PREFACE

In a bid to standardize higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. *core, discipline specific, generic elective, ability and skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit tranafer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry their acquired credits. I am happy to note that the University has been recently accredited by National Assessment and Accreditation Council of India (NAAC) with grade "A".

UGC (Open and Distance Learning Programmes and Online Programmes) Regulations, 2020 have mandated compliance with CBCS for U. G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the six semesters of the Programme.

Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English/Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

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Netaji Subhas Open University

Under Graduate Degree Programme
Choice Based Credit System (CBCS)
Subject : Honours in Chemistry (HCH)
Course : Physical Chemistry–II
Course Code : CC-CH-10

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(HCH)

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Physical Chemistry-II

Unit - 1 ❑ Application of Thermodynamics – I

Structure

1.1 Objective

On completion of this unit, the learner will be able to

- Define chemical potential and relate it to Gibbs free energy and other thermodynamic state functions

- Comprehend partial molar properties and their variations with different parameters
- Explain the variation of thermodynamic functions for systems with variable composition
- Explain the variation of chemical potential (μ) with temperature and pressure
- Derive the Gibbs-Duhem equation and explain the changes of thermodynamic parameters in binary mixtures
- Interpret the concept of standard states and chemical potential of pure solids and pure liquids
- Explain the fundamentals of chemical equilibrium and derive vant-Hoff's reaction isotherm.
- Define equilibrium constants in terms of concentration and pressure, establish their relationship with free energy and explain changes in equilibrium due to change in external conditions,
- Understand and apply Le Chatelier's principle and Nernst distribution law.

1.2 Introduction

Thermodynamics is the study of heat (energy) and work. Thermodynamics studies the interconversion of heat and work in a system and its surroundings. The term "thermodynamics" was first coined by William Thomson who was later known as Lord Kelvin. Thermodynamics is studied across all the branches of science and engineering. In chemistry, we are concerned about the energy changes happening during physical and chemical transformations. Thus, thermodynamics paves the way for us to understand and control chemical changes. We also use thermodynamics to understand the level of organization and disorganization happening during the changes. Thermodynamics is a powerful tool for chemists.

In previous course units you have already been in introduced to the basic concepts of thermodynamics such as systems, surroundings, reversible and irreversible processes, state and path functions, isothermal and adiabatic processes etc. The first, second and the third law of thermodynamics were also introduced. You have also learned that whether a chemical change or physical transformation will happen depends on enthalpy and entropy, and we can understand the spontaneity of a process from free energy calculations which is a combination of enthalpy and entropy. Most of the discussions in the introduction to thermodynamics were based on processes happening in closed or isolated systems. The basic or the fundamentals of thermodynamics are also applicable to open systems where exchange of both mass and energy with surroundings is allowed. Open systems are most common in nature. Living beings including humans are examples of such system. We continuously exchange mass and energy with our surroundings. In most cases, chemical reactions are performed in open systems. Solutions are another common example of open systems.So it is important to discuss the thermodynamics of open systems. The most important consideration in this case is the exchange of matter. In this unit, we will learn how fundamentals of thermodynamics is applied to open systems and how chemical processes are described using thermodynamics.

1.3 Chemical Potential

J. Willard Gibbs introduced chemical potential in his famous paper, "On the Equilibrium of Heterogeneous Substances," published in two parts, in 1876 and 1878. He denoted a system's energy and entropy by lower-case Greek letters ε and η respectively. Hence presumably he chose the letter μ to provide a mnemonic for a derivative with respect to mass. Early in the paper, Gibbs called his derivative merely the "potential". Later, he found it necessary to distinguish his derivative from the electric and gravitational potentials.He introduced the term "intrinsic potential" for a derivative that is "entirely determined at any point in a mass by the nature and state of the mass about that point. Nowhere in his major paper does Gibbs use the term "chemical potential". That coinage seems to be introduced by Wilder D. Bancroft, a Ph.D. student of Wilhelm Ostwald. Here we will discuss the thermodynamic aspects of the chemical potential.

1.3.1 Chemical Potential and Gibbs Free Energy

We have studied systems in **Material Equilibrium**. Material equilibrium means that the number of components present in each phase remains the same. Material equilibrium generally occurs in isolated and closed systems. Along with material equilibrium, there can be thermal and mechanical equilibrium. Two physical systems are in **thermal equilibrium** if there is no net flow of thermal energy between them when they are connected by a path permeable to heat. A system is said to be in thermal equilibrium with itself if the temperature within the system is spatially uniform and temporally constant. A **mechanical equilibrium** exists when all the mechanical forces within a system are balanced so that there is no net acceleration. We have learned about thermodynamic properties and their changes for systems in equilibrium. Now let us consider a system which is in thermal and mechanical equilibrium but not in material equilibrium. These types of situation are very common in irreversible chemical reactions or in case of material transport between different phases.

Consider a system consisting of one phase only, which is in thermal and mechanical equilibrium but not in material equilibrium. Here, exchange of material with surroundings is allowed and composition of the system is variable. From now on we will refer to such systems as **nonequilibrium systems**. But since the system is in thermal and mechanical equilibrium, variables such as pressure, temperature etc. are well defined in it. In other words, the P-V work and changes are valid in this system and we can write thermodynamic variables as functions of pressure, temperature. The new consideration in this case is that we need to take into account variation of composition of the system. Suppose, the system is composed of a total of k components in one phase. The number of moles of each of the components is denoted by n_i (i = 1, 2, 3....k). So, the number of moles of component 1 is n_1, for component 2 is n_2, for component 3 is n_3 and so on. At any instant during a chemical process, we can express the Gibbs free energy of the system as a function of pressure (P), temperature (T) and the concentration of components of the system as $\mathbf{G = G\ (T, P, n_1, n_2......n_k)}$. We have an open system; matter can be transported in and out of the system. Suppose, an irreversible chemical reaction or irreversible transport of matter into the system takes place. Due to this process, P, T and n'_is changes by infinitesimal amounts dP, dT and $dn_1....dn_k$. We need to know the Gibbs free energy change for this process. Remember from your earlier thermodynamic knowledge that **Gibbs free energy (G) is a state function**. A state function only depends on the initial and final states of the system and does not depend on whether the process occurs reversibly or irreversibly. It also means that while calculating the change in Gibbs free energy for an irreversible process, we can treat the process as reversible and end up getting the same value. Here, we can consider the process as reversible, where one or more component of the system change(s) infinitesimally and as a consequence, the pressure and temperature change. The outcome of this idea is that we can use partial derivatives for this process. So the change in Gibbs free energy for the process may be written as

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_j \neq 1} dn_1$$

$$+ \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_j \neq 2} dn_2 + \cdots + \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_j \neq k} dn_k \ (1.1)$$

Here, the convention should be indicated and understood. The subscript n_i on a partial derivative means i^{th} molar concentration is constant i.e. the concentration of each component is constant. For example, in the first term in the right-hand side of the equation $\left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT$, pressure and all molar concentrations are kept constant. The subscript $n_{j \neq 1}$ on a partial derivative means that all molar concentrations except n_1 are kept constant. So, in future when we encounter a subscript to a partial derivative which says $n_{j \neq i}$, it will imply that the molar concentrations of all components except the ith component n_i are kept constant.

Now, recall that for a reversible process where only pressure-volume work is performed and no change of composition occurs, the change in Gibbs free energy is written as

$$dG = -SdT + VdP \ \ldots\ldots(1.2)$$

Here, S is entropy and V is volume. Now comparing equation 1.2 with 1.1 we can write $\left(\frac{\partial G}{\partial T}\right)_{P,n_i} = -S$ and $\left(\frac{\partial G}{\partial T}\right)_{P,n_i} = V$. Remember that the subscript n_i denotes constant composition. Using these two equalities in equation 1.1 give us

$$dG = -SdT + VdP + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}} dn_i \ \ldots\ldots(1.3)$$

This equation gives the fundamental idea of free energy change in an open system. The last term in the equation is the variation of Gibbs free energy with the change in concentration of i^{th} component in the mixture keeping temperature, pressure and concentration of other components fixed. This term is known as the **chemical potential** (μ) and is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad ......(1.4)$$

Chemical potential can also be defined as the slope of a plot of Gibbs energy against the amount of the ith component, with the pressure, temperature, and the amounts of the other substances held constant. Chemical potential can be called partial molar Gibbs free energy. Defining chemical potential converts equation 1.3 to the following

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad ......(1.5)$$

Equation 1.5 is extremely important in thermodynamics, as we will see in further discussions that this equation is used to explain chemical reactions, solutions and many other chemical phenomena.

1.3.2 Chemical Potential and Other Thermodynamic State Functions

Chemical potential can be related to thermodynamic state functions such as internal energy (U), Helmholtz free energy (A) and enthalpy. In each case, we can derive the relation starting from definition of the individual terms and using the methodology discussed in the last section. However, since we have already defined chemical potential in terms of Gibbs free energy, we can arrive at the individual relations from that. Let us first obtain the equation for internal energy (U). We know that G = U + PV – TS and therefore dG = dU + PdV + VdP – TdS – SdT. We can replace dG from equation 1.5, and obtain the equation

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad ......(1.6)$$

Similarly for Helmholtz free energy (A), we know A = U – TS and so dA = dU –TdS – SdT. Replacing the value of dU from equation 1.6, we arrive at the equation

$$dA = -SdT - PdV + \sum_i \mu_i dn_i \quad ......(1.7)$$

We further extend the idea to enthalpy (H), which is related to the internal energy via the equation H = U + PV. Henced H = dU + PdV + VdP. Using equation 1.6, we get

$$dH = TdS + VdP + \sum_i \mu_i dn_i \quad ......(1.8)$$

Equation 1.6, 1.7 and 1.8 are extensions of Gibbs equation 1.5 to processes involving exchange of matter with the surroundings or irreversible composition changes. The independent variables on the right side of each of these equations are natural variables of the corresponding thermodynamic potentials. In each of the equation from 1.5 to 1.8, the first two terms incorporate thermal and mechanical properties/ processes in the system, and the extra $\Sigma_i \mu_i dn_i$ term allows for the effect of composition change on the state functions. Gibbs himself termed these four equations (i.e. equation 1.5 – 1.8) as the **fundamental equations of thermodynamics**. We can now define chemical potential in terms of each of these state functions based on the fundamental equations. In each of the expression of chemical potential, the natural variables for that particular state function will be kept constant. The partial derivatives defining chemical potential are

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} \quad ......(1.9)$$

1.3.3 Features of Chemical Potential

Here a few points will be mentioned which are some of the characteristics of chemical potential.

(i) Chemical potential μ_i (T, P, n_i) is an intensive variable.

(ii) Chemical potential is a function of number of moles of all the components already present in the system.

(iii) By definition, chemical potential is the work to be done to add the substance per mole, in a system of given composition.

(iv) For pure substances, chemical potential is equal to free energy per mole i.e. $\mu_i = \overline{G_{P,T}}$.

(v) Chemical potential is the tendency of a substance to react with other substances, to transform into another state, to redistribute in space. The numerical value of μ is the magnitude of this tendency.

(vi) At equilibrium, chemical potential of a species is the same everywhere in the system. This point can be proved very easily in the following manner.

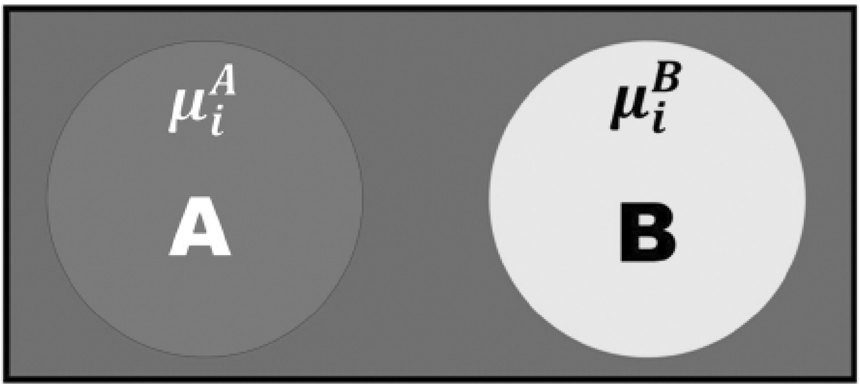


Figure 1.1: Schematic Representation of a Thermodynamic System

Suppose in figure 1.1, the box represents our system. The circles A and B represent two areas within the system. Let us transfer dn_i amount of substance i from A to B. The chemical potentials of the substances in A and B have been designated as μ_i^A and μ_i^B. Now total change of Gibbs free energy of the system will be

$$dG = dG^A + dG^B = \mu_i^A(-dn_i) + \mu_i^B(dn_i) = (\mu_i^B - \mu_i^A)\,dn_i \quad ......(1.10)$$

In equation 1.10, if $\mu_i^B > \mu_i^A$, then $dG > 0$ which signifies that the process is non-spontaneous and if $\mu_i^B < \mu_i^A$ then $dG < 0$ which means the process is spontaneous. So substance i flows from a region with higher chemical potential to a region with lower chemical potential and the opposite process is not possible. This flow will remain spontaneous until $dG = 0$ i.e. until $\mu_i^A = \mu_i^B$ which means the system attains equilibrium when chemical potential becomes the same everywhere in the system.

