, it is said that a radioactive decay series is consecutive. Considering the simplest case of the so called *parent-daughter* relation

$$A \longrightarrow B \longrightarrow C$$

A being the parent, *B* is the daughter, and *C* is the final product. Significant differences may arise depending on the relative half lives of the parent and the daughter. A very important difference between a radioactive decay and chemical reactions is that the former goes essentially to completion but the latter tends to an equilibrium. If N_A , N_B and N_C represent the number of nuclei of the parent *A*, the daughter *B* and, the final product *C*, respectively, at time *t*, then

$$N_A = N_A^0 e^{-k_1 t}$$
 [by Eq. (5.66)] and, (5.72)

$$N_B = \frac{k_1 N_A^{\ 0}}{(k_1 - k_2)} \left[e^{-k_2 t} - e^{-k_1 t} \right] \left[(\text{by Eq. 5.68}) \right]$$
(5.73)

Notice, that the second group of terms represents the growth of the daughter from the parents and the first represents the decay of these daughters.

Case-1: Transient Equilibrium

If the parent is long lived than the daughter, i.e. $k_2 > k_1$, a state of so-called *radioactive* equilibrium is reached. Therefore, after a long span of the time, the term e^{-k_2t} becomes negligible compared to e^{-k_1t} . Therefore, neglecting this terms (e^{-k_2t}) , we have at a time t

$$N_B = \frac{k_1 N_A^0}{(k_2 - k_1)} e^{-k_1 t} = \frac{k_1 N_A}{(k_2 - k_1)}$$
 [(using Eq. (5.72)]

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$$\Rightarrow \qquad \qquad \frac{N_A}{N_B} = \frac{k_2 - k_1}{k_1} \tag{5.74}$$

If the counting efficiencies of the parent and daughter are the same, the numbers of nuclei can be replaced by the corresponding activities; this gives us

$$\frac{A_A}{A_B} = \frac{k_2 - k_1}{k_1} \tag{5.75}$$

Since $k_2 > k_1$, the daughter *B* is decaying faster than the relatively long lived parent *A*, which decays to produce the daughter. After a very short span of time, therefore, the total activity passes through a maximum and then decreases at approximately a constant rate. Moreover, at this stage of transient equilibrium, both the activities decay with parent's half-life. This interesting story is shown in Figure 5.16, where the logarithms of the total activity and the activities of the parent and daughter are plotted versus time.



Figure 5.16 Activity of parent and daughter and total activity during transient equilibrium. Note how the activity of the daughter becomes virtually equal to that of the parent at longer times. Data are based on a parent having a half-life of 10 hours and a daughter having a half life of 1.0 hour. Activity is in arbitrary units.

Case II: Secular Equilibrium

If $k_2 \gg k_1$, the half life of the parent A is much greater than that of the daughter B. Under this condition, the activity from the decay of the parent does not decrease measurably during many daughter half lives. Using Eq. (5.74) we then find

$$\frac{N_A}{N_B} = \frac{k_2}{k_1} \text{ or, } k_1 N_A = k_2 N_B$$
(5.76)

5.7.2.2 Steady State Approximation

Consider the consecutive reaction given in Sec. 5.6.2.2

$$R \xrightarrow{k_1} I \xrightarrow{k_2} P$$

After a long mathematical journey, there we have arrived at for the concentration of the final product P as [(Eq. 5.69)]

$$C_P = C_R^{\ 0} \left[1 - \frac{k_1}{(k_1 - k_2)} e^{-k_2 t} - \frac{k_2}{(k_2 - k_1)} e^{-k_1 t} \right]$$

If k_1 is much greater than k_2 ($k_1 \gg k_2$), then the intermediate concentration C_I grows up to a significant concentration and, thereafter slopes down. The variation of the concentration of R, I and P with time are then as shown in Figure 5.17. However, if k_2 is much much greater than k_1 ($k_2 \gg k_1$), the story is completely different. Since the intermediate I is very short-lived, the moment the intermediate I is produced, it takes practically no time to give P. The first step ($R \rightarrow I$) then determines the rate of the overall reaction. This may be checked from the equation for C_p :



Figure 5.17 Concentration in a consecutive reaction when $k_1 = 10 k_2$.

in the limit $k_2 \gg k_1$, Eq. (5.69) changes to

$$C_P = C_R^0 \ (1 - e^{-k_1 t}) \tag{5.77}$$

as $(k_2 - k_1) \approx k_2$ and $e^{-k_2 t} \approx 0$.

This condition is shown in Figure 5.18.

We have arrived at Eq. (5.77), after a long mathematical journey. Let us now see that, how the same result could be obtained by the *Steady State Approximation*.

The basic point is that, $k_2 \gg k_1$; the specific rate at which the intermediate *I* is destroyed is very much faster than, that at which it is produced. The result is then, the intermediate concentration C_I grows to its maximum over a very short period of time (the induction period) to a very little concentration (Figure 5.18) and then, decays down to zero. It is evident from Figure 5.18, that, after the induction period



Figure 5.18 Concentration in consecutive reaction when $k_2 = 10k_1$.

and, $\frac{dC_I}{dt}$ is so much smaller than the other two rates $\left(\frac{-dC_R}{dt} \text{ and } \frac{dC_P}{dt}\right)$, we can safely make the approximation

make the approximation

$$\frac{dC_I}{dt} = 0 \tag{5.78}$$

which implies that the *concentration of the intermediate remains fixed over, practically, the entire course of the reaction.* The rate at which the intermediate is produced is equal (on an approximation) to the rate of its destruction. Let us now see that how this approximation can save our mathematical volume.

From Eq. (5.67a) and using the steady state approximation [Eq. (5.78)], we find

$$C_{I} = \frac{k_{1}}{k_{2}} C_{R}$$

$$C_{I} = \frac{k_{1}}{k_{2}} C_{R}^{0} e^{-k_{1}t} \qquad \text{[using Eq. (5.66)]}$$

..

and therefore

 \Rightarrow

$$\begin{split} C_P &= C_R^0 - C_R - C_I \\ &= C_R^0 - C_R^0 e^{-k_1 t} - \frac{k_1}{k_2} C_R^0 e^{-k_1 t} \\ &= C_R^0 \left[1 - e^{-k_1 t} \left(1 + \frac{k_1}{k_2} \right) \right] \\ &= C_R^0 \left[1 - e^{-k_1 t} \frac{(k_1 + k_2)}{k_2} \right] \end{split}$$

or,

 $C_P = C_R^{\ 0} \ [1 - e^{-k_1 t}]$

on approximation, $k_1 + k_2 \approx k_2$. This is exactly the same as derived earlier [(Eq. (5.77)].

Example 5.24

Ozone depletion in the stratosphere is one of the most important siren-calls for life on the earth's surface. The gas-phase decomposition of ozone is believed to follow the mechanism

I:
$$O_3 + M \rightleftharpoons k_1 \longrightarrow O_2 + O + M$$

II: $O + O_3 \longrightarrow 2O_2$

where M is any molecule present in the reaction vessel. Applying the steady state approximation, analyse the overall kinetics of the O₃ depletion.

Solution

The rate of formation of O_2 is

$$\frac{dC_{O_2}}{dt} = k_1 C_{O_3} C_M - k_{-1} C_{O_2} C_O C_M + 2k_2 C_{O_3} C_O$$
(i)

the multiplier 2 is required for the last term because for each step (II), two $\rm O_2$ molecules are produced.

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The rate of destruction of ozone is

$$\frac{-dC_{O_3}}{dt} = k_1 C_{O_3} C_M - k_{-1} C_{O_2} C_O C_M + k_2 C_{O_3} C_O$$
(ii)

The rate of the reaction v is given by

$$v = -\frac{1}{2} \frac{dC_{O_3}}{dt} = \frac{1}{3} \frac{dC_{O_2}}{dt}$$
(iii)

Applying the steady state approximation on the concentration of the transient species O, we get

$$\frac{dC_{\rm O}}{dt} = k_1 C_{\rm O_3} C_M - k_{-1} C_{\rm O_3} C_{\rm O} C_M - k_2 C_{\rm O_3} C_{\rm O} = 0$$
(iv)

$$C_{\rm O} = \frac{k_1 C_{\rm O_3} C_M}{(k_{-1} C_{\rm O_3} C_M + k_2 C_{\rm O_3})} \tag{v}$$

The rate of formation of O_2 is [from Eq. (i)]

$$\frac{dC_{O_2}}{dt} = 3 k_2 C_{O_3} C_0 \text{ [using Eq. (iv)]}$$

and, then using the expression of $C_{\rm O}$ [Eqn. (v)]

$$\frac{dC_{O_2}}{dt} = \frac{3 k_1 k_2 C_{O_3}^2 C_M}{(k_{-1} C_{O_2} C_M + k_2 C_{O_3})}$$

Therefore, the rate of the reaction v is

$$v = \frac{1}{3} \frac{dC_{O_2}}{dt} = \frac{k_1 k_2 C_{O_3}^2 C_M}{(k_{-1} C_{O_2} C_M + k_2 C_{O_3})}$$
(vi)

The rate of destruction of O_3 is

$$\frac{-dC_{O_3}}{dt} = k_1 C_{O_3} C_M - k_{-1} C_{O_2} C_O C_M + k_2 C_{O_3} C_O$$
$$= 2 k_2 C_{O_3} C_O$$

and finally,

$$-\frac{dC_{O_3}}{dt} = \frac{2k_1k_2C_{O_3}^2C_M}{(k_{-1}C_{O_2}C_M + k_2C_{O_3})}$$

and, the rate of reaction

$$v = -\frac{1}{2} \frac{dC_{O_3}}{dt} = \frac{k_1 k_2 C_{O_3}^2 C_M}{(k_{-1} C_{O_2} C_M + k_2 C_{O_3})}$$
(vii)

using (vi) and (vii), we then write

$$v = -\frac{1}{2} \frac{dC_{O_3}}{dt} = \frac{1}{3} \frac{dC_{O_2}}{dt} = \frac{k_1 k_2 C_{O_3}^2 C_M}{(k_{-1} C_{O_2} C_M + k_2 C_{O_3})}$$

At very high pressure, C_M is large enough, so that, $(k_{-1}C_{O_2}C_M + k_2C_{O_3}) \approx k_{-1}C_{O_3}C_M$ The rate law then becomes

$$v = \frac{k_1 k_2}{k_{-1}} C_{O_3}^2 C_{O_2}^{-1}$$

an example, where a reaction may have a negative order with respect to a component.

5.7.3 Opposing Reaction

Perhaps the most basic mechanism in chemical kinetics is the opposing reaction; as the reactant R produces the product P, the P can also react back to give R. Basically the mechanism is an outcome of the *principle of microscopic reversibility*, first noted by R.C. Tolman. It says that in the microscopic world there is no one-way traffic; what can happen in one direction can also happen in the reverse direction. It is a consequence of the time-reversal symmetry of classical and quantum mechanics. Considering the simplest opposing reaction, where both the forward and backward processes are first-order with rate constants k_1 and k_{-1}

$$R \xleftarrow{k_1}{\leftarrow k_{-1}} P$$

at $t = 0$ $C_R^{\ 0}$ O
at t C_R C_P ; $C_R + C_P = C_R^{\ 0}$

where C_R^{0} is the initial concentration of the reactant, and C_R and C_P are the concentrations of the reactant and product at time *t*, respectively.

In terms of the reactant concentration the rate law is

$$\frac{dC_P}{dt} = \frac{-dC_R}{dt} = k_1 C_R - k_{-1} C_P = k_1 C_R - k_{-1} (C_R^{\ 0} - C_R)$$
(5.79a)

$$\Rightarrow$$

$$\frac{d[(k_1 + k_{-1})C_R - k_{-1}C_R^0]}{[(k_1 + k_{-1})C_R - k_{-1}C_R^0]} = -(k_1 + k_{-1})dt$$
(5.79b)

on integration we find

$$\ln \left[(k_1 + k_{-1}) C_R - k_{-1} C_R^0 \right] = -(k_1 + k_{-1})t + z \quad \text{(integration const.)}$$

using the fact that at t = 0, $C_R = C_R^{0}$, we get

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$$z = \ln k_1 C_R^{0}$$

using this, we find

$$\ln \frac{(k_1 + k_{-1}) C_R - k_{-1} C_R^{0}}{k_1 C_R^{0}} = -(k_1 + k_{-1})t$$

and simplifying the reactant concentration at time t is

$$C_R = \frac{C_R^0}{(k_1 + k_{-1})} [k_{-1} + k_1 e^{-(k_1 + k_{-1})t}]$$
(5.80)

The product concentration at time t is then

$$C_{P} = C_{R}^{0} - C_{R}$$

$$C_{P} = \frac{k_{1}C_{R}^{0}}{(k_{1} + k_{-1})} [1 - e^{-(k_{1} + k_{-1})t}]$$
(5.81)

The concentration-time profile of the reactant R and the product P are shown in the Figures 5.19(a) and (b) for two different cases. The reactant concentration C_R decays exponentially, with a fixed residue $(C_R)_e$ which is attained at equilibrium $(C_R)_e$. C_P also grows exponentially, and gives the final equilibrium residue $(C_P)_e$ as the equilibrium is attained. The equilibrium is attained when the two opposing rates are equal.



Figure 5.19(a) $k_1 > k_{-1}$; $k_{eqm} > 1$. Product concentration is more than the reactant concentration at equilibrium.

5.64

 \Rightarrow

 \Rightarrow



Figure 5.19(b) $k_1 < k_1$; $k_{eqm} < 1$. Product concentration is more than the reactant concentration at equilibrium.

$$k_{1}(C_{R})_{e} = k_{-1}(C_{P})_{e}$$

$$k_{eqm} = \frac{k_{1}}{k_{-1}} = \frac{(C_{P})_{e}}{(C_{R})_{e}}$$
(5.82)

when $k_1 > k_{-1}$, $K_{eqm} > 1$; the equilibrium is favoured with respect to the product *P* (Figure 5.19a). If $k_1 < k_{-1}$, $K_{eqm} < 1$; at equilibrium only a small amount of the product *P* is formed (Figure 5.19b)

The Integrated Rate Equation of an opposing reaction, first order in either direction can be put into a form, which is very similar of a uni-directional first-order process.

Using the Eq. (5.79a) we may write

$$\frac{dx}{dt} = k_1 (C_R^0 - x) - k_{-1} x = k_1 C_R^0 - (k_1 + k_{-1}) x$$
(5.83)

where *x* is the concentration of the product formed at time *t*.

At equilibrium, $\frac{dx}{dt} = 0$ $\Rightarrow \qquad k_1 C_R^{0} = (k_1 + k_{-1}) x_e$

 x_e being the equilibrium value of x. Using this identity in Eq. (5.83), we get

$$\frac{dx}{dt} = (k_1 + k_{-1})(x_e - x)$$

and integrating between limits

$$\int_{0}^{x} \frac{d(x_{e} - x)}{(x_{e} - x)} = -(k_{1} + k_{-1}) \int_{0}^{t} dt$$

$$\ln \frac{x_{e}}{(x_{e} - x)} = (k_{1} + k_{-1})t$$
(5.84)

 \Rightarrow

a first-order-like equation.

5.8 THE EQUILIBRIUM APPROXIMATION

Besides the steady state approximation, another approximation is also used judiciously to solve the differential rate law of a complex reaction. Let us consider the reaction

 $2A + B \longrightarrow \text{product}(s)$

which goes through the mechanism

(i) $A + B \xrightarrow{k_1} I$ (fast) (ii) $I + A \xrightarrow{k_2} P$ (slow)

The process (i) cannot be considered as a true equilibrium as there is the drainage process (ii) which drifts the intermediate I to produce the product *P*. However, if the situation is such that $k_1, k_{-1} >> k_2$, i.e. the equilibrium (i) is tend to be attained very fast, compared to the decay process (ii), then on a first approximation we may write (using Eq. (5.82)]

$$K_{\text{eqm}} = \frac{k_1}{k_{-1}} = \frac{C_I}{C_A C_B}$$
$$C_I = K_{\text{eqm}} C_A C_B$$

The rate of the reaction is the rate at which the product P is formed, and is therefore

$$v = k_2 C_I C_A = k_2 K_{eqm} C_A^2 C_B$$
or, $v = \left(\frac{k_1 k_2}{k_{-1}}\right) C_A^2 C_B$
(5.85)

an overall third order reaction, second order with respect to A and first order with respect to B.

5.9 EFFECT OF TEMPERATURE ON REACTION RATE

Reaction rates have been found to depend on temperature in various different ways. Three most common variations are shown in Figure 5.20.



Figure 5.20 The most common three types of variations of reaction rate with temperature.

All elementary reactions and most of the complex reactions follow the type A (Figure 5.20); the rate increases exponentially with temperature. Type B represents an explosive process, where the rate increases sluggishly over a low temperature range, and then shoots to infinity on explosion. The third type C represents the enzyme catalyzed metabolic processes in living bodies. The later two types will be taken up in due course; we first take up the type A variation. This is referred to as the Arrhenius-type temperature dependence.

Svante August Arrhenius * suggested in the late 1800s that the rate of most reactions vary with temperature (as shown in Figure 5.20A) in an exponential way

$$k = Ae^{-E/RT} \tag{5.86}$$

where k is the rate constant, A is the frequency factor (or, pre-exponential factor), R is the universal gas constant and T is the temperature in the kelvin scale; E is the activation energy of the process. An easier way to testify the law is to take the natural logarithm on both sides

$$\ln k = \ln A - \frac{E}{RT} \tag{5.87}$$

A plot of $\ln k$ versus $\left(\frac{1}{T}\right)$ should be a straight line, with slope $\left(-\frac{E}{R}\right)$ and intercept $\ln A$.

Such a plot is shown in Figure 5.21. The activation energy E and the frequency factor A can be evaluated from such a plot. Any non-linearity in the plot may be attributed to the temperature dependence of the activation energy E. The Arrhenius equation is sometimes written in the differential form

^{*} Svante August Arrhenius* (1859–1927; Stockholm, (Sweden) have an interesting academic career. He was turned away from chemistry twice in his career, once as a under graduate and once when his Ph.D. thesis was awarded only as a fourth-class. He then went on to join as a school teacher and started working under Van't Hoff, at his own cost. Eventually, due to his research work on electrolytic solutions, he was rewarded with a Nobel prize in Chemistry in 1903.



Figure 5.21 An Arrhenius plot of ln k versus 1/T.

$$\frac{d\ln k}{dT} = \frac{E}{RT^2} \tag{5.88}$$

or, in the integrated form at two different temperatures T_1 and T_2 as (considering E to be independent of temperature)

$$\ln \frac{k_2}{k_1} = \frac{E}{R} \frac{(T_2 - T_1)}{T_2 T_1}$$
(5.89)

 k_1 and k_2 are the rate constants at the temperatures T_1 and T_2 , respectively The increase in the rate constant of a reaction due to change in temperature then depends obviously on the activation energy of the reaction. Nevertheless, a common rule of thumb is that the rate doubles itself for every 10°C rise in temperature. This is illustrated in Figures 5.22 and 5.23.

Figure 5.22 is drawn using the Eq. (5.89).



Figure 5.22 The effect of 10°C rise in temperature.

$$E = \frac{R T_1 T_2}{(T_2 - T_1)} \ln \frac{k_2}{k_1}$$

Choosing $T_2 = 305$ K and $T_1 = 295$ K, the ratio $\left(\frac{k_2}{k_1}\right)$ is plotted for different activation energies. From Figure 5.22 it is seen that $\left(\frac{k_2}{k_1}\right) = 2$ (which means that the rate doubles) only if the activation energy is about 50 kJ mol⁻¹. But, for reactions with high activation energy, say E = 100 kJ mol⁻¹, the ratio $\left(\frac{k_2}{k_1}\right)$ is about 4. This dependence is more clearly demonstrated in Figure 5.23. For three different activation energies, the ratio $\left(\frac{k_2}{k_1}\right)$ is

now plotted versus T. The *distinct dependence* of the variation of k with T on the activation energy now becomes more clear.

Although the Arrhenius equation [Eq. (5.86)] has been found excellent to fit with the experimental data, some systematic deviations from the straight line (Figure 5.21) have been observed. A better fit is obtained by an equation of the form



Figure 5.23 The dependence of the variation of k with T on the activation energy of the reaction. For the curves a, b and c, the corresponding activation energies are: 100, 75 and 50 kJ mol⁻¹.

$$k = A' \sqrt{T} e^{-E/RT}$$

This equation will be justified later by a theory of reaction rate (see the collision theory).

Example 5.25

For the gas phases reaction, $H_2 + I_2 \rightarrow 2HI$ at 373.15 K, the rate constant is found to be $8.74 \times 10^{-15} \text{ L mol}^{-1}\text{s}^{-1}$. At 473.15 K the rate constant increases to $9.53 \times 10^{-10} \text{ L mol}^{-1}\text{s}^{-1}$. Find the activation energy *E* and the pre-exponential factor *A*.

Solution

Using Eq. (5.89), we find

$$E = \frac{R T_1 T_2}{(T_2 - T_1)} ln \frac{k_2}{k_1}$$

or,

$$E = \frac{(8.314 \ J \ \text{K}^{-1} \ \text{mol}^{-1}) \ (373.15 \ \text{K}) \ (473.15 \ \text{K})}{(473.15 \ \text{J} \ \text{S}^{-1})} \ln \frac{(9.53 \times 10^{-10} \ \text{M}^{-1} \ \text{s}^{-1})}{(8.74 \times 10^{-15} \ \text{M}^{-1} \ \text{s}^{-1})}$$

or,

$$E = 1.70 \times 10^5 \,\mathrm{Jmol}^{-1}$$

Then using the equation

$$k = Ae^{-E/RT}$$

and using the first set of data

$$A = k e^{E/RT}$$

or,

$$A = (8.74 \times 10^{-15} \ M^{-1} \text{s}^{-1} \exp \left[\frac{(1.70 \times 10^5 \ \text{J mol}^{-1})}{(8.314 \ \text{J K}^{-1} \ \text{mol}^{-1})(373.15 \ \text{K})}\right]$$
$$A = 5.5 \times 10^9 \ \text{M}^{-1} \text{s}^{-1}$$

or,

Example 5.26

Find the activation energy of a reaction whose rate constant doubles itself if the temperature is raised from 20 to 30°C and, if the temperature rise is from 90 to 100°C.

Solution

Using Eq. (5.89), we find for 20 to 30°C temperature gap

$$E = \frac{R T_1 T_2}{(T_2 - T_1)} \ln \frac{k_2}{k_1}$$
$$E = \frac{(8.314 \text{ J/K}^{-1} \text{ mol}^{-1}) (293 \text{ /K}) (303 \text{ /K})}{(10 \text{ /K})} \ln 2 = 51.2 \text{ kJ mol}^{-1}$$

or

Similarly, for 90 to 100°C temperature gap

$$E = \frac{(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (363 \text{ K}) (373 \text{ K})}{(10 \text{ K})} \ln 2 = 78 \text{ kJ mol}^{-1}$$

Example 5.27

The rate constant of a reaction increases by 2.4% per kelvin rise in temperature at 227°C. Calculate the activation energy of the reaction at 227°C.

Solution

This kind of problem is solved by using the differential form of the Arrhenius equation [Eq. 5.88)]. If k be the rate constant at temperature T and, it increases to k + dk on increasing the temperature by dT, then $(dk/k) = d \ln k$ is the fractional change in the rate constant due to the change in temperature by dT. Therefore, according to the problem

$$\frac{E}{RT^2} = 0.024 \ K^{-1}$$
$$E = (0.024 \ K^{-1}) \ (8.314 \ J \ K^{-1} \ mol^{-1}) \ (500 \ K)^2$$
$$E = 49.9 \ kJ \ mol^{-1}$$

or

 \Rightarrow

Example 5.28

The expiry time on some milk-product cartons are as follows: 1/3 day at 299.8 K; 1/2 day at 294.26 K; 1 day at 288.71 K and, 2 days at 283.15 K. Calculate the activation energy for the process that spoils the milk-product.

Solution

This is a case of bacterial decay which usually follows a first order kinetics. The expiry time that is generally given for a certain definite fraction ϕ of the product is lost. From Eq. (5.9) we may write

$$k = \frac{1}{t} \ln \frac{Co}{Co - \phi Co} = \frac{1}{t} \ln \frac{1}{(1 - \phi)}$$

For our problem ϕ is a fixed number; therefore, $\ln \frac{1}{(1-\phi)}$ is a constant; let it be z. The above equation then changes to

$$k = \frac{z}{t} \tag{i}$$

The Arrhenius equation [Eq. (5.86)] is

$$k = Ae^{-E/RT}$$

which, on using Eq. (i) changes to

$$\frac{z}{t} = Ae^{-E/RT}$$

$$\ln t = \ln\left(\frac{z}{A}\right) + \frac{E}{RT}$$
(ii)

A plot of $\ln t$ versus $\frac{1}{T}$ should then be a straight line with slope $\left(\frac{E}{R}\right)$, from which the activation energy E may be estimated. From the given data such a plot is made (Figure 5.24). The slope is found to be 9900 K.



Figure 5.24 The plot of ln *t* versus (1/*T*).

 \Rightarrow

Therefore, the activation energy of the reaction is

 $E = (9900 \text{ K}) (8.314 \text{ JK}^{-1} \text{ mol}^{-1})$

or

5.10 SOME APPLICATIONS OF ARRHENIUS LAW

 $E = 82.3 \text{ kJ mol}^{-1}$

The Arrhenius rate law [Eq. (5.86)] has some interesting applications beside the *elementary chemical reactions*. One such example is given already in Example 28.

Bacterial Colony 5.10.1

Consider the bacterial decay of a food product. Cell division produces a bacterial colony, and, as the colony increases, the quality of the food product decreases. A bacterial colony grows like a compound interest on an investment. If P_{o} be the initial purity of the food product and P at instant t, then following the first-order rate law we may write

$$P = P_o e^{-kt} \tag{5.91}$$

..

If r be the percent decay of the food product per unit time interval t_1 , then the purity after time t_1 goes down to $P_o(1 - rt_1)$; after the second period of t_1 , it goes down to $P_o(1 - rt_1)(1 - rt_1)$, i.e. $P_o(1 - rt_1)^2$. After *n* such periods the purity drops down to ŀ)

$$P = P_0 (1 - rt_1)^n \tag{5.92}$$

If the total time elapsed is *t*, then $n = \frac{t}{t_1}$; we then have

$$P = P_o \left(1 - rt_1\right)^{\frac{t}{t_1}}$$
$$= P_o \left[\left(1 - \frac{r}{\left(\frac{1}{t_1}\right)}\right)^{\frac{1}{t_1}} \right]^t$$
(5.93)

By definition, we know that

$$\lim_{n \to \infty} \left(1 \pm \frac{x}{n} \right)^n = e^{\pm x}$$
(5.94)

by selecting the time period t_1 infinitesimally small, which is rational, we write Eq. (5.93) as

$$P = P_o \begin{bmatrix} 1 \\ \left(\frac{1}{t_1}\right) \rightarrow \infty \end{bmatrix}^{1} \begin{bmatrix} 1 - \frac{n}{\left(\frac{1}{t_1}\right)} \end{bmatrix}^{\frac{1}{t_1}} \end{bmatrix}^{t}$$

 $P = P_0 e^{-rt}$ [using Eq. (5.94)]

or

The quality of the food product therefore, decreases exponentially.