1.4 Partial Molar Quantities

In case of open systems, we learned that not only work and heat but matter is also exchanged with surroundings. So, in a multicomponent open system, the amounts of various components are treated like variables in a thermodynamic system. Some thermodynamic properties like entropy, enthalpy, internal energy, etc. are known as extensive properties, because their values change by varying mass of the system. In case of open systems, the extensive property must be function of number of moles of various components of the system, in addition to temperature and pressure of the system.

1.4.1 Expression of Partial Molar Quantities

In general, the partial derivative of a thermodynamic function Y with respect to the amount of component i of a mixture – when T, P and amounts of other constituents of the system are kept constant – is known as the partial molar quantity of the ith component. So if Y is any extensive property of a system/solution, the corresponding partial molar property $\overline{Y}_i$ of the component i of the mixture is defined as

$$\overline{Y}_i = \left(\frac{\partial Y}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad ......(1.11)$$

Thus, the partial molar quantity can be defined as the change in Y when 1 mole of component i is added to the system which is so large that this addition has a negligible effect on the composition of the system. The quantity $\overline{Y}_i$ represents the actual value of Y per mole of the ith component of the system. This value may be the same or different from the actual molar value of Y in its pure state. These two values i.e., partial molar value and actual molar value of a substance are the same only in case of an ideal system. In case of non-ideal systems, these two values are different because of interactions between the constituents, i.e. actual molar value gets modified to partial molar value. This partial molar value may not be the same throughout the whole system since the extent of interactions vary according to the amount of the constituents in the system. Hence the partial molar value is dependent on the composition of the system. Therefore, the partial molar quantities are meant for the individual components of the system, but their values are not only dependent on the nature of the particular component in consideration but also on the nature and amounts of the other components of the system.

1.4.2 Partial Molar Volume

Of all the extensive thermodynamic properties, volume is the easiest to visualize. Thus, partial molar volume of a substance (say ith component) in a mixture is the change in volume per mole of substance 'i' added to a large volume of the mixture. It is expressed as

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad ......(1.12)$$

Here, V is the total volume of the solution/system. In case of an ideal solution, the partial molar volume of the i-th component will be equal to its molar volume in the pure state, whereas in the case of non-ideal solution the partial molar volume is the molar volume actually occupied by the substance in a solution of known composition. The volume of a pure substance i is $V_i^* = n_i V_{m,i}^*$ i.e. its molar volume $V_{m,i}^*$ multiplied by the number of moles of pure substance. Now pure substance means the substance is not present in any mixture. However, if we take the pure substance as a special case of solution within itself (for example we can consider pure water as a solution of water in water) then we can define the partial molar volume and as a consequence

$$\bar{V}_i^* = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial V_i^*}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left\{\frac{\partial}{\partial n}\left(n_i V_{m,i}^*\right)\right\}_{T,P,n_{j\neq i}} = V_{m,i}^* \quad ......(1.13)$$

Equation 1.13 clearly shows that the partial volume of a pure substance is equal to its molar volume.

Relation between Solution Volume and Partial Molar Volume

We now find an expression for total volume V of the solution. V depends on temperature, pressure and the mole numbers of the components present. For fixed values of T, P and mole fraction of the components x_i we can write solution volume as $V = nf(T, P, x_1, x_2......)$. Here $n = \Sigma n_i$ that is the sum of all the mole numbers.

$$V = \sum_i n_i \bar{V}_i \quad ......(1.14)$$

For a system having two components, the equation is

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \quad ......(1.15)$$

If the solution is ideal then the partial volumes are the molar volumes of the pure components. This equation is applicable to real solutions also and it can reveal interactions present among the components of a real solution. Let us take two examples. Benzene and toluene form an (almost) ideal solution. The volume of 1 mole pure benzene is 88.9 ml and the same for toluene is 106.4 ml. According to equation 1.15, when 1 mol benzene is mixed with 1 mole toluene, the volume of the solution should be 88.9 ml + 106.4 ml = 195.3 ml. The experiment will also validate this prediction because the solution is ideal. But for real solutions we need the partial molar volumes. For example, water and ethanol does not form an ideal solution. The volume of 1 mole pure ethanol and pure water is 58 ml and 18 ml respectively. If we mix 1 mol water and 1 mol ethanol, we expect the volume to be 58 ml + 18 ml = 76 ml. But the actual volume is 74.3 ml. Clearly, partial molar volume in this case does not correspond to the molar volume of the pure components. Now when we mix 1 mole of each substance, the final mole fraction of water and ethanol in the solution becomes 0.5 each. When the mole fraction is 0.5, the partial molar volumes of ethanol and water are 57.4 ml and 16.9 ml. Using this, we calculate the total volume of the solution = (1 mole ethanol) × (57.4 ml/mol) + (1 mole water) × (16.9 ml/mol) = 74.3 ml which is exactly what is observed.

1.4.3 Other Partial Molar Quantities

What we learned for volume can be applied to any extensive property in solution. For example, the **partial molar internal energy** $\bar{U}_i$ of component i in a solution is defined as

$$\bar{U}_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad ......(1.16)$$

We can find the total internal energy of the system exactly in the same way we did for volume that is $U = \Sigma_i n_i \bar{U}_i$. We can also define the **partial molar Gibbs free energy, partial molar Helmholtz free energy, partial molar enthalpy**, partial molar enthalpy in a similar way.

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i \quad ......(1.17)$$

$$\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad ......(1.19)$$

$$\bar{A}_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad ......(1.18)$$

$$\bar{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad ......(1.20)$$

As we can see in equation 1.17, partial molar Gibbs free energy is chemical potential as we have discussed in the previous section. But let us not confuse partial molar internal energy or partial molar enthalpy with the definition of chemical potential in terms of internal energy or enthalpy. Please note that in case of partial molar quantities the constants are temperature and pressure always.

1.4.4 Variation of Chemical Potential (μ) with Temperature and Pressure

Variation of chemical potential with pressure and temperature can be established from the relations between partial molar quantities. For most of the thermodynamic relations between extensive properties of a homogeneous system, there are corresponding relations involving partial molar quantities of the same extensive variable. For instance, we know that G = H − TS. Now if we differentiate with respect to n_i at constant T, P, $n_{j\neq i}$ then we will get

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad ......(1.21)$$

Now using the definitions given in equation 1.17 to 1.20, we get

$$\mu_i = \bar{G}_i = \bar{H}_i - T\bar{S}_i \quad ......(1.22)$$

Equation 1.22 is another expression for chemical potential of a component in a solution. While deriving equation 1.3, we have learned that $\left(\frac{\partial G}{\partial T}\right)_{P,n_i} = -S$ Partial differentiation of this equation with respect to n_i gives

$$-\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial T}\right)_{P,n_j}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}\right)_{P,n_j} \quad ......(1.23)$$

Here we have used the relation $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$. Using the definitions given in equation 1.17 and 1.20 in equation 1.23 we can write

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j} = \left(\frac{\partial \bar{G}_i}{\partial T}\right)_{P,n_j} = -\bar{S}_i \quad ......(1.24)$$

Similarly, we have learned that $\left(\frac{\partial G}{\partial P}\right)_{T,n_j}$ = V and partial differentiation of this equation with n_i gives us

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j} = \left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,n_j} = \bar{V}_i \quad ......(1.25)$$

One important point is to be mentioned here about use of subscript n_j instead of subscript $n_{j\neq i}$. In equation 1.24 and 1.25 subscript n_j means all the mole numbers of all the components are held constant. However sometimes n_j is not written while writing the equation. Equation 1.24 and 1.25 leads us to the fact that partial molar volume and entropy can also be known from chemical potential which is one more significance of the term.

1.5 The Gibbs-Duhem Equation

In thermodynamics, the Gibbs–Duhem equation describes the relationship between changes in chemical potential for components in a system. This equation shows that in thermodynamics, intensive properties are not independent but are interrelated, making it a mathematical statement of the state postulate. The equation is extremely important in the study of solutions. However it cannot be used for very small thermodynamic systems due to the influence of surface effects and other microscopic phenomena.The equation is named after Josiah Willard Gibbs and Pierre Duhem. The derivation of the equation is straightforward. It starts from the idea of the partial derivatives. While discussing partial molar properties, we have found that equation 1.14 can be written for other extensive variables such as internal energy, Gibbs free energy etc. Moreover, we have learned that chemical potential is the partial molar Gibbs free energy. Combining these two facts, especially for total Gibbs free energy G of a system, we can write

$$G = \sum_i n_i \mu_i \quad ......(1.26)$$

Taking the derivative of the both sides of equation 1.26 yields

$$dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \quad ......(1.27)$$

Previously, in equation 1.5, we have seen that Gibbs free energy can also be expressed as $dG = -SdT + VdP + \Sigma_i\mu_i dn_i$. So equation 1.27 and equation 1.5 must be the same. Setting these two equations equal to each other and cancelling the common terms we get

$$\sum_i n_i d\mu_i = VdP - SdT \quad ......(1.28)$$

This is more generalized form of Gibbs-Duhem equation. For a system at constant pressure and temperature the right-hand side of equation 1.28 becomes zero which means

$$\sum_i n_i d\mu_i = 0 \quad ......(1.29)$$

This is Gibbs-Duhem equation for a system in constant pressure (isobar) and temperature (isothermal). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium. This form of the equation is particularly useful in case of binary systems or binary mixtures. Suppose a system consists of two components A and B. So for this system at constant P and T we can write

$$n_A d\mu_A + n_B d\mu_B = 0 \quad ......(1.30)$$

We can derive the Gibbs-Duhem equation for multicomponent system in terms of mole fraction of each of the components with the help of more mathematical understanding.

1.6 Chemical Potential of an Ideal Gas

In this section we will derive the chemical potential of an ideal gas. But first we need to understand the **chemical potential of a pure substance**. It was briefly mentioned while discussing the definition of chemical potential in section 1.3. Ideal gases are pure substances. A pure substance contains only one type of matter. So, the chemical potential of a pure substance is defined as

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} \quad ......(1.31)$$

Here, we don't need to incorporate the subscript "i" since only one component is present. n is the number of moles of the pure substance. This equation describes how the Gibbs free energy of a system changes as the pure substance is added to it. For a pure substance, the Gibbs free energy is given by G = n × G_m where G_m is the molar Gibbs free energy. This is also designated as $\bar{G}$. Thus, the chemical potential of a pure substance is simply G_m since

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial (nG_m)}{\partial n}\right)_{T.P} = G_m \quad ......(1.32)$$

Let us now derive an expression of G_m for a perfect gas (pure substance) at a pressure P. We know that the fundamental equation of thermodynamics for a pure substance is given by dG = – SdT + VdP. So at constant temperature dG = VdP.

For n moles of an ideal gas PV = nRT. Thus, we can write dG = $\frac{nRT}{P}$ dP. Now for a change of pressure from P° = 1 atm to a pressure of P atm, the Gibbs free change is given by

$$\Delta G = G(P) - G(P^\circ) = nRT \int_{P^\circ}^{P} \frac{dP}{P} = nRT\, \ell n \left(\frac{P}{P^\circ}\right) \quad ......(1.33)$$

Thus, for one mole of an ideal gas (n = 1), the molar Gibbs free energy at pressure P atm is

$$G_m = G^\circ{}_m + RT\, \ell n \left(\frac{P}{P^\circ}\right) \quad ......(1.34)$$

In the above equation, G°_m is the molar Gibbs free energy at the standard state. Similarly in terms of chemical potential

$$\mu = \mu^\circ + RT\, \ell n \left(\frac{P}{P^\circ}\right) \quad ......(1.35)$$

Here, μ° is the chemical potential at the standard state.

Concept of Standard State

In chemistry, the standard state of a material (pure substance, mixture or solution) is a reference point used to calculate its properties under different conditions.

A superscript circle is used to designate a thermodynamic quantity in the standard state, such as change in enthalpy (ΔH°), change in entropy (ΔS°), or change in Gibbs free energy (ΔG°). It is also denoted by a symbol $\ominus$ in the subscript. In principle, the choice of standard state is arbitrary, although the International Union of Pure and Applied Chemistry (IUPAC) recommends a conventional set of standard states for general use. The standard state is defined at pressure 1 atm. Strictly speaking, temperature is not part of standard state definition but it is recommended that 298.15 K (25.00 °C; 77.00 °F) should be used. Many standard states are non-physical states, often referred to as "hypothetical states". Nevertheless, their thermodynamic properties are well-defined, usually by an extrapolation from some limiting condition, such as zero pressure or zero concentration, to a specified condition (usually unit concentration or pressure) using an ideal extrapolating function, such as ideal solution or ideal gas behavior, or by empirical measurements.The standard state for a gas is the hypothetical state it would have as a pure substance obeying the ideal gas equation at standard pressure (1 atm). No real gas has perfectly ideal behavior, but this definition of the standard state allows corrections for non-ideality to be made consistently for all the different gases.The standard state should not be confused with standard temperature and pressure (STP) for gases nor with the standard solutions used in chemistry. STP is commonly used for calculations involving gases that approximate an ideal gas, whereas standard state conditions are used for thermodynamic calculations.

1.7 Fugacity and Fugacity Coefficient

Fugacity was introduced by the American chemist Gilbert Newton Lewis (1875–1946) in 1908 to calculate the chemical potential of components in gas mixtures. The word fugacity is coined from the Latin *fuga* meaning escape and the word *capacity* which is also of Latin origin, thus referring to the "capacity to escape" of the gas. To calculate the change in molar Gibbs free energy or the chemical potential of a **real gas**, we need to perform the integration $\int_{P_1}^{P_2} dG = \int_{P_1}^{P_2} VdP$. This procedure will, however, depend upon the nature of the gas. G. N. Lewis removed the above dependence by proposing an alternative procedure which does not depend uponthe nature of the gas. So, for real gases, a function, **fugacity** of the gas is defined in such a way that it satisfies the relation

$$\Delta\mu = RT\ \ell n\left(\frac{f_2}{f_1}\right) \quad ......(1.36)$$

Fugacity is important in case of real gases since the effect of intermolecular interaction needs to be taken care of. Thus, fugacity f plays the role of pressure and need not be equal to the actual pressure of the real gas. It may be known as corrected pressure which applies to real gases.

The Fugacity Coefficient

In general, the fugacity of a real gas is related to its pressure by an equation

$$\frac{f}{P} = \varphi \quad ......(1.37)$$

where φ is known as the fugacity coefficient and is a measure of deviations of a real gas from the ideal gas behavior. We know that a gas behaves ideally in the limiting condition of pressure tending to zero.

$$\lim_{P\to 0}\frac{f}{P} = \lim_{P\to 0}\varphi = 1 \quad ......(1.38)$$

One important point is that the fugacity is expressed in the same dimension as pressure meaning fugacity has the unit of pressure. Thus, fugacity coefficient is a dimensionless number.

The Standard State of Real Gases

The chemical potential of a real gas at fugacity f relative to that at standard-state fugacity f^o following equation 1.36 is

$$\mu = \mu^\circ + RT\ \ell n\left(\frac{f}{f^\circ}\right) \quad ......(1.39)$$

where μ and μ° are the chemical potentials at fugacities f and f^o, respectively. Please note that here μ° is the chemical potential of the real gas in the standard state. Substituting fugacity in terms of pressure using equation 1.37 we get

$$\mu = \mu^\circ + RT\ \ell n\left(\frac{\varphi P}{f^\circ}\right) = \mu^\circ + RT\,\ell n\left(\frac{P}{f^\circ}\right) + RT\,\ell n\varphi \quad ......(1.40)$$

Examination of equation 1.40 reveals that the first two terms on the right-hand side resembles the chemical potential equation of the ideal gas. So, we can say that the the third term measures the deviations of a real gas from ideality. If whole of the deviations is to be ascribed to φ, then it is obvious that μ° in equation 1.40 must be identical with that appeared in Eq. (1.35) which is applicable to ideal gases, i.e. μ° of Eq. (1.40) must have the characteristics of ideal gas. Thus, the standard state of a real gas is, in fact, some hypothetical state in which the gas behaves ideally at $f^\circ = 1$ atm. At this point however, $\varphi = 1$ which renders the fact that pressure tends to zero. It is counter-intuitive and is the reason behind calling this state hypothetical.

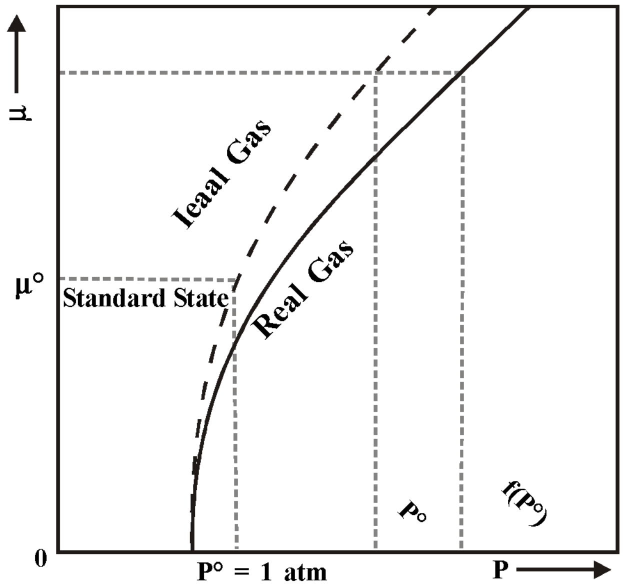


Figure 1.2 : Chemical potential as a function of pressure at constant temperature.

1.8 Chemical Potential of an Ideal Gas in an Ideal Gas Mixture

Now, we need to relate the chemical potential of a constituent of a gas mixture to its partial pressure. We cannot measure the absolute value of a chemical potential, but we can evaluate its value relative to the chemical potential in a standard state. Here, we are considering an ideal gas in a mixture of ideal gases. The standard state of a substance “i” in a gas mixture is the same as the standard state of the pure gas described in section 1.6. To derive an expression for μ_i in an ideal gas mixture relative to μ_i^0 of the ideal gas, we make an assumption based on the following argument.

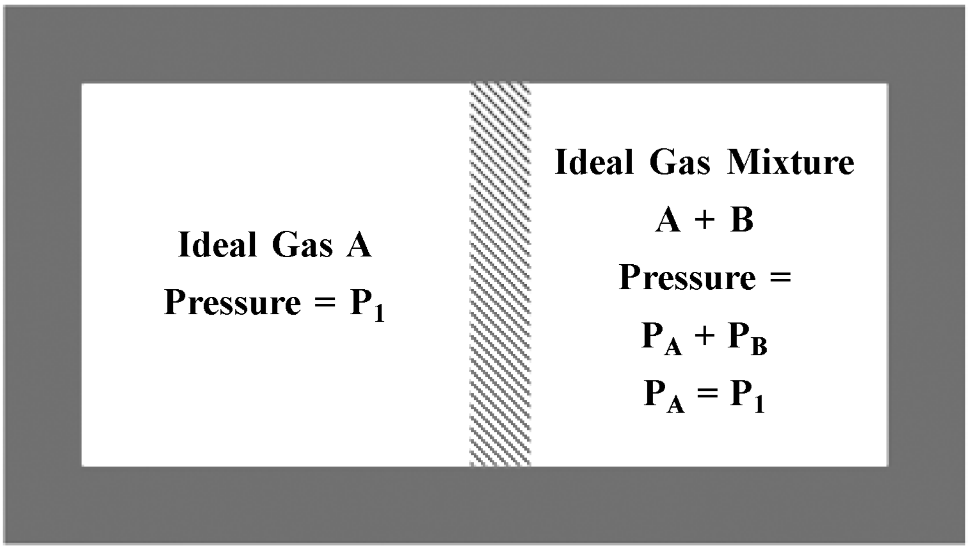


Figure 1.3 : System with two gas phases, pure A and a mixture of A and B, separated by a semipermeable membrane through which only A can pass. Both phases are ideal gases at the same temperature.

Suppose we place pure A, an ideal gas, in a rigid box at pressure P_1. We then slide a rigid membrane into the box so as to divide the box into two compartments. The membrane is permeable to A; that is, molecules of A pass freely through its pores. The membrane does not affect the pressures on either side, which remain equal to P_1. Finally, without changing the volume of either compartment, we add a second gaseous substance, B, to one side of the membrane to form an ideal gas mixture, as shown in Fig 1.3. The membrane is impermeable to B, so the molecules of B stay in one compartment and cause a pressure increase there. Since the mixture is an ideal gas, the molecules of A and B do not interact, and the addition of gas B causes no change in the amounts of A on either side of the membrane. Thus, the pressure of A in the pure phase and the partial pressure of A in the mixture are both equal to P_1. So our assumption is that the partial pressureof gas A in an ideal gas mixture in equilibrium with pure ideal gas A is equal to the pressure of the pure gas.Because the system shown in Fig. 1.3 is in an equilibrium state, gas A must have the same chemical potential in both phases. This is true even though the phases have different pressures. Since the chemical potential of the pure ideal gas is given by equation 1.35 and we assumed that P_A in the mixture is equal to pressure in the pure gas, the chemical potential of A in the mixture is given by

$$\mu_A = \mu_A^o + RT\,\ell n\left(\frac{P_A}{P^o}\right)$$

By the same analogy, we can generalize the idea for an ideal gas in a multicomponent ideal gas mixture. So, for each substance "i" in an ideal gas mixture, we have the relation

$$\mu_i = \mu_i^o + RT\,\ell n\left(\frac{P_i}{P^o}\right) \quad ......(1.41)$$

Equation 1.41shows that if the partial pressure of a constituent of an ideal gas mixture is equal to P°, so that ln $\left(\frac{P_i}{P^o}\right) = 0$, the chemical potential is equal to the standard chemical potential. Conceptually, a standard state should be a well-defined state of the system, which in the case of a gas is the pure ideal gas at P = P°. Thus, although a constituent of an ideal gas mixture with a partial pressure of 1 atm is not in its standard state, it has the same chemical potential as in its standard state. Equation 1.41 will be taken as the **thermodynamic definition of an ideal gas mixture**. Any gas mixture in which each constituent obeys this relation at all compositions is by definition an ideal gas mixture.

Now we can use this expression to get the partial molar quantities of the gas mixture. By substituting the expression 1.41 into equation 1.24 we obtain an expression for the partial molar entropy of substance "i" in an ideal gas mixture.

$$\overline{S}_i = -\left(\frac{\partial \mu_i^o}{\partial T}\right)_{P,n_j} - R\,\ell n\left(\frac{P_i}{P^o}\right) = S_i^o - R\,\ell n\left(\frac{P_i}{P^o}\right) \quad ......(1.42)$$

The quantity S_i^o is the **standard molar entropy** of constituent "i". It is the molar entropy of i in its standard state of pure ideal gas at pressure 1 atm. We have mentioned that the partial properties also obey thermodynamic relations. So, for partial molar enthalpy $\overline{H}_i$ we can write

$$\mu_i = \overline{H}_i - T\overline{S}_i \quad ......(1.43)$$

Now if we use equation 1.41 and 1.42 in equation 1.43, we will get

$$\bar{H}_i = \mu_i + T\bar{S}_i = \mu_i^o + RT\,\ell n\left(\frac{P_i}{P^o}\right) + TS_i^o - RT\,\ell n\left(\frac{P_i}{P^o}\right) = \mu_i^o + TS_i^o = H_i^o \quad ......(1.44)$$

Here H_i^o is the **standard molar enthalpy of the ideal gas**. Equation 1.44 tells us that the partial molar enthalpy of a constituent of an ideal gas mixture at a given temperature is **independent of the partial pressure or mixture composition**; it is a function only of T.

Now, from equation 1.24 we can find the partial molar volume of the ideal gas in the mixture. The partial molar volume $\bar{V}_i$ is given by

$$V_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j} = \left(\frac{\partial \mu_i^o}{\partial P}\right)_{T,n_j} + RT\left[\frac{\partial\,\ell n\left(\frac{P_i}{P^o}\right)}{\partial P}\right]_{T,n_j} \quad ......(1.45)$$

The first partial derivative on the right is zero because μ_i^o is a function of T only. For the second partial derivative, we write $\frac{P_i}{P^o} = \frac{x_i P}{P^o}$ where x_i is the mole fraction of the i^{th} component. The mole fractionis constant when the amount of each substance is constant and so we have $\left[\frac{\partial\,\ell n\left(\frac{P_i}{P^o}\right)}{\partial P}\right]_{T,n_j} = \frac{1}{P}$. The partial molar volume is therefore given by

$$\bar{V}_i = \frac{RT}{P} \quad ......(1.46)$$

which is what we would expect simply from the ideal gas equation. The partial molar volume is not necessarily equal to the standard molar volume. In the similar way, for partial molar internal energy $\bar{U}_i$ using the relation $\bar{U}_i = \bar{H}_i - P\bar{V}_i$ we get $\bar{U}_i = U_i^o$. For the partial molar heat capacity at constant pressure, $\overline{Cp_i}$ we will get $\overline{Cp_i} = Cp_i^o$. Thus, in an ideal gas mixture the partial molar internal energy and the partial molar heat capacity at constant pressure, like the partial molar enthalpy, are functions only of T. Thus, the definition of an ideal gas mixture given by the above equations is consistent with the criteria for an ideal gas.

1.9 Condensed Phase and Ideal Solutions

In the last sections we have discussed ideal gas and gas mixtures. Now in this section we will deal with thermodynamic properties of solutions in condensed phases. Solids and liquids have particles that are fairly close to one another, and are thus called “condensed phases” to distinguish them from gases. To start our discussion, we first need to define the standard states for ideal solution components. Please note that in this section when the word solution is mentioned it means liquid solutions unless mentioned otherwise.