5.10.2 Flashing of Firefly

The frequency of flashing of firefly is recorded as a function of temperature. The experimental data is given below.

Let us calculate the activation energy of the process

Frequency (min ⁻¹)	15.9	14.8	12.5	12	11.5	10	8
Т(К)	302	301	300	299	297	296	292

Applying the Arrhenius equation

$$\ln k = \ln A - \frac{E}{RT}$$

A plot of $\ln k$ versus $\left(\frac{1}{T}\right)$ is made; (Figure 5.25). From the slope $\left(-\frac{E}{R}\right)$ it is found that the

activation energy of the flashing of firefly is 57.4 kJ mol^{-1} .



Figure 5.25 Arrhenius plot for the flashing of firefly.

5.10.3 Terrapin's Heart Beat^{*}

Terrapin is a small turtle; the heart beat of terrapin has been studied under a variety of conditions. Figure 5.26 shows an Arrhenius plot of one set of data. It is observed that the Arrhenius law is obeyed satisfactorily with an activation energy of 18.3 kcal mol⁻¹, in the temperature range 18 to 34° C. Below 18° C the activation energy is much higher. In this region of temperature the terrapin was presumably not feeling quite himself. For more interesting facts, students are referred to the original paper by K.J. Laidler.



Figure 5.26 Arrhenius plot for the rate of a terrapin's heart beat.

5.11 ACTIVATION ENERGY OF A REACTION

In order for the reactant molecules to be transformed into the product molecules, the former must pass through an energy state which is higher than that corresponding to either the reactant or product. Consider, the transformation: *cis*-2-butene to *trans*-2-butene.



For the transformation to occur, it is necessary that the π -bond is broken, and then the unit $-CH(CH_3)$ is rotated by 180°; during this rotation there is no overlap between the two atomic *p*-orbitals. Finally, after 180° rotation, again there is an overlap between the two *p*-orbitals and the bond is formed leading to the *trans*-product. The essential idea is then: the reactant molecules must first be excited, so as to bent, stretch or even break some bonds, and produce an excited state of the reactant, often called, the *transition state* or, the *activated complex*, which then produces the final product. This is illustrated in Figure 5.27. Similarly, if the product molecules are to be converted into the reactant

^{*} K.J. Laidler; *J.Chem. Edu.*; 49, 343, 1972.

molecules, the former must again have to climb up to the top of the barrier, and then, slopes down to the reactant valley. The minimum energy which is required to climb up to the top of the potential energy hill is called the *activation energy*. As Figure 5.27(a) shows the activation energy of the forward process E_1 is less than that (E_{-1}) for the backward process; it is then an exothermic reaction because, the net energy change $\Delta E = (E_1 - E_{-1})$ is negative. Figure 5.27b represents an endothermic process for which $\Delta E = (E_1 - E_{-1})$ is positive. This concept of activation energy may also be put forward as follows:





Figure 5.27(a) The energy profile of an exothermic reaction $E_1 < E_{-1}$; $\Delta E < 0$.



Figure 5.27(b) The energy profile of an endothermic reaction $E_1 > E_{-1}$; $\Delta E > 0$.

Every stable molecule has its own potential energy well; it is constituted by a manifold of vibrational levels, which gradually becomes closer and closer as the vibrational energy increases and, finally forms the continuum. Considering a simple elementary reaction $R \rightarrow P$: the potential energy versus the reaction coordinate (a qualitative axis representing the progress of the reaction) of R and P, and their crossing is shown in Figure 5.28. It is clear that the R molecules must first be excited to the crossing point O, and then slides down to the product valley. Can you give an example where the activation energy for a chemical process is zero?



Figure 5.28 The passage of the reactant *R* into the product *P*.

5.12 CHEMICAL DYNAMICS: THEORY OF REACTION RATES

Several different theories have been proposed to account for the experimentally observed rate of the processes and their dependence on various factors like concentration of the reacting species, temperature, etc. The trivial and perhaps the most simple one is the *Collision Theory*.

5.12.1 Collision Theory of Reaction Rate (Hard Sphere Collision Theory)

The rate of a bi-molecular gas phase reaction

 $A(g) + B(g) \xrightarrow{k_r} product(s)$

is given by $v = k_r C_A C_B$.

Hard Sphere Collision Theory (HSCT) is now used to estimate rate constant.

If one uses the naive assumption that every collision between a A and B molecule leads to a fruitful reaction, then we may write the rate of the reaction as

$$v = Z_{AB} = \sigma_{AB} \langle v_r \rangle n_A n_B \tag{5.96}$$

where, Z_{AB} = number of binary A–B collisions per unit volume per second.

 $\langle v_r \rangle$ is the relative average speed of the colliding A and B molecules.

 n_A and n_B are the numbers of A and B molecules, respectively, per unit volume.

 σ_{AB} is the hard sphere collision cross-section

and
$$\langle v_r \rangle = \sqrt{\frac{8 kT}{\pi \mu}}; \ \mu = \frac{m_A m_B}{(m_A + m_B)}; \ \sigma_{AB} = \pi d_{AB}^2 = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2$$

(5.95)



the rate constant k_r of the reaction would then be

$$k_r = \sigma_{AB} \left\langle v_r \right\rangle \tag{5.97}$$

Let us take a simple reaction

 $H_{2}\left(g\right)+C_{2}H_{4}\left(g\right) \; \longrightarrow \; C_{2}H_{6}\left(g\right)$

The molecular diameters are $\sigma_{\text{H}_2} = 270 \text{ pm}$ and $\sigma_{\text{C}_{2\text{H}_4}} = 430 \text{ pm}$. σ_{AB} is therefore 3.85 × 10⁻¹⁹ m². The reduced mass is $\mu = 3 \times 10^{-27}$ kg. The relative average speed is (at 298.15 K) $\langle v_r \rangle = 1830 \text{ ms}^{-1}$. The value of k_r (in units of mol⁻¹ dm³ s⁻¹) is then

$$k_r = N_0 \sigma_{AB} \langle v_r
angle = 4 imes 10^{11} ext{ mol}^{-1} ext{ dm}^3 ext{ s}^{-1}$$

..

Per litre, roughly 10^{12} mole of reactants are consumed every second. This is unbelievable because, experiments suggest a *very low value of k*_r, about 10^{-26} mol⁻¹ dm³ s⁻¹.

Moreover, this part of the theory suggests that the rate constant should have a temperature dependence as $T^{1/2}$ (contained within $\langle v_r \rangle$); the experimental results, on the other hand, shows an exponential increases like exp(-const./T). Our immediate conclusion is then *All* collisions cannot take away the reaction successfully.

In this naive approach, we assumed that each pair of reactant molecules approach each other at a relative speed (whose average value is $\langle v_r \rangle$) and make a hit; and the reaction is done. But, in the real situation this cannot happen because, the molecules are moving along all possible directions with speeds in the range 0 to \propto , and , when they come closer, their valence electrons must repel one another. Therefore, no collision can give us reaction unless, their relative speed of approach is sufficiently high to overcome this repulsion. We may solve this problem in two different ways.

Method 1

Let the minimum energy required by the couple of the reacting molecules in order to overcome the electronic cloud repulsion and make the collision successful be ε_0 , and let

the corresponding relative speed be v_0 (i.e. $\varepsilon_0 = \frac{1}{2}\mu v_0^2$; μ is the reduced mass). Therefore,

only those collisions per unit volume per second are to be counted as equal to the rate of the reaction, in which the relative average energy exceeds ε_0 .

From the kinetic theory we know that the frequency of collision of molecules moving with speeds in the range $v \rightarrow v + dv$ on a unit area of the wall is given by vf(v) dv, not just by f(v)dv because, f(v)dv gives the probability that the molecules have their speeds in the range $v \rightarrow v + dv$ at any point, say near the wall. The frequency must also depend on how many of them can arrive at that point in one second from other regions. This last factor is proportional to v, because they can move over a distance v in one second; there is a sweep or swarm of molecules through a distance v. Drawing the same analogy, we can write

 $v_r f(v_r) dv_r$ or, $v_r^3 \exp\left(-\frac{\mu v_r^2}{2kT}\right) dv_r$ as the frequency of collision between molecules moving

with relative speeds in the range $v_r \rightarrow v_r + dv_r$. The only change we have made is to replace

the mass of a molecule *m* by its reduced mass $\mu\left(\frac{m_A m_B}{m_A + m_B}\right)$. This is a molecule-molecule

collision; the masses are comparable. For a molecule-wall collision, the wall is of infinite mass; therefore only m was there

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{m_{\text{wall}}} \implies \mu \approx m ; \quad \because \frac{1}{m_{\text{wall}}} \approx 0$$

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Therefore, we may write

$$dZ_{AB}(v_r) = Av_r^3 e^{-\frac{\mu v_r^2}{2kT}} dv_r$$
(5.98)

as the number of collisions between *A* and *B* molecules per unit volume per second, with relative speeds in the range v_r to $v_r + dv_r$. The normalization constant *A* may be evaluated if we recall that the integral of $dZ_{AB}(v_r)$ for all possible values of v_r (from 0 to ∞) must give Z_{AB} [Eq. (5.96)]. This gives us (assuming the molecules as hard spheres of collision cross-section $\sigma_{AB} = \pi d_{AB}^{-2}$)

$$A\int_{0}^{\infty} e^{-\frac{\mu v_r^2}{2kT}} v_r^3 dv_r = \sigma_{AB} \langle v_r \rangle n_A n_B$$
$$\frac{A}{2} \int_{0}^{\infty} e^{-\frac{\mu}{2kt} v_r^2} (v_r^2)^{2-1} d(v_r^2) = \sigma_{AB} \sqrt{\frac{8kT}{\pi\mu}} n_A n_B$$
$$\frac{A}{2} \left(\frac{2kT}{\mu}\right)^2 = \sigma_{AB} \sqrt{\frac{8kT}{\pi\mu}} n_A n_B$$

$$A = \sqrt{\frac{2}{\pi}} \left(\frac{\mu}{kT}\right)^{\frac{3}{2}} \sigma_{AB} n_A n_B \tag{5.99}$$

Equation (5.98) then becomes

$$dZ_{AB}(v_{r}) = \sigma_{AB} (n_{A} \cdot n_{B}) \sqrt{\frac{2}{\pi}} \left(\frac{\mu}{kT}\right)^{\frac{3}{2}} v_{r}^{3} e^{-\frac{\mu v_{r}^{2}}{2kT}} dv_{r}$$
$$dZ_{AB} (v_{r}) = \sigma_{AB} (n_{A} \cdot n_{B}) F(v_{r}) dv_{r}$$
(5.100)

or

 \Rightarrow

 \Rightarrow

 \Rightarrow

 $F(v_r)dv_r$ is the fraction of the total number of A - B collisions in which the relative speeds are in the range v_r to $v_r + dv_r$. We then write

$$F(v_r)dv_r = \sqrt{\frac{2}{\pi}} \left(\frac{\mu}{kT}\right)^{\frac{3}{2}} v_r^3 e^{-\frac{\mu v_r^2}{2kT}} dv_r$$
(5.101)

 $\frac{1}{2}\mu v_2^2$ is the kinetic energy of the relative motion, i.e. the relative kinetic energy of the two colliding molecules. For the corresponding energy distribution we set

$$\varepsilon_r = \frac{1}{2} \mu v_r^2 \implies d\varepsilon_r = \mu v_r dv_r$$

or

$$v_r^2 = \frac{2\varepsilon_r}{\mu}$$
 or, $v_r dv_r = \frac{1}{\mu} d\varepsilon_r$

combining these two equations we find

$$v_r^3 dv_r = \frac{2\varepsilon_r}{\mu^2} d\varepsilon_r$$

Equation (5.101) may be written as, setting $F(\varepsilon_r)d\varepsilon_r = F(v_r)dv_r$

$$F(\varepsilon_r)d\varepsilon_r = \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{\left(kT\right)^{\frac{3}{2}}} \varepsilon_r e^{-\frac{\varepsilon_r}{kT}} d\varepsilon_r$$
(5.102)

as the fraction of the total number of binary collisions in which the relative kinetic energy of translation is in the range $\varepsilon_r \rightarrow \varepsilon_r + d\varepsilon_r$. Equation (5.100) may now be written as

$$dZ_{AB}(\varepsilon_r) = dZ_{AB}(v_r) = \sigma_{AB} \ n_A \cdot n_B \ F(\varepsilon_r) d\varepsilon_r$$
$$dZ_{AB}(\varepsilon_r) = \sigma_{AB}(n_A \cdot n_B) \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{(kT)^{\frac{3}{2}}} \varepsilon_r \ e^{-\frac{\varepsilon_r}{kT}} \ d\varepsilon_r \tag{5.103}$$

Therefore, according to our postulate laid down in the first paragraph (Method 1), the rate of the reaction is obtained by integrating Eq. (5.103) from ε_0 to ∞ .

$$v = \int_{\varepsilon_0}^{\infty} dZ_{AB}(\varepsilon_r) = \sigma_{AB}(n_A \cdot n_B) \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{(kT)^{\frac{3}{2}}} \int_{\varepsilon_0}^{\infty} \varepsilon_r \ e^{-\frac{\varepsilon_r}{kT}} \ d\varepsilon_r$$

$$k_r = \sigma_{AB} \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{(kT)^{\frac{3}{2}}} \int_{\varepsilon_0}^{\infty} \varepsilon_r \ e^{-\frac{\varepsilon_r}{kT}} \ d\varepsilon_r$$
(5.104)

or,

 \Rightarrow

To evaluate the integral in Eq. (5.104), we set

$$Z = e^{-\frac{\varepsilon_r}{kT}}$$
$$dZ = d(e^{-\frac{\varepsilon_r}{kT}}) = -\frac{1}{kT} e^{-\frac{\varepsilon_r}{kT}} d\varepsilon_r$$
$$e^{-\frac{\varepsilon_r}{kT}} d\varepsilon_r = -kT d(e^{-\frac{\varepsilon_r}{kT}})$$

or

Therefore,

$$\int_{\varepsilon_0}^{\infty} \varepsilon_r \, e^{-\frac{\varepsilon_r}{kT}} \, d\varepsilon_r = -kT \int_{\varepsilon_0}^{\infty} \varepsilon_r \, d(e^{-\frac{\varepsilon_r}{kT}})$$
$$= -kT \left[\left| \varepsilon_r \, e^{-\frac{\varepsilon_r}{kT}} \right|_{\varepsilon_0}^{\infty} - \int_{\varepsilon_0}^{\infty} e^{-\frac{\varepsilon_r}{kT}} \, d\varepsilon_r \right]$$
$$= -kT \left[\lim_{\varepsilon_r \to \infty} \frac{\varepsilon_r}{e^{\frac{\varepsilon_r}{kT}}} - \varepsilon_0 e^{-\frac{\varepsilon_0}{kT}} + kT \left| e^{-\frac{\varepsilon_r}{kT}} \right|_{\varepsilon_0}^{\infty} \right]$$

Using the L'Hospital's rule, we get

$$\int_{\varepsilon_0}^{\infty} \varepsilon_r \, e^{-\frac{\varepsilon_r}{kT}} \, d\varepsilon_r = -kT \Biggl[\lim_{\varepsilon_r \to \infty} \frac{1}{\frac{1}{kT} e^{\frac{\varepsilon_r}{kT}}} -\varepsilon_0 \, e^{-\frac{\varepsilon_0}{kT}} - kT e^{-\frac{\varepsilon_0}{kT}} \Biggr]$$
$$= -kT [0 - \varepsilon_0 \, e^{-\frac{\varepsilon_0}{kT}} - kT \, e^{-\frac{\varepsilon_0}{kT}}]$$
$$= (kT)^2 \left(1 + \frac{\varepsilon_0}{kT} \right) e^{-\frac{\varepsilon_0}{kT}}$$

Equation (5.104) then finally takes the form

$$k_r = \sigma_{AB} \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} \left(1 + \frac{\varepsilon_0}{kT}\right) e^{-\frac{\varepsilon_0}{kT}}$$
(5.105)

We have incorporated an approximation that will make clear our next approach.

Method 2

Here we do the same thing exactly that we have done in method 1, but slightly in a different way. Here, we replace the hard sphere collision cross-section σ_{AB} by the reaction cross-section $\sigma(v_p)^*$, that depends on the relative speed v_r of the two colliding molecules. Rewriting Equation (5.100) as

$$dZ_{AB}(v_r) = [\sigma(v_r) F(v_r) dv_r] n_A n_B$$
(5.106)

as the frequency of collision between *A* and *B* molecules per unit volume with relative speeds in the range v_r to $v_r + dv_r$ or, in terms of the relative energy ε_r (cf. Eq. 5.102) as

^{*} The reaction cross-section is supposed to be a cross-sectional area about the target molecule on which, if the projectile molecule hits, there will be fruitful reaction.

$$dZ_{AB}(\varepsilon_r) = [\sigma(\varepsilon_r) F(\varepsilon_r) d\varepsilon_r] n_A \cdot n_B = dv(\varepsilon_r)$$
(5.107)

We correctly identify $dZ_{AB}(\varepsilon_r)$ as equal $dv(\varepsilon_r)$, i.e. the rate of the reaction between the molecule A and B colliding with the relative energy ε_r . The net rate is then obtained by integrating $dv(\varepsilon_r)$ for all possible values of ε_r :

$$v = \int_{0}^{\infty} dv(\varepsilon_r) = \int_{0}^{\infty} [\sigma(\varepsilon_r) F(\varepsilon_r) d\varepsilon_r] n_A \cdot n_B$$
(5.108)

The overall rate-constant of the reaction k_r is therefore given by

$$k_r = \int_0^\infty \sigma(\varepsilon_r) \ F(\varepsilon_r) d\varepsilon_r$$
(5.109)

We now impose the Hard Sphere Collision Cross-section, the simplest one as

$$\sigma(\varepsilon_r) \begin{cases} = 0 \text{ for } \varepsilon_r < \varepsilon_0 \\ = \sigma_{AB} = (\pi d_{AB}^2 \text{ for } \varepsilon_r > \varepsilon_0) \end{cases}$$
(5.110)

i.e. the collision cross-section is zero for all relative energy $\varepsilon_r < \varepsilon_0$, and it is constant and, equal to the hard sphere collision cross-section σ_{AB} for all $\varepsilon_r > \varepsilon_0$. Equation (5.109) then becomes

$$\begin{aligned} k_r &= \sigma_{AB} \int_{\varepsilon_0}^{\infty} F(\varepsilon_r) d\varepsilon_r \\ k_r &= \sigma_{AB} \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{(kT)^{\frac{3}{2}}} \int_{\varepsilon_0}^{\infty} \varepsilon_r \, e^{-\frac{\varepsilon_r}{kT}} \, d\varepsilon_r \qquad \text{[using Eq. (5.102)]} \\ k_r &= \sigma_{AB} \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} \left(1 + \frac{\varepsilon_0}{kT}\right) e^{-\frac{\varepsilon_0}{kT}} \end{aligned}$$
(5.111)

or

 \Rightarrow

Exactly the same as in Eq. (5.105). This is quite expected that only those collisions in which
$$\varepsilon_r > \varepsilon_0$$
 are effective for the reaction, and for all these collisions the reaction cross-section $\sigma(\varepsilon_r)$ is equal to the hard sphere collision cross-section σ_{AB} . The energy requirement of the reaction is then looked upon as the energy dependence of $\sigma(\varepsilon_r)$. For all value of $\varepsilon_r < \varepsilon_0$, $\sigma(\varepsilon_r) = 0$, and for $\varepsilon_r > \varepsilon_0$, $\sigma(\varepsilon_r) = \sigma_{AB}$. This is the hard sphere collision cross-section model.

5.12.2 Line-of-Centres (LOC) Model

In the hard sphere collision model it is assumed that for any energy $\varepsilon_r > \varepsilon_0$, the reaction takes place. This is clearly an overestimation. It is not difficult to understand, why? In
Figure 5.30, two set of collisions are shown. Consider the collision shown in Figure 5.30a. There is a head-on-collision between the two molecules A and B, and it is legitimate to believe that the entire relative translational kinetic energy ε_r of the two molecules along the line they are approaching will be used up in overcoming the electron cloud repulsion. But if the collision was like that in Figure 5.30b. Then it is not the entire relative kinetic energy ε_r but, only that part of ε_r which is along the line-of-centres of the two colliding molecules at the time of impact. The rest part goes to sideswiping of the molecules, and would not be expected to be useful for the reaction (Figure 5.30 b).



Figure 5.30 (a) Entirely, the total translational kinetic energy of the two colliding molecules $\left(\frac{1}{2}m_A v_A^2 + \frac{1}{2}m_B v_B^2\right)$

may be used in overcoming the electron repulsion as, momentarily the molecules come to a stop on collision.



Figure 5.30 (b) Only a part of the translational kinetic energy of the two colliding molecules along the line AB joining their centres at the time of impact will be used because the two molecules continue their motion even after they collide; some energy is retained for this motion and could not be used for the reaction as in (a).

5.12.2.1 How to Express $\sigma(\varepsilon_r)$?

Let v_r be the relative speed of the molecule A with respect to the B (assumed stationary) at the time of impact. Not the whole of v_r would be used for the reaction. Only the component of v_r along the line-of-centres ($v_{r(loc)}$) may be used for the reaction. From Figure 5.31, we proceed as





$$\cos\theta = \frac{v_{r(\text{loc})}}{v_r} \implies v_{r(\text{loc})} = v_r \cos\theta$$
$$v_{r(\text{loc})} = v_r \left(\frac{d^2 - a^2}{d^2}\right)^{\frac{1}{2}}$$

 \Rightarrow

The corresponding kinetic energy along the line-of-centres is therefore

$$\varepsilon_{r,\text{loc}} = \frac{1}{2} \mu v_{r,\text{loc}}^2 = \frac{1}{2} \mu v_r^2 \left(1 - \frac{a^2}{d^2} \right)$$
$$\varepsilon_{r,\text{loc}} = \varepsilon_r \left(1 - \frac{a^2}{d^2} \right)$$
(5.112)

 \Rightarrow

where μ is the reduced mass.

The first point to note is that, $a' \ge d'$, for then, there will be no collision Figure 5.32a. So, a must be less than d'; a' < d'.

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If 'a' is zero, then the situation cannot be *even more favourable for the reaction* because, it is a *head-on-collision*; the entire of ε_r goes to $\varepsilon_{r,\text{loc}}$. To find the maximum permissible value of 'a', we recognize the requirement of the minimum threshold energy ε_0 which, the $\varepsilon_{r,\text{loc}}$ must succeed. Naturally, there is a maximum value of a (a_{max}) for a given value ε_r (ε_r may vary from 0 to ∞) corresponding to the critical ε_0 , and this is obtained as [using Eq. (5.112)]

$$\varepsilon_0 = \varepsilon_r \left(1 - \frac{a_{\max}^2}{d^2} \right) \tag{5.113}$$

As because ε_0 and d are fixed constants, it is observed form Eq. (5.113) that, a_{\max} increases with ε_r . Students may get a feeling of this from Figures 5.32 (b) and (c). Solving for a_{\max} , we get

$$a_{\max}^{2} = \left(1 - \frac{\varepsilon_{0}}{\varepsilon_{r}}\right) d^{2}$$
$$\pi a_{\max}^{2} = \left(1 - \frac{\varepsilon_{0}}{\varepsilon_{r}}\right) \pi d^{2} \quad (\text{for } \varepsilon_{r} > \varepsilon_{0})$$

We define the left hand side as the reaction cross-section $\sigma(\varepsilon_r)$. We have then

$$\sigma(\varepsilon_r) = \left(1 - \frac{\varepsilon_0}{\varepsilon_r}\right) \sigma_{AB} \quad \text{(for } \varepsilon_r > \varepsilon_0\text{)} \tag{5.114}$$

For $\varepsilon_r < \varepsilon_0$, there is no chance of any reaction. Let us analyze Figures 5.32 (a), (b) and c. In Figure 5.32a there is no collision; therefore no reaction because a > d. For $\varepsilon_r = 200$ J and $\varepsilon_0 = 100$ J; for Figure 5.32(b)

Let
$$a < d$$
; say, $\frac{a^2}{d^2} = 0.75$, then [using Eq. (5.112)]

$$\varepsilon_r (1 - 0.75) = 200 \text{ J} (0.25) = 50 \text{ J} < \varepsilon_0 (= 100 \text{ J})$$

..

The result is no reaction as 'a' is too high.

Let

$$\frac{a^2}{d^2} = 0.5$$
 (Fig 5.32c)

 \Rightarrow $\varepsilon_r(1-0.5) = 100 \text{ J}$; just equal to the threshold energy ε_0 .

The maximum permissible *a* is then given by $a_{\max} = d\sqrt{0.5}$ for $\varepsilon_r = 200$ J. All collisions with '*a*' less then this value are reactive for $\varepsilon_r = 200$ J. As ε_r increases, a_{\max} also needs to be increased because, ε_0 is fixed for a given reaction. Greater cross-section $\sigma(\varepsilon_r)$ is available for the reaction between molecules moving with greater ε_r .

Figure 5.33 shows the variation of the reaction cross-section with the relative kinetic energy. $\sigma(\varepsilon_r)$ increases with ε_r . No reaction for $\varepsilon_r < \varepsilon_0$. In the region of $\varepsilon_r > \varepsilon_0$, $\sigma(\varepsilon_r)$ increases with ε_r . For low ε_r the collision must be more closer to the head-on situation (i.e. θ must be more acute) for the reaction to occur; $\sigma(\varepsilon_r)$ is then small. For collisions with high ε_r , a slight touch between the molecules may give rise to the product(s); $\sigma(\varepsilon_r)$ is then large.



Figure 5.33 The variation of the reaction cross-section with relative kinetic energy ε_r .

5.12.2.2 Final Calculation of k_r

Starting from Eq. (5.109) and using Eq. (5.114) for $\sigma(\varepsilon_r)$, and Eq. (5.102) for $F(\varepsilon_r)d\varepsilon_r$, we get,

$$k_{r} = \int_{\varepsilon_{0}}^{\infty} \left(1 - \frac{\varepsilon_{0}}{\varepsilon_{r}}\right) \sigma_{AB} \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{(kT)^{\frac{3}{2}}} \varepsilon_{r} e^{-\frac{\varepsilon_{r}}{kT}} d\varepsilon_{r}$$
$$= \sigma_{AB} \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{(kT)^{\frac{3}{2}}} \left[\int_{\varepsilon_{0}}^{\infty} \varepsilon_{r} e^{-\frac{\varepsilon_{r}}{kT}} d\varepsilon_{r} - \varepsilon_{0} \int_{\varepsilon_{0}}^{\infty} e^{-\frac{\varepsilon_{r}}{kT}} d\varepsilon_{r}\right]$$

where the lower limit is put at ε_0 (for all collisions with $\varepsilon_r < \varepsilon_0$, there is no reaction).

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$$k_{r} = \sigma_{AB} \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{\left(kT\right)^{\frac{3}{2}}} \left[-kT \left(\varepsilon_{r} e^{-\frac{\varepsilon_{r}}{kT}}\right)_{\varepsilon_{0}}^{\infty} + kT \int_{\varepsilon_{0}}^{\infty} e^{-\frac{\varepsilon_{r}}{kT}} d\varepsilon_{r} + \varepsilon_{0} kT \left|_{e}^{-\frac{\varepsilon_{r}}{kT}}\right|_{\varepsilon_{0}}^{\infty} \right]$$
$$k_{r} = \sigma_{AB} \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{\left(kT\right)^{\frac{3}{2}}} \left[-kT \left(0 - \varepsilon_{0} e^{-\frac{\varepsilon_{0}}{kT}}\right) - \left(kT\right)^{2} \left|_{e}^{-\frac{\varepsilon_{r}}{kT}}\right|_{\varepsilon_{0}}^{\infty} + \varepsilon_{0} kT \left|_{e}^{-\frac{\varepsilon_{r}}{kT}}\right|_{\varepsilon_{0}}^{\infty} \right]$$

$$k_r = \sigma_{AB} \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{\left(kT\right)^{\frac{3}{2}}} \left[\varepsilon_{\theta} kTe^{\frac{\varepsilon_0}{kT}} + (kT)^2 e^{-\frac{\varepsilon_0}{kT}} - \varepsilon_{\theta} kTe^{\frac{\varepsilon_0}{kT}}\right]$$

or,
$$k_r = \sigma_{AB} \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{(kT)^{\frac{3}{2}}} (kT)^2 e^{-\frac{\varepsilon_0}{kT}}$$

$$k_r = \sigma_{AB} \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} e^{-\frac{\varepsilon_0}{kT}}$$
(5.115)

which was the equation first derived by Lewis and Trautz. This result differs from the hard-sphere-collision theory by the factor $\left(1 + \frac{\varepsilon_0}{kT}\right)$ [cf. Eq. (5.111)]. This is quite expected.

The hard-sphere-collision theory considers the entire ε_r for any value of θ , going to be used for the reaction. This is clearly an overestimation. On the other hand, the LOC model uses only that part of ε_r which is along their centre joining line; this is more realistic.

5.13 HOW GOOD IS COLLISION THEORY OF REACTION RATE?

When the theoretically calculated rate constants from the collision theory are compared with those experimentally observed rate constants, it is found that the theory gives excellent result for reactions between atoms and, between geometrically simple molecules. But, as the geometry of the reactant molecules becomes complex, the theoretically calculated values of k are found to be much more than those experimentally observed. The theory is therefore counting more successful encounters between the reactant molecules than what is happening in fact. To account for this Eq. (5.115) has been modified as

$$k = P \sigma_{AB} \left(\frac{8 kT}{\pi \mu}\right)^{1/2} e^{-\varepsilon_0/kT} = \rho z' e^{-\varepsilon_0/kT^*}$$
(5.116)

5.88

 \Rightarrow

 \Rightarrow

or,

z' is the number of binary collision at the hypothetical concentration of 1 molecule per unit volume.

where *P* is called the *probability factor* or, the *steric factor*. Naturally *P* is much less than unity, e.g., for the reaction between C_2H_4 + butadiene \rightarrow cyclohexane, *P* has been found to be 4×10^{-5} . This is explained as follows:

The acquirement of the activation energy during a collision between the reactant molecules is not only necessary for the reaction to occur; the collision must take place at the vulnerable point. It may happen that the two colliding molecules have acquired the required activation energy but, they were not property oriented during the collision so as to form the product. Certainly, it is a useless collision. Hence, a fraction of the activated collisions becomes fruitless just because of the proper geometric orientation of the two colliding molecules. For atoms and geometrically simple molecules, this factor of orientation is not important; therefore we got the theoretical k matching with the experimental k. But, when the reactant molecules are geometrically complex, there may be a number of collisions, which acquires the activation energy but, they were not properly *geometrically oriented*; such an energetic collision yields nothing.

There are also examples where, the experimental value of the rate constant is much higher than the theoretical value. This anomaly is explained as follows:

We have considered, in the collision theory, the contribution of only the translational mode of energy towards acquiring the activation energy. If, however, the rotational and vibrational modes also contribute in the process of acquiring the activation energy then, naturally the reaction rate would be more faster.

5.14 THEORY OF UNIMOLECULAR REACTION

The Collision Theory of Reaction Rate fails apparently, to explain the elementary first order reactions. The theory requires two molecules to collide, suggesting that such reactions should be second-order. The decomposition of N_2O_5 follows a first-order kinetics at sufficiently high pressure of N_2O_5 , however, at low pressure, the reaction follows a second-order kinetics. Lindemann proposed a satisfactory explanation of these observations (1922).

Energy transfer between two molecules occurs during a collision; according to Lindemann, the translational energy of one molecule is transferred onto the other into its vibrational mode (during the collision) and, the second molecule gets vibrationally excited. The activation of molecules can thus be made.

This activated molecule now has two fates. It may become deactivated again by suffering a collision with another molecule. On the other hand, it may also happen that, the vibrationally activated molecule has concentrated the energy into one of its vibrational mode, which ruptures and give the product.

The whole scheme may be represented as:

$$A + A \xrightarrow[k_{-1}]{k_{-1}} A + A^*$$

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$$A^* \xrightarrow{k_2} \operatorname{Product}(s)$$

where A^* is the vibrationally activated reactant molecule A.

The rate of the reaction is

$$v = k_2 C_{A^*} \tag{5.116}$$

 C_{A^*} is then evaluated by applying the steady state approximation to C_{A^*} ; we get

 $\frac{d}{dt}C_{A^*} = k_1 C_A^2 - k_{-1} C_A C_{A^*} - k_2 C_{A^*} = 0$ $C_{A^*} = \frac{k_1 C_A^2}{(k_1 C_A + k_2)}$ (5.117)

Substituting this result in Eq. (5.116), we find

$$v = \frac{k_1 k_2 C_A^2}{(k_1 C_A + k_2)} \tag{5.118}$$

At high enough pressure, the number density of A molecules is large, and therefore, the possibility is that, the activated molecule A^* makes frequent collision with the other A molecules in their ground state and, becomes quenched. Under this condition, we will consider the rate of deactivation of A^* to be large compared to its decomposition to form the product. This means that, $k_1C_A >> k_2$ and therefore Eq. (5.118) changes to

$$v = \frac{k_1 k_2}{k_1} C_A = k_{\text{obs}} C_A$$
(5.119)

where $k_{obs} = \frac{k_1 k_2}{k_1}$. It then shows that at high pressure of *A*, the reaction follows a first-

order kinetics (unimolecular). At low pressure, fewer molecules of A is available for the A^* molecules to strike, and therefore A^* gets the chance to concentrate its excess energy into that particular mode of vibration to be ruptured; the bond breaking happens and, we get the final product(s). Under this condition $k_1 >> k_1C_A$, and the rate law goes to

$$v = k_1 C_A^2$$
(5.120)

a second order process (bimolecular). It is thus predicted as a second order dependence at low pressure, and a first order dependence at high pressure. The mechanism involves, however, the activation of molecules by collision. It can also be concluded that at low pressure, the life time of A^* is longer at low pressure than that it has at high enough pressure.

In the above section, we have considered the excitation of a A molecule with collision with another A molecule. It is however possible that, there is a third body M (non-reacting) which collides with a A molecule and, excites it vibrationally. The reaction scheme is then

5.90

 $A + M \xleftarrow{k_1} A^* + M$ $A^* \xrightarrow{k_2} \text{Product(s)}$

The rate of the reaction is

$$v = k_2 C_{A^*} \tag{5.121}$$

We find C_{A^*} by applying the steady state approximation: $k_1C_AC_M - k_{-1}C_{A^*}C_M - k_2C_{A^*} = 0$

$$\Rightarrow \qquad \qquad C_{A^*} = \frac{k_1 C_A C_M}{(k_{-1} C_M + k_2)}$$

Using this result in Eq. (5.121), we get

$$v = \frac{k_1 k_2 C_A C_M}{(k_{-1} C_M + k_2)} \tag{5.122}$$

Comparison between the activation of A by its own kind, and by a third body M is now compared.

At high pressure the deactivation of A^* by M is more likely than its decomposition to give the product(s); i.e., $k_1C_M >> k_2$. The rate law [Eq. (5.122)] then becomes

$$v = \frac{k_1 k_2}{k_1} C_A = k_{\text{obs}} C_A \tag{5.123}$$

which shows that the reaction follows a first-order kinetics.

At low pressure, the concentration of the quenching particles (*M*) is low; therefore, $k_{-1}C_M \ll k_2$. Equation (5.122) then becomes

$$v = k_1 C_A C_M \tag{5.124}$$

The reaction then becomes first-order in A and first-order in M. If M is now a A molecule, Eq. (5.124) becomes the same as Eq. (5.120).

5.15 TRANSITION STATE THEORY

The collision theory of reaction rates is not totally satisfactory, particularly with the steric factor *P*, which is evaluated empirically as $P = k_{expt}/k_{theo}$.

Henry Eyring proposed the *transition state theory* which takes a somewhat different approach.

According to this theory, it is proposed that the reactant molecule(s) first form an activated complex which may then breaks up to give the product(s). The theory cleverly evades how is the complex is formed. It may be formed by some loose association among the reactant molecules. If it is a unimolecular reaction, the complex could be formed by a stretching or bending of some bonds.

The essential feature of the transition state theory is that, there is a potential barrier between the reactant and the product. Not all the activated complexes can lead to the product; only those complexes which are at the cole point of the potential energy diagram can form the products. These activated complexes are said to be at the *transition state*.

These activated complexes at the transition state are assumed to be in equilibrium with the reactant molecules. It is also postulated that the activated complexes at the transition state are considered as a transient species, having all the normal modes of motion, excepting one vibrational mode, along which it breaks open to form the products. This vibration happens to have a large amplitude and a low frequency such that the vibrational energy is of the order of the thermal energy kT, i.e., hv = kT. The basic idea is that when the bond vibrating with energy hv breaks open, it produces two translational modes, each

of energy $\frac{1}{2}kT$, i.e., a total of $2\left(\frac{1}{2}kT\right) = kT$ (if a vibrating string is cut at any point, the two ends just translate). So we may write

$$hv = kT$$
, or $v = \frac{kT}{h}$ (5.125)

Now, according to our postulates the reaction scheme may be represented as

$$A + B \Longrightarrow AB^{\#} \to \operatorname{Product}(s) \tag{5.126}$$

For the formation of the transition state, the equilibrium constant is

$$k^{\neq} = \frac{[AB^{\neq}]}{[A][B]}$$
(5.127)

and, we find the concentration of the transition state is

$$[AB^{\neq}] + K^{\neq} [A][B]$$
 (5.128)

The concentration of the transition state is not the only factor involved; the frequency of its dissociation must come into play because, the rate at which it decomposes must also be considered. Therefore, the rate v can be expressed as

 $v = (\text{Transition state concentration}) \times (\text{frequency of decomposition})$ $v = K^{\neq} \text{[A][B]} \cdot v$

then using Eq. (5.125),

 \Rightarrow

$$v = \frac{kT}{h} K^{\neq}[\mathbf{A}][\mathbf{B}]$$

If k_r be the rate constant of the reaction, then we find

$$k_r = \frac{kT}{h} K^{\neq}$$
(5.129)

k is the Boltzmann constant and h is the Planck's constant. This is the famous Eyring equation. The equilibrium constant can be expressed either in terms of

thermodynamic quantities or it terms of partition functions. In the following, we take the first approach.

$$K^{\neq} = e^{-\Delta G^{\neq}/RT} = e^{\Delta S^{\neq}/R} \cdot e^{-\Delta H^{\neq}/RT}$$
(5.130)

where, ΔG^{\neq} , ΔS^{\neq} and ΔH^{\neq} are the standard free energy change, the standard entropy change and, the standards enthalpy change for one mole of the complex to be formed. Equation (5.129) then changes to

$$k_r = \frac{kT}{h} e^{-\Delta S^{\neq}/R} \cdot e^{\Delta H^{\neq}/RT}$$
(5.131)

From Eq. (5.129), we may write

$$\ln k_r = \ln \frac{k}{h} + \ln T + \ln K^{\neq}$$

 \Rightarrow

 $\frac{d\ln k_r}{dT} = \frac{1}{T} + \frac{d\ln K^{\neq}}{dT}$

then using the Arrhenius equation, we get

$$\frac{E}{RT^2} = \frac{1}{T} + \frac{d\ln K^*}{dT}$$

 \Rightarrow

$$E = RT + RT^2 \frac{d \ln K}{dT}$$

 $\Rightarrow \qquad E = RT + \Delta u^{\neq} \quad (\text{from the van't Hoff isochore})$

$$\Rightarrow \qquad \qquad E = RT + \Delta H^{\neq} - \Delta n^{\neq} RT$$

where Δn^{\neq} is the change in the number of moles during the complex formation step. Therefore,

$$\Delta H^{\neq} = E - RT + \Delta n^{\neq} RT = E + (\Delta n^{\neq} - 1) RT$$
(5.132)

Substituting this into Eq. (5.131), we get

$$k_r = \frac{kT}{h} e^{\Delta S^{\neq}/R} e^{(1 - \Delta n^{\neq})} e^{-E/RT}$$
(5.133)

Comparing with the Arrhenius equation, we find the frequency factor A as

$$A = \frac{kT}{h} e^{\Delta S^{\neq}/R} e^{(1 - \Delta n^{\neq})}$$
(5.134)

For a unimolecular reaction, $\Delta n = 0$

$$k_r = e \, \frac{kT}{h} \, e^{\Delta S^{\neq}/R} \, e^{-E/RT}$$
(5.135)

For a bimolecular process,

$$k_r = e^2 \frac{kT}{h} e^{\Delta S^{\neq}/R} e^{-E/RT}$$
(5.136)

Equation (5.133) can be written as

$$\ln k_r = -\frac{E}{RT} + \ln T + \left[\frac{\Delta S^{\neq}}{R} + \ln \frac{k}{h} \left(1 - \Delta n^{\neq}\right)\right]$$
(5.137)

Since ΔS^{\neq} is almost independent of temperature and, the variation of $\ln T$ is negligible in comparison to $\frac{E}{RT}$, a plot of $\ln k_r$ versus 1/T would be linear. This has already been established by Arrhenius.

5.16 COMPARISON OF COLLISION THEORY WITH TRANSITION STATE THEORY

The collision theory starts with the assumption that, there is a binary collision between two reactant molecules to initiate the reaction. This concept faces the problem of explaining the unimolecular reactions; however, with the Lindemann hypothesis, the theory could have enabled to explain how a reaction may be unimolecular. On the other hand, the great advantage of the transition state theory is that, it evades the question of how the complex is formed and, how many atoms/molecules will have to be there.

Comparing Eqs (5.116) and (5.133) we may write

$$Pz' \approx rac{kT}{h} e^{\Delta S^{\neq}/R}$$

Since z' is constant, and kT/h is constant, it is clear that for different reactions, the probability factor P is related to the entropy of activation ΔS^{\neq} . If ΔS^{\neq} is positive, then P is large and the reaction will be fast. But if ΔS^{\neq} is negative the reaction will be a slow one.

For gaseous reaction ΔS^{\neq} is generally negative. This may be understood as: when two molecules unite and form a complex, the translational degrees of freedom is reduced from 6 to 3; the rotational degrees of freedom is also reduced; This may however be compensated by an increase of the vibrational degrees of freedom. But, the definite orientation required to form the complex will inevitably reduce the entropy.

When the reactant molecules are simple, e.g., for a reaction between two atoms or, between two simple molecules, there is a little rearrangement of energy among the various degrees of freedom during the formation of the activated complex. Under this condition ΔS^{\neq} has a small negative value. The transition state theory and the collision theory give results of the same order. But when complex molecules are involved in forming the activated complex, there would be a large decrease in entropy; naturally the reaction rate will be slow [cf. Eq. (5.133)]. This has been explain in the collision theory by making *P* much less than unity; for the reaction to occur the molecules are to be properly oriented, which then makes some energetic collision fruitless due to improper geometric orientation of the reactant molecules.

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5.17 CHAIN REACTIONS

A complex reaction pathway may sometimes include a cycle of reactions, such that certain reaction intermediates consumed in one step are regenerated in another. The intermediates may be atoms, free radicals, or ions. If such a cycle is repeated more than once, the reaction is said as a chain reaction. The ending of the chain is being done by the combination of the atoms or free radicals. For example, if H_2 and Br_2 react and the product HBr is removed as fast as it is formed, then the following scheme may be given for the reaction:

$$\begin{array}{l} \operatorname{Br}_{2} \xrightarrow{k_{1}} 2\operatorname{Br} & \text{Initiation} \\ \\ \operatorname{Br} + \operatorname{H}_{2} \xrightarrow{k_{2}} \operatorname{HBr} + \operatorname{H} \\ \\ \operatorname{H} + \operatorname{Br}_{2} \xrightarrow{k_{3}} \operatorname{HBr} + \operatorname{Br} \end{array} \end{array} \begin{array}{l} \text{Chain propagation} \\ \\ \\ \operatorname{Br} + \operatorname{Br} \xrightarrow{k_{4}} \operatorname{Br}_{2} & \text{Termination} \end{array}$$

In the initiating step two Br atoms are formed; one of them reacts with H_2 to produce a product (HBr) and a chain carrier H atom; this in turns reacts with Br_2 to produce the product HBr, and the chain carrier Br atom. *If this cycle continues a number of times, the reaction is said to be a chain reaction*. This sequence is called the chain propagation step. Finally, two atoms of Br may unite to bring an end of this chain. This process is called termination. In the following we shall discuss some of its special kinds.

(i) Decomposition of Acetaldehyde

$CH_3CHO \rightarrow CH_4 + CO$

Rice and Herzfeld proposed a mechanism for this thermal decomposition:

$$\begin{array}{ll} \operatorname{CH}_{3}\operatorname{CHO} & \stackrel{k_{1}}{\longrightarrow} \operatorname{CH}_{3} + \operatorname{CHO} & \text{Initiation} \\ \\ \operatorname{CH}_{3} + \operatorname{CH}_{3}\operatorname{CHO} & \stackrel{k_{2}}{\longrightarrow} \operatorname{CH}_{4} + \operatorname{CH}_{3}\operatorname{CO} \\ \\ \operatorname{CH}_{3}\operatorname{CO} & \stackrel{k_{3}}{\longrightarrow} \operatorname{CO} + \operatorname{CH}_{3} \end{array} \end{array} \right\} \operatorname{Propagation} \\ \\ \operatorname{CH}_{3} + \operatorname{CH}_{3} & \stackrel{k_{4}}{\longrightarrow} \operatorname{C}_{2}\operatorname{H}_{6} \end{array}$$
 Termination

The rate of the reaction v, may be expressed as the rate at which the product(s) is formed; we write

$$\frac{d}{dt}[CH_4] = v = k_2[CH_3CHO][CH_3]$$
(5.138)

Applying the steady state concept to the methyl radicals

$$k_1[CH_3CHO] - k_2[CH_3CHO][CH_3] + k_3[CH_3CO] - 2 k_4[CH_3]^2 = 0$$
(5.139)

and for the CH₃CO radicals

$$k_2[CH_3CHO][CH_3] - k_3[CH_3CO] = 0$$
 (5.140)

Adding these two equations, we get

 k_1 [CH₃CHO] = 2 k_4 [CH₃]²

$$[CH_3] = \left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3CHO]^2$$
(5.141)

Using this in Eq. (5.138) we have, for the rate of the reaction

$$v = k_2 \left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3 CHO]^{3/2}$$
 (5.142)

$$v = k_{\rm obs} [\rm CH_3 CHO]^{3/2}$$
 (5.143)

Thus, the mechanism predicts the three-halves order; this has been experimentally verified. The radical CHO undergoes further reaction:

$$\label{eq:CHO} \begin{array}{l} {\rm CHO} \rightarrow {\rm CO} + {\rm H} \\ \\ {\rm H} + {\rm CH}_{3} {\rm CHO} \rightarrow {\rm H}_{2} + {\rm CH}_{3} {\rm CO} \end{array}$$

These two steps are ignored for, their inclusion complicates the mathematical steps but, at the end, it is found that equation for the rate [Eq. (5.143)] is just multipled by a constant factor.

 $\ln \mathbf{k}_{\text{obs}} = \ln k_2 + \frac{1}{2} \ln \left(\frac{k_1}{2k_4} \right) = \ln k_2 + \frac{1}{2} \ln k_1 - \frac{1}{2} \ln 2 - \frac{1}{2} \ln k_4$

The overall rate constant $k_{\rm obs}$ is related to those of the elementary steps as

$$k_{\rm obs} = k_2 \left(\frac{k_1}{2 k_4}\right)^{1/2}$$

 \Rightarrow

 \Rightarrow

$$\frac{d\ln k_{\rm obs}}{dT} = \frac{d\ln k_2}{dT} + \frac{1}{2}\frac{d\ln k_1}{dT} - \frac{1}{2}\frac{d\ln k_4}{dT}$$

$$\Rightarrow \qquad \frac{E}{RT^2} = \frac{E_2}{RT^2} + \frac{1}{2} \left(\frac{E_1 - E_4}{RT^2} \right)$$

or

$$E = E_2 + \frac{1}{2} \left(E_1 - E_4 \right) \tag{5.144}$$

That is how, the overall activation energy E is related to the activation energies of the elementary steps.

The chain length γ of a chain reaction is defined as:

$$\gamma = \frac{\text{rate of the overall reaction}}{\text{rate of the initiation step}}$$

 \Rightarrow

For the thermal decomposition of CH₃CHO, the chain length is then

$$\gamma = \frac{k_2 \left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3 CHO]^{3/2}}{k_1 [CH_3 CHO]}$$
$$\gamma = \frac{k_2}{\sqrt{2k_1 k_4}} [CH_3 CHO]^{1/2}$$
(5.145)

 \Rightarrow

The chain length then depends on the concentration of the reactant.

This reaction changes its order if the termination step is changed. Thus, for the scheme

$$\begin{array}{c} \mathrm{CH}_{3}\mathrm{CHO} & \stackrel{k_{1}}{\longrightarrow} \mathrm{CH}_{3} + \mathrm{CHO} \\\\ \mathrm{CH}_{3} + \mathrm{CH}_{3}\mathrm{CHO} & \stackrel{k_{2}}{\longrightarrow} \mathrm{CH}_{4} + \mathrm{CH}_{3}\mathrm{CO} \\\\\\ \mathrm{CH}_{3} & \mathrm{CO} & \stackrel{k_{3}}{\longrightarrow} \mathrm{CO} + \mathrm{CH}_{3} \\\\\\ 2 & \mathrm{CH}_{3} & \mathrm{CO} & \stackrel{k_{4}}{\longrightarrow} \mathrm{CH}_{3}\mathrm{COCOCH}_{3} \end{array}$$

The steady state equation for CH₃ is

$$k_1[CH_3CHO] - k_2[CH_3CHO][CH_3] - 2 k_3[CH_3CO] = 0$$
 (5.146)
and for CH_CO

and for CH₃CO,

$$k_2[CH_3CHO][CH_3] - k_3[CH_3CO] - 2 k_4[CH_3CO]^2 = 0$$
(5.147)
Addition of these two equations, we get

 k_1 [CH₃CHO] = 2 k_4 [CH₃CO]²

$$[CH_{3}CO] = \left(\frac{k_{1}}{2k_{4}}\right)^{1/2} [CH_{3}CHO]^{1/2}$$
(5.148)

The rate of formation of CO^* is therefore

$$v = \frac{d}{dt} [CO] = k_3 [CH_3 CO]$$
$$v = \frac{d}{dt} [CO] = k_3 \left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3 CHO]^{1/2}$$
(5.149)

 \Rightarrow

 \Rightarrow

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^{*} In these schemes the rate of formation of CO and CH_4 are very close to each other, but are not identical. In the present scheme it is simpler to considered the rate of formation of CO, whereas in the three-halves order scheme, it was better to consider the rate of formation of CH_4 .

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The overall activation energy is now

$$E = E_3 + \frac{1}{2}(E_1 - E_4) \tag{5.150}$$

and the chain length is

$$\gamma = \frac{k_3 \left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3 CHO]^{1/2}}{k_1 [CH_3 CHO]}$$
$$\gamma = \frac{k_3}{\sqrt{2k_1 k_4}} [CH_3 CHO]^{-1/2}$$
(5.151)

(ii) Goldfinger-Letort-Niclause Rules

The above examples show that the order of the overall reaction depends on the manner in which the chains are broken. The problem has been solved by Goldfinger, Letort and Niclause, who distinguished between two types of radicals:

- 1. Radicals that are involved in second-order propagation are referred to as β radicals. In the above examples CH₃ is a β radical.
- 2. Radicals that are involved in first-order propagation are referred to as μ radicals. CH₃CO is a μ radical.

Their proposal is given as the following.

Termination	Overall order
$\beta\beta$	3/2
βμ	1
$\mu\mu$	1/2

(iii) Hydrogen-Bromine Reaction

M. Bodenstein and S.C. Lind (1906) first addressed the gas phase reaction between H_2 and Br_2 . For this thermal reaction over the temperature range 205–302°C, they found empirically that the rate of consumption of H_2 or Br_2 as:

$$v = \frac{k[\mathrm{H}_2][\mathrm{Br}_2]^2}{m = [\mathrm{HBr}]/[\mathrm{Br}_2]}$$
(5.152)

There was no interpretation of this curious rate law for thirteen years. Then the problem was solved independently and almost simultaneously by Christiansen, Herzfeld and Polani. They proposed a chain of reactions as follows:

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 $\begin{array}{lll} \text{Chain initiation (1)} & \operatorname{Br}_2 + \operatorname{H}_2 & \xrightarrow{k_1} & 2 \operatorname{Br} \\ \\ \text{Chain propagation} & \begin{cases} (2) \operatorname{Br} + \operatorname{H}_2 & \xrightarrow{k_2} & \operatorname{HBr} + \operatorname{H} \\ (3) \operatorname{H} + \operatorname{Br}_2 & \xrightarrow{k_3} & \operatorname{HBr} + \operatorname{Br} \\ \\ \\ \text{Chain inhibition (4)} & \operatorname{H} + \operatorname{HBr} & \xrightarrow{k_4} & \operatorname{H}_2 + \operatorname{Br} \\ \\ \\ \text{Chain termination (5)} & \operatorname{Br} + \operatorname{Br} & \xrightarrow{k_5} & \operatorname{Br}_2 \end{cases}$

The reaction is initiated by the formation of bromine atom from the thermal dissociation of Br_2 . The chain propagating steps (2) and (3) form two molecules of HBr and regenerate the Br atom, ready for another cycle. Step (4) is introduced to account for the observed inhibition by HBr. Since this inhibition is proportional to the ratio [HBr]/[Br₂] [cf. Eq. (5.152)], it is evident that HBr and Br_2 compete, so that the atom being removed must be H rather than Br.