1.9.1 Standard State of Pure Liquids and Solids

We have already defined the conditions for standard state of pure substances in section 1.6. The same conditions are applicable in this case also. The standard state of each component i of an ideal liquid solution is defined to be pure liquid i at temperature T and pressure P of the solution. For solid solutions, we use the pure solids. So, we have for a liquid

$$\mu_i^o = \mu_i^*(P,T) \quad ......(1.47)$$

The “o” or the degree superscript denotes the standard state and the * or star superscript indicates a pure substance. We will use this idea to explore the thermodynamics of solutions.

1.9.2 Ideal Solutions and Raoult’s Law

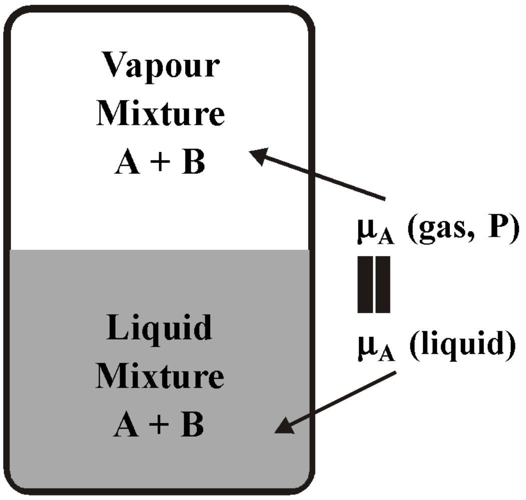


Figure 1.4 : An Ideal Liquid Mixture in Equilibrium with Vapour

Suppose we consider an ideal liquid mixture of A and B in a container as shown in figure 1.4. The solution will be in equilibrium with its vapour which contains A and B in gaseous form. At equilibrium, the chemical potential of the gaseous form of a substance A is equal to the chemical potential of its condensed phase. The equality is preserved if a solute is also present. Because the chemical potential of A in the vapour phase depends on its partial vapour pressure, it follows that the chemical potential of liquid A can be related to its partial vapour pressure. Now consider that first only pure A was present in the container. We will treat liquid and gaseous A as ideal. So, from the discussion we know that at equilibrium for pure A

$$\mu_A^* = \mu_A^o + RT\,\ell n\left(\frac{P_A^*}{P^o}\right) \quad ......(1.48)$$

μ_A^* is the chemical potential of pure liquid A, μ_A^o is the standard chemical potential of A gas and P_A^* is the vapour pressure of A. If another substance, a solute, is also present in the liquid, the chemical potential of A in the liquid is changed to μ_A and its vapour pressure is changed to P_A. The vapour and solvent are still in equilibrium, so we can write

$$\mu_A = \mu_A^o + RT\,\ell n\left(\frac{P_A}{P^o}\right) \quad ......(1.49)$$

Next, we combine these two equations to eliminate the standard chemical potential of the gas. To do so, we write equation 1.48 as $\mu_A^o = \mu_A^* - RT\,\ell n\left(\frac{P_A^*}{P^o}\right)$ and substitute it in equation 1.49.

$$\mu_A = \mu_A^* - RT\,\ell n\left(\frac{P_A^*}{P^o}\right) + RT\,\ell n\left(\frac{P_A}{P^o}\right) = \mu_A^* + RT\,\ell n\left(\frac{P_A}{P_A^*}\right) \quad ......(1.50)$$

In the final step we draw on additional experimental information about the relation between the ratio of vapour pressures and the composition of the liquid.

Raoult's law

In the 1880s, in a series of experiments on mixtures of closely related liquids (such as benzene and methylbenzene), the French chemist François Raoult found that when a substance is dissolved in a solution, the vapour pressure of the solution will generally decrease. This observation depends on two variables :

(i) mole fraction of the amount of dissolved solute present and

(ii) the original vapour pressure (pure solvent).

At any given temperature for a particular solid or liquid, there is a pressure at which the vapour formed above the substance is in dynamic equilibrium with its liquid or solid form. This is the **vapour pressure of the substance** at that temperature. At equilibrium, the rate at which the solid or liquid evaporates is equal to the rate that the gas is condensing back to its original form. All solids and liquids have a vapour pressure, and this pressure is constant regardless of how much of the substance is present. Thus, he established that the ratio of the partial vapour pressure of each component to its vapour pressure as a pure liquid $\frac{P_A}{P_A^*}$ is approximately equal to the mole fraction of A in the liquid mixture. This is now known as the

Raoult's law

$$P_A = x_A P_A^* \quad ......(1.51)$$

Some mixtures obey Raoult's law very well, especially when the components are structurally similar. Mixtures that obey the law throughout the composition range from pure A to pure B are called ideal solutions. For an ideal solution, it follows from equation 1.50 and 1.51 that

$$\mu_A = \mu_A^* + RT\,\ell n\, x_A \quad ......(1.52)$$

Equation 1.52 gives the chemical potential of a component of an ideal solution. We will learn about Raoult's law in more details in unit 2.

1.9.3 Mixing Properties of Solutions

Thermodynamics can provide insight into the properties of liquid mixtures, and a few simple ideas can bring the whole field of study together. The Gibbs energy of mixing of two liquids to form an ideal solution is calculated in exactly the same way as for two gases. The total Gibbs energy before liquid are mixed is

$$G_i = n_A \mu_A^* + n_B \mu_B^* \quad ......(1.53)$$

Equation 1.53 is basically the sum of Gibbs free energy of two pure liquids. Now when they are mixed together, the individual chemical potentials are given by equation 1.52 and the total Gibbs free energy is

$$G_f = n_A(\mu_A^* + RT\,\ell n\,x_A) + n_B(\mu_B^* + RT\,\ell n\,x_B) \quad ......(1.54)$$

So, the Gibbs free energy of mixing is the difference between these two quantities.

$$\Delta_{mix}G = G_f - G_i = n_A RT\,\ell n\,x_A + n_B RT\,\ell n\,x_B$$

$$= nRT\left(\frac{n_A}{n}RT\,\ell n\,x_A + \frac{n_B}{n}RT\,\ell n\,x_B\right)$$

$$= nRT(x_A\ell n\,x_A + x_B\ell n\,x_B) \quad ......(1.55)$$

Here, n = n_A + n_B i.e. n is the total number of moles. Based on the same method, we can obtain the Gibbs free energy of mixing for a solution having more than two components

$$\Delta_{mix}G = RT\sum_i n_i\ell n\,x_i = nRT\sum_i x_i\ell n\,x_i \quad ......(1.56)$$

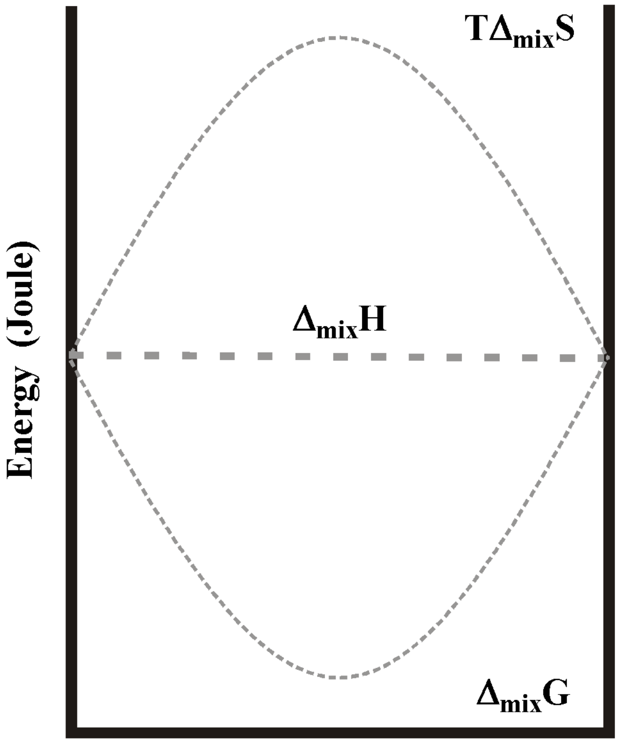
Since $0 < x_i < 1$, we have $\ln x_i < 0$ (always) and $\Delta_{mix}G < 0$ as must be true for an irreversible (spontaneous) process at constant T and P.We know that $\Delta_{mix}V = \left(\frac{\partial \Delta_{mix}G}{\partial P}\right)_T$. But for the ideal solution $\Delta_{mix}G$ does not depend on P. So, $\Delta_{mix}V = 0$. The ideal entropy of mixing of two liquids can be found from the relation $\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial P}\right)_{T,n_i}$

$$\Delta_{mix}S = -nR(x_A\ell n\,x_A + x_B\ell n\,x_B) ......(1.57)$$

$$\Delta_{mix}S = -nR\sum_i x_i\ell n\,x_i \quad ......(1.58)$$

Because $\Delta_{mix}H = \Delta_{mix}G + T\,\Delta_{mix}S = 0$; the ideal enthalpy of mixing is zero.Equation 1.57 (and eqn. 1.58) is the same as that for two perfect gases, however, it should be noted that an ideal solution means something different from an ideal gas. In a perfect gas there are no forces acting between molecules. In ideal solutions there are interactions, but the average energy of A – B interactions in the mixture is the same as the average energy of A – A and B – B interactions in the pure liquids.

In figure 1.5, the plots for $\Delta_{mix}G$, $\Delta_{mix}S$ and $\Delta_{mix}H$ for and ideal two component solution have been shown.



Mole Fraction of a Component A

Figure 1.5 : Variation of Thermodynamic Functions in a Binary Ideal Solution with respect to change in Mole Fraction of a Component

1.10 Chemical Potential and Activity : Non-ideal Solutions

The discussion thus far has shown that the chemical potential is a key thermodynamic property as other state functions can be derived from chemical potential. Now for an ideal liquid or ideally diluted solution, the chemical potential for each component can be written using equation 1.47 and 1.52 as

$$\mu_i^{ideal} = \mu_i^o + RT\ell n\, x_i \quad ......(1.59)$$

where μ_i^o is the standard state of the liquid or the solid component and x_i is its mole fraction. One may notice that specifically the superscript "ideal" has been used in this case. A non-ideal solution is defined as one that is neither ideal nor ideally dilute. So for nonideal solutions we need to modify equation 1.59. To keep the format same for ideal and non-ideal solution we define the **activity of the solution** (a_i) in terms of chemical potential as

$$a_i = \exp\left[\frac{(\mu_i - \mu_i^o}{RT}\right] \quad ......(1.60)$$

In this equation, μ_i is the chemical potential of the solution, μ_i^o is the chemical potential of standard state of the component. This definition actually works for any solution regardless of the solution being ideal or non-ideal. So taking log of both side of equation 1.60 yields

$$\mu_i = \mu_i^o + RT\,\ell n\, a_i \quad ......(1.61)$$

Comparing equation 1.61 with equation 1.59 clearly shows that for an ideal solution $a_i = x_i$. Also, when the activity of the component i is unity i.e. $a_i = 1$, $\mu_i = \mu_i^o$ and the component is in its standard state. Thus, activity can be defined as the measure of the effective concentration of a species under non-ideal (e.g., concentrated) conditions. The difference in chemical potential of the non-ideal solution and the corresponding ideal solution is

$$\mu_i - \mu_i^{ideal} = RT\,\ell n\, a_i - RT\,\ell n\, x_i = RT\,\ell n \frac{a_i}{x_i} \quad ......(1.62)$$

The ratio $\frac{a_i}{x_i}$ is thus a measure of the departure from ideal behaviour. We therefore define the **activity coefficient** of the component i as

$$a_i = \gamma_i x_i \quad ......(1.62)$$

Activities and concentrations can both be used to calculate equilibrium constants and reaction rates. However, most of the time, we use concentration even though activity is also a measure of composition, similar to concentration. It is satisfactory to use concentration for diluted solutions, but when you are dealing with more concentrated solutions, the difference in the observed concentration and the calculated concentration in equilibrium increases. This is the reason that the activity was initially created.

1.11 Chemical Equilibrium

In all the discussion of thermodynamics till now, we have mentioned that the species are "non-reactive" or there is no chemical reaction happening in the system. Even when we have discussed about thermodynamics of mixing of gases and liquids, we have maintained the criterion that the components do not react with each other. Now let us introduce chemical reactions into the system and learn how to study chemical reactions thermodynamically. We will begin our learning by first understanding the concept of reversible reactions.

1.11.1 Reversible Reaction and Fundamental Concept of Chemical Equilibrium

While learning general chemistry, we have encountered reversible and irreversible reactions. However, it is probable that all chemical reactions can take place in both directions, but in many cases the extent of the reverse reaction is so small as to be negligible. Consider, for example, the reaction between two parts of hydrogen and one part of oxygen. Explosion of a mixture of these gases at ordinary temperatures, by means of an electric spark, results in complete conversion into water. There is no detectable residue of the reacting gases, provided they were present in the correct proportion in the reaction vessel. Nevertheless, at temperatures above about 1500°C, water vapour is decomposed to an appreciable extent into hydrogen and oxygen. The reverse reaction thus definitely occurs at high temperatures, and it undoubtedly takes place to some extent under ordinary conditions. Because this is so small as to be virtually undetectable, the combination of hydrogen and oxygen is regarded as a reaction which proceeds to completion at normal temperatures and pressures.