Applying the steady state approximation to [Br], we have

$$\frac{d[Br]}{dt} = 2 k_1 [Br_2] - [Br] [H_2] + k_3 [H] [Br_2] + k_4 [H] [HBr] - 2 k_5 [Br]^2 = 0$$
(5.153)

and for [H], we have

$$\frac{d[H]}{dt} = k_2 \,[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0$$
(5.154)

Adding these two equations, we get

 $2 k_1[Br_2] = 2 k_5[Br]^2$

 \Rightarrow

$$[Br] = \sqrt{\frac{k_1}{k_5}} [Br_2]^{1/2}$$
(5.155)

From Eq. (5.154), we may write

$$[{\rm H}] = \frac{k_2 [{\rm Br}] + {\rm H}_2]}{k_3 [{\rm Br}_2] + k_4 [{\rm HBr}]}$$

and using Eq. (5.155) for [Br] we get,

$$[H] = \frac{k_2 \sqrt{\frac{k_1}{k_5}} [Br]^{1/2} + [H_2]}{k_3 [Br_2] + k_4 [HBr]}$$
(5.156)

The rate of formation of HBr is,

(

$$\frac{d[\text{HBr}]}{dt} = k_2 [\text{Br}][\text{H}_2] + k_3 [\text{H}][\text{Br}_2] - k_4 [\text{H}][\text{HBr}]$$
(4)

Using Eq. (5.154)

$$\frac{d[\text{HBr}]}{dt} = 2 k_3 [\text{H}][\text{Br}_2]$$

and, finally using the expression of [H] from Eq. (5.156)

$$\begin{aligned} \frac{d[\text{HBr}]}{dt} &= 2k_3 \, \frac{k_2 \left(\frac{k_1}{k_5}\right)^{1/2} \, [\text{Br}_2]^{1/2} \, [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} [\text{Br}_2] \\ \\ \frac{d[\text{HBr}]}{dt} &= \frac{2k_2 \left(\frac{k_1}{k_5}\right)^{1/2} \, [\text{H}_2]^{1/2} \, [\text{Br}_2]^{1/2}}{1 + \frac{k_4}{k_3} \frac{[\text{HBr}]}{[\text{Br}_2]}} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k_4 [\text{HBr}] / k_3 [\text{Br}_2]} \end{aligned}$$

This agrees exactly with the empirical expression [Eq. (5.152)]. The second term in the denominator is just the ratio of rates of step (3) to that of (4)

$$\frac{v_4}{v_3} = \frac{k_4 \,[\text{H}][\text{HBr}]}{k_3 \,[\text{H}][\text{Br}_2]} = \frac{k_4 \,[\text{HBr}]}{k_3 \,[\text{Br}_2]}$$
(5.158)

which indicates that, to what extent the reaction is inhibited. As this quotient increases, the rate decreases.

(iv) Hydrogen-Chlorine Reaction

The reaction between H_2 and Cl_2 occurs both thermally a photochemically; only the thermal reaction is considered here. The mechanism is not as clear-cut as in the H_2 -Br₂ reaction, and a large number of elementary steps play a significant role. Only an approximate interpretation of the overall kinetic law can be given in terms of a reaction scheme.

The thermal reaction between H_2 and Cl_2 occurs at conveniently measurable rates above 200°C. The rate is strongly affected by O_2 , and is extremely great in its complete absence. Most workers have therefore worked using a small but known concentration of O_2 . This effect of O_2 was not found in the H_2 -Br₂ reaction.

The rate of the thermal reaction approximately obeys the rate law

$$\frac{d[\text{HCl}]}{dt} = \frac{k[\text{H}_2][\text{Cl}_2]^2}{m[\text{Cl}_2] + [\text{O}_2]\left([\text{H}_2 + n[\text{Cl}_2]\right)}$$
(5.159)

where k, m and n are constants. The rate is quite sensitive to the shape and size of the vessel, and to the nature of the surface. A mechanism that gives a reasonably satisfactory interpretation of this empirical law is

- 1. $\operatorname{Cl}_2 + M \xrightarrow{k_1} 2\operatorname{Cl} + M$
- 2. $\operatorname{Cl} + \operatorname{H}_2 \xrightarrow{h_2} \operatorname{HCl} + \operatorname{H}$
- 3. $H + Cl_2 \xrightarrow{k_3} HCl + Cl$
- 4. $H + O_2 \xrightarrow{k_4} HO_2$

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- 5. $\operatorname{Cl} + \operatorname{O}_2 \xrightarrow{k_5} \operatorname{ClO}_2$
- 6. $Cl + X \xrightarrow{k_6} ClX$

Here, M is any third boy (including the surface) that aids the dissociation of the Cl_2 molecule, and X is another third body that removes Cl atoms. Except in the complete absence of O_2 , the reaction

 $2 \operatorname{Cl} \rightarrow \operatorname{Cl}_2$

does not play a prominent role as a chain-terminating step. The above reaction scheme gives, with the neglect of some small terms, a rate equation that agrees approximately with the empirical Eq. (5.159).

The H₂—I₂ reaction does not follow a chain mechanism.

The reason is that activation energy of the process $I + H_2 \rightarrow HI + H$ is relatively high (E = 33 k cal mol⁻¹) and hence it follows the easier path of bimolecular collision^{*}.

5.18 DECOMPOSITION OF OZONE

The gas phase decomposition of ozone

$$2\mathrm{O}_3 \to 3\mathrm{O}_2$$

is believed (according to Benson and Axworthy) to have the mechanism

$$O_3 + M \xrightarrow[k_1]{k_{-1}} O_2 + O + M$$
$$O + O_3 \xrightarrow{k_2} 2O_2$$

where M is any third body.

The rate of formation of O_2 is given by

$$\frac{d[O_2]}{dt} = 2 k_2 [O][O_3] + k_1[O_3][M] - k_1[O_2][O][M]$$
(5.160)

and of consumption of O_3 as

$$\frac{d[O_3]}{dt} = k_1[O_3][M] - k_1[O_2][O][M] + k_2[O][O_3]$$
(5.161)

Applying the steady state approximation to [O], we have

$$\frac{d[O]}{dt} = k_1[O_3][M] - k_1[O_2][O][M] - k_2[O][O_3] = 0$$
(5.162)

 \Rightarrow

$$[O] = \frac{k_1[O_3][M]}{k_1[O_2][M] + k_2[O_3]}$$
(5.163)

From Eq. (5.162) we get

^{*} see K.J. Laidler; Chemical Kinetics.

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 $k_1[O_3][M] - k_1[O_2][O][M] - k_2[O][O_3]$

and using this is Eq. (5.160)

$$\frac{d[O_2]}{dt} = 3 k_2[O]O_3]$$
(5.164)

Similarly, using Eq. (5.162)

$$-\frac{d[O_3]}{dt} = 2 k_2[O][O_3]$$
(5.165)

The rate of formation of O_2 is then

$$\frac{d[O_2]}{dt} = \frac{3k_1k_2[O_3]^2[M]}{k_{-1}[O_2][M] + k_2[O_3]}$$

The rate of the reaction is then

$$v = \frac{1}{3} \frac{d[O_2]}{dt} = \frac{k_1 k_2 [O_3]^2 [M]}{k_1 [O_2] [M] + k_2 [O_3]}$$
(5.166)

5.19 DECOMPOSITION OF N₂O₅

The mechanism now accepted for N_2O_5 decomposition was first proposed by R.A. Ogg (1950) and is as follows:

$$N_{2}O_{5} \xrightarrow{k_{1}} NO_{2} + NO_{3}$$
$$NO_{2} + NO_{3} \xrightarrow{k_{2}} NO_{2} + O_{2} + NO_{3}$$
$$NO + N_{2}O_{5} \xrightarrow{k_{3}} 3NO_{2}$$

giving us finally, 2 $\mathrm{N_2O_5} \rightarrow 4$ $\mathrm{NO_2}$ + $\mathrm{O_2}.$

The intermediates NO_3 and NO are present is smaller amounts than N_2O_5 ; the steady state approximation applied to these species gives

$$\frac{d[\text{NO}_3]}{dt} = \text{O} = k_1 [\text{N}_2 \text{O}_5] - k_1 [\text{NO}_2] [\text{NO}_3] - k_2 [\text{NO}_2] [\text{NO}_3]$$
$$k_1 [\text{N}_2 \text{O}_5] - (k_1 + k_2) [\text{NO}_2] [\text{NO}_3] = 0$$
(5.167)

 \Rightarrow

$$\frac{d[\text{NO}]}{dt} = k_2[\text{NO}_2] \ [\text{NO}_3] - k_3 \ [\text{NO}][\text{N}_2\text{O}_5] = 0$$
(5.168)

The rate of consumption of N_2O_5 is

$$\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2]NO_3] + k_3[NO][N_2O_5]$$

with Eq. (5.168), this becomes

$$-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] + (k_2 - k_{-1})[NO_2]NO_3]$$
(5.169)

Using Eq. (5.167) (eliminating $[NO_2][NO_3]$)

$$-\frac{d[\mathbf{N}_{2}\mathbf{O}_{5}]}{dt} = k_{1}[\mathbf{N}_{2}\mathbf{O}_{5}] + (k_{2} - k_{1})\frac{k_{1}}{(k_{-1} + k_{2})}[\mathbf{N}_{2}\mathbf{O}_{5}]$$
$$= \frac{2k_{1}k_{2}[\mathbf{N}_{2}\mathbf{O}_{5}]}{(k_{-1} + k_{2})}$$
(5.170)

The mechanism thus explains the first order kinetics. The rate constant k_2 is expected to be much smaller than k_{-1} , so that to a good approximation

$$\frac{d[N_2O_5]}{dt} = \frac{2k_1k_2}{k_{-1}} [N_2O_5]$$
(5.171)

Under this condition, the overall activation energy E is related to those of the elementary steps as

$$E = (E_1 + E_2 - E_{-1}) \tag{5.172}$$

5.20 THERMAL PARA-ORTHO HYDROGEN CONVERSION

The rate of conversion of *para*-hydrogen into *ortho*-hydrogen takes place homogeneously between 700 – 800°C. The mechanism suggested is

- 1. $H_2 \rightleftharpoons K 2H$ (fast)
- 2. $H + p-H_2 \xrightarrow{k_2} o-H_2 + H$ (slow)

The equilibrium constant of the step (1) is

$$K = \frac{C_{\rm H}^2}{C_{\rm H_2}} \implies C_{\rm H}^2 = KC_{\rm H_2}$$
(5.173)

The rate of the reaction is therefore

$$\frac{d[o-H_2]}{dt} \Rightarrow k_2 C_H C_{p-H_2} = k_2 K^{1/2} C_{p-H_2}^{3/2}$$

The activation energy of the process is given by

$$E = E_2 + \frac{1}{2}D \tag{5.174}$$

where D is the dissociation energy of H_2 ; it is about 435^{-1} . E_2 is about 38 kJ mol⁻¹. It then follows that the overall activation energy is about 256 kJ mol⁻¹, which has experimentally been found.

5.103

5.21 BRANCHING CHAIN: EXPLOSION

In the chain reactions, so far considered, during a propagation step, one free radical (or atom) reacts with a reactant molecule, producing the product and another free radical, the chain carrier; this chain carrier then combines with another reactant producing a product molecule and another chain carrier, i.e., a radical or atom. Under ordinary condition, the concentration of these chain carriers are very small and, the steady state approximation is used to express their concentrations.

For some gas phase reactions, e.g., the oxidation of H_2 , CO, PH_3 , CS_2 etc., the reaction proceeds through a chain mechanism, but, in these cases when a free radical combines with the reactant molecule to produce a product molecule, it produces more than one free radical (chain carrier). This results into an increase of these free radicals very rapidly with time, naturally with a consequent increase in the reaction rate. This, in turn, will increase the reaction rate further, producing more and more free radicals, which are ready to carry on the reaction more faster. This is said to be a branching chain. Eventually, the reaction may go to so fast a rate that, an explosion may occur.

The mechanism of H_2 and O_2 is believed to be as:

1. $H_2 \rightarrow 2 H$ Initiation

2.
$$H + O_2 \rightarrow OH + O$$

- 3. $O + H_2 \rightarrow OH + H$ Branching
- 4. $OH + H_2 \rightarrow H_2O + H$ Propagation

In the steps (2) and (3) it is seen that two radicals are produced at the cost of one; this is branching. These radicals propagate the reaction to a large extent, than normally observed. In this way the concentrations of the chain carriers increase to such an extent and, as a result increases the reaction rate so fast, that explosion occurs. The chain carriers may also be destroyed, mainly by collision with the walls of the container.

It is observed that (Figure 5.34), the rate increases smoothly, as the pressure is increased. Suddenly the reaction comes to an explosion (1^{st} limit) ; this continues upto a 2^{nd} limit, where the reaction again comes down to a smooth rate; a steady reaction is followed.



Figure 5.34 Explosion limits.

This continues with increase in pressure, until the final 3^{rd} limit is attained, where the rate again shoots to infinity.

It is easy to understand the reason. At low pressure the radicals get a free access to collide with the walls, and are destroyed there. This counterbalances the increase in the rate of production of the radical from the branching steps. The reaction proceeds smoothly.

As the pressure is gradually increased, through the branching, the concentration of the radical increases tremendous and their journey towards the wall is diminished. The destruction of the radicals cools down. A pressure eventually is reached, where the rate of branching is much more rapid than the slow rate of destruction of the radicals at the walls. We get the first explosion limit. Obviously, this pressure limit depends upon the shape and size of the vessel. At further higher pressure, the radicals are destroyed in the gas phase than at the walls. This is because of the three body collisions:

$$H + O_2 + X \rightarrow HO_2$$

a kind of quenching, where X may be any foreign gas or H_2 , or O_2 molecule, resulting into a reduction of the free radicals. The reaction then comes down to a smooth rate.

Finally, we get the third limit due to thermal explosion. In these exothermic reactions, the heat generated cannot be conducted out; and the temperature rises. This increases the rate further, and eventually we get the third explosion limit, which is thermal.

The mechanistic scheme of a branched chain reaction may then be represented as:

1.
$$A \xrightarrow{k_1} R$$

2.
$$A + R \xrightarrow{k_2} P + \alpha R$$

3. $R \xrightarrow{k_3}$ destruction

where A is the reactant; branching occurs in step (2) and, finally, the radicals are destroyed in step (3). The chain carriers are destroyed in two ways: (i) diffusing to the walls and combining with a surface atom and, (ii) by a three-body collision in the gas phase. This means that the rate constant k_3 is the sum of two rate constants, k_g for the gas phase destruction and k_w for wall destruction.

The steady state condition, $\frac{dC_R}{dt} = 0$, must be there to get a smooth reaction; hence

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_A C_R + \alpha \, k_2 C_A C_R - k_3 \, C_R = 0$$

 \Rightarrow

$$C_R = \frac{k_1 \ C_A}{k_3 + k_2 \ C_A (1 - \alpha)}$$

$$C_{R} = rac{k_{1} C_{A}}{k_{w} + k_{g} + k_{2} C_{A}(1 - \alpha)}$$

Normally, in chain reactions $\alpha = 1$ and $C_R = k'C_A$.

Branching occurs when $\alpha > 1$. Very soon from the start of the reaction, α increases to such an extent that $k_2C_A(\alpha - 1)$ become equal to $(k_w + k_g)$; C_R then shoots to infinity. The extremely high concentration of the chain carriers is responsible for the rapid rate of the reaction, and explosion occurs.

When the pressure is low, the diffusion of the carriers to the wall is an easy access and hence, k_w is large. Over the period of pressure, when $(k_w + k_g)$ is greater than $k_2C_A(\alpha - 1)$, i.e., the rate of destruction is more than that of the formation of the carriers, we observe a smooth reaction. As the pressure is increased, the journey of the radicals towards the walls decreases and k_w falls; $k_2C_A(\alpha - 1)$ then becomes relatively large and finally explosion occurs; the first limit is reached.

If the pressure is gradually increased k_w decreases and k_g will increase. Finally, when the destructive collisions in the gas phase overcomes the branching of chain, the concentration of the radicals decreases, and we then get a slow rate of the reaction. This is how the second limit is reached.

PROBLEMS

- **5.1** (i) Show that for a first order reaction the time required for 75% reaction is twice the time for 50% reaction.
 - (ii) A first order reaction is 25% complete at the end of 20 minutes. How long will it take to complete 75% reaction [Ans.: 96.27 min]
- **5.2** The first order decomposition of H_2O_2 in a suitable medium has the rate constant $3 \times 10^{-2} \text{ min}^{-1}$. Find the time to complete one-third of the reaction.

[Ans.: 13.5 min]

- **5.3** For the reaction $2NO + Cl_2 \rightarrow 2$ NOCl, it was found that on doubling the concentration of both the reactants, the rate increases eight fold. But on doubling the concentration of Cl_2 alone, the rate only doubles itself. What are the orders of the reaction with respect to the reactants. [Ans.: 2 for NO; 1 for Cl_2]
- **5.4** The decomposition of azomethane is a first-order reaction.

$$CH_3 - N = N - CH_3 \rightarrow N_2 + C_2H_6$$

the rate constant is 4×10^{-4} s⁻¹. If initially azomethane be taken at 200 Torr pressure, what will be the partial pressures of the components after half an hour? [Ans.: $P_{azo} = 97.35$ Torr; $P_{N_2} = P_{C_2H_6} = 102.65$ Torr]

- **5.5** The gas phase reaction $2 \text{ NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2$ has the rate constant $k = 2 \times 10^4$ dm³ mol⁻¹ at 300 K. What is the order of the reaction. [Ans.: 2nd order]
- **5.6** The rate of decomposition of HI is given by, $-\frac{dC_{HI}}{dt} = kC_{HI}^2$, where $k = 4 \times 10^{-6}$ L mol⁻¹ s⁻¹, at 327°C. How many molecules of HI would decompose per second at 1 atm pressure? [*Ans.*: 9.93 × 10¹⁴ molecule L⁻¹]

- 5.7 At 100°C the gaseous reaction $A \times 2B + C$ is observed to be first-order. On starting with pure A it is found that at the end of 10 minutes the total pressure of the system is 176 Torr, and after a long time 270 Torr. From these data find
 - (i) the initial pressure of A
 - (ii) the pressure of A at the end of 10 minutes
 - (iii) the rate constant of the reaction
 - (iv) the half life period of the reaction

[Ans.: (i) 90 Torr; (ii) 47 Torr; (iii) 0.065 min⁻¹; (iv) 10.7 min]

- **5.8** For the gas phase reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, the rate constant k is 1.73×10^{-5} s⁻¹ at 25°C. The observed rate low is $v = k[N_2O_5]$.
 - (i) Calculate v and $J\left(=\frac{1}{v}\frac{dnt}{dt}\right)$ for the reaction in a 12 dm³ container with $P_{N_{0}O_{r}} = 0.1$ atm at 25°C.
 - (ii) Calculate $\frac{d[N_2O_5]}{dt}$ for the condition of part (a).
 - (iii) Calculate the number of N_2O_5 molecules decomposed per second for the condition of (a).
 - (iv) What are k, v and J for the condition of (a) if the reaction is written as N₂O₅ $\rightarrow 2NO_2 + \frac{1}{2}O_2$?

 $\begin{array}{l} [Ans.: (\mathrm{i}) \; v = 7.1 \times 10^{-8} \; \mathrm{mol} \; \mathrm{L^{-1} \; s^{-1}}; \; \mathrm{J} = 5.12 \times 10^{17} \; \mathrm{molecules \; s^{-1}}; \\ (\mathrm{ii}) \; -1.42 \times 10^{-7} \; \mathrm{mol} \; \mathrm{L^{-1} \; s^{-1}}; \; (\mathrm{iii}) \; 8.6 \times 10^{16} \; \mathrm{molecules \; L^{-1} s^{-1}}; \end{array}$

(iv) k remains the same; v and J will be half of the above values]

5.9 The stoichiometric equation for the oxidation of bromide ions by H_2O_2 in acid solution is:

 $2 \ \mathrm{Br}^{-} + \mathrm{H}_2\mathrm{O}_2 + 2\mathrm{H}^{+} \rightarrow \mathrm{Br}_2 + 2 \ \mathrm{H}_2\mathrm{O}$

the rate equation has been found to be

$$v = k[H_2O_2] [H^+][Br^-]$$

- (i) If the concentration of H_2O_2 in increased by a factor of 3; by what factor the rate of consumption of Br^- ions increased?
- (ii) If the rate of consumption of Br⁻ ions is 7.2×10^{-3} mol dm⁻³s⁻¹, what is the rate of consumption of H₂O₂? What is the rate of production of Br₂?
- (iii) What is the effect on the rate constant k of increasing the concentration of bromide ions?
- (iv) If by the addition of water to the reaction mixture, the total volume were doubled, what would be the effect on the rate of change of the concentration of Br⁻? What would be the effect on the rate constant k?

 $\label{eq:ans.: (i) 3; (ii) both rates are 3.6 <math display="inline">\times$ 10^{-3} mol dm^{-3} s^{-1}; (iii) No effect; (iv) decreased by a factor of 8; nothing]

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5.10 A reaction has the stoichiometric equation

$$A + 2B \rightarrow 2z$$

The rates of formation of z at various concentrations of A and B are as follows:

$[A]/mol L^{-1}$	$[\mathrm{B}]/\mathrm{mol}\ \mathrm{L}^{-1}$	Rate/mol $L^{-1} s^{-1}$
$3.5 imes10^{-2}$	$2.3 imes10^{-2}$	$5.0 imes10^{-7}$
$7.0 imes10^{-2}$	$4.6 imes10^{-2}$	$2.0 imes10^{-6}$
$7.0 imes10^{-2}$	$9.2 imes10^{-2}$	$4.0 imes10^{-6}$

what are α and β in the rate equation

 $v = k[A] \alpha [B] \beta$

and what is the rate constant *k*?

[*Ans.*: $\alpha = 1$; $\beta = 1$; $k = 6.21 \text{ L mol}^{-1}\text{s}^{-1}$]

- **5.11** The half life for the disintegration of Ra is 1590 years. Calculate the mate constant. In how many years will three-quarter of a given amount of Ra have disappeared? $[Ans.: 1.38 \times 10^{-11} s^{-1}: 3180 \text{ years}]$
- **5.12** Find out the rate constant in the decomposition of a gas which is of three-halves order, when 60% decomposition took place in an hour; the initial pressure is 1 atm.

[Ans.: 1.162 atm^{-1/2} h⁻¹]

- **5.13** At 327°C, for the second order decomposition of NO₂, $k = 6 \times 10^2 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$. Calculate the time required for 75% decomposition of a sample of NO₂ at 300 Torr at the same temperature. [Ans.: 624.5 s]
- **5.14** In the thermal decomposition of malonic acid

 $CH_2(COOH)_2 \rightarrow CH_3COOH + CO_2$

the pressure at different time intervals are

<i>t</i> (min)	10	20	35	56	×
p(Torr)	37	67	108	155	303

what is the order of the reaction. Also find out the rate constant.

[Ans.: 1st order; 0.013 min]

5.15 When ethyl acetate is saponified by NaOH, the progress of the reaction can be followed by titrating unchanged alkali with a standard acid. Using equal concentrations of ester and alkali, the following results were obtained.

$t(\min)$	0	5	25	55	120	×
vol. of acid (cm ³)	16	10.24	4.32	2.31	1.1	0

Show that the reaction is of the second order. What is the value of the rate constant? What fraction of the ester will be saponified at the end of 30 minutes?

[Ans.: $6.9 \times 10^{-3} \text{ min}^{-1}$; 0.77]

5.16 At 25°C, the rate constant for the hydrolysis of ethyl acetate by NaOH is 6.36 $\text{mol}^{-1}\text{L} \text{min}^{-1}$. Starting with concentrations of base and ester of 0.02 mol L⁻¹, what proportion of the ester will be hydrolyzed in 10 minutes? [Ans.: 0.56]

5.108

5.17 For the reduction 2 $\text{FeCl}_3 + \text{SnCl}_2 \rightarrow 2\text{FeCl}_2 + \text{SnCl}_4$ in aqueous solution the following data were obtained at 25°C.

$t(\min)$	1	3	7	1	40
У	0.01434	0.02664	0.03612	0.04102	0.05058

where y is the amount of FeCl₃ reacted in moles per liter. The initial concentrations of SnCl₂ and FeCl₃ were respectively 0.03125 and 0.0625 molL⁻¹. Show that the reaction is third order, and calculate the rate constant.

[Ans.: 86 (mol L^{-1})⁻² mim⁻¹]

- **5.18** The rate constant of a reaction at 30°C is found to be exactly twice the value at 20°C. Calculate the activation energy. $[Ans.: 51.2 \text{ kJ mol}^{-1}]$
- **5.19** Two second order reactions have identical preexponential factors and activation energies differing by 20 kJ mol⁻¹. Calculate the ratio of their rate constants at 0°C. [Ans.: 1.48×10^{-4}]
- **5.20** The water flea *Daphnia* performs a constant number of heartbeats and then dies. The flea lives twice as long at 15°C as at 25°C. Calculate the activation energy for the reaction that controls the rate of its heartbeat. $[Ans.: 49.5 \text{ kJ mol}^{-1}]$
- **5.21** A sampling of milk kept at 25°C is found to sour 40 times as rapidly as when it is kept at 4°C. Estimate the activation energy for the souring process.

[Ans.: 120.6 kJ mol⁻¹]

5.22 For a parallel reaction from the reactant *R*.



with rate constants and activation energies for the formation of P_1 and P_2 as k_1 , E_1 and K_2 , E_2 , respectively, show that the overall activation energy is

$$E = \frac{k_1 E_1 + k_2 E_2}{k}$$

where $k = k_1 + k_2$.

- **5.23** Two reactions of the same order have identical activation energies and their entropies of activation differ by 50 $JK^{-1}mol^{-1}$. Calculate the ratio of their rate constants at any temperature. [Ans.: 409]
- **5.24** The gas phase reaction

$$H_2 + I_2 \rightarrow 2HI$$

is second order. The rate constant at 400°C is 2.34×10^{-2} L mol⁻¹s⁻¹, and its activation energy is 150 kJ mol⁻¹. Calculate ΔH^{\neq} , ΔS^{\neq} and ΔG^{\neq} at 400°C, and the preexponential factor.

 $[138.8 \text{ kJmol}^{-1}; -76.7 \text{ JK}^{-1} \text{ mol}^{-1}; 190.4 \text{ kJmol}^{-1}; 1.02 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}]$

5.109

6 CHAPTER

CATALYST

6.1 INTRODUCTION

It was known from the early part of the nineteenth century that some substances can increase the rate of a chemical reaction, and can be removed chemically unchanged at the end of the process. Such substances are called catalysts and the process as catalysis. Some definitions of catalysts are given below:

- A catalyst is any substance that alters the rate of a chemical reaction without modification of the energy factors of the reaction. —W. Ostwald (1895)
- A catalyst is any substance that alters the rate of a chemical reaction without appearing in the end product of the reaction. —W. Ostwald (1902)
- A substance is said to be a catalyst for a reaction when its concentration occurs in the rate expression to a higher power than it does in the stoichiometric equation.

6.2 CHARACTERISTIC FEATURES OF A CATALYST

Some of the characteristic features of catalyst are as follows:

- (i) A catalyst only increases the rate of chemical reaction but remains chemically unchanged at the end of the process; its physical form may be changed. For example, a catalyst initially introduced as a solid metallic chunk may be regenerated in a finely powdered form.
- (ii) A catalyst cannot start a reaction, nor can it affect the magnitude of the standard free energy change of the reaction ΔG° . Since $\Delta G^{\circ} = -\operatorname{RT} \ln K_{eqm}$, it follows therefore that the equilibrium constant K_{eqm} , also remains unaffected.

Therefore the equilibrium yields are also remained unchanged; only the attainment of the equilibrium is hastened up.

(iii) Since for an elementary opposing reaction, the equilibrium constant K_{eqm} is related to the rate constants k_1 and k_{-1} for the forward and the backward processes as $K_{eqm} = k_1/k_{-1}$, and since the K_{eqm} remains unaltered during catalysis, both the rate constants are increased by the same factor. Therefore a catalyst does not only increase the forward rate, it also increases the rate of the backward reaction by the same factor.

(iv) Generally, it is found that a very minute amount of the catalyst may bring about a large increase in the reaction rate, e.g. colloidal platinum at a concentration of 10^{-8} M can catalyse the decomposition of H_2O_2 at a considerable rate.

6.2.1 Thermodynamic Proof of that a Catalyst cannot Modify the Value of *K*_{eam}

Let us start the reaction at any arbitrary composition in absence of the catalyst, and attain the equilibrium position. We now add the catalyst and let it affect the equilibrium by shifting it further to the right. If the reaction is exothermic to the right, then during this shift an amount of heat would be liberated, that can be converted completely into work; let it be done. Since the catalyst remains unchanged, it is now taken off the system; the reaction will then be back home to its original position of equilibrium by absorbing, from the surroundings, exactly the same amount of heat it has released before. At the end of this cyclic process, nothing changes permanently except the conversion of an amount of heat into work under isothermal condition. This certainly is going to violate the Kelvin Planck statement of the second law of thermodynamics.

6.3 MECHANISM OF CATALYSIS

Although a catalyst remains chemically unchanged at the end of the chemical reaction, it does involve itself into the actual chemical union and is regenerated at the end of process. In fact, the catalyst finds an alternative path for the reaction in which the required activation energy is less than that of the uncatalysed path; that is how the rate is increased.

There are a number of different mechanisms through which catalysed reactions take place. Among these, an important type is the reaction of a *single substrate* catalysed by solid surfaces, enzymes, acids and bases. At the start, we undertake a reaction scheme that can focus on the similarities among reactions being catalysed by different kinds of catalyst.

The scheme proposed is

(i)
$$C + S \xrightarrow{k_1} X + Y$$

(ii) $X + W \xrightarrow{k_2} P + Z$
(6.1)

C is catalyst, and X and Y are intermediates; the species X then reacts with a species W to produce the product P with an additional substance Z. The species Y and Z may undergo other processes, but these have hardly any effect on our reaction of interest.

In the step (ii) of Eq. (6.1), if the product P is removed from the reaction vessel, as soon as it is formed, then the reverse process of step (ii) can be neglected. There is a possibility that the intermediate X undergoes the step (ii) very slowly, and so much so, that the step (i) may be considered to be at equilibrium. The corresponding condition is

$$k_2[X][W] <\!\!< k_{-1}[X][Y] \tag{6.2}$$

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It is the Arrhenius-concept of equilibrium between the reactant (s) with the intermediates. These intermediates are called Arrhenius intermediates.

On the other hand, if $k_2[X][W] >> k_{-1}[X][Y]$ then the concentration of X is very small, and the steady state approximation may be applied to [X]. This is called the *van't Hoff* intermediate.

Arrhenius Intermediate: Applying Equilibrium Approximation 6.3.1

From (i) of Eq. (6.1), we may write

$$\frac{[X][Y]}{[C][S]} = \frac{k_1}{k_{-1}} = K$$
(6.3)

(applying equilibrium approximation). The concentrations of C, S and X are related to their initial concentrations as

$$[C]_0 = [C] + [X] \tag{6.4}$$

and

 \Rightarrow

and fin

$$[S]_0 = [S] + [X] \tag{6.5}$$

If we are interested to the initial rates, Eq. (6.3) then becomes

$$\frac{[X][Y]}{([C]_0 - [X])([S]_0 - [X])} = K$$
(6.6)

Equation (6.6), being quadratic in [X] can be solved for [X], and then the rate of the reaction $v = k_2[X][W]$ can be evaluated. However, two special cases make the problem easier.

Case 1: If the initial concentration of the substrate is much greater than that of the catalyst, i.e. $[S]_0 >> [C]_0$, then $[S]_0 - [X] \approx [S]$ (:: [X] cannot exceed $[C]_0$). Equation (6.6) then changes to

$$\frac{[X][Y]}{([C]_0 - [X])[S]_0} = K$$

$$[X][Y] = K[S]_0([C]_0 - [X])$$

$$[X][Y] = K[C]_0[S]_0 - K[X][S]_0$$
(6.7)

$$\Rightarrow \qquad [X][Y] = K[C]_0 \ [S]_0 - K[X][$$

$$\Rightarrow \qquad \qquad K[X][S]_0 + [X][Y] = K[C]_0 [S]_0$$

ally,
$$[X] = \frac{K[C]_0[S]_0}{K[S]_0 + [Y]}$$
(6.8)

The rate of the reaction v, is then [step (ii); Eq. (6.1)]

$$v = k_2[X][W] = \frac{k_2 \ K[C]_0[S]_0[W]}{K[S]_0 + [Y]}$$
(6.9)

The variation of the rate v versus $[S]_0$ is shown in Figure **6.1(a)**. At lower region of $[S]_0$, $K[S]_0 \ll [Y]$, v varies almost linearly with $[S]_0$. At higher initial concentration of the substrate, $[S]_0$, $K[S]_0 \gg [Y]$, the rate becomes independent of $[S]_0$. Moreover, as long as $[S]_0 \gg [C]_0$, the rate v varies linearly with $[C]_0$.

The reactions between a single substrate on solid surfaces and with enzymes show this kind of characteristic behaviour. For both of these catalysts, Y and W have no role to play; Eq. (6.9) changes to



Figure 6.1(a) The rate of the reaction v versus initial substrate concentration for the condition $[S]_0 >> [C]_0$.



Figure 6.1(b) A plot of v versus the initial concentration of the catalyst. Here $[C]_0 >> [S]_0$.

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$$v = \frac{k_2 K[C]_0[S]_0}{K[S]_0 + 1} \tag{6.10}$$

Case 2: If the initial concentration of the catalyst is much more than that of $[S]_0$, i.e. $[C]_0 >> [S]_0$, then Eq. (6.6) changes to

$$\frac{[X][Y]}{[C]_0 ([S]_0 - [X])} = K$$
(6.11)

After finding out the expression of [X], as done just earlier, the rate of the reaction v (using the expression of [X]) is given by

$$v = \frac{k_2 K[C]_0[S]_0[W]}{K[C]_0 + [Y]}$$
(6.12)

As long as the condition $[C]_0 >> [S]_0$, v now varies with the initial concentration of the substrate, $[S]_0$; the variation of v with $[C]_0$ is shown in the Figure 6.1(b).

6.3.2 Van't Hoff Intermediates: Applying Steady-state Treatment

From Eq. (6.1), it is clear that if $k_2[W] >> k_{-1}[Y]$, then althroughout the entire period of the reaction, the concentration of X is very small, and we apply the steady-state approximation. The corresponding equation using Eq. (6.1) is

$$\frac{d}{dt}[X] = k_1[C][S] - k_{-1}[X][Y] - k_2[X][W] = 0$$
(6.13)

But $[C] = [C]_0 - [X]$ and $[S] = [S]_0 - [X]$

Equation (6.13) then becomes

$$k_{1}([C]_{0} - [X])([S]_{0} - [X]) - k_{-1}[X][Y] - k_{2}[X][W] = 0$$

$$k_{1}\{[C]_{0}[S]_{0} - [C]_{0}[X] - [S]_{0}[X] + [X]^{2}\} - k_{-1}[X][Y] - k_{2}[X][W] = 0$$
(6.15)

$$(-k_1[C]_0 - k_1[S]_0)[X] - (k_{-1}[Y] + k_2[W])[X] + k_1[C]_0[S]_0 = 0$$

$$\Rightarrow \qquad \{k_1([C]_0 + [S]_0) + (k_{-1}[Y] + k_2[W])\}[X] = k_1[C]_0[S]_0$$

and finally,

 \Rightarrow

 \Rightarrow

$$[X] = \frac{k_1[C]_0[S]_0}{k_1([C]_0 + [S]_0) + k_{-1}[Y] + k_2[W]}$$
(6.16)

[X] being a very small concentration, the term $[X]^2$ is further smaller and is neglected.

The rate of the reaction [(Eq. (6.1)] is then

$$v = k_2[X][W]$$

(6.15)

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Using Eq. (6.16), we get

$$v = \frac{k_1 k_2 [C]_0 [S]_0 [W]}{k_1 ([C]_0 + [S]_0) + k_{-1} [Y] + k_2 [W]}$$
(6.17)

In catalytic processes on solid surface, and by enzymes, the species W and Y are not present; the rate then becomes

$$v = \frac{k_1 k_2 [C]_0 [S]_0}{k_1 ([C]_0 + [S]_0) + k_{-1} + k_2}$$
(6.18)

6.3.3 Activation Energy of Catalysed Reactions

Let us consider the case of an Arrhenius complex. When the initial concentration of the reactant $[S]_0$ is low, the rate constant of the reaction [(Eq. (6.9)] is given by

$$k = k_2 K_{\text{eqm}} = (k_1 k_2 / k_{-1}) \tag{6.19}$$

If E_1 , E_2 and E_{-1} are the activation energies of the elementary steps [cf: Figure 6.2(a)], and A_1 , A_2 and A_{-1} are the corresponding frequency factors, then using the Arrhenius equation, we have

$$k = (A_1 A_2 / A_{-1}) \exp\{-(E_1 + E_2 - E_{-1})/RT\}$$
(6.20)

The net activation energy is then given by

$$E_{\rm low} = E_2 + (E_1 - E_{-1}) = E_1 + E_2 - E_{-1} \tag{6.21}$$

On the other hand, when the initial concentration of the reactant is very high the rate is $k_2[C]_0$ and the rate constant of the reaction becomes equal to k_2 , and therefore the activation energy of the reaction is

$$E_{\text{high}} = E_2 \tag{6.22}$$

The interpretation of Eqs (6.21) and (6.22) is as follows:

When the reactant concentration is low, almost every reactant molecule is in its own potential well and hence in order to surmount the final barrier E_2 , it has to form the complex first which is an exothermic process (note that $E_2 > E_1 - E_{-1}$). The net activation energy required is therefore less than E_2 by an amount $E_{-1} - E_1$. This is shown in Figure 6.2(a). On the other hand, when the reactant concentration is high, most of the molecules are in the complex state, and therefore the activation energy is now E_2 [Figure 6.2(b)]

Catalyst



C + P

..

Figure 6.2(a) The potential energy diagram for Arrhenius model of catalysed reactions. From Figure 6.2(a) it is clear that $k_{-1} >> k_2$. The rate-determining step is the surmounting of the second barriers.

Potential energy

E

C + R



Figure 6.2(b) The potential energy diagram for the van't Hoff model of catalysed reactions. From this Figure 6.2(b) it is clear that $k_{-1} \ll k_2$. To surmount the first barrier is now the rate-determining step.

Equations (6.21) and (6.22) are equivalent to Figure 6.3. In the van't Hoff's model, where the steady state approximation is applied, Eq. (6.18) is applied. At high substrate concentration, the activation energy is $E_{\rm high} = E_{\rm low}$ [(Eq. (6.22)].

6.7



Figure 6.3 Energy diagram for a unimolecular surface reaction. The difference ΔE between the energy of R - S and the R + S is always negative (adsorption is exothermic). R is the reactant.

Under the condition that, both the concentrations of the substrate and the catalyst are low, Eq. (6.18) changes to

$$v = \frac{k_1 k_2}{(k_{-1} + k_2)} [C]_0 [S]_0$$
(6.23)

The Arrhenius rate law does not apply to the above equation; nevertheless, Eq. (6.23) can be recasted, so that the Arrhenius equation appears.

Case 1: If $k_2 >> k_{-1}$, Eq. (6.23) becomes

 $v_{\text{low}} = k_1 [C]_0 [S]_0$ (an Arrhenius type) (6.24)

The activation energy is then

$$E_{\text{low}} = E_1(\because k_1 = A_1 e^{-E_1/RT})$$
(6.25)

Figure 6.2(b) represents this situation.

Case 2: If $k_{-1} >> k_2$, Eq. (6.23) becomes

$$v_{\text{low}} = \frac{k_1 k_2}{k_{-1}} \left[C \right]_0 \left[S \right]_0; \text{ again an Arrhenius type}$$
(6.26)

The activation energy is then

$$E_{\rm low} = E_1 + E_2 - E_{-1}.$$

It is also interesting to note that the condition, $k_{-1} >> k_2$, the *steady-state treatment* and the *equilibrium treatment* are the same.

Catalyst

Example 6.1

(a) Show that, for a reaction occurring by the mechanism

$$C + S \xrightarrow[k_{-1}]{k_1} \times \xrightarrow{k_2} C + Y$$

where total catalyst concentration $[C]_0$ is much less than the substrate concentration [S], the rate equation at low substrate concentration is

$$v_{\text{low}} = \frac{k_1 k_2}{(k_{-1} + k_2)} [C]_0 [S]$$

(b) Prove that the observed activation energy under these conditions is

$$E_{\rm low} = \frac{k_{-1}}{(k_{-1}+k_2)} \left(E_1 + E_2 - E_{-1}\right) + \frac{k_2}{(k_{-1}+k_2)} E_1$$

Solution

(a) The condition imposed is $[C]_0 \ll [S]_0$

Applying the steady-state approximation to [X], we find

$$\begin{aligned} k_1[C][S] - k_{-1}[X] - k_2[X] &= 0\\ k_1\left([C]_0 - [X]\right) \left[S\right] &= (k_{-1} + k_2)[X]\\ [X] &= \frac{k_1([C]_0 - [X])[S]}{(k_{-1} + k_2)} \end{aligned} \tag{1}$$

and finally,

The rate of the reaction v is then

$$v = k_2[X] = \frac{k_1 k_2 ([C]_0 - [X])[S]}{(k_{-1} + k_2)}$$

$$v = \frac{k_1 \times k_2}{(k_{-1} + k_2)} \left([C]_0 - [X] \right) [S] = \frac{k_1 k_2}{(k_{-1} + k_2)} \left([C]_0 [S] - [X][S] \right)$$
(2)

Since the equilibrium constant of the first equilibrium is given by,

$$K = \frac{k_1}{k_{-1}} = \frac{[X]}{[C][S]}; \Rightarrow [X] = K[C][S]$$

$$[X] [S] = K[C] [S]^2$$
(3)

Since [S] is very small, $[S]^2$ is further smaller and the term can be neglected. Therefore,

$$v_{\text{low}} = k_2[X] = \frac{k_1 k_2}{(k_{-1} + k_2)} \left([C]_0[S] - [X][S] \right)$$
(4)

6.9

 \Rightarrow

 \Rightarrow
(6)

Therefore, using Eq. (3), which is neglected, we have

$$v_{\text{low}} = \frac{k_1 k_2}{(k_{-1} + k_2)} [C]_0 [S]; \text{ where Eq. (3) is utilized.}$$

(b)
$$v_{\text{low}} = \frac{k_1 k_2}{(k_{-1} + k_2)} [C]_0 [S]$$

Moreover, we can write

 $v_{\text{low}} = k_{\text{low}} f$ (concentration terms)

Therefore,

$$k_{\rm low} = \frac{k_1 k_2}{(k_{-1} + k_2)}; \tag{5}$$

 $\frac{dk}{dT} = \frac{kE}{RT^2}$

and the Arrhenius equation can be written as

Then,
$$\frac{d k_{\text{low}}}{dT} = \frac{\left[(k_{-1} + k_2) \frac{d}{dT} (k_1 k_2) - k_1 k_2 \frac{d}{dT} (k_{-1} + k_2) \right]}{(k_{-1} + k_2)^2}$$

$$\Rightarrow \qquad \qquad \frac{d}{dT} k_{\text{low}} = \frac{(k_{-1} + k_2) \left(k_2 \frac{dk_1}{dT} + k_1 \frac{dk_2}{dT}\right) - \left\{k_1 k_2 \left(\frac{dk_{-1}}{dT} + \frac{dk_2}{dT}\right)\right\}}{(k_{-1} + k_2)^2}$$

$$\Rightarrow \qquad \qquad \frac{k_{\text{low}} E_{\text{low}}}{RT^2} = \frac{\left\{ (k_{-1} + k_2) \left(\frac{k_2 k_1 E_1}{RT^2} + \frac{k_1 k_2 E_2}{RT^2} \right) \right\} - \left\{ \frac{k_1 k_2 k_{-1} E_{-1}}{RT^2} + \frac{k_1 k_2^2 E_2}{RT^2} \right\}}{(k_{-1} + k_2)^2}$$

$$\Rightarrow \qquad \qquad \frac{k_{\text{low}} E_{\text{low}}}{RT^2} = \frac{k_{-1}k_1k_2 E_1 + k_{-1}k_1k_2 E_2 + k_1k_2 E_1 + k_1k_2 E_2 - k_1k_2 E_2 - k_1k_2 E_{-1} - k_1k_2 E_2}{RT^2 (k_{-1} + k_2)^2}$$

using Eq. (5)

$$\frac{k_1k_2}{(k_{-1}+k_2)}\frac{E_{\text{low}}}{RT^2} = \frac{1}{(RT^2)(k_{-1}+k_2)^2} [k_{-1}k_1k_2E_1 + k_1k_2^2E_1 + k_{-1}k_1k_2E_2 + k_1k_2^2E_2 - k_1k_2k_{-1}E_{-1} - k_1k_2^2E_2]$$

$$\Rightarrow \qquad \frac{k_1 k_2}{(k_{-1} + k_2)} \frac{E_{\text{low}}}{(\mathcal{RT}^2)} = \frac{1}{(\mathcal{RT}^2)(k_{-1} + k_2)^2} [k_{-1} k_1 k_2 (E_1 + E_2 - E_{-1}) + k_1 k_2^2 E_1]$$

6.10

$$\Rightarrow \qquad \qquad k_1 k_2 E_{\text{low}} = \frac{k_1 k_2}{(k_{-1} + k_2)} [k_{-1} (E_1 + E_2 - E_{-1}) + k_2 E_1]$$

$$\Rightarrow$$

$$E_{\rm low} = \frac{k_{-1}}{(k_{-1}+k_2)} \left(E_1 + E_2 - E_{-1}\right) + \frac{k_2}{(k_{-1}+k_2)} E_1$$

6.4 CATALYSIS BY ACIDS AND BASES

Reactions catalysed by acids and bases were studied in the earliest part of the development of this subject. In fact, the kinetic investigations of these reactions and the work on the electrolytic dissociation theory were undergoing at the same time. Ostwald and Arrhenius first suggested that the rates of acid catalysed reactions are independent of the nature of the anion, but are directly proportional to the electrical conductivity of the solution. Their interpretation was that the conductivity of these solutions was a measure of the strength of the acid, i.e. the degree of dissociation of the acid solution. The catalysing species were therefore regarded as H^+ ions. Similarly, it was shown that the rates of the base catalysed reactions are directly proportional to the concentration of OH^- ions, but are independent of the nature of the nature of the cation. In fact, they had identified a number of reactions in which H^+ and OH^+ ions are the only catalysts.

In a very strong acidic solution, where the concentration of OH⁻ ions is very small so that we can neglect any catalysis by the OH⁻ ions, the rate of the reaction may be written as

$$v = k_{\rm H^+}[{\rm H^+}][{\rm R}]$$
 (6.27)

..

where k_{H^+} is the catalytic coefficient of the hydrogen ions for the reactions and [R] is the reactant concentration. The rate is therefore directly proportional to the concentration of the hydrogen ion. However, in a particular run, the concentration of the species H⁺ is kept fixed; the reaction then follows a pseudo-first kinetics.

$$v = k[\mathbf{R}] \tag{6.28}$$

where the pseudo-first order rate constant k is related to the catalytic coefficient $k_{\rm H^+}$ as

$$k = k_{\rm H^+}[{\rm H^+}] \tag{6.29}$$

Similarly, in a very strong basic solution the rate is given by

$$v = k_{\rm OH^{-}}[\rm OH^{-}] [R]$$
 (6.30)

which, in a particular run, follows a pseudo-first order kinetics v = k[R]; the pseudo-first order rate constant is given by,

$$k = k_{\rm OH^-}[\rm OH^-] \tag{6.31}$$

Now, if the acidity of the solution be such that catalysis by both H^+ and OH^- ions is significant, and moreover, if the spontaneous part of the reaction rate be important then the overall rate is given by

6.11

$$v = k_0 [R] + k_{H^+} [H^+] [R] + k_{OH^-} [OH^-] [R]$$
(6.32)

and the pseudo-first order rate constant is given by

$$k = k_0 + k_{\rm H^+}[{\rm H^+}] + k_{\rm OH^-}[{\rm OH^-}]$$
(6.33)

Depending on the acidity or basicity, one or more terms in the above expression may be important. The various possibilities that may arise have been considered by Scrabal who potted log k versus the pH of the solution (Figure 6.4). In sufficiently acidic solution,





or,
$$\log k = \log k_{\mathrm{H}^+} - p\mathrm{H}$$
(6.34)

A plot of log k versus pH would then be a straight line with slope – 1; plot a. Similarly, in sufficiently basic solution

$$k = k_{\rm OH^-}[{\rm OH^-}] = k_{\rm OH^-} K_{\rm w} / [{\rm H^+}]$$

log k = log (k_{\rm OH^-} K_{\rm w}) + p{\rm H} (6.35)

The plot will then have a slope +1 (plot b). The most general type of behaviour is shown by plot c. The regions of H⁺ and OH⁻ ions catalysis (with slopes 1 and -1, respectively) are separated by a horizontal slope, where the spontaneous part of the rate is the only important. This has been experimentally verified by the mutarotation of glucose (plot c). If, however, the spontaneous part is very small then the two slopes meet fairly sharply (plot d). If, on the other hand, $k_{\rm H^+}$ is very small then plot e is obtained when the spontaneous part is considerable. Plot *f* is obtained when $k_{\rm OH^-}$ is very small, and the spontaneous part is considerable. Examples of all these cases are known.

6.4.1 Generalized Acid-base Catalysis

H.S. Taylor, H.M. Dawson and F. Powis first showed clearly that there may be some other species which are acids and bases according to the more general concepts by the

6.12

or,

same, which can catalyse the reaction in addition to H^+ and OH^- ions. The results of the iodination of acetone at high iodine concentration may be taken as an illustration. One probable mechanism of the reaction is

$$\mathrm{CH}_3\mathrm{COCH}_3 \xrightarrow[r/d]{\mathrm{slow}} \mathrm{CH}_3\mathrm{C(OH)} = \mathrm{CH}_2 \xrightarrow[I_2]{I_2} \mathrm{CH}_3\mathrm{C(OH)(I)CH}_2\mathrm{I}$$

They carried out the reaction in a series of chloroacetic acid solutions of increasing concentrations and measured the initial rates of the reaction. It was found that the experimentally observed rate constant, i.e. the pseudo-first order rate constant, increases steadily with increase in the concentration of chloroacetic acid. This result by itself is not alarming; what is alarming is that $K/[H^+]$ increases steadily with increase in the chloroacetic acid concentration. A plot of $K/[H^+]$ versus [acid]/[H^+] (K is the ionization constant of chloroacetic acid) is shown in Figure 6.4. If H⁺ ions were the only catalysing species then $K/[H^+]$ should have remained constant with increase in the total acid concentration. It was therefore concluded that besides H⁺ ions, the undissociated chloroacetic acid molecules could also catalyse the reaction. Neglecting the spontaneous part, the pseudo-first order rate constant is, therefore, given by

$$k = k_{\rm H}^{+}[{\rm H}^+] + k_{\rm acid} \,[{\rm acid}]$$
 (6.36)

It is now clear that as the concentration of the acid is increased, the ratio $K/[H^+]$ increases linearly with [acid]/[H⁺].

Example 6.2

The half life time for the inversion of cane sugar has been found to be 50 min at pH 3. What will be its half life time at pH 4? Also find out the value of k_{H^+} .

Solution

This is an example of H^+ ion catalysis, where [Eq. (6.29)] will be applied. The pseudo-first order rate constant is related to the half life time as

$$\frac{0.693}{t_{1/2}} = k = k_{\mathrm{H}^+} [\mathrm{H}^+]$$

and at two different H⁺ ion concentrations, $[H^+]_1$ and $[H^+]_2$, with half life times $(t_{1/2})_1$ and $(t_{1/2})_2$, respectively, we have,

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{[\mathrm{H}^+]_1}{[\mathrm{H}^+]_2} \implies (t_{1/2})_2 = \frac{[\mathrm{H}^+]_1}{[\mathrm{H}^+]_2} (t_{1/2})_1 = \frac{10^{-3} \mathrm{M}}{10^{-4} \mathrm{M}} (50 \mathrm{min}) = 500 \mathrm{min}.$$

Using any acid solution, say of pH 3, k_{H^+} is now calculated as

$$k_{\rm H^+}[{\rm H^+}] = {0.693 \over t_{1/2}} \implies k_{\rm H^+} = {0.693 \over (50 {\rm ~min}) \, 10^{-3} {\rm ~M}} = 13.86 {\rm ~min} {\rm ~M^{-1}}.$$

Exactly in the same way the catalysis by basic species BOH other than OH^- ions has been identified. If, in general, a acid-base catalysis is taking place then the pseudo-first order rate constant, say in an acid solution HA, would be given by, where the base BOH is also present,

$$k = k_0 + k_{\rm H^+}[{\rm H^+}] + k_{\rm OH^-}[{\rm OH^-}] [{\rm BOH}] + k_{\rm A^-}[{\rm A^-}] + k_{\rm HA}[{\rm HA}] k_{\rm BOH}$$
 (6.37)

6.5 AUTOCATALYSIS

A reaction is said to be auto-catalysed when one of the products of the reaction can catalyse the same. A classical example of such a reaction may be the hydrolysis of ester catalysed by a weak acid. When methyl acetate is hydrolysed by an acetic acid the reaction that follows is

$$\mathrm{CH}_3\mathrm{CO}_2\mathrm{CH}_3 + \mathrm{H}_2\mathrm{O} \xrightarrow{\mathrm{H}^+} \mathrm{CH}_3\mathrm{CO}_2\mathrm{H} + \mathrm{CH}_3\mathrm{OH}$$

Apart from the H⁺ ion catalysis, the produced acetic acid may also catalyse the reaction

Let the initial concentration of the ester be [Ester], and that of acetic acid be [AcOH]. If [x] be the concentration of the ester hydrolysed at time *t*, then

$$\frac{d[x]}{dt} = k[\text{AcOH}]([\text{Ester}] - [x]) + k[x]([\text{Ester}] - [x])$$
$$= k[(\text{Ester}) - [x])([\text{AcOH}] + [x])$$

[Later it will be shown that the rate of a homogeneous catalysis is directly proportional to the catalyst concentration.] On integration of the above equation, with the lower limit, at t = 0, [x] = 0, we have

$$k = \frac{1}{t([\text{Ester}] + [\text{AcOH}])} \ln \frac{[\text{Ester}] [\text{AcOH} + (\text{H}^+)]}{[\text{AcOH}] ([\text{Ester}] - [\text{H}^+])}$$

The general example may be like, $R \rightarrow P$, with the P as the product as well as the autocatalyst. The rate law, in the simplest form is

$$v = k[R][P]$$

Let $[R]_0$ and $[P]_0$ are the initial concentrations of R and P, respectively, and let $[R]_0 - x$ and $[P]_0 + x$ are the corresponding concentrations at time t, then

$$v = \frac{dx}{dt} = k([R]_0 - x)([P]_0 + x)$$

or,
$$\frac{dx}{([R]_0 - x)([P]_0 + x)} = k dt$$

which on integration by partial fraction gives

$$k([R]_0 + [P]_0) t = \ln \frac{([P]_0 + x)[R]_0}{([R]_0 - x)[P]_0}$$
(6.38)

writing, $k([R]_0 + [P]_0)$ as *m*, we find

$$mt = \ln \frac{([P]_0 + x)[R]_0}{([R]_0 - x)[P]_0}$$
(6.39)

$$\Rightarrow \qquad e^{mt} = \frac{([P]_0 + x)[R]_0}{([R]_0 - x)[P]_0} \quad \Rightarrow \quad \frac{[P]_0}{[R]_0} e^{mt} = \frac{([P]_0 + x)}{([R]_0 - x)}$$

$$\Rightarrow \qquad ne^{mt} = \frac{([P]_0 + x)}{([R]_0 - x)}; \text{ where, } n = \frac{[P]_0}{[R]_0}$$

$$\Rightarrow \qquad 1 + ne^{mt} = \frac{([R]_0 + [P]_0)}{[R]_0 - x} \tag{6.40}$$

As already shown, $e^{mt} = \frac{([P]_0 + x)[R]_0}{([R]_0 - x)[P]_0}$

$$\Rightarrow \qquad e^{mt} - 1 = \frac{x([R]_0 + [P]_0)}{([R]_0 - x)[P]_0} \tag{6.41}$$

Dividing Eq. (6.27) by Eq. (6.26), we get

$$\frac{(e^{mt}-1)}{1+ne^{mt}} = \frac{\frac{x\left([R]_{0}+[P]_{0}\right)}{([R]_{0}-x)\left[P]_{0}}}{\frac{([R]_{0}+[P]_{0}\right)}{([R]_{0}-x)}}$$

$$\frac{(e^{mt}-1)}{(1+ne^{mt})} = \frac{x}{[P]_{0}}$$
(6.42)

or,

where $n = [P]_0/[R]_0$. A plot of $x/[P]_0$ versus *mt* is shown in Figure 6.5. Initially, the rate is slow, because a little *P* is present; then increases due to autocatalysis, and finally becomes slow again when *R* has almost disappeared. It can also be shown that the time at which the rate becomes maximum is given by



Figure 6.5 The plot of $\frac{x}{[P]_0}$ versus *mt* where $m = ([R]_0 + [P]_0)k$. $t_{\text{max}} = \text{m}^{-1} \ln(n^{-1})$ (6.43)

Other examples of autocatalytic reaction are

- (i) Oxidation of oxalic acid by $KMnO_4;$ the product $Mn^{\rm ++}$ is the autocatalyst.
- (ii) Dissolution of Cu in nitric acid; the product HNO_2 is the autocatalyst.