In fact, the problem of incomplete and reversible reactions was already known to chemists long ago. At the beginning of 19^{th} century, these unusual reactions were given a new explanation by the French chemist C. L. Berthollet. His ideas developed from experience with chemical reactions carried out on a large scale. In 1798, he made a trip to Egypt accompanying Napoleon's expedition. He observed the continuous formation of sodium carbonate on the edge of 'natron lakes.' He came to the conclusion that although in the reaction of sodium carbonate and calcium chloride, calcium carbonate is precipitated; in presence of excess sodium chloride, calcium carbonate dissolves and forms sodium carbonate. The reaction can be expressed in the following manner

$$Na_2CO_3 + CaCl_2 \rightleftharpoons NaCl + CaCO_3$$

By definition, when the conditions are such that forward and reverse reactions can both occur to a noticeable extent, the process is described as a **reversible reaction**. It should be noted that the term "reversible" is not used here in the thermodynamic sense. A reversible chemical reaction, like other chemical reactions, takes place spontaneously and so the actual process is thermodynamically irreversible. The example of a reversible reaction in low temperature is the formation of hydrogen iodide by the reaction between hydrogen and iodine gas.

$$H_2 + I_2 \rightleftharpoons 2HI$$

Esterification reaction between ethanol and acetic acid leading to the formation of ethyl acetate and water is an example of room temperature reversible reaction in liquid phase.

After a sufficient interval of time has elapsed all reversible reactions reach **a state of chemical equilibrium**, that is, "a state in which no further change in the composition with time can be detected, provided the temperature and pressure are not altered".Another important point is that this equilibrium state can be reached from either the reactant side or the product side of the reaction. Once the reaction has reached chemical equilibrium, no change in concentration of reactants or products can be detected. This can mean two possibilities : (i) the overall reaction has stopped or (ii) the forward and reverse reactions are taking place simultaneously at the same speed. Obviously the first possibility is not true. The second possibility means that the reaction will continue to happen till the system stays in chemical equilibrium. Thus, chemical equilibrium is also known as dynamic equilibrium. So the rate of forward reaction (formation of products from reactants) and the rate of reverse reaction (formation of reactants from products) are different before the equilibrium is reached. But once chemical equilibrium is reached, these two rates become exactly equal and they will remain so until any condition such as pressure or temperature is changed. This phenomenon has been explained graphically in figure 1.6.

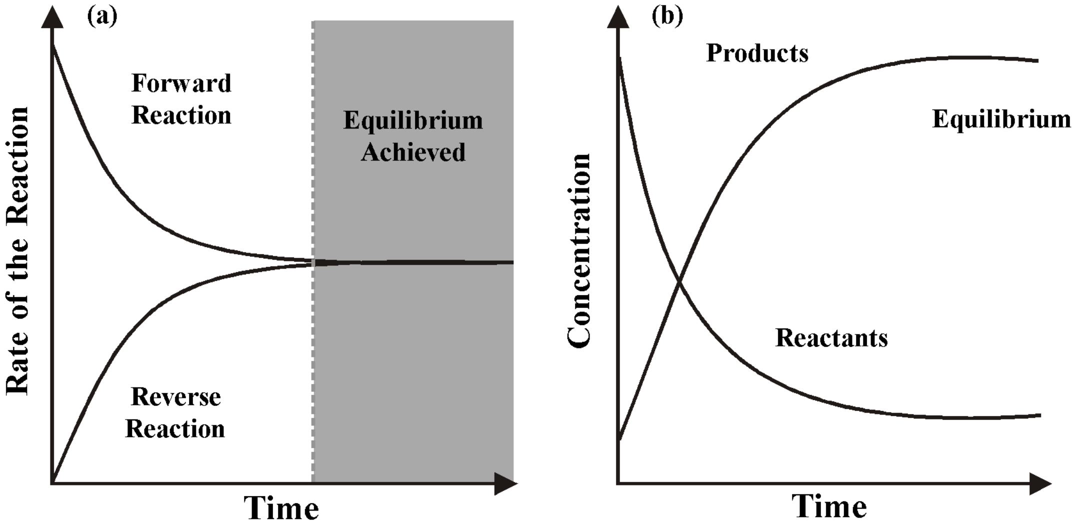


Figure 1.6 : (a) Variation of the Rate Reaction and (b) Concentration of Reactants and Products with Time

1.11.2 The Law of Mass Action

The concept of dynamic equilibrium provides a simple means for determining the relationship between the quantities of reactants and products that are present at equilibrium. This type of relationship was first derived from the second law of thermodynamics by A. Horstmann in 1873 and J. H. van't Hoff in 1877. The most important aspect of this relation is that it does not depend on the mechanism of the reaction. It says "the driving force of a chemical reaction is proportional to the active masses of the reacting substances". This is the so-called **law of mass action** as proposed by C. M. Guldberg and P. Waage. In a more modern physical chemistry textbook, one can find the statement "the rate of a chemical reaction is proportional to the molar concentration of the reacting substances". This is also the law of mass action.

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

Consider the above reaction. According to the law given above, the rate of the forward reaction will be proportional to the molar concentrations of A and B; if the proportionality constant is taken as k_1, then according to the law rate of forward reaction

$$v_f = k_1 C_A^{\alpha} C_B^{\beta} \quad ......(1.64)$$

where C is used to represent the molar concentration of the species. Similarly, the rate of the reverse reaction will be

$$v_r = k_2 C_c^{\gamma} C_D^{\delta} \quad .....(1.65)$$

k_2 is the proportionality constant for the backward reaction. Now, when the state of chemical equilibrium is attained, the rates of forward and reverse reactions must be equal $v_f = v_r$

$$k_1 C_A^{\alpha} C_B^{\beta} = k_2 C_c^{\gamma} C_d^{\delta} \quad ......(1.66)$$

where the various concentration terms now refer to the values at equilibrium. Rearranging equation 1.66 gives

$$K_c = \frac{k_1}{k_2} = \frac{C_c^{\gamma} C_D^{\delta}}{C_A^{\alpha} C_B^{\beta}} \quad ......(1.67)$$

The constant K_c is called the **equilibrium constant of the reaction**, the subscript c indicating that the equilibrium condition is expressed **in terms of the concentrations units**, e.g. moles per liter, of the various species.It should be noted that the reciprocal of K_c as defined by equation 1.67 would also be a constant; however, the convention adopted by physical chemists when expressing the equilibrium constant of a reaction is to place in the numerator the concentrations of the reaction products, i.e. of the substances on the right-hand side of the reaction as written. Please note that the **equilibrium constant varies with temperature** of the reaction.

1.11.3 Thermodynamic Derivation

The thermodynamic method for deriving the expression for the equilibrium constant do not require any postulated reaction mechanism and therefore any arbitrary (suitable) rate equation may be used in this derivation. Let us consider any general reaction

$$aA + bB + ... \rightleftharpoons lL + mM + ...$$

In the beginning, let us assume that the reactants A, B, etc., and the products L, M, etc., are not necessarily present in their equilibrium amountsbut in any arbitrarily chosen state. Here the word "state" means the partial pressure or concentration of any substance present in the system may be defined at constant temperature. The reaction mixture is an open system whose composition can vary with progress of time (due to the reaction itself) and thus partial molar quantities can be applied in this case. So, the Gibbs free energy for the reactants and products can be written as

$$G_{\text{reactants}} = a\mu_A + b\mu_B + \ldots\ \ldots$$

$$G_{\text{products}} = l\mu_l + m\mu_M + \ldots\ \ldots$$

So the change in Gibbs free energy is the difference between these two quantities; hence, at constant temperature and pressure is

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} = (\ell\mu_L + m\mu_M + \cdots\cdots) - (a\mu_A + b\mu_B + \cdots\cdots) \quad \ldots(1.68)$$

$$\Delta G = \left\{l\left(\mu_L^0 + RT\,\ell n\, a_L\right) + m\left(\mu_M^0 + RT\,\ell n\, a_M\right) + \cdots\right\}$$

$$-\left\{a\left(\mu_A^0 + RT\,\ell n\, a_A\right) + b\left(\mu_B^0 + RT\,\ell n\, a_B\right) + \cdots\right\} \quad \ldots\ldots(1.69)$$

where a_A, a_B etc denotes the activity of that particular species. Rearranging the equation and using the standard state definition, we can write

$$\Delta G = \Delta G^\circ + RT\,\ell n \frac{a_L^l a_M^m \cdots\cdots}{a_A^a a_B^b \cdots\cdots} \quad \ldots\ldots(1.70)$$

Here, ΔG° is the change in free energy accompanying the reaction when all the reactants and products are in their respective standard states. From the basic idea of thermodynamics, we know that for a system in equilibrium the free energy change ΔG is zero, provided the temperature and pressure at equilibrium are not allowed to alter. So, for the reaction at chemical equilibrium ΔG = 0 and thus at equilibrium equation 1.70 reduces to

$$\Delta G^\circ = -RT\ell n\left(\frac{a_L^l a_M^m \cdots\cdots}{a_A^a a_B^b \cdots\cdots}\right)_{eq} \quad \ldots\ldots(1.71)$$

Here a subscript "eq" has been used to denote that these are equilibrium activities. Since the standard free energy change ΔG° refers to the reactants and products in the definite states of unit activity, it is apparent that ΔG° must be a constant at that temperature, pressure etc. The gas constant R is a constant, and so if the temperature T is constant then

$$\left(\frac{a_L^l a_M^m \cdots\cdots}{a_A^a a_B^b \cdots\cdots}\right)_{eq} = \text{constant} = K \quad \ldots\ldots \ (1.72)$$

where K is the equilibrium constant for the reaction in terms of activities. This result is applicable to reversible reactions of all types, irrespective of whether gases, liquids or solids are involved. Since activities do not have any units, the equilibrium constant K is also unitless.

1.11.4 Different Forms of Equilibrium Constant

Gas Reactions

The equilibrium constant depicted in equation 1.72 is in terms of activities. So according to the states of matter of the reactants and products it can be specified. If the reactants and the products of the reaction are ideal gases or approximate closely to ideal behavior, the activity of each substance is proportional to its partial pressure and also to its molar concentration. So again, let us consider the reaction

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

The equilibrium constant in terms of partial pressure K_p and molar concentration is written as

$$K_p = \frac{P_c^\gamma P_D^\delta}{P_a^\alpha P_B^\beta} \quad \ldots\ldots(1.73)$$

$$K_c = \frac{C_c^\gamma C_D^\delta}{C_a^\alpha C_B^\beta} \quad \ldots\ldots(1.74)$$

where the P and the C terms are the partial pressures and the molar concentration of the components at equilibrium. Apart from these two representations, we can also represent the equilibrium constant in terms of mole fractions as

$$K_x = \frac{x_c^\gamma x_D^\delta}{x_a^\alpha x_B^\beta} \quad \ldots\ldots(1.75)$$

Here the x-terms represent the mole fractions of the components at equilibrium. It should be mentioned that equations 1.73 to 1.75 is applicable only to a system involving ideal gases. For real gases, the actual concentration (or partial pressure) must be replaced by the activity, or fugacity. However, if the reaction takes place at moderate pressures and relatively high temperatures, the deviations from ideal behavior are not much, and equations 1.73 and 1.74 may be employed. Now assuming ideal gas behaviour, relationship between the equilibrium constants can be established. The partial pressure of any gas P_i occupying a volume V at temperature T is given by $P_iV = n_iRT$; n_i is the number of moles of the component. From this equation it follows that $P_i = \frac{n_i}{V} RT = C_iRT$. If the equilibrium partial pressures in equation (1.74) are replaced by the corresponding values of C_iRT, then we get

$$K_P = \frac{C_c^{\gamma} C_D^{\delta}}{C_A^{\alpha} C_B^{\beta}} \times \frac{(RT)^{\gamma+\delta}}{(RT)^{\alpha+\beta}} = K_c \times (RT)^{\Delta n} \quad ......(1.76)$$

Where $\Delta n = (\gamma + \delta) - (\alpha + \beta)$ is equal to the change in the number of molecules in the chemical reaction as written. If in the reaction the number of molecules of reactant is equal to the number of molecules of products, Δn is zero; for such a reaction K_p and K_c are equal. Similarly using the relation $P_i = x_i P$, we can show that

$$K_p = K_x \times (P)^{\Delta n} \quad ......(1.77)$$

1.11.5 Thermodynamic conditions for equilibrium

We have learned in thermodynamics that the criterion for spontaneous change is to lower the Gibbs free energy of the system. This idea is absolutely general and can be applied to reaction equilibrium too. We locate the equilibrium composition of a reaction mixture by calculating the Gibbs energy of the reaction mixture and identifying the composition that corresponds to minimum value of G. Let us consider a simple equilibrium $A \rightleftharpoons B$. There are many examples of it, such as the isomerization of pentane to 2-methylbutane and the conversion of l-alanine to d-alanine etc. Suppose an infinitesimal amount $d\xi$ of A turns into B; then the change in the amount of A present is $\mathbf{dn_A = -\ d\xi}$ and the change in the amount of B present is $\mathbf{dn_b = d\xi}$. The quantity ξ **(xi)** is called the **extent of reaction**; it has the dimensions of amount of substance and is reported in moles. When extent of reaction changes by a finite amount $\Delta\xi$, the amount of A present changes from $n_{A,0}$ to $n_{A,0} - \Delta\xi$ and the amount of B changes from $n_{B,0}$ to $n_{B,0} + \Delta\xi$. **The reaction Gibbs free energy** is defined as the slope of the graph of the Gibbs energy plotted against the extent of reaction.

$$\Delta_{rxn}G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} \quad ......(1.78)$$

Now for the reaction we considered above, the change in Gibbs energy is

$$dG = \mu_A dn_A + \mu_B dn_B = -\ \mu_A d\xi + \mu_B d\xi \quad ......(1.79)$$

So, the reaction free energy becomes

$$\Delta_{rxn}G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \mu_B - \mu_A \quad ......(1.80)$$

So $\Delta_{rxn}G$ can also be interpreted as the difference between the chemical potentials (the partial molar Gibbs energies) of the reactants and products at the composition of the reaction mixture. Because chemical potentials vary with composition, the slope of the plot of Gibbs energy against extent of reaction, that is the reaction Gibbs energy, changes as the reaction proceeds. The spontaneous direction of reaction lies in the direction of decreasing G (that is, down the slope of G plotted against ξ). From equation 1.80 it is understood that the reaction A → B is spontaneous when $\mu_A > \mu_B$, whereas the reverse reaction is spontaneous when $\mu_B > \mu_A$. The slope is zero when $\Delta_{rxn}G = 0$ and at this point the reaction is at equilibrium and spontaneous in neither direction. This condition occurs when $\mu_B = \mu_A$. It follows that, if we can find the composition of the reaction mixture that ensures $\mu_B = \mu_A$, then we can identify the composition of the reaction mixture at equilibrium. Note that the chemical potentialis now fulfilling the role its name suggests : it represents the potential for chemical change, and equilibrium is attained when these potentials are in balance.

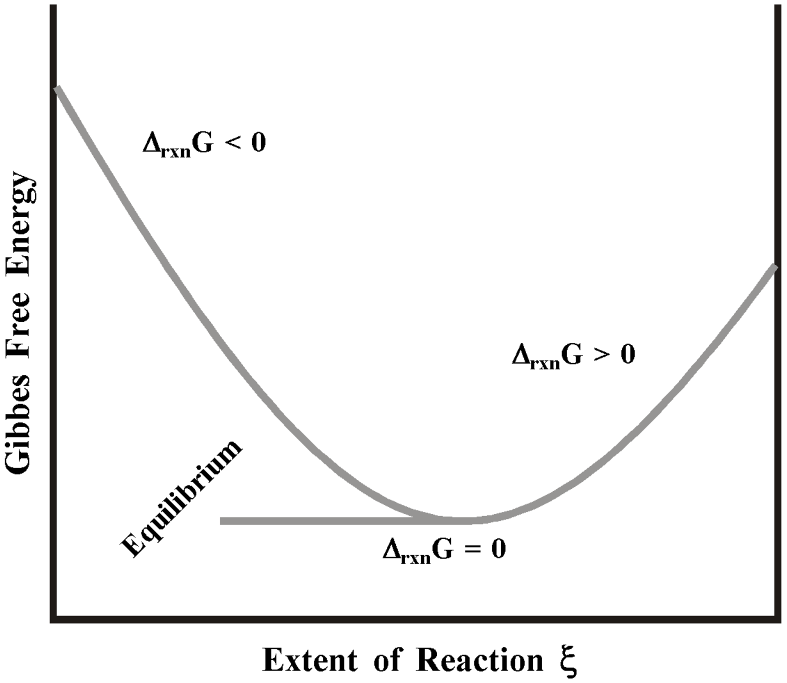


Figure 1.7 : Variation of Gibbs Free Energy with the Extent of the Reaction. Equilibrium corresponds to zero slope, at the foot of the valley

We can express the spontaneity of a reaction at constant temperature and pressure in terms of the reaction Gibbs energy as

- If $\Delta_{rxn}G < 0$, the forward reaction is spontaneous.
- If $\Delta_{rxn}G > 0$, the reverse reaction is spontaneous.
- If $\Delta_{rxn}G = 0$, the reaction is at equilibrium.

A reaction for which $\Delta_{rxn}G < 0$ is called **exergonic** (from the Greek words for work producing) and a reaction for which $\Delta_{rxn}G > 0$ is called **endergonic** (signifying work consuming).

1.11.6 The van't Hoff Equation

An exact relation between temperature and equilibrium constant can be derived from thermodynamics. Equation 1.71 and 1.72 can be combined as

$$\Delta G^\circ = -RT \ln K \quad ......(1.81)$$

This equation is very important and used throughout in chemistry. For a gas reaction in which the gases approach ideal behavior, equation 1.81 is written as

$$\Delta G^\circ = -RT \ln K_P \;......(1.82)$$

The left-hand side refers to a process in which each of the reactants and products is in its standard state of 1 atm pressure, assuming ideal behavior. The right-hand side contains two variables T and K_P and is independent of pressure. It is thus possible to differentiate equation 1.82 with respect to temperature at constant pressure. Now let us write equation 1.82 as $\ln K_P = -\frac{1}{R}.\frac{\Delta G^\circ}{T}$ and differentiate with respect to temperature.

$$\frac{d\ell n K_P}{dT} = -\frac{1}{R} \times \left(\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T} \right)_P \;......(1.83)$$

The subscript P indicates constant pressure. From Gibbs-Helmholtz equation we know that $\left(\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T} \right)_P = -\frac{\Delta H^\circ}{T^2}$. Using this equation in 1.83 we get

$$\frac{d\ell n K_P}{dT} = \frac{\Delta H^\circ}{RT^2} \;......(1.84)$$

Equation 1.84 is known as the **van't Hoff equation**, and ΔH° is the **change in enthalpy for the reaction**, i.e. the heat of reaction at constant pressure with the reactants and products in their standard states. In order to utilize equation 1.84 for purposes of calculation, it must be integrated. Integration of equation 1.84 gives us

$$\ell n \left(\frac{K_{P_2}}{K_{P_1}} \right) = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \;......(1.85)$$

Here K_{P_1} and K_{P_2} are the equilibrium constants in terms of pressure for the reaction at temperature T_1 and T_2 respectively. By means of equation 1.85 it is possible to calculate the equilibrium constant at the absolute temperature if the other parameters are known. Alternatively, if the equilibrium constants have been determined at two temperatures, the heat of reaction can be evaluated. These procedures can be applied to both homogeneous and heterogeneous equilibria. Since pressure is kept constant in this equation it is also sometimes called **isobar equation**. It should be mentioned that equation 1.85 is based on the approximation that ΔH° value is constant with temperature. Now integration of equation 1.84 can also be written as

$$\ell n K_P = -\frac{\Delta H^\circ}{RT} + \text{Constant} \quad ......(1.86)$$

So, the slope of ln K_P vs $\frac{1}{T}$ plot will give us ΔH°.

1.11.7 The Reaction Isotherm

From equation 1.70 and 1.81 we can write the free energy change for the reaction with reactants and products in any arbitrary states as

$$\Delta G = -RT\,\ell n K + RT\,\ell n \frac{a_L^l a_M^m \cdots\cdots}{a_A^a a_B^b \cdots\cdots} \quad ......(1.87)$$

Here the activities refer to the arbitrary reaction state (not necessary equilibrium). So at any point in the reaction, equation 1.87 is valid and the logarithm of activities term in equation 1.87 is called the **reaction quotient**. It is exactly similar in form to the expression for the equilibrium constant but the activities correspond to any state which may or may not be equilibrium.The reaction quotient in terms of activities is represented as

$$Q_a = \frac{a_L^l a_M^m \cdots\cdots}{a_A^a a_B^b \cdots\cdots} \quad ......(1.88)$$

So the equation 1.87 in terms of reaction quotient becomes

$$\Delta G = -RT\,\ell n K + RT\,\ell n Q_a = RT\,\ell n \frac{Q_a}{K_a} \quad ......(1.89)$$

This form is known as the **reaction isotherm or van't Hoff reaction isotherm**. It is evident that if the arbitrary states happen to correspond to those for the system at equilibrium, Q_a will become identical with the equilibrium constant K, since the expressions for both these quantities are of exactly the same. For gases, it is the usual practice to choose the state of unit activity as the ideal gas at 1 atm pressure; consequently, for gas reactions equation 1.89 becomes

$$\Delta G = -RT\,\ell n K_P + RT\,\ell n Q_P = RT\,\ell n \frac{Q_P}{K_P} \quad ......(1.90)$$

where K_P is the equilibrium constant with partial pressures expressed in atm, and Q_P is now the reaction quotient with the arbitrary states of reactants and products given in the same pressure units.For reactions in dilute solution, the standard state is chosen as the (hypothetical) ideal solution of unit concentration and in this condition the reaction isotherm becomes

$$\Delta G = -RT\,\ell n\,K_C + RT\,\ell n\,Q_C = RT\,\ell n\frac{Q_C}{K_C} \quad \ldots\ldots(1.91)$$

where Q_C is the reaction quotient with the states of the reactants and products expressed in terms of concentrations in their ideal solutions. If the solutions are sufficiently dilute, the actual concentrations may be employed in place of the ideal values.

The essential importance of the reaction isotherm lies in the fact that it provides a means of determining whether a particular reaction is possible or not, under a given set of conditions. For a thermodynamically irreversible process taking place at constant temperature and pressure, ΔG must be negative, that is the free energy of the system must decrease. If a particular physical or chemical change is to be theoretically possible it must be able to occur spontaneously. Spontaneous processes are, however, irreversible in the thermodynamic sense. So a reaction can take place spontaneously only if it is accompanied by a decrease of free energy, i.e. ΔG must be negative, at constant temperature and pressure.So from the above equation we can directly arrive at the conclusion that reaction will be able to take place spontaneously if Q is less than K, but not if Q is greater than K. Now here we have considered reaction in terms of reactants to products. So we can say that

- When $Q < K$, the activities (or concentrations) of the products are relatively less than those in the equilibrium state. The reaction will proceed forward, converting reactants into products.
- When $Q > K$ the products will be present in excess of the equilibrium activities and the reaction will proceed in the reverse direction, converting products into reactants.
- When $Q = K$ the system is in equilibrium.

1.11.8 The Le Chatelier's Principle

In 1884 the French chemist and engineer Henry-Louis Le Chatelier proposed one of the central concepts of chemical equilibria. The principle, which is based fundamentally on the second law of thermodynamics, may be stated in the following form

"A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance."

Consider, first, the effect of pressure on the position of equilibrium.An increase in pressure will cause the composition of the equilibrium system to change in such a manner as to decrease the number of molecules, since this implies a tendency for the pressure to decrease. Similarly, an increase of temperature will change the composition at equilibrium in the direction leading to an absorption of heat.

1.11.8.1 Shifting of equilibrium due to change in external parameters

This discussion will also be the thermodynamic proof of the Le Chatelier's Principle. We have seen that the reaction Gibbs free energy or the "reaction potential" is a function of temperature, pressure and the extent of reaction i.e. $\Delta_{rxn}G = f\ (T, P, \xi)$. Differential form of the relation gives

$$d(\Delta_{rxn}G) = \left(\frac{\partial}{\partial T}\Delta_{rxn}G\right)_{P,\xi} dT + \left(\frac{\partial}{\partial P}\Delta_{rxn}G\right)_{T,\xi} dP + \left(\frac{\partial}{\partial \xi}\Delta_{rxn}G\right)_{T,P} d\xi \quad ......(1.92)$$

Following the basic principles we can write equation 1.92 as

$$d(\Delta_{rxn}G) = -\Delta_{rxn}S\ dT + \Delta_{rxn}V\ dP + G''\ d\xi \quad ......(1.93)$$

In this equation,

$$G'' = \left(\frac{\partial}{\partial \xi}\Delta_{rxn}G\right)_{T,P} = \left(\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial \xi}\right)_{P,T}\right)_{T,P} \quad ......(1.94)$$

If the reaction is in equilibrium, then $d(\Delta_{rxn}G) = 0$. Also $\Delta_{rxn}S = \frac{\Delta_{rxn}H}{T}$ at equilibrium. So equation 1.93 becomes

$$0 = -\frac{\Delta_{rxn}H}{T}(\partial T)_{eq} + \Delta_{rxn}V\ (\partial P)_{eq} + G''_{eq}\ (\partial \xi)_{eq} \quad ......(1.95)$$

G''_{eq} is the value of G'' at equilibrium and is positive. At constant pressure, $dP = 0$ and the above equation gives

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{\Delta_{rxn}H}{TG''_{eq}} \quad ......(1.96)$$

This equation signifies that when heat is added to the reaction mixture or temperature is raised then the equilibrium shifts in the endothermic direction, i.e. it is shifted to high enthalpy side. If $\Delta_{rxn}H$ is positive, i.e. the reaction is endothermic, then $\left(\frac{\partial \xi}{\partial T}\right)_P$ is also positive, i.e. an increase in temperature increases the extent of reaction at equilibrium. For an exothermic reaction, $\Delta_{rxn}H$ is negative and thus $\left(\frac{\partial \xi}{\partial T}\right)_P$ is negative, i.e. increase in temperature decreases the equilibrium extent of the reaction. At constant temperature $dT = 0$, the equation 1.95 gives

$$\left(\frac{\partial \xi}{\partial P}\right)_T = -\frac{\Delta_{rxn}V}{G''_{eq}} \quad ......(1.97)$$

This equation signifies that if pressure increase reaction will shift in a direction where the number of gaseous molecules is reduced, thus lowering the pressure P. If $\Delta_{rxn}V$ is negative, i.e. the sum of stoichiometric numbers of gaseous products is less than that of gaseous reactants, the derivative $\left(\frac{\partial \xi}{\partial P}\right)_T$ has a positive value. Thus, increase in pressure increases the extent of reaction. If $\Delta_{rxn}V$ is positive, then $\left(\frac{\partial \xi}{\partial P}\right)_T$ is negative and thus increase in pressure decreases the extent of reaction. Hence, the net effect of increasing pressure is to shift the reaction in a direction where the sum of stoichiometric numbers of gaseous molecules is lowered, thus lowering P.