Figure 6.6 Undissociated acids also catalyse the reaction in addition of H⁺ ions.

Example 6.3

Show that the time at which the rate becomes maximum is given $t_{\text{max}} = \frac{1}{m} \ln \left(\frac{1}{n} \right)$.

Solution

The rate of the autocatalysed reaction may be written as

$$v = k([R]_0 - x)([P] + x)$$

 $[R]_0$ and $[P]_0$ are the initial concentrations of the reactant and product, respectively, and x is the amount reacted at time t, when the rate is v.

Differentiating v with respect to time t,

$$\frac{dv}{dt} = k([R]_0 - x)\frac{dx}{dt} - k([P]_0 + x)\frac{dx}{dt}$$

at the maximum, $\frac{dv}{dt} = 0$; this gives us

$$k'([R]_0 - x) \frac{dx}{dt} = k'([P]_0 + x) \frac{dx}{dt}$$

 \Rightarrow

 \Rightarrow

$$[R]_{0} - x = [P]_{0} + x$$

$$x = \frac{[R]_{0} - [P]_{0}}{2}$$
(7)

From Eq. (6.28), we write

$$x = \frac{[P]_0 (e^{mt_{\text{max}}} - 1)}{(1 + ne^{mt_{\text{max}}})}$$
(8)

Equating Eqs. (7) and (8), we write

$$\begin{split} \frac{[R]_0 - [P]_0}{2[P]_0} &= \frac{(e^{mt_{\max}} - 1)}{(1 + ne^{mt_{\max}})} \\ & \frac{1}{2} \left(\frac{[R]_0}{[P]_0} - 1 \right) + 1 = \frac{(e^{mt_{\max}} - 1)}{(1 + ne^{mt_{\max}})} + 1 \\ & \frac{1}{2} \left(\frac{[R]_0}{[P]_0} \right) - \frac{1}{2} + 1 = \frac{e^{mt_{\max}} - \cancel{1} + \cancel{1} + ne^{mt_{\max}}}{(1 + ne^{mt_{\max}})} \\ \Rightarrow & \frac{1}{2} \frac{\cancel{1 + n}}{n} = \frac{\cancel{1 + n}e^{mt_{\max}}}{(1 + ne^{mt_{\max}})} \\ \Rightarrow & \frac{1 + ne^{mt_{\max}}}{e^{mt_{\max}}} = 2n \\ \Rightarrow & e^{-mt_{\max}} = n \\ \Rightarrow & mt_{\max} = \ln \frac{1}{n} \end{split}$$

and finally,

$$t_{\max} = \frac{1}{m} \ln\left(\frac{1}{n}\right) \tag{9}$$

6.6 PRIMARY KINETIC SALT EFFECT

The influence of the ionic strength of the medium by the addition of inert electrolytes onto the *rates of reactions between ions* is known as the *primary kinetic salt effect*. The effect arises due to the change in the activity coefficients of the participating ions.

Bronsted, Bjerrum and Christiansen gave the first successful theoretical treatment of this effect. The most general scheme is:

$$\mathbf{M}^{\mathbf{Z}_m} + \mathbf{N}^{\mathbf{Z}_n} \stackrel{K^{\ddagger}}{\rightleftharpoons} \mathbf{X}^{(\mathbf{Z}_m + \mathbf{Z}_n)} \xrightarrow{k_2} \operatorname{Product}(\mathbf{s})$$

where M^{Z_m} and N^{Z_n} are the reactants, carrying electrical charges Z_m and Z_n ; X is an activated complex. The pre-equilibrium approximation is used to find the concentration of X, and the basis of the treatment is that the rate of the reaction is directly proportional to the concentration of the complex not to its activity. The equilibrium constant for the

formation of the complex K^{\ddagger} is given by

$$K^{\ddagger} = \frac{a_x}{a_m a_n} = \frac{C_x}{C_m C_n} \frac{\gamma_x}{\gamma_m \gamma_n} \implies C_x = K^{\pm} \frac{\gamma_m \gamma_n}{\gamma_x} C_m C_n$$

The rate of the reaction is therefore given by,

$$v = k_2 C_x = k_2 K^{\pm} \frac{\gamma_m \gamma_n}{\gamma_x} C_m C_n$$

The observed rate constant of the reaction is therefore given by

$$k_{\rm obs} = k_2 K^{\pm} \frac{\gamma_m \gamma_n}{\gamma_x}$$
(6.44a)

If k_0 be the rate constant of the reaction at zero ionic strength, i.e. when all the activity coefficients are unity, then Eq. (6.44a) changes to

$$k_{\rm obs} = k_0 \frac{\gamma_m \gamma_n}{\gamma_x} \implies \log\left(\frac{k_{\rm obs}}{k_0}\right) = \log \gamma_m + \log \gamma_n - \log \gamma_x$$
 (6.44b)

If the concentration of the ions in the solution is not too high then the Debye-Hückel limiting law can be used in correlating the activity coefficients with the ionic strength of the medium I.

$$\log \gamma_m = -AZ_m^2 \sqrt{I} \log \gamma_n = -AZ_n^2 \sqrt{I} \text{ and } \log \gamma_x = -A(Z_m + Z_n)^2 \sqrt{I}$$
 (6.45)

6.18

where the value of A at 25°C in aqueous solution is 0.509. Using these relations in Eq. (6.44b), we find

$$\log\left(\frac{k_{\rm obs}}{k_0}\right) = 2AZ_m Z_n \sqrt{I} \tag{6.46}$$

Three cases are there. If both the reactant ions are of like charges (+, + or -, -) then the right hand side of Eq. (6.46) is positive. The rate of such reactions will therefore increase on increasing the ionic strength. Such a prediction can be experimentally tested by plotting $\log(k_{obs}/k_0)$ versus \sqrt{I} ; a straight line with slope $2AZ_mZ_n$ will be observed. This has been really confirmed experimentally (Figure 6.7). On the other hand, if the two reactant ions are of two opposing charges then the rate decreases with increase in *I*. Finally, if either of the reactant ions is neutral then the rate remains unaffected with the changing ionic strength.



Figure 6.7 Plot of log $\frac{k_{obs}}{K_0}$ vs \sqrt{I} of some ionic reactions.

- $1. \quad \mathrm{CO(NH_3)_5\,Br^{2+}+Hg^{2+}+H_2O} \rightarrow \mathrm{Co(NH_3)_5\,(H_2O)^{3-}+HgBr^+}$
- 2. $S_2O_8^{2-} + I^- + (SIO_4^- + SO_4^{2-}) \rightarrow I_2^- + 2SO_4^{2-}$
- 3. O_2N N— $COOC_2H_5^- + OH^- \rightarrow N_2O + CO_3^{2-} + C_2H_5OH$
- 4. cane sugar + $OH^- \rightarrow invert$ sugar
- 5. $H_2O_2 + H^+ + Br^- \rightarrow H_2O + \frac{1}{2}Br_2 (not \ balanced)$
- 6. $CO(NH_3)_5 Br^{2+} + OH^- \rightarrow CO(NH_3)_5(OH)^{2+} + Br^-$
- 7. $\operatorname{Fe}^{2+} + \operatorname{CO}(\operatorname{C}_2\operatorname{O}_4)_3^{3-} \to \operatorname{Fe}^{3+} + \operatorname{CO}(\operatorname{C}_2\operatorname{O}_4)_4^{3-}$

The physical interpretation of this is as follows: for ions of like charges, the charge density of the activated complex is more than that of the either ion and this makes the complex more stable by increased solvation. A higher concentration of the complex is thereby produced due to the lowering of γ_x , and the rate therefore increases. Just the opposite thing happens in case of reacting ions of opposite charges. When one of the reactant ions is neutral there is no change in the charge density during the formation of the complex, and therefore the rate remains unaltered.

6.7 SECONDARY KINETIC SALT EFFECT

A change in the concentration of the *catalytically active ions may have an effect on the rate* of reaction in solution, particularly between ions. This is the secondary kinetic salt effect. The effect is pronounced when the catalytic ions are produced from a *weak electrolyte;* but it is negligible when a strong acid or base is the catalyst.

Let us have a mixture of a weak acid HA and its salt at definite concentrations; the H^+ ions are the catalyst. For the acid ionisation we may write

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

 $C_{\rm H_3O^+} = K_a \frac{C_{\rm HA}}{C_{\rm A^-}} \frac{\gamma_{\rm HA}}{\gamma_{\rm HaO^+} \gamma_{\rm A^-}}$

The ionisation constant K_a is then

$$K_a = rac{a_{
m H_3O^+} \ a_{
m A^-}}{a_{
m HA}} = rac{C_{
m H_3O^+} \ C_{
m A^-}}{C_{
m HA}} rac{\gamma_{
m H_3O^+} \ \gamma_{
m A^-}}{\gamma_{
m HA}}$$

 \Rightarrow

In a buffered solution, the quotient $\frac{C_{\text{HA}}}{C_{\text{A}'}}$ is constant, and therefore, at a fixed temperature the quantity $K_a \frac{C_{\text{HA}}}{C_{\text{A}^-}}$ is constant; let it be represented by *K*. We then have

$$C_{\rm H_3O^+} = K \frac{\gamma_{\rm HA}}{\gamma_{\rm H_3O^+} \ \gamma_{\rm A^-}}$$
(6.47)

Since the activity coefficient terms vary with the ionic strength of the solution, $C_{\rm H_3O^+}$ will also vary; *this produces the secondary kinetic salt effect*.

Since the rate of the reaction is directly proportional to the catalyst H_3O^+ , and if there is no primary kinetic salt effect, the rate constant of the reaction may be written as

$$k = k_0 \frac{\gamma_{\rm HA}}{\gamma_{\rm H_3O^+} \gamma_{\rm A^-}} \tag{6.48}$$

where k_0 is a constant, the value of k is at infinite dilution where all the activity coefficients are unity.

Using the Debye-Hückel limiting law for the variation of activity coefficients with ionic strength in dilute solution

 $\log \gamma_i = -0.509 Z_i^2 \sqrt{I}$ at 25°C and in aqueous solution.

From Eq. (6.48)

$$\log k = \log k_0 + \log \gamma_{\text{HA}} - \log \gamma_{\text{H}_2\text{O}^+} - \log \gamma_{\text{A}^-}$$

 \Rightarrow

$$\log k = \log k_0 + 0 + 0.509\sqrt{I} + 0.509\sqrt{I}$$

It is assumed that for the undissociated acid, $\gamma_{\rm HA}$ = 1. Therefore,

$$\log k = \log k_0 + 1.018\sqrt{I} \qquad [at 25^{\circ}C \text{ in aqueous solution}] \quad (6.49)$$

..

Therefore, in an acid-salt mixture the secondary salt effect will increase the rate constant with increasing concentration of the electrolyte (i.e. increasing I).

If the catalysing species are, e.g. NH_4^+ or $[Fe(H_2O)_6]^{3+}$, then the effects are fairly interesting.

For NH_4^+ ion, we write the equilibrium as

$$\mathrm{NH}_{3} + \mathrm{H}_{3}\mathrm{O}^{+} \underbrace{K_{a}}{\mathrm{NH}_{4}^{+}} + \mathrm{H}_{2}\mathrm{O}$$

$$(6.50)$$

$$K_{a} = \frac{[\mathrm{NH}_{4}^{+}]}{[\mathrm{NH}_{3}][\mathrm{H}_{3}\mathrm{O}^{+}]} \frac{\gamma_{\mathrm{NH}_{4}^{+}}}{\gamma_{\mathrm{NH}_{3}} \gamma_{\mathrm{H}_{3}\mathrm{O}^{+}}}$$
(6.51)

$$\Rightarrow \qquad [\mathrm{NH}_{4}^{+}] = K_{a}[\mathrm{NH}_{3}][\mathrm{H}_{3}\mathrm{O}^{+}] \frac{\gamma_{\mathrm{NH}_{3}} \gamma_{\mathrm{H}_{3}\mathrm{O}^{+}}}{\gamma_{\mathrm{NH}_{4}^{+}}}$$

as previously explained, we write

$$k = k_0 \frac{\gamma_{\rm NH_3} \gamma_{\rm H_3O^+}}{\gamma_{\rm NH_4^+}}$$
(6.52)

 \Rightarrow

 \Rightarrow

$$\log k = \log k_0 + \log \gamma_{\mathrm{NH}_3} + \log \gamma_{\mathrm{H}_3\mathrm{O}^+} - \log \gamma_{\mathrm{NH}_4^+}$$

 $\Rightarrow \qquad \log k = \log k_0 + 0 - 9.509 \sqrt{I} + 9.509 \sqrt{I} = \log k_0 \quad (\text{at } 25^{\circ}\text{C}; \text{aqueous solution})$

 $(\rm NH_3$ being a neutral undissociated molecule, it is assumed that $\gamma_{\rm NH_3}$ to be unity.)

The specific rate constant will be independent of the ionic-strength (I) of the medium, provided the solution is not too concentrated; obviously, it is assumed that there is no primary-salt effect.

(6.54)

For the catalyzing species $[Fe(H_2O)_6]^{3+}$, we write the equilibrium as

$$[\operatorname{Fe}(\operatorname{H}_2\operatorname{O})_5(\operatorname{OH}^-)]^{2+} + \operatorname{H}_3\operatorname{O}^+ \xleftarrow{K} [\operatorname{Fe}(\operatorname{H}_2\operatorname{O})_6]^{3+} + \operatorname{H}_2\operatorname{O}$$

The equilibrium constant K is then

$$K = \frac{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}{[\text{Fe}(\text{H}_2\text{O})_5 \text{ OH}^-]^{2+} [\text{H}_3\text{O}^+]} \times \frac{\gamma_3}{\gamma_2 \gamma_{\text{H}_3\text{O}^+}}$$

This equation can be rewritten as (explained earlier)

$$k = k_0 \frac{\gamma_3}{\gamma_2 \,\gamma_{\rm H_3O^+}} \tag{6.53}$$

where k_0 is the rate constant k at infinite dilution, i.e. when all the activity-coefficients are unity. Taking logarithm on Eq. (6.53), we have

$$\log k = \log k_0 + \log \gamma_3 - \log \gamma_2 - \gamma_{H_3O^+}$$
$$\log k = \log k_0 - 0.509(9)\sqrt{I} + 0.509(4)\sqrt{I} + 0.509\sqrt{I}$$
$$\log k = k_0 + (-0.509(9)\sqrt{I} + 0.509\sqrt{I})$$

⇒

 \Rightarrow

$$\log k = k_0 + (-9 + 4 + 1) \ 0.509\sqrt{I}$$

and finally, $\log k = \log k_0 - 2.04\sqrt{I}$

at 25°C and in aqueous solution. Here, we find that the secondary kinetic salt effect is negative. Other examples of secondary kinetic salt effect are (i) catalytic decomposition of nitrosotriacetoneamine by OH^- ions, (ii) hydrolysis of ethyl acetate with H^+ ions as the catalyst, among many others.

6.8 ENZYME CATALYSIS

Enzymes are proteins; they are called biological catalysts, and are responsible of carrying out a number of metabolic processes. They function in a much more specific way; for example, urease can catalyse only the hydrolysis of urea. Some enzymes show group specificity that they can catalyse the hydrolysis of any peptide linkage provided certain groups are present nearby. Some enzymes show stereo-specificity in that they can hydrolyse the peptide linkage in which the amino acid groups are of L-configuration. It is now evident that the catalytic activity of an enzyme is confined over a very small region of the protein molecule which is usually referred to as the active centre.

Up to date, only a little information is accumulated regarding their structure, reactivity and kinetics. In the following we will discuss very briefly on the dependence of the rate of enzyme catalysed reaction on the substrate concentration, temperature and pH of the medium.

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In general, the characteristic features of an enzyme may be summarized as

- 1. *Absolute Specificity*: In this type of behaviour, an enzyme can catalyse a single reaction.
- 2. *Group Specificity*: A reaction having single type of functional group is catalysed by the enzyme.
- 3. Linkage Specificity: In this type, the enzyme makes a specific type of bond labile.
- 4. *Stereochemical Specificity*: They catalyse the reaction of one stereochemical form and not the other; the proteolytic enzymes, for example, only catalyse the hydrolysis of peptides made up from amino acids in the *L*-configuration.
- 5. *The turn-over number*^{*}: of an enzyme is much more than any inorganic catalyst. A comparative figure of the three cases in given in figure.



Figure 6.8 A comparison of uncatalysed, chemically catalysed and enzyme catalytic process.

In order to avoid possible complications, measuring the initial rate of the reaction at different substrate concentrations keeping the enzyme concentration fixed generally does the kinetic study of enzyme-catalysed reactions. The result is shown in Figure 6.9. Normally, the substrate concentration is much higher than that of the enzyme; and under this condition, it is found that the rate increases linearly with the substrate concentration (first order kinetics) in the low concentration range, and becomes independent of the substrate concentration (zero order kinetics) in the higher concentration range. Apart from this behaviour, it is found that at any substrate concentration, $[S]_0 >> [E]_0$, the rate is directly proportional to $[E]_0$. Michaelis and Menten first attempted to account for these observations successfully.

^{*} The turnover number is defined as the number of molecules transformed per minute by one molecule of the catalyst.

6.8.1 Michaelis-Menten Analysis

In this method, at a fixed enzyme concentration, a series of the substrate with increasing concentration is made. This is done over a wide range of concentration of the substrate; in every case the initial rate v is measured. It is observed that the rate v increases linearly in the low substrate concentration range; this is a first order process. Thereafter, the increase in v slows down; and at higher substrate concentration, the rate saturates to v_{max} ; it becomes a zeroth-order kinetics.

Since $[S]_0 >> [E]_0$ at low concentration of the substrate, the enzyme-substrate complex *ES* is formed, and the decomposition of the complex to produce the final product along with the

free enzyme takes place. As the substrate concentration increases, the ratio $\frac{[S]_0}{[E]_0}$ increases;

the probability of the binding of S and E decreases. At large substrate concentration all the enzyme molecules are complexed ($[S]_0 >> [E]_0$). Therefore any further increase in the substrate concentration cannot form any further enzyme-substrate complex any more; there comes a kind of saturation, and the rate saturates to its maximum value, v_{max} . This is clarified in Figure 6.9.

The reaction pathway may be written as

$$E + S \xrightarrow[k_{-1}]{k_{-1}} ES \xrightarrow[k_{-2}]{k_{-2}} P + E$$
(6.55)

where S is the substrate, P is the product, E is the enzyme and ES is the enzyme-substrate complex. k_1 and k_{-1} are the rate constants for the forward and backward process for the first step and, k_2 and k_{-2} are the corresponding rate constants for the second step.

In most of the kinetic studies of enzyme catalysed reactions $[S]_0 >> [E]_0$, and consequently the enzyme-substrate concentration [ES] is much less than that of $[S]_0$. Therefore, the steady state approximation may be applied to the species ES. Secondly, since the concentration of ES at the early stage of the reaction is very small, we can neglect the backward reaction $P + E \rightarrow ES$ with rate constant k_{-2} . Applying the steady state approximation to [ES], we find

$$\frac{d}{dt}[ES] = 0 = k_1 [E][S] - k_{-1}[ES] - k_2 [ES]$$
$$k_1 [E][S] = (k_{-1} + k_2) [ES]$$

Since it is difficult to estimate [E] during the reaction but, its initial concentration is known exactly, we rewrite the above equation as

$$\begin{split} k_1([E]_0 - [ES])[S] &= (k_{-1} + k_2) \, [ES] \\ k_1[E]_0 \, [S] - k_1[ES][S] &= k_{-1}[ES] + k_2[ES] \end{split}$$

 \Rightarrow

 \Rightarrow

 \Rightarrow

 \Rightarrow

$$k_1[E]_0[S] = k_{-1}[ES] + k_2[ES] + k_1[ES][S]$$

[

 $v = \frac{k_2 [E]_0 [S]}{K_m + [S]}$

$$ES] = \frac{k_1[E]_0[S]}{k_{-1} + k_2 + k_1[S]}$$
(6.56)

The rate of the reaction is then

$$v = k_2[ES] = \frac{k_1 \ k_2[E]_0[S]}{k_{-1} + k_2 + k_1[S]}$$

$$v = \frac{k_2[E]_0[S]}{\frac{k_{-1} + k_2}{k_1} + [S]}$$
(6.57)

$$\mathbf{or}$$

or

This is the Michaelis-Menten equation, and the constant $\frac{k_{-1} + k_2}{k_1}$ is called the Michaelis constant K_m .

The addition of K_m to a concentration term [S] indicates that K_m also has the units of concentration

units of

$$K_m = \frac{k_{-1} + k_2}{k_1} = \frac{s^{-1} + s^{-1}}{L \text{ mol}^{-1} \text{ s}^{-1}} = \text{mol} L^{-1}$$

At high substrate concentration, as $[S] >> K_m, K_m + [S] \approx [S]$. Equation (6.58) then changes to

$$v = \frac{k_2 [E]_0 [S]}{[S]} = k_2 [E]_0 \tag{6.59}$$

This is the maximum attainable rate. v_{max} (Figure 6.7).

We then write

$$v_{\max} = k_2 [E]_0 \tag{6.60}$$

The physical interpretation of this equation is that, at high enough substrate concentration [S], all the enzyme molecules are complexed; therefore any further increase in the substrate concentration is useless. The maximum rate will be given when all the enzyme molecules are blocked.

Using Eqs. (6.58) and (6.60), we may write

$$v = \frac{v_{\max}[S]}{K_m + [S]} \tag{6.61}$$

(6.58)

The Michaelis constant K_m has a special significance. It has already shown that K_m has the units of concentration. If, during the reaction K_m becomes equal to [S], i.e. $K_m = [S]$, then Eq. (6.61) changes to

$$v = \frac{v_{\max}[S]}{[S] + [S]} = \frac{1}{2} v_{\max}$$
(6.62)

Therefore, we find that K_m is equal to that substrate concentration at which the rate of the process is half of maximum attainable rate (Figure 6.9). It has earlier been shown that under condition $[S] >> K_m$ we get the maximum attainable rate

$$v_{\text{max}} = k_2 [E]_0$$

The rate follows a zero-order rate law with respect to the substrate concentration. But, when $K_m >> [S]$, the rate law becomes

$$v = \frac{k_2 \left[E\right]_0 \left[S\right]}{K_m} \tag{6.63}$$

The reaction then follows a first-order kinetics with respect to the substrate concentration [S]. The regions of first-order kinetics and zero-order kinetics with respect to the substrate are also shown in Figure 6.9. The Mechaelis constant bears two important features about the enzyme which are discussed as follows:



Figure 6.9 Reaction rate versus substrate concentration for a reaction following Michaelis-Menten kinetics.

It gives the concentration of the substrate just required to bind the half of the available sites of the enzyme, and it gives a qualitative strength to the binding affinity of the substrate on the active sites of the enzyme.

The Michaelis-Menten model of enzyme catalysed reactions bears a close similarity with the heterogeneous catalysis; this will be taken up in the topic of heterogeneous catalysis, Eq. (6.55) may also be written as

1 [7] [0]

..

$$-\frac{d}{dt}[S] = \frac{k_2[E]_0[S]}{K_m + [S]}$$

$$\Rightarrow \qquad -\frac{d[S]}{dt}\frac{(K_m + [S])}{[S]} = k_2[E]_0$$

$$\Rightarrow \qquad -d[S]\left(\frac{K_m}{[S]} + 1\right) = k_2[E]_0 dt$$

$$\Rightarrow \qquad -K_m \frac{d[S]}{[S]} - d[S] = k_2[E]_0 dt$$

[S]

Integrating between limits

$$-K_{m} \int_{[S_{0}]}^{[S]} \frac{d[S]}{[S]} - \int_{[S]_{0}}^{[S]} d[S] = k_{2}[E]_{0} \int_{0}^{t} dt$$
$$K_{m} \ln \frac{[S]_{0}}{[S]} + ([S]_{0} - [S]) = k_{2}[E]_{0}t$$
(6.64)

 \Rightarrow

The first term on the left hand side represents a first-order kinetic and, the second term representing a zero-order kinetic; it has already been seen in Figure 6.9.

Lineweaver-Burk and Eadie Plots 6.8.2

The data of enzyme catalysed reactions have been analyzed in a number of methods. One most commonly used method is to take the reciprocal of Eq. (6.58)

$$\frac{1}{v} = \frac{K_m + [S]}{k_2 [E]_0 [S]} = \frac{K_m}{k_2 [E]_0 [S]} + \frac{1}{k_2 [E]_0}$$
(6.65)

Therefore a plot of $\frac{1}{v}$ versus $\frac{1}{[S]}$ will give a straight line with slope $\frac{K_m}{k_2[E]_0}$ and intercept of $\frac{1}{k_2[E]_0}$. Such a plot is known as Lineweaver-Burk plot, shown in Figure 6.10(a).







Figure 6.10(b) The Eadie plot of v / [S] versus v.

Multiplying Eq. (6.65) by [S], we get

$$\frac{[S]}{v} = \frac{[S]}{k_2[E]_0} + \frac{K_m}{k_2[E_0]}$$
(6.66)

Therefore a plot of $\frac{[S]}{v}$ versus [S] will be a straight line with slope $\frac{1}{v_{\max}}$ and intercept $\frac{K_m}{v_{\max}}$. This type of plot is known as Hanes-Wolff plot (Figure 6.11).



Figure 6.11 A Hanes-Wolff (single reciprocal) plot.

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The parameters $v_{\text{max}} (=k_2[E]_0)$ and K_m can be obtained from such a plot. If the initial concentration of the enzyme $[E]_0$ is known, k_2 can also be evaluated because $v_{\text{max}} = k_2[E]_0$.

The Michaelis-Menten Eq. (6.61) can be rewritten as

$$vK_m + v[S] = v_{\max}[S] \tag{6.67}$$

$$\Rightarrow$$

 \Rightarrow

$$\frac{v}{[S]}K_m + v = v_{\max}$$

$$\frac{v}{[S]} = \frac{v_{\max}}{K_m} - \frac{v}{K_m}$$
(6.68)

Therefore a plot of $\frac{v}{[S]}$ versus v, would have an intercept of $\frac{v_{\max}}{K_m}$ and a slope of $-\frac{1}{K_m}$. This is shown in Figure 6.10(b). This kind of plot was first suggested by Eadie (1942); it has the advantage over the Lineweaver-Burk plot in that, it can spread out the points to a greater extent.

Another way of plotting the data for enzyme-catalysed reaction is as follows:

Using Eq. (6.68), we may write

$$v(\mathbf{K}_{m} + [S]) = k_{2}[E]_{0}[S]$$

 $vK_{m} + v[S] = k_{2}[E]_{0}[S]$

 \Rightarrow

Dividing althrough by [S]

$$\frac{vK_m}{[S]} + v = k_2[E]_0$$

 \Rightarrow

 \Rightarrow

 $v = k_2[E]_0 - \frac{vK_m}{[S]}$

 $v = v_{\max} - \frac{v}{[S]} K_m \tag{6.69}$

Therefore a plot of v versus $\frac{v}{[S]}$ would be a straight line with slope $-K_m$ and intercept v_{max} . This is called Eadie-Hofstee plot (Figure 6.12).



Figure 6.12 An Eadi-Hofstee (single reciprocal) plot.

6.8.3 Effect of Temperature

Enzymes generally function by complexing to the substrate. The phenomenon is called the *'lock and key'* model; this is shown in Figure 6.13. The *active sites* of an enzyme are the locations where the spatial geometry of the enzyme and the substrate match. This is one of the reasons as to why enzymes are *highly specific*.



Figure 6.13 The 'lock and key' model for the enzyme-substrate complex.

Enzymes may undergo denaturation even at temperatures around 40° C; this is because, enzymes are proteins which are highly temperature sensitive. If there is a slight change in the configuration of the enzyme, the enzyme-substrate complex would not be formed resulting into a decrease in the reaction rate. Generally, the rate first increases with temperature and then forming a maximum slows down due to denaturation. This is shown in Figure 6.14. There is a common saying that, enzymes act most efficiently at that temperature which favours life.

..



Figure 6.14 Variation of enzyme activity with temperature.

6.8.4 Effect of pH

The pH of the medium has a great influence on the activity of an enzyme. A detailed explanation of the effect of pH may be made by Michaelis-Menten model. In general, an enzyme has one or more active sites from where H^+ ion can be removed or added. This depends upon the pH of the solution. Representing the enzyme as EH, the deprotonated form as E^- and the protonated form as EH_2^+ , the net equilibria may be constructed as

$$\begin{array}{c}
\mathbf{E}^{-} + \mathbf{H}^{+} \\
K_{2} \\
\mathbb{E} \\
\mathbf{E} \\
\mathbf{K}_{1} \\
\mathbb{E} \\
\mathbf{K}_{1} \\
\mathbb{E} \\
\mathbf{H}_{2}^{+}
\end{array} \xrightarrow{k_{1}} \mathbf{E} \\
\mathbf{H} \\
\mathbf{K}_{2} \\
\mathbb{E} \\
\mathbf{K}_{2} \\
\mathbb{E} \\
\mathbb{E} \\
\mathbf{K}_{2} \\
\mathbb{E} \\
\mathbb{E}$$

The total enzyme concentration is

$$[E]_{0} = [EH] + [E^{-}] + [EH_{2}^{+}] + [EHS]$$
(6.71)

Three equilibrium constants are to be considered

$$K_{1} = \frac{[\text{EH}][\text{H}^{+}]}{[\text{EH}_{2}^{+}]}; \ K_{2} \ \frac{[\text{E}^{-}][\text{H}^{+}]}{[\text{EH}]}; \ K_{S} = \frac{[\text{EH}][\text{S}]}{[\text{EHS}]}$$
(6.72)

Using Eqs. (6.69) and (6.70), we have

$$[\mathbf{E}]_{0} = \frac{[\mathbf{E}^{-}][\mathbf{H}^{+}]}{K_{2}} + \frac{K_{2}[\mathbf{E}\mathbf{H}]}{[\mathbf{H}^{+}]} + \frac{[\mathbf{E}\mathbf{H}][\mathbf{H}^{+}]}{K_{1}} + [\mathbf{E}\mathbf{H}\mathbf{S}]$$
(6.73)

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Dividing althoughout by [EHS], we get

$$\frac{[E]_0}{[\text{EHS}]} = \frac{[\text{E}^-][\text{H}^+]}{K_2[\text{EHS}]} + \frac{K_2[\text{EH}]}{[\text{H}^+][\text{EHS}]} + \frac{[\text{EH}][\text{H}^+]}{K_1[\text{EHS}]} + 1$$
(6.74)

Substituting $\frac{[\text{EH}][\text{S}]}{K_{S}}$ for [EHS] on the right and side, we get $\frac{[\text{E}]_{0}}{[\text{EHS}]} = \frac{[\text{E}^{-}][\text{H}^{+}]K_{S}}{K_{2}[\text{EH}][\text{S}]} + \frac{K_{2}[\text{EH}]K_{S}}{[\text{H}^{+}][\text{EH}][\text{S}]} + \frac{[\text{EH}][\text{H}^{+}]K_{S}}{K_{1}[\text{EH}][\text{S}]} + 1 \qquad (6.75)$ $\Rightarrow \qquad \frac{[\text{E}]_{0}}{[\text{EHS}]} = \frac{[\text{E}^{-}][\text{H}^{+}]K_{S}}{K_{2}[\text{EH}][\text{S}]} + \frac{K_{2}K_{S}}{[\text{H}^{+}][\text{S}]} + \frac{K_{S}[\text{H}^{+}]}{K_{1}[\text{S}]} + 1 \qquad (6.76)$

$$\begin{aligned} \operatorname{Recognising that} & \frac{[\mathrm{E}^{-}][\mathrm{H}^{+}]}{K_{2}[\mathrm{EH}]} = 1, \text{ we get} \\ & \frac{[\mathrm{E}]_{0}}{[\mathrm{EHS}]} = \frac{K_{S}}{[\mathrm{S}]} + \frac{K_{2}}{[\mathrm{H}^{+}]} \cdot \frac{K_{S}}{[\mathrm{S}]} + \frac{[\mathrm{H}^{+}]}{K_{1}} \cdot \frac{K_{S}}{[\mathrm{S}]} + 1 \\ \Rightarrow & \frac{[\mathrm{E}]_{0}}{[\mathrm{EHS}]} = 1 + \frac{K_{S}}{[\mathrm{S}]} \left(1 + \frac{K_{2}}{[\mathrm{H}^{+}]} + \frac{[\mathrm{H}^{+}]}{K_{1}} \right) \end{aligned}$$
(6.77)
$$\Rightarrow & [\mathrm{EHS}] = \frac{[\mathrm{EI}]_{0}}{1 + \frac{K_{S}}{[\mathrm{S}]} \left(1 + \frac{K_{2}}{[\mathrm{H}^{+}]} + \frac{[\mathrm{H}^{+}]}{K_{1}} \right) \end{aligned}$$

The rate of the reaction for the formation of the product P is [cf. Eq. (6.55)]

$$v = K_{2}[\text{EHS}] = \frac{k_{2}[\text{EI}]_{0}}{1 + \frac{K_{S}}{[\text{S}]} \left(1 + \frac{K_{2}}{[\text{H}^{+}]} + \frac{[\text{H}^{+}]}{K_{1}}\right)}$$
(6.78)

writing $1 = \frac{[S]}{[S]}$ in the denominator, and simplifying we get

$$v = \frac{k_2 [E]_0 [S]}{[S] + K_s \left(1 + \frac{K_2}{[H^+]} + \frac{[H^+]}{K_1}\right)}$$
(6.79)

This equation resemblance the Michaelis-Menten [Eq. (6.58)] with

$$K_m = K_s \left(1 + \frac{K_2}{[\mathrm{H}^+)} + \frac{[\mathrm{H}^+]}{K_1} \right)$$
(6.80)

In the numerator of Eq. (6.79), there is no [H⁺] term; therefore the maximum rate v_{max} does not depend on pH. At low pH where [H⁺] is sufficiently high, the term $\frac{K_2}{[\text{H}^+]} \ll \frac{[\text{H}^+]}{K_1}$. Equation (6.79) therefore changes to

$$v = \frac{v_{\max}[S]}{[S] + K_S \left(1 + \frac{[H^+]}{K_1}\right)} \quad (v_{\max} = K_2[E]_0)$$
(6.81)

Later on, it will be shown that Eq. (6.81) is similar to the equation of competitive inhibition, where H⁺ acts as the inhibitor.

A plot of pK_m versus pH can be made [(using Eq. (6.65)] to find, how does the Michaelis constant K_m vary with pH Standard value of K_S , K_1 and K_2 which are taken as 5×10^{-4} , 10^{-5} and 10^{-7} , respectively. The plot of pK_m versus pH is shown in Figure 6.15. The pH scale is scanned from 1 to 11. Quite expectedly pK_m first increases, forms a maximum and then decreases. The maximum occurs at pH 6. If the experiment is carried at different pH values, pK_m gives a horizontal line touching the maximum of the curve. The tangents from either sides intersect this horizontal line. It may be shown that the intersecting points correspond to pK_1 and pK_2 .



Figure 6.15 A plot of the logarithm of the apparent K_m versus pH for the enzyme-catalysed process shown in Eq. (6.68), the dissociation constant for the EHS complex was taken as 5.0×10^{-4} , K_1 as 10^{-5} mol/L, and K_2 as 10^{-7} mol/L.

6.33

INHIBITION OF ENZYME ACTION 6.9

Enzymes are molecules of high molecular weights, whereas substrates are molecules of relatively very low molecular weights. For example, the decomposition of H_2O_2 (mol. wt. 34) is catalysed by the enzyme catalyse whose molecular weight is about 2,50,000. The enzyme lowers the activation energy for the decomposition from 75 to only 8 kJ mol⁻¹ (Figure 6.8). Generally, the active site is located to a small region of the large enzyme molecule. If some foreign substance gets bound to the active sites then the enzyme loses its activity fully or partially. This is the inhibition of enzyme action.

In the following, three simplest kinetic models of enzyme inhibition will be discussed; (1) competitive inhibition, (2) non-competitive inhibition and (3) uncompetitive inhibition.

6.9.1 **Competitive Inhibition**

In this kind of inhibition, a foreign substance, i.e. the *inhibitor I competes with the substrate* S to get bound to the *active sites* of the enzyme; this reduces the activity of the enzyme. This is called *competitive inhibition*. There is a competition between the I and S to occupy the active sites of the enzyme.

The two equilibria involved are

$$\mathbf{E} + \mathbf{S} \xrightarrow[k_{-1}]{k_{-1}} \mathbf{E} \mathbf{S} \xrightarrow[k_{-2}]{k_{-2}} \mathbf{P} + \mathbf{E}$$
(6.82)

and

 \Rightarrow

 \Rightarrow

$$\mathbf{E} + \mathbf{I} \underbrace{\xrightarrow{k_3}}_{k_{-3}} \mathbf{E} \mathbf{I}$$
(6.83)

In this system, the free enzyme concentration can be written as

$$E] = [E]_0 - [ES] - [EI]$$
(6.84)

The equilibrium constant of the equilibrium [Eq. (6.83)] is

[]

$$K = \frac{k_3}{k_{-3}} = \frac{[\text{EI}]}{[\text{E}][\text{I}]} = \frac{[\text{EI}]}{([\text{E}]_0 - [\text{ES}] - [\text{EI}])[\text{I}]}$$
(6.85)

If K_i is the equilibrium constant for the dissociation of the EI complex then $K_i = \frac{1}{K}$. Solving for [EI] goes as follows. Starting from Eq. (6.85), we write

$$\begin{split} \frac{1}{K_i} &= \frac{[\text{EI}]}{([\text{E}]_0 - [\text{ES}] - [\text{EI}])[\text{I}]} \\ K_i &= \frac{([\text{E}]_0 - [\text{ES}] - [\text{EI}])[\text{I}]}{[\text{EI}]} \\ K_i &= \left\lceil \frac{[\text{E}]_0 - [\text{ES}]}{[\text{EI}]} - 1 \right\rceil [\text{I}] \end{split}$$

$$K_i = \frac{[\mathbf{I}] \left([\mathbf{E}]_0 - [\mathbf{ES}] \right)}{[\mathbf{EI}]} - [\mathbf{I}]$$

 $K_i + [\mathbf{I}] = \frac{[\mathbf{I}]([\mathbf{E}]_0 - [\mathbf{ES}])}{[\mathbf{EI}]}$

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and finally
$$[EI] = \frac{[I]([E]_0 - [ES])}{K_i + [I]}$$
 (6.86)

The enzyme-substrace complex is very short lived, i.e., *transient*; hence we can apply the *steady state approximation*, and neglect the step $P + E \xrightarrow{k_{-2}} ES$. The equation is then

$$\begin{aligned} \frac{d[\text{ES}]}{dt} &= k_1[\text{E}][\text{S}] - k_{-1}[\text{ES}] - k_2[\text{ES}] = 0 \\ \Rightarrow & k_1 \left([\text{E}]_0 - [\text{ES}] - [\text{EI}] \right) [\text{S}] = (k_{-1} + k_2) [\text{ES}] \\ \Rightarrow & ([\text{E}]_0 - [\text{ES}] - [\text{EI}])[\text{S}] = \frac{(k_{-1} + k_2)}{k_1} [\text{ES}] = K_m [\text{ES}] \end{aligned}$$

Using the expression of [EI] from Eq. (6.86), we get

$$\Rightarrow \qquad [E]_0 [S] (K_i + [I]) - [ES] [S] (K_i + [I] - ([E]_0 - [ES]) [I] [S] \\ = K_m [ES] (K_i + [I])$$

$$\Rightarrow \qquad K_i [E]_0 [S] + [E]_0 [S] [I] - K_i [ES] [S] - [ES] [S] [I] - [E]_0 [H] [S] + [ES] [I] [S] \\ = K_m K_i [ES] + K_m [ES] [I]$$

$$\Rightarrow \qquad K_i [E]_0 [S] - K_i [ES] [S] = K_m K_i [ES] + K_m [ES] [I]$$

$$\Rightarrow \qquad K_i [E]_0 [S] = (K_m K_i + K_m [I] + K_i [S]) [ES]$$
and finally

$$[ES] = \frac{K_i [E]_0 [S]}{K_i [S] + K_m K_i + K_m [I]}$$
(6.87)

The rate of formation of the product is

$$v = k_2$$
 [ES]

and using the expression of [ES] from Eq. (6.87), we get

$$v = \frac{k_2 K_i [E]_0 [S]}{K_i [S] + K_m K_i + K_m [I]}$$
(6.88)

The maximum rate v_{max} is obtained when [S] is large enough, so that all the enzyme molecules are complexed; therefore, $v_{\text{max}} = k_2$ [E]₀. Equation (6.88) then changes to

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$$v = \frac{v_{\max} K_i [S]}{K_i [S] + K_m K_i + K_m [I]}$$
(6.89)

Note that this Eq. (6.89) is equivalent to Eq. (6.81), where λ/H^+ ion is the catalyst. Taking the inverse of Eq. (6.89), we find

$$\frac{1}{v} = \frac{K_i[S] + K_m K_i + K_m[I]}{v_{\max} K_i[S]} = \frac{K_i[S]}{v_{\max} K_i[S]} + \frac{K_m K_i}{v_{\max} K_i[S]} + \frac{K_m[I]}{v_{\max} K_i[S]}$$

 $\frac{1}{v} = \frac{1}{v_{\max}} + \frac{K_m}{v_{\max}[\mathbf{S}]} + \frac{K_m[\mathbf{I}]}{v_{\max} K_i[\mathbf{S}]}$

$$\Rightarrow \qquad \frac{1}{v} = \frac{1}{v_{\max}} \left(K_m + \frac{K_m[\mathbf{I}]}{K_i} \right) \frac{1}{[\mathbf{S}]} + \frac{1}{v_{\max}}$$
(6.90)

$$\frac{1}{v} = \frac{K_m}{v_{\text{max}}} \left(1 + \frac{[\text{I}]}{K_i} \right) \frac{1}{[\text{S}]} + \frac{1}{v_{\text{max}}}$$
(6.91)

Therefore, a plot of $\frac{1}{v}$ versus $\frac{1}{[S]}$ should be linear with slope $\frac{K_m}{V_{\text{max}}} \left(1 + \frac{[I]}{K_i}\right)$ and intercept

 $\frac{1}{v_{\text{max}}}$. For different concentrations of the inhibitor I, different straight lines will be obtained

but all with the same intercept on the ordinate whereas the slopes will be different; higher the concentration of the inhibitor, greater will be the slope. This has been confirmed experimentally. This is shown in Figure 6.16.



Figure 6.16 The Linewever-Burk plot of competitive enzyme inhibition at three different inhibitor concentrations.

6.36

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In a noncompetitive inhibition, the inhibitor does not bind to an active site; it binds at some other sites. This changes the conformation of the enzyme molecule, and therefore the binding of the substrate to the active sites becomes a hindered process.

The inhibition of urease by Ag^+ , Pb^{2+} or Hg^{2+} is due to the binding of these metal ions to the -SH groups on the enzyme. The following equilibria may be written as

$$E + I \rightleftharpoons EI$$
 (6.92)

$$\mathrm{ES} + \mathrm{I} \rightleftharpoons \mathrm{ESI} \tag{6.93}$$

where both the complexes EI and ESI are inactive to form the product. Let K_i (EI) and K_i (ESI) are the dissociation constants of the complexes EI and ESI, respectively. Following the same procedure as done in the previous section, it can be shown that

$$\frac{1}{v} = \frac{K_m}{v_{\text{max}}} \left(1 + \frac{[\text{I}]}{K_i} \right) \frac{1}{[\text{S}]} + \frac{1}{v_{\text{max}}} \left(1 + \frac{[\text{I}]}{K_i} \right)$$
(6.94)

Here, K_i represents the combined effects of both K_i (EI) and K_i (ESI). Therefore a plot of $\frac{1}{v}$

versus $\frac{1}{[S]}$ will be a straight line with slope $\frac{K_m}{v_{\max}} \left[1 + \frac{[I]}{K_i} \right]$ and intercept $\frac{1}{v_{\max}} \left[1 + \frac{[I]}{K_i} \right]$. Different inhibitor concentrations will give different straight lines but with the same intercept along the $\frac{1}{[S]}$ axis; we work it out as follows:

From Eq. (6.94), we may write

$$0 = \frac{K_m}{v_{\text{max}}} \left(1 + \frac{[\text{II}]}{K_i} \right) \frac{1}{[\text{S}]} + \frac{1}{v_{\text{max}}} \left(1 + \frac{[\text{II}]}{K_i} \right)$$

$$\Rightarrow \qquad \frac{K_m}{v_{\text{max}}} \left(1 + \frac{[\text{II}]}{K_i} \right) \frac{1}{[\text{S}]} = -\frac{1}{v_{\text{max}}} \left(1 + \frac{[\text{II}]}{K_i} \right)$$

$$\Rightarrow \qquad \frac{1}{[\text{S}]} = -\frac{1}{K_m}$$
(6.95)

This is shown in Figure 6.17; and this has been experimentally proved.

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Figure 6.17 The Lineweaver-Burk plot for a noncompetitive inhibition at three different [I].

6.9.3 Uncompetitive Inhibition

In this category, the inhibitor combines with the enzyme-substrate complex reversibly, and the combined complex is so much stable that it cannot form the expected product. If the complexes were not so strong then the situation would have been the noncompetitive inhibition. The formation if the ESI complex may be written as

$$\text{ES} + I \rightleftharpoons \text{ESI}$$
 (6.96)

and the equilibrium constant K is

$$K = \frac{[\text{ESI}]}{[\text{ES}][\text{I}]} \tag{6.97}$$

Following the same procedure as done earlier, it can be shown that

$$\frac{1}{v} = \frac{K_m}{v_{\text{max}}} \frac{1}{[S]} + \frac{1}{v_{\text{max}}} \left(1 + \frac{[I]}{K_i} \right)$$
(6.98)

According to Eq. (6.98), a plot of $\frac{1}{v}$ versus $\frac{1}{s}$ will be straight line with slope $\frac{K_m}{v_{\max}}$ and an intercept of $\frac{1}{v_{\max}} \left(1 + \frac{[I]}{K_i}\right)$. For a series of concentrations of the inhibitor a series of parallel lines with the same slope $\frac{K_m}{v_{\max}}$ will be obtained; the intercepts are also dependent on [I]. This is shown in Figure 6.18.



1/[S]

Figure 6.18 A Lineweaver-Burk plot for the case of uncompetitive inhibition at three concentrations of inhibitor.

Finally, the kinetics of enzyme-catalysed reactions may be more complex. Sometimes it may happen that the product forms a stable complex with the enzyme. The result is a decrease in the rate of the reaction due to: (i) some substrate is consumed and, (ii) the effective concentration of the enzyme is decreased.

6.10 HETEROGENEOUS CATALYSIS: REACTIONS ON SURFACE

Reaction between gases in the presence of solid surface is a very common kind, and most general catalytic processes are of this kind. The process is supposed to consist of five consecutive steps.

- 1. Diffusion of the reactant molecules towards the surface.
- 2. Adsorption of these molecules on the surface.
- 3. Reaction on the surface.
- 4. Desorption of the product molecules off the surface and
- 5. Diffusion of the desorbed products into the bulk of the gas.

Initially it was thought that the steps 1 and 5 are the slowest and therefore are rate determining. However, detailed study has shown that this could not be the case because heterogeneous catalytic processes involve appreciable activation energies, whereas diffusion in the gas phase requires no activation energy. Today, it is proved that one of the steps among 3, 4 and 5 could be the rate determining. However, since one cannot measure the rate of desorption, the step 3, i.e. *the reaction of the adsorbed reactant on the surface is considered to be the rate-determining step*. A comparison of the potential energy diagram of a simple heterogeneous reaction of a gas with the corresponding homogeneous process is given in Figure 6.19.



Figure 6.19 Potential-energy diagram for a reaction occurring homogeneously (solid curve) and heterogeneously (dashed curve).

6.10.1 A Single Reacting Gas

The scheme which is widely used to explain the reaction of a single reactant molecule R on the surface is

$$\mathbf{R}(\mathbf{g}) + - \overset{\mathbf{k}}{\mathbf{S}} - \overset{\mathbf{k}}{\underset{k_d}{\overset{\mathbf{k}}{\longrightarrow}}} - \overset{\mathbf{R}}{\mathbf{S}} - \overset{\mathbf{k}}{\underset{k_d}{\overset{\mathbf{k}}{\longrightarrow}}} \mathbf{P}(\mathbf{g}) + - \overset{\mathbf{k}}{\mathbf{S}} - \tag{6.99}$$

The Langmur adsorption is used to find the surface coverage of R on the surface, and it is assumed that the slow reaction of the adsorbed reactant does not disturb the adsorption equilibrium. Under this condition, the rate of the reaction is proportional to the surface coverage θ , i.e. $v = k_2 \theta$. In Chapter 4 we found θ to be given by Eq. (4.63b)

$$\theta = \frac{KP}{1 + KP}; \quad K = \frac{k_a}{k_d} \tag{6.100}$$

The rate of the reaction is therefore given by

$$v = \frac{k_2 K P}{1 + K P} \tag{6.101}$$

where *P* is the pressure of the overlying reactant at equilibrium. There are two limiting cases: (1) at sufficiently low pressure, when $KP \ll 1$

$$v = k_2 KP$$
; $v = kP$: (6.102)

We get a first-order kinetics. On the other hand, at extremely high pressure, when KP >> 1

$$v = k_2 \tag{6.103}$$

gives a zero-order kinetics. At the intermediate pressures, the order of the reaction n, is then between 0 and 1. The explanation to the change in order is as follows. At low pressure, the surface is only sparsely covered, and an increase in the pressure of the overlying reacting gas increases the surface coverage proportionately; this increases the rate linearly with pressure. When the pressure is very high, almost all the surface sites are occupied and therefore, a further increase in the pressure of the overlying reacting gas cannot change θ anymore and hence v. Examples include decomposition of NH₃ on electrically heated tungsten (Figure 6.20), decomposition of PH₃, AsH₃ on glass, etc.



Figure 6.20 The variation of the rate with change in the overlying gas pressure for a simple unimolecular process.

6.10.2 Inhibition

Inhibition is frequently encountered in heterogeneously catalysed processes. Sometimes a nonreacting gaseous substance I, or a product P gets adsorbed on the surface, thereby reducing the number of available active sites for the reactant molecules. This will inevitably reduce the rate of the reaction, which is then said to be inhibited. The nonreacting substance is an *inhibitor* or a *poison*. If θ be the surface coverage of the reactant molecules and P and P_i , respectively, are the partial pressure of the overlying reactant and I then θ is given as follows.

Competitive Adsorption

If two substances adsorb on the same surface, then regarding inhibition and the kinetics of surface reaction adsorbing two substances, the subject is of great importance. Let θ_A be the fraction of the sites occupied by molecules of type A, and θ_B be the same for the molecules of types B. The vacant fraction is $(1 - \theta_A - \theta_B)$. If both the adsorptions of A and B are nondissociative then the rates of adsorption of A and B are

$$v_{a(A)} = k_{a(A)} \left[A \right] \left(1 - \theta_A - \theta_B \right) \tag{a}$$

$$v_{a(B)} = k_{a(B)} \left[B \right] (1 - \theta_A - \theta_B) \tag{b}$$

The rate of desorptions are

$$v_{d(A)} = k_{d(A)} \theta_A \tag{c}$$

$$v_{d(B)} = k_{d(B)} \,\theta_B \tag{d}$$

At equilibrium, the rates of adsorption and desorption [Eqs. (a) and (c)] are equal; therefore, equating these two expressions, we get

$$v_{a(A)}\left[A\right]\left(1-\theta_{A}-\theta_{B}\right) = k_{d(A)} \theta_{A}$$
(e)

$$\frac{\theta_A}{1 - \theta_A - \theta_B} = \frac{k_{a(A)}}{k_{d(A)}} [A] = K_A [A]$$
(f)

where the equilibrium constant for the adsorption of *A* is $K_A = \frac{k_{a(A)}}{k_{d(A)}}$.