In the following table few examples of Le Chatelier's principle has been shown.

Table 1.11.1: Example of Le Chatelier's principle

System	Change	Result
$CO_2 + H_2 \rightarrow H_2O(g) + CO$	a drying agent is added to absorb H_2O	Shift to the right. Continuous removal of a product will force any reaction to the right

System	Change	Result
$H_2(g) + I_2(g) \rightarrow 2HI(g)$	Some nitrogen gas is added	No change; N_2 is not a component of this reaction system.
$NaCl(s) + H_2SO_4\ (l) \rightarrow Na_2SO_4(s) + HCl(g)$	reaction is carried out in an open container	Because HCl is a gas that can escape from the system, the reaction is forced to theright. This is the basis for the commercial production of hydrochloric acid.
$H_2O(l) \rightarrow H_2O(g)$	water evaporates from an open container	Continuous removal of water vapor forces the reaction to theright, so equilibrium is never achieved.
HCN (aq) $\rightarrow$ H + (aq) + CN^- (aq)	the solution is diluted	Shift toright; the product [H+][CN—] diminishes more rapidly than does [HCN].
$AgCl(s) \rightarrow Ag^+(aq) + Cl^-\ (aq)$	some NaCl is added to the solution	Shift toleftdue to increase in Cl– concentration. This is known as the common ion effect on solubility.
$N_2 + 3H_2 \rightarrow 2NH_3$	a catalyst is added to speed up this reaction	No change. Catalysts affect only the rate of a reaction;

1.11.8.2 The LeChâtelier's principle in physiology : hemoglobin and oxygen transport

Many of the chemical reactions that occur in living organisms are regulated through the Le Chatelier's principle. Few of these are more important to warm-blooded organisms than those that relate to aerobic respiration, in which oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.

$$\text{Hemoglobin} + O_2 \rightleftharpoons \text{Oxyhemoglobin}$$

The partial pressure of O_2 in the air is 0.2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the O_2 concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells. Carbon dioxide reacts with water to form the weak acid H_2CO_3 which would cause the blood acidity to become dangerously high if it were not promptly removed as it is excreted by the cells. This is accomplished by combining it with carbonate ion through the reaction

$$H_2CO_3 + CO_3^{2-} \rightleftharpoons 2HCO_3^-$$

which is forced to the right by the high local CO_2 concentration within the tissues. Once the hydrogen carbonate (bicarbonate) ions reach the lung tissues where the CO_2 partial pressure is much smaller, the reaction reverses and the CO_2 is expelled.

1.11.8.3 Industrial Application of Le Chatelier's Principle

Haber Process

In Haber process, ammonia is synthesized by combining pure nitrogen and hydrogen gases in 1 : 3 ratio in presence of finely powdered iron catalyst and molybdenum promoter at around 450°C and at about 250 atm. of pressure.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \ \Delta H = -\ 92.2 \text{ kJ/mol}$$

The Le Chatelier's principle helps in choosing these conditions to improve the yields of ammonia. **Effect of pressure :** In the forward reaction (synthesis of ammonia), the number of moles of gaseous components is decreasing. i.e., $\Delta n_g = (2) - (1+3) = -2$. Hence the synthesis of ammonia is favored by increasing the pressure of the system. Industrially, 100 – 250 atm. of pressure is employed. **Effect of temperature :** Since the forward reaction is exothermic, the increase in temperature favors the backward reaction i.e., the dissociation of ammonia. That means according to Le Chatelier's principle, the synthesis of ammonia is favored at lower temperatures. However, the reaction will be too slow at lower temperatures (a kinetic restriction). Hence this reaction is carried out at optimal temperatures i.e., at about 450 - 550°C to overcome the kinetic barrier. **Removal of ammonia :** The forward reaction can also be favored by removing ammonia from the system from time to time by liquefying it. **Catalyst :** To increase the speed of the reaction, finely powdered or porous iron is used as catalyst. Its efficiency can be improved by adding molybdenum or oxides of potassium and aluminium.

Contact Process

In the contact process, sulfuric acid is manufactured on large scale. The major steps involved in the process are

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

$$2SO_2(g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g) \quad \Delta H = -197\ kJ/mol$$

$$2SO_3(g) + H_2SO_4\ (l) \rightarrow H_2S_2O_7\ (l)$$

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2\ H_2SO_4\ (l)$$

The crucial step is the oxidation of sulfur dioxide, SO_2 to sulfur trioxide, SO_3. It is a reversible reaction. At normal conditions, the equilibrium lies far to the left and the amount of sulfur trioxide formed is very small. To improve the yield of sulfur trioxide, the reaction is carried out at around 450°C and 2 atm pressure in presence of V_2O_5 or Pt, which acts as a catalyst. These conditions are chosen by applying le Chatelier's principle. **Effect of pressure :** In the forward reaction (formation of sulfur trioxide), the number of moles of gaseous components is decreasing. i.e. $\Delta ng = (2) - (2 + 1) = -1$. Hence the forward reaction is favored by increasing the pressure of the system. However, at high pressures, the iron towers used in the contact process are corroded. Hence the process is carried out at optimal pressures like 2 atm. **Effect of temperature :** Since the forward reaction is exothermic, at higher temperatures the backward reaction i.e. the dissociation of sulfur dioxide is more favored. However the reaction will be too slow at lower temperatures. Hence this reaction is carried out at optimal temperatures i.e. around 450°C. **Catalyst :** To increase the speed of the reaction, V_2O_5 or Pt is used as catalyst.

1.11.9 Variation of Equilibrium Constant with Addition to Inert Gas

Now we will analyse the effect of addition of inert gas on reaction equilibrium constant. For a gas reaction at equilibrium $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$, we have previously written the equilibrium constant in terms of pressure in equation 1.73 and in terms of mole fraction in equation 1.75. Now let us express equation 1.75 in terms of number of moles of the reactants and products. We know mole fraction of a component can be expressed as

$$x_i = \frac{n_i}{\Sigma_i n_i} \quad ......(1.98)$$

Using this in the expression of

$$K_X = \frac{n_C^{\gamma} n_D^{\delta}}{n_A^{\alpha} n_B^{\beta}} \times \frac{1}{(\Sigma n)^{\Delta n}} \quad ......(1.99)$$

Here $\Delta n = (\gamma + \delta) - (\alpha + \beta)$. Now using this equation in equation 1.77 we get

$$K_P = \frac{n_C^{\gamma} n_D^{\delta}}{n_A^{\alpha} n_B^{\beta}} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n} \quad ......(1.100)$$

Equation 1.100 will give us the result of addition of inert gas in a reaction mixture. Now, an inert gas can be added in two different conditions.

(i) **At constant volume :** Addition of inert gas will not have any effect on the equilibrium or products at this condition. Since volume is constant and total pressure of the reaction will change, the partial pressure of each of the reactants and products remains unchanged and therefore the equilibrium constant K_P will remain unchanged.

(ii) **At constant pressure :** When inert gas is added at constant pressure, it will change the equilibrium. Here three situations may arise. If there is no change in number of gaseous species i.e. if $\Delta n = 0$ then the expression of K_P becomes independent of P and Σn. Hence no change in equilibrium occurs. If there is an increase in the number of gaseous species in the reaction i.e. if $\Delta n > 0$, then after addition of inert gas in order to keep K_P constant the first term i.e. $\frac{n_C^{\gamma} n_D^{\delta}}{n_A^{\alpha} n_B^{\beta}}$ in the equation 1.100 has to increase. It means more reactants will be consumed and more products will be formed. If there is an decrease in the number of gaseous species in the reaction i.e. if $\Delta n < 0$, then after addition of inert gas in order to keep K_P constant the first term i.e. $\frac{n_C^{\gamma} n_D^{\delta}}{n_A^{\alpha} n_B^{\beta}}$ in the equation 1.100 has to decrease. So, the reaction will shift towards the reactant side and more products will be consumed to form the reactants.

1.11.10 Nernst's Distribution Law

When two immiscible solvents A and B are taken in a beaker, they form separate layers. Now a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from B to A. Finally, a dynamic equilibrium is set up. At equilibrium, the rate at which molecules of X pass from one solvent to the other is balanced. W. Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called **Nernst's Distribution law** or **Nernst's Partition law** or simply **Distribution law** or **Partition law**. It states that

"If a solute distributes itself between two immiscible solvents at constant temperature and the solute is in the same molecular condition in both solvents, then at equilibrium, the ratio of the concentrations of the solute component in two liquid phases is a constant."

If C_1 denotes the concentration of the solute in solvent A and C_2 the concentration in solvent B, Nernst's Distribution law can be expressed as

$$\frac{C_1}{C_2} = K_D \quad ......(1.101)$$

The constant K_D (or simply K) is called the distribution coefficient or partition coefficient or distribution ratio. When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, the Nernst Distribution Law can also be expressed in terms of solubilities.

Thermodynamic Derivation of the Distribution Law

The thermodynamic derivation of the distribution law is based upon the principle that if there are two phases in equilibrium (i.e. two immiscible solvents containing the same solute dissolved in them), the chemical potential of a substance present in them must be same in both the phases. Suppose a solute is distributed in two immiscible liquid A and B. The chemical potential of the solute in solvent A is given by

$$(\mu_i)^A = \left(\mu_i^0\right)^A + RT\,\ell n\, a_i^A \quad ......(1.102)$$

where the superscript A denotes solvent A and the subscript i denotes solute i. Similarly the chemical potential of the solute i in solvent B is given as

$$(\mu_i)^B = \left(\mu_i^0\right)^B + RT\ \ell n\, a_i^B \quad ......(1.103)$$

But as already stated, the liquids A and B are in equilibrium and thus $(\mu_i)^A = (\mu_i)^B$. From this equality we get

$$\ell n\left(\frac{a_i^A}{a_i^B}\right) = \frac{\left(\mu_i^o\right)^B - \left(\mu_i^o\right)^A}{RT} \quad ......(1.104)$$

Further at a given temperature, $\left(\mu_i^o\right)^A$ and $\left(\mu_i^o\right)^B$ are constants for a given substance in the particular solvents. Hence at constant temperature,

$$\frac{a_i^A}{a_i^B} = \text{constant} = K_D \quad ......(1.105)$$

This is the exact expression of the distribution law. However, if the solutions are dilute, the activities are equal to the concentrations so that the expression 1.105 is modified to

$$\frac{C_i^A}{C_i^B} = \text{constant} = K_D \quad ......(1.106)$$

Equation 1.106 is the original form of Nernst's Distribution law.

Limitations of the Nernst Distribution Law

The law is valid when the molecular state of the solute is same in both the solvents. If the solute undergoes dissociation or association in any one of the solvents, then in such cases the distribution law no longer holds good in its original form. The distribution law can be applied in such cases with some modifications.

1.11.11 Application of Nernst Distribution Law

There are several applications of Nernst Distribution law such as (1) solvent extraction; (2) partition chromatography; (3) release of drug from dosage forms;

(4) passage of drug through membranes; (5) preservation of emulsions and creams etc. We will discuss two very common applications.

Determination of equilibrium constant from distribution coefficient

Distribution law helps in determining the equilibrium constant of a reaction when one of the reactants is soluble in two non-miscible solvents. Let us illustrate by taking example of the reaction when potassium iodide reacts with iodine to form potassium triiodide.

$$KI + I_2 \rightleftharpoons KI_3$$

This reaction can be carried in water, while iodine is soluble in both water and benzene. So in water layer if KI is added this reaction will happen but in benzene layer KI is insoluble.

Procedure

To find the distribution coefficient of I_2 Iodine is shaken with water and benzene in a bottle. The concentration of iodine in the two layers is then determined by titration against standard thiosulphate solution. Thus $\frac{C_{\text{iodine}}^{\text{water}}}{C_{\text{iodine}}^{\text{Benezene}}}$ = constant = K_D.

To find the equilibrium constant using the value of K a solution of KI of concentration "a" is shaken with iodine in a bottle. To this is added some benzene and shaken. On standing, the mixture separates into two layers. The concentration of iodine is determined in the two layers by titration against standard thiosulphate solution. Let "b" be the concentration of I_2 in benzene layer, "c" be the concentration of I_2 in water layer which is really the total of the concentration of free I_2 and KI_3. K_D is the value of distribution coefficient of iodine between water and iodine as determined earlier. So

$$\text{Concentration of free } I_2 \text{ in water layer} = K_D \times b$$

Concentration of KI_3 in water layer = $c - K_D\, b$; Concentration of KI in water layer = $a - (c - K_D\, b) = a - c + K_D\, b$. We can now say that the equilibrium constant of the reaction

$$K_c = \frac{[KI_3]}{[KI][I_2]} = \frac{c - K_D b}{(a - c + K_D b).(K_D b)} \quad \text{......(1.107)}$$

Since all the quantities on the right-hand side are known, the equilibrium constant (K_c) can be calculated.

Association of Solute Molecules

When solute molecules undergo association or dissociation in a solvent, then it can be calculated from Nernst Distribution Law. For example, benzoic acid forms dimer in benzene but stays as monomer in water. Water and benzene are two immiscible liquids. So following the distribution of benzoic acid in water and benzene layer, we can understand its association properties. Suppose the solute is present as simple molecules X in solvent A. In solvent B, n molecules of X associate to form X_n molecules. Let C_1 be concentration of X in solvent A, C_3 be concentration of X in solvent B and C_2 be concentration of X_n in solvent B. Applying distribution law to the equilibrium,

$$\frac{C_1}{C_3} = K_D \quad ......(1.108)$$

According to chemical equilibrium, $nX \rightleftharpoons X_n$,

$$\frac{C_3^n}{C_2} = K_C \quad ......(1.109)$$

Taking nth root on both sides in equation,

$$\frac{C_3}{\sqrt[n]{C_2}} = \sqrt[n]{K_C} \quad ......(1.110)$$

Dividing equation 1.108 by 1.110 we get

$$\frac{C_1}{\sqrt[n]{C_2}} = \frac{K_D}{\sqrt[n]{K_C}} = K \quad ......(1.111)$$

The constant K can be experimentally determined. This is a modified form of Nernst distribution law for solute undergoing association in one solvent.

1.12 Summary

In this unit we discussed open systems. An open system allows material transfer with the surroundings or a chemical reaction. We learned about the chemical potential which is the most important function in studying open systems and by extension all of chemical thermodynamics. Chemical potential was defined in terms of thermodynamic state functions. We then learned about the partial molar quantities and defined them for extensive thermodynamic properties. Chemical potential is also a partial molar property. Various thermodynamic relations were established in terms of partial molar quantities. Variation of chemical potential for a system was established using the Gibbs Duhem equation. We looked at ideal gas and real gases in terms of chemical potential and fugacity, then extended those ideas in the condensed phase. In the second part we explored chemical equilibrium, defined equilibrium constants and various forms. We learned about the van'tHoff reaction isotherm and the Le Chatelier principle. Finally, we explored the Nernst Distribution law.

1.13 Self-Assessment Questions

1. For a system of variable composition, the internal energy depends on (a) entropy (b) volume (c) moles (d) all of the mentioned.
2. Pick out the wrong statement. (i)Activity co-efficient is dimensionless, (ii) In case of an ideal gas, the fugacity is equal to its pressure, (iii) In a mixture of ideal gases, the fugacity of a component is equal to the partial pressure of the component, (iv) The fugacity co-efficient is zero for an ideal gas.
3. "The chemical potential of i-th species (μ_i) in an ideal gas mixture approaches zero as the pressure or mole fraction (x_i) tends to be zero at constant temperature" – this statement is true or false?
4. Use equation 1.6 to show that $dq = TdS + \Sigma_i\mu_i dn_i$ for a one phase closed system with P-V work only.
5. True or false- The chemical potential of sucrose in a solution of sucrose in water at 300K and 1 atm must be equal to the molar Gibbs free energy of solid sucrose at 300K and 1 atm.
6. When you add 5 ml acetone to 5 ml water what will be the volume of the resulting mixture if (i) it behaves ideally, (ii) it behaves non-ideally

7. What will be the slope and intercept of the plot of total molar volume vs mole fraction of component 1 plot in case of a binary component mixture?
8. The volume of a binary mixture has a molar volume, V, that depends on its composition as

   $V = 75x_1 + 95x_2 + 3.7x_1x_2$ cm^3/mol. For a mixture with $x_1 = 0.60$, determine (a) the molar volume of the mixture, and (b) the partial molar volume of component 1.
9. For an ideal solution, the partial molar entropy for a component _____ as the mole fraction of that component increases.
10. The partial molar enthalpies for mixing for benzene (1) and cyclohexane (2) is $\bar{H}_1 = 300x_2^2$ and $\bar{H}_2 = 300x_1^2$. When 1 mol of benzene is mixed with 2 moles of cyclohexane what is the enthalpy change?
11. Gibbs-Duhem equation relates composition in liquid phase and the __________ at constant temperature & pressure.
12. At constant temperature and pressure, for one mole of a pure substance, the ratio of the free energy to the chemical potential is what?
13. When liquid and vapour phases of one component system are in equilibrium (at a given temperature and pressure), the molar free energy is A. more in vapour phase B. more in liquid phase C. same in both the phases D. replaced by chemical potential which is more in vapour phase.
14. Fugacity is a measure of the____________________?

    (A) Escaping tendencies of the same substance in different phases of a system, (B) Relative volatility of a mixture of two miscible liquids, (C) Behaviour of ideal gases, (D) None of these
15. The activity of a pure gas is numerically equal to its pressure. True or False?
16. A mixture of NO_3 and SO_2 has 25 moles and 100 moles respectively. The total pressure exerted by the gases is 100 atm. What is the partial pressure of NO_3?
17. A binary liquid solution is prepared by mixing n-heptane and ethanol. Is this solution ideal or non-ideal?

18. Which condition is not satisfied by an ideal solution?

    (A) $\Delta_{mix}H = 0$, (B) $\Delta_{mix}S = 0$, (C) $\Delta_{mix}V = 0$

19. What is meant when a reaction is described as "having reached equilibrium"? What does this statement mean regarding the forward and reverse reaction rates? What does this statement mean regarding the amounts or concentrations of the reactants and the products?

20. Which of these systems exists in a state of chemical equilibrium?

    (a) oxygen and hemoglobin in the human circulatory system, (b) iodine crystals in an open beaker, (c) the combustion of wood, (d) the amount of ^{14}C in a decomposing organism

21. Write the equilibrium constant expressions for K and Kp for each reaction.

    (a) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

    (b) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

    (c) $2O_3(g) \rightleftharpoons 3O_2(g)$

22. Write the equilibrium constant expression for each reaction. Are these equilibrium constant expressions equivalent? Explain.

    (a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

    (b) $\frac{1}{2} N_2O_4(g) \rightleftharpoons NO_2(g)$

23. For the following equilibrium, $K = 6.3 \times 10^{14}$ at 1000K. $NO(g) + O_3 \longrightarrow NO_2(g) + O_2(g)$, both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c for the reverse reaction?

24. Calculate Kc and Kp for each reaction.

    (a) $N_2O4(g) \rightleftharpoons 2NO_2(g)$: at the equilibrium temperature of −40°C, a 0.150 M sample of N_2O_4 undergoes a decomposition of 0.456%.

    (b) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$: an equilibrium is reached at 227°C in a 15.5 L reaction vessel with a total pressure of 6.71×10^2 atm. It is found to contain 37.8 g of hydrogen gas, 457.7 g of carbon monoxide, and 7.193 g of methanol.

25. Write an equilibrium constant expression, Kp, based on the formation of one mole of each of the following gaseous compounds from its elements at 25 °C.

    (a) NO(g) (b) $NH_3(g)$ (c) NOCl(g)

26. In the equilibrium reaction A + B $\rightleftharpoons$ C, what happens to K if the concentrations of the reactants are doubled? tripled? Can the same be said about the equilibrium reaction 2A $\rightleftharpoons$ B + C?

27. In what manner will increase of pressure affect the following equation : C(s) + $H_2O \rightarrow CO(g) + H_2(g)$

    (a) shift in the reverse direction, (b) shift in the forward direction, (c) increase in the yield of hydrogen, (d) no effect

28. A vessel at equilibrium contains SO_3, SO_2 and O_2. Now some helium gas is added so that total pressure increases while temperature and volume remain constant. According to Le Chatelier's Principle the dissociation of SO_3^2

    (a) decreases, (b) remain constant, (c) increases, (d)changes unpredictably

29. The equilibrium constant of a reaction is 300. If the volume of reaction flask is tripled thenwhat will happen to the equilibrium constant?

30. The Haber Process for the manufacture of ammonia from nitrogen and hydrogen involves this reversible reaction : The ΔH value shows that the reaction is exothermic.

    (a) What would be the effect on the position of equilibrium if you increased the pressure? Explain your answer using Le Chatelier's Principle. (b) In order to get the maximum possible percentage of ammonia in the equilibrium mixture, would you choose to use a high or a low temperature? Explain your answer using Le Chatelier's Principle. (c) If you were a manufacturer, would there be any disadvantages in using the temperature you chose in part (b)?

1.14 Answers of Self-Assessment Questions

1. (d) 2. (iv) 3. False; It approaches standard state potential.

4. dU = dq + dw. For a mechanically reversible process in a closed system considering only work dU = dq – PdV. Use the expression of dU from equation 1.6 to arrive at the result.

5. False. 6. For ideal case exactly 10 ml. For non-ideal case less than 10 ml

7. From eqn. $V = n_1\bar{V}_1 + n_2\bar{V}_2$, total molar volume $V_m = \frac{V}{\Sigma_i n_i} = x_1\bar{V}_1 + x_2\bar{V}_2 = x_1\bar{V}_1 + (1 - x_1)\bar{V}_2 = \bar{V}_2 + x_1\left(\bar{V}_1 - \bar{V}_2\right)$ So for plot of V_m vs x_1 slope = $\left(\bar{V}_1 - \bar{V}_2\right)$ intercept = $\bar{V}_2$

8. (a) 83.9 cm3/mol. (B) 75.6 cm^3/mol; 9. Decreases

10. After mixing $x_1 = \frac{1}{3}$ and $x_2 = \frac{2}{3}$. So enthalpy of mixing = $x_1\bar{H}_1 + x_2\bar{H}_2 =$ $x_1(300x_2^2) + x_2\left(3600x_1^2\right)$ = 800 J

12. 1 13. C 14. A

15. True. Activity (a) of a pure ideal gas is defined as : a = (fugacity at a temperature and pressure of interest) / (fugacity at same temperature and standard pressure) usually the, standard pressure = 1 atm and for ideal gas fugacity at a temperature and pressure = pressure at that condition. So a = P

16. 20 atm. $P_i = (X_i)\ (P_{total})$.

17. The solution is non-ideal, showing +ve deviation from Raoult's Law. n-Heptane is non-polar and ethanol is polar. Hence the mixture formed by these two liquids is non-ideal. The stronger forces of attraction between n-heptane-n-heptane and ethanol-ethanol are replaced by weaker forces of attraction between n-heptane-ethanol in the solution. Therefore, the escaping tendency of the liquid molecules into the vapour phase increases. This will increase the vapour pressure more than expected from Raoult's law. This is a positive deviation.

18. B

20. (a) Exists in a state of equilibrium as the chemical reaction that occurs in the body is : $Hb(aq) + 4H_2O(l) \rightleftharpoons Hb(O_2)_4(aq)$.

    (b) Exists in a state of equilibrium as the chemical reaction occurs is: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(c) Does not exist in a state of equilibrium as it is not a reversible process. The chemical reaction that takes place is: $6C_{10}H_{15}O_7(s) + \text{heat} \rightarrow C_{50}H_{10}O(s) + 10CH_2O(g)$.

(d) Does not exist in a state of chemical equilibrium as it is not a reversible process. The chemical reaction that takes place is: $CH_2O + O_2 \rightarrow H_2O(l) + CO_2(g) + \text{nutrients}$.

22. (a) $K=[NO_2]^2/[N_2O_4]$; (b) $K=[NO_2]/[N_2O_4]^{1/2}$. We would need to square it to get the K value for b

23. 1.59 x 10 – 15

25. In each case, first write the balanced chemical reaction and then use the stoichiometric coefficients in the mass action expression to give the equilibrium constant expression.

26. In both cases, the equilibrium constant will remain the same as it does not depend on the concentrations

27. (a) 28. (b)

1.15 Suggested Readings

(a) Physical Chemistry by Peter W. Atkins and Julio De Paula, Oxford University Press

(b) Physical