In the same way, equating Eq. (b) and (d), we find,

$$\frac{\theta_B}{1 - \theta_A - \theta_B} = K_B[B] = K_B = \frac{k_{a(B)}}{k_{d(B)}}$$
(g)

Solving the two simultaneous Eqs. (f) and (g), we get

$$\theta_A = \frac{K_A [A]}{1 + K_A [A] + K_B [B]} \tag{h}$$

and

 \Rightarrow

$$\theta_B = \frac{K_B[B]}{1 + K_A[A] + K_B[B]} \tag{i}$$

It is note worthy to see that, if either [B] = 0 or $K_B = 0$, which means that *B* is not adsorbed, then Eq. (h) goes to Eq. (4.63b), where [A] is replaced by the pressure *P*. Another interesting feature about Eqs. (h) and (i) is that, if the surface is predominantly adsorbed by *A* then the adsorption of the other component *B* is decreased, and vice-versa. The reason is that

the substances *A* and *B* are competing with each other for a limited number of active sites; hence it is called *competitive adsorption*.

$$\theta = \frac{KP}{1 + KP + K_I P_I} \tag{6.104}$$

..

where K and K_I are the adsorption-desorption equilibrium constants for the reactant and the inhibitor I. The rate of the reaction is therefore given by

$$v = \frac{k_2 KP}{1 + KP + K_1 P_1} \tag{6.105}$$

A simplest case may be as follows. If the pressure of the reactant is very low then

$$v = \frac{k_2 KP}{1 + K_{\rm I} P_{\rm I}} \tag{6.106}$$

and furthermore, if the inhibitor is strongly adsorbed then

$$v = \frac{k_2 K P}{K_{\rm I} P_{\rm I}} \tag{6.107}$$

The rate is then first-order with respect to the reactant concentration and inversely proportional to the partial pressure of the inhibitor. Exactly the same kinetics is followed when one of the products is adsorbed; $P_{\rm I}$ is then replaced by the partial pressure of the product. *P* and $P_{\rm I}$, respectively, which are the partial pressures of the overlying reactant and I. For example, Hinshelwood found that the decomposition of ammonia over platinum was inhibited by the hydrogen produced in the reaction and by externally added hydrogen; the rate law obtained is

$$v = \frac{kP_{\rm NH_3}}{P_{\rm H_2}}$$
(6.108)

6.10.3 Activation Energy

The constant k_2 and K in Eq. (6.101) vary with temperature as

From Arrhenius rate equation:
$$\frac{d \ln k_2}{dT} = \frac{E_2}{RT^2}$$
 (6.109)

From van't Hoff isochore:
$$\frac{d \ln K}{dT} = \frac{\Delta E_{ad}}{RT^2}$$
 (6.110)

Where E_2 is the activation energy of the step in which the adsorbed reactant reacts and $\Delta E_{\rm ad}$ is the heat of adsorption at constant volume. With these equations, the temperature dependence of the rate in Eq. (6.102) can be deduced at two limiting conditions.

6.43

In the low-pressure region, the rate constant of the reaction is given by

$$k = k_2 K \implies \frac{d \ln k}{dT} = \frac{d \ln k_2}{dT} + \frac{d \ln K}{dT}$$
$$\frac{d \ln k}{dT} = \frac{E_2}{RT^2} + \frac{\Delta E_{ad}}{RT^2} \qquad \text{[using Eq. (6.109) and (6.110)]}$$
$$\frac{d \ln k}{dT} = \frac{E_2 + \Delta E_{ad}}{RT^2} \qquad (6.111)$$

The activation energy of the reaction is then lowered by ΔE_{ad} from the true activation energy E_2 : $E = E_2 + \Delta E_{ad}$ (note that ΔE_{ad} is negative).

In the high-pressure region, the rate becomes zero-order and under this condition the rate constant of the reaction is k_2 , i.e.

$$k = k_2 \implies \frac{d\ln k}{dT} = \frac{d\ln k_2}{dT} \implies \frac{d\ln k}{dT} = \frac{E_2}{RT^2} \qquad \text{[using Eq. (6.109)]} \qquad (6.112)$$

At high pressure, the activation energy of the reaction is therefore E_2 . This is shown in Figure 6.21. The physical interpretation of these two results is exactly the same as discussed earlier.



Figure 6.21 Energy diagram for a unimolecular surface reaction. The difference ΔU° between the energy of R - S and R + S is always negative (adsorption is exothermic).

6.44

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6.10.4 Reaction between Two Adsorbed Molecules

 $v = k_2 \theta_A \theta_B$

Here the reaction takes place between two reactant molecules adsorbed on neighbouring sites:

$$A(g) + B(g) + - \overset{|}{S} \xrightarrow{=} \overset{|}{S} \xrightarrow{=} - S(A) \xrightarrow{=} S(B) \xrightarrow{k_2} P + - \overset{|}{S} \xrightarrow{=} \overset{|}{S} \xrightarrow{=} (6.113)$$

If θ_A and θ_B are the surface coverages of A and B, and if P_A and P_B are the partial pressures of A and B, respectively, in the overlying gas, then as shown in Eq. (6.104), θ_A and θ_B are given by

$$\theta_{A} = \frac{K_{A} P_{A}}{1 + K_{A} P_{A} + K_{B} P_{B}}; \text{ and } \theta_{B} = \frac{K_{B} P_{B}}{1 + K_{A} P_{A} + K_{B} P_{B}}$$

For the above reaction the rate is proportional to the product of θ_A and θ_B , i.e., the rate is

$$v = \frac{k_2 K_A K_B P_A P_B}{\left(1 + K_A P_A + K_B P_B\right)^2}$$
(6.114)

If the pressure of one reactant, say P_B , is held fixed and the other P_A is varied, then the rate initially increases, then forms a maximum and finally decreases. This is shown in Figure 6.22. The maximum of the curve corresponds to the situation, when maximum equal number of A and B molecules are adsorbed.



Figure 6.22 Biomolecular process occurring by a Langmuir-Hinshelwood model.

At extremely high pressure of A some adsorbed B molecules are replaced by A molecules, and since the reaction demands simultaneous existence of A and B molecules, the rate drops down. Two special cases can now be discussed

1. The surface coverage of both the reactants are low When the partial pressures of both A and B are sufficiently low, so that both $K_A P_A$ and $K_B P_B$ can be neglected in comparison to unity, Eq (6.114) changes to

$$v = k_2 K_A K_B P_A P_B \tag{6.115}$$
Under this condition, the rate is overall second-order, being first-order with respect to each of A and B. An example is the reaction between NO and O_2 over glass.

2. **One reactant in weakly adsorbed** If the reactant A is very weakly adsorbed, $K_A[A]$ in the denominator of Eq. (6.114) may be neglected, and the rate equation becomes

$$v = \frac{k_2 K_A K_B[A][B]}{(1 + K_B[B])^2}$$
; (where the partial pressure terms are replaced by molar concentration) (6.116)

Here, also the rate passes through a maximum as [B] increases; however, as long as the condition $K_A[A] \ll 1 + K_B[B]$ holds, the rate is proportional to [A].

A classic example of this kind of behaviour has been observed in the reaction between $\rm H_2$ and $\rm CO_2$ on Pt-surface.

If the reactant *B* is strongly adsorbed, while [A] is adsorbed weakly so that K_B [B] >> 1, Eq. (6.114) becomes

$$v = \frac{k_2 K_A[A]}{K_B[B]}$$
 (6.117)

The order of the reaction with respect to B is -1. Common examples are the reaction between CO and O₂ on quartz, and on platinum.

Example 6.4

Consider a surface catalysed bimolecular reaction between molecules A and B, which has a rate law of the form $v = k_3 \theta_A \theta_B$, where θ_A is the fraction of surface sites occupied by reactant A, and θ_B is the fraction of surface sites occupied by reactant B. The mechanism proposed is as follows

$$A(g) + - \overset{|}{S} - \underbrace{\overset{k_a(A)}{\overleftarrow{k_d(A)}}}_{k_d(A)} - \overset{A}{\overset{|}{S}} -$$
 (fast equilibrium) (10)

$$B(g) + -S - \underbrace{\stackrel{k_a(B)}{\longleftarrow}}_{k_d(B)} - \stackrel{B}{S} - \quad (fast equilibrium)$$
(11)

$$\overset{A}{\stackrel{|}{\overset{|}{}} =} \overset{B}{\stackrel{|}{}} \overset{B}{\overset{|}{}} \rightarrow \text{Product(s)}$$
(12)

If K_A and K_B are the equilibrium constants for reactions 10 and 11, respectively, derive expressions for θ_A and θ_B in terms of [A], [B], K_A and K_B . Finally, show that the rate law can be written as

$$v = \frac{k_3 K_A K_B[A][B]}{(1 + K_A[A] + K_B[B])^2}$$
(13)

Catalyst

Solution

At any instant, the fraction of the vacant surface sites is $(1 - \theta_A - \theta_B)$. From Eq. (10), equating the rate of adsorption and desorption at equilibrium

$$v_a(A) = k_a(A)[A](1 - \theta_A - \theta_B) \times \sigma_0 = v_{d(A)} = k_d(A) \theta_A \sigma_0$$
(14)

where σ_0 is the concentration of surface sites (active) in units of m⁻².

$$\Rightarrow \qquad \qquad k_d (A) \theta_A = k_a (A) [A] (1 - \theta_A - \theta_B)$$

 \Rightarrow

$$\frac{\theta_A}{(1-\theta_A-\theta_B)} = \frac{k_a(A)}{k_d(A)} [A] = K_A [A]$$
(15)

Similarly for *B*, $\frac{\theta_B}{1 - \theta_A - \theta_B} = K_B[B]$

$$\frac{\theta_B}{1 - \theta_A - \theta_B} = K_B[B] \tag{16}$$

Solving Eqs. (15) and (16) simultaneously, e.g. Eq. (16), we write

$$\begin{split} \frac{1-\theta_A-\theta_B}{\theta_B} &= \frac{1}{K_B[\mathrm{B}]} \Rightarrow \frac{1}{\theta_B} - \frac{\theta_A}{\theta_B} - 1 = \frac{1}{K_B[\mathrm{B}]} \\ \frac{1}{\theta_B} &= 1 + \frac{1}{K_B[\mathrm{B}]} + \frac{K_A[\mathrm{A}]}{K_B[\mathrm{B}]} = \frac{K_B[\mathrm{B}] + K_A[\mathrm{A}] + 1}{K_B[\mathrm{B}]} \\ \theta_B &= \frac{K_B[\mathrm{B}]}{1 + K_A[\mathrm{A}] + K_B[\mathrm{B}]}; \text{ and similarly} \end{split}$$

⇒

 \Rightarrow

$$\theta_{B} = \frac{K_{B}[B]}{1 + K_{A}[A] + K_{B}[B]}; \text{ and similarly}$$

$$\theta_{A} = \frac{K_{A}[A]}{1 + K_{A}[A] + K_{B}[B]}$$

$$(17)$$

Using these expressions for θ_A and θ_B in the rate law gives

$$v = \frac{k_3 K_A K_B[A][B]}{(1 + K_A[A] + K_B[B])^2}$$

Example 6.5

Consider the surface-catalysed bimolecular process in Example 6.4. If A(g) and B(g) do not compete for similar surface sites, but each molecule binds uniquely to different types of surface site, show that the rate law is given by

$$v = \frac{k_3 K_A K_B [A][B]}{(1 + K_A [A])(1 + K_B [B])}$$
(18)

(19)

Solution

In this case, *A* can adsorb only on its specific sites; similar is also for case *B*. The fraction of the sites available to *A* is $(1 - \theta_A)$ and that for *B* is $(1 - \theta_B)$.^{*} Equating the adsorption and desorption rates at equilibrium for both the species *A* and *B*, we have

and

 \Rightarrow

 $\begin{array}{c} k_a(A)[\mathbf{A}] \left(1 - \theta_A \right) = k_d(A) \; \theta_A \\ k_a(B)[\mathbf{B}] \left(1 - \theta_B \right) = k_d(B) \; \theta_B \end{array} \right)$

To solve for θ_A , we proceed as

and finally, $\theta_A = \frac{K_A[A]}{1 + K_A[A]}$; and similarly, $\theta_B = \frac{K_B[B]}{1 + K_B[B]}$

The rate law is

$$v = k_3 \,\theta_A \,\theta_B$$

Substituting θ_A and θ_B in the above equation, we get the final result

$$v = \frac{k_{3}K_{A}K_{B}[A][B]}{(1 + K_{A}[A]) \times (1 + K_{B}[B])}$$

6.11 LANGMUIR-HINSHELWOOD MECHANISM

A model for bimolecular reactions on a surface catalyst

The rate expression for the reaction between two gaseous reactants A and B, forming product(s) may be developed by assuming an irreversible adsorption of both A and B, bimolecular surface reaction

(i)
$$A + - \stackrel{i}{S} - \rightleftharpoons - \stackrel{i}{S} -$$
 (quasi-equilibrated adsorption of A)
(ii) $B + - \stackrel{i}{S} - \rightleftharpoons - \stackrel{i}{S} -$ (quasi-equilibrated adsorption of B)
(iii) $\frac{\stackrel{i}{-S} - + - \stackrel{i}{S} - + 2(-\stackrel{i}{S} -) - \stackrel{k_2}{\longrightarrow}}{A + B \longrightarrow Product(s)}$ (reaction on the surface; the rate-determining step)
(overall reaction)

^{*} Where θ_A and θ_B are, respectively, the fraction of the total number of sites occupied by A and B.

Catalyst

A and *B* to react on the catalyst surface, they have to be adsorbed first. Then there is an elementary step through which the adsorbed species react; this step is referred to as the *Langmuir-Hinshelwood* step. Let us understand the concept through a problem.

Example 6.6

The rate law for the oxidation reaction

$$2CO_2(g) + O_2(g) \longrightarrow 2CO_2(g)$$
(20)

is given by

$$v = \frac{k_3 \ b_{\rm CO} \ b_{\rm O_2}^{1/2} \ P_{\rm CO} \ P_{\rm O_2}^{1/2}}{\left(1 + \left(b_{\rm O_2} \ P_{\rm O_2}\right)^{1/2} + b_{\rm CO} \ P_{\rm CO}\right)^2} \tag{21}$$

Assuming that the reaction occurs by the *Langmuir-Hinshelwood model*, prove the above rate law. The overall rate law for this mechanism is

$$v = k_3 \theta_{\rm CO} \theta_{\rm O_2}$$

Also show that

$$\theta_{O_2} = \frac{(K_{O_2}[O_2])^{1/2}}{1 + (K_{O_2}[O_2])^{1/2} + K_{CO}[CO]}$$

 $\theta_{\rm CO} = \frac{K_{\rm CO}[{\rm CO}]}{1 + (K_{\rm O_2}[{\rm O_2}])^{1/2} + K_{\rm CO}[{\rm CO}]}$

and

Use these expressions and the relation
$$b_C = \frac{K_C}{kT}$$
 to obtain the rate expression (Assume ideal gas behaviour).

Solution The Langmuir-Hinshelwood mechanism for the reaction (20) is as follows:

- 1. $CO(g) \rightleftharpoons CO(ads)$ (fast-equilibrium)
- 2. $O_2(g) \rightleftharpoons 2 O(ads)$ (fast-equilibrium)
- 3. $CO(ads) + O(ads) \xrightarrow{k_3} CO_2(g)$

For the step (1), $k_a(\text{CO})[\text{CO}](1 - \theta_{\text{CO}} - \theta_{\text{O}_2}) = k_d(\text{CO})\theta_{\text{CO}}$ (22)

For the step (2), since two O atoms are produced

$$k_a(O_2)[O_2](1 - \theta_{CO} - \theta_{O_2})^2 \sigma_0^2 = k_d \theta_{O_2}^2 \sigma_0^2$$
(23)

A pictorial diagram of Eq. (23) may be as follows:

$$O_2(g) + - S - S - \stackrel{|}{\rightleftharpoons} - S - S - \stackrel{|}{\rightleftharpoons} - S - S - S - (S \text{ represent the surface atom}).$$

 σ_0 is the total number of surface sites (active).

Cancelling σ_0^2 from either side of Eq. (23), we get

$$k_a(O_2)[O_2](1 - \theta_{CO} - \theta_{O_2})^2 = k_d (CO) \theta_{O_2}^2$$
(24)

taking the square root on both sides of this equation,

$$[k_a(O_2)[O_2]]^{1/2} (1 - \theta_{CO} - \theta_{O_2}) = (k_d (O_2)^{1/2} \theta_{O_2}$$
(25)

Using the adsorption-desorption equilibrium constant as

$$K_{\rm CO} = \frac{k_a \,({\rm CO})}{k_d \,({\rm CO})}$$
 and, $K_{\rm O_2} = \frac{k_a \,({\rm O_2})}{k_d \,({\rm O_2})}$,

Equation (25) gives

$$\left(\frac{k_a(O_2)}{k_d(O_2)} \right)^{1/2} [O_2]^{1/2} = \frac{\theta_{O_2}}{1 - \theta_{CO} - \theta_{O_2}}$$

$$(K_{O_2}[O_2]^{1/2} = \frac{\theta_{O_2}}{1 - \theta_{CO} - \theta_{O_2}}$$

$$(26)$$

and,

 \Rightarrow

$$[CO] = \frac{\theta_{CO}}{1 - \theta_{CO} - \theta_{O_2}} \qquad [using Eq. (22)]$$
(27)

Adding Eqs. (26) and (27) with 1, we get

 $K_{\rm CO}$

1 10

$$1 + (K_{O_2}[O_2]^{1/2} + K_{CO}[CO] = 1 + \frac{\theta_{O_2}}{1 - \theta_{CO} - \theta_{O_2}} + \frac{\theta_{CO}}{1 - \theta_{CO} - \theta_{O_2}}$$

$$\Rightarrow 1 + (K_{O_2}[O_2])^{1/2} + K_{CO}[CO] = \frac{1 - \theta/CO - \theta/O_2 + \theta/O_2 - \theta/CO}{(1 - \theta_{CO} - \theta_{O_2})} = \frac{1}{(1 - \theta_{CO} - \theta_{O_2})}$$
(28)

From Eq. (26), $\theta_{O_2} = (K_{O_2}[O_2])^{1/2} (1 - \theta_{CO} - \theta_{O_2})$ and using Eqs. (25) and (28)

Catalyst

$$\theta_{O_2} = \frac{(K_{O_2}[O_2])^{1/2}}{1 + (K_{O_2}[O_2])^{1/2} + K_{CO}[CO]}$$
ame way,
$$\left\{ \text{QED} \right\}$$
(29)

and, in the same way,

$$\theta_{\rm CO} = \frac{K_{\rm CO}[\rm CO]}{1 + (K_{\rm O_2}[\rm O_2])^{1/2} + K_{\rm CO}[\rm CO]}$$
(30)

Substituting these results in the equation given

$$v = k_3 \ \theta_{\rm CO} \ \theta_{\rm CO_2} = \frac{k_3 \ K_{\rm CO} [\rm CO] \ K_{O_2}^{1/2} \ [\rm O_2]^{1/2}}{\left[1 + (K_{O_2} \ [\rm O_2])^{1/2} + K_{\rm CO} [\rm CO]\right]^2}$$
(31)

Since ideal gas behaviour is to be assumed for O_2 and CO, we may write

$$[O_2] = \frac{P_{O_2}}{k_B T}$$
 and $[CO] = \frac{P_{CO}}{k_B T}$ (k_B is the Boltzmann constant),

and since, $b_{\rm CO} = \frac{K_{\rm CO}}{k_B T}$ and $b_{\rm O_2} = \frac{K_{\rm O_2}}{k_B T}$, substituting these results in Eq. (31) changes to

$$v = \frac{k_3 K_{\rm CO} [\rm CO] K_{O_2}^{1/2} [O_2]^{1/2}}{(1 + K_{O_2}^{1/2} [O_2]^{1/2} + K_{\rm CO} [\rm CO])^2}$$

 \Rightarrow

$$= \frac{k_{3} b_{CO} (k_{B}T) P_{CO} b_{O_{2}}^{1/2} (k_{B}T)^{1/2} P_{O_{2}}^{1/2}}{(k_{B}T)^{1/2} \left(1 + b_{O_{2}}^{1/2} (k_{B}T)^{1/2} - \frac{P_{O_{2}}^{1/2}}{(k_{B}T)^{1/2}} + b_{CO} (k_{B}T) \frac{P_{CO}}{(k_{B}T)}\right)^{2}}$$

and finally,

v

$$v = \frac{k_3 \ b_{\rm CO} \ P_{\rm CO} \ b_{\rm O_2}^{1/2} \ P_{\rm O_2}^{1/2}}{(1 + b_{\rm O_2}^{1/2} P_{\rm O_2}^{1/2} + b_{\rm CO} \ P_{\rm CO})^2}; \ \rm QED^*$$
(23)

6.11.1 Rideal-Fley Mechanism: Another Model for bi-molecular Reactions on Surface Catalyst

A fairly rare elementary reaction between A and B, often called a Rideal-Eley step, occurs by direct reaction of gaseous B with adsorbed A according to the following sequence:

^{*} A Latin word: quod erat demonstrandum; That is what I wanted to prove, and I have proved it.



Normally, if reactions are able to proceed through either a Rideal-Eley step or a Langmuir-Hinshelwood step, the latter route is much more preferred due to the extremely short time scale (~picosecond) of a gas-surface collision. The Rideal-Eley step can however become important at extreme conditions.

One of the classical examples of Rideal-Eley mechanism is the oxidation of CO to CO_2 , which occurs by three steps

1.
$$O_2(g) \rightleftharpoons 2O \text{ (ads)}$$

2.
$$CO(g) \rightleftharpoons CO (ads)$$

3. $CO(g) + O(ads) \xrightarrow{k_3} CO_2(g)$; or 2CO(g) + 2O(ads)

Although, both CO(g) and $O_2(g)$ adsorb on the surface, the reaction does not occur between the adsorbed reactants. In the Rideal-Eley model, the $O_2(g)$ chemisorbs dissociatively on the surface. Then, there is a subsequent collision between a CO(g) molecule and an adsorbed O-atom to generate $CO_2(g)$. Effectively a CO(g) molecule captures an O atom from the surface.

If we assume ideal gas behaviour, then the first two steps are in fast equilibrium during the course of the reaction and, the 3rd-step is the rate determining. The rate law is now evaluated as

The rate law for the oxidation reaction $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$; assuming that the reaction occurs by the Rideal-Eley model, the overall rate law is

$$v = k_3 \theta_{O_2}$$
 [CO]

The step of the mechanism for the adsorption of O_2 is the same as that discussed in Example 6.5. Therefore,

$$\theta_{\rm O_2} = \frac{(k_2[{\rm O_2}])^{1/2}}{1 + (K_{\rm O_2}[{\rm O_2}])^{1/2} + K_{\rm CO} [\rm CO]}$$

Assuming ideal behaviour, $[O_2] = \frac{P_{O_2}}{k_B T}$; $[CO] = \frac{P_{CO}}{k_B T}$; $b_{CO} = \frac{K_{CO}}{k_B T}$ and $b_{O_2} = \frac{k_{O_2}}{k_B T}$.

Substituting this θ_{O_2} in the above equation one gets the final expression of v;

$$v = k_3 \frac{(k_2[O_2])^{1/2}[CO]}{\left[1 + (K_{O_2}[O_2])^{1/2} + K_{CO}[CO]\right]}$$
(24)

6.11.2 Negative Catalysis and Inhibition

When a substance is able to decrease the rate of a reaction, it is said to be a **negative catalyst or an inhibitor**. For example, the oxidation of sodium sulfite solution by oxygen gas is inhibited by small amounts of mannitol, benzyl alcohol, aniline, benzaldehyde and certain alkaloids, particularly brucine. The explanation first proposed to account for inhibition was that the inhibitor combined with and so removed a positive catalyst already present. A Titoff showed that a very minute concentration of cupric ions was able to catalyse the reaction between sulfite solution and oxygen, and the effect of the positive catalyst could be counteracted by the addition of mannitol or cyanide ions; these act as inhibitors.

We have seen that in a reaction between two gases on a surface, if one component is strongly adsorbed, then it would reduce the reaction rate. The strongly adsorbed component inhibits the reaction.

There are also examples where the product is also adsorbed on the surface of the catalyst. We then have a competitive adsorption between the reactant and the product for the active sites on the surface. In the dissociation of NH_3 on platinum surface: $2NH_3 \rightarrow N_2 + 3H_2$, there is a keen rivalry between NH_3 and H_2 ; the latter being strong by adsorbed. The kinetic equation is then given by

$$-\frac{dP}{dt} = k \frac{P_{\rm NH_3}}{P_{\rm H_2}}$$

Foreign substances may also inhibit a reaction. These are called **poisons**. Generally the poisons are adsorbed on the active sites of the surface, retarding the reaction, for it could have been effective in bringing about the reaction. Moreover, a poison may form definite chemical compounds with the atoms of the catalyst. For example, minute quantities of As destroy the catalytic activity of Pt, by forming platinum arsenide at the surface in the manufacture of H_2SO_4 .

6.11.3 Induced Reactions

Sodium sulphite is spontaneously oxidized in air, but sodium arsenite is not. However, a mixture of a sodium sulphite and sodium arsenite, when kept in air, both of them are found to be oxidised. These are called **induced reactions**.

6.11.4 Promoters

The catalytic effect of a mixture is often greater than the sum of the separate effects of the constituents. In the extreme case, a small quantity of a material, which itself is noncatalytic on a feeble catalyst, is able to increase appreciably the activity of a given catalyst. Such a substance is called a promoter. For example, in the combination of N_2 and H_2 the catalyst is iron, promoted by the addition of small amounts of potassium and aluminium oxides.

6.11.5 Catalysis in Industry

A number of industrial preparations depend on catalytic reactions. To mention a few, we may give the examples of the production of H_2 , NH_3 , H_2SO_4 , HNO_3 , synthetic liquid fuels, cracking of petroleum, polymers, hydrogenated oils, etc. Enzymes are used in the production of wine, vinegar, curd, cheese, etc. Sodium benzoate is used as a food preservative; barbituric acid preserves H_2O_2 . As anti-knocks, lead tetraethyl is used in motor fuels.

PROBLEMS

- 6.1 What is meant by catalysis? Discuss the general characteristics of a catalyst.
- **6.2** Differentiate between homogeneous and heterogeneous catalysis. Explain the following on the basis of heterogeneous catalysis:
 - (i) Active centers; (ii) specificity of a catalyst; (iii) the action of catalytic poisons;(iv) the action of promoters; (v) the activity of finely divided catalyst.
- **6.3** Select the correct statements from the following for a catalysed reaction.
 - (i) The use of a catalyst provides an alternative path of lower activation energy.
 - (ii) The catalyst does not change the position of equilibrium.
 - (iii) The equilibrium position is attained earlier.
 - (iv) An enzyme has an optimum temperature at which its catalytic action is maximum.
 - $\left(v\right)$ $% \left(v\right)$ The use of a catalyst changes the rate constant of the reaction.
 - (vi) The catalyst remains unchanged at the end of the reaction. It may, however, undergo a change in its physical state [True statements: (i), (ii), (iv), (vi)]
- **6.4** When oxalic acid is added to an acidified solution of $KMnO_4$, no appreciable decolourization occurs for a long period of time. But once decolourization occurs, it proceeds rapidly.

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 $1 Langmuir = 10^{-6} Torr s 4.53$

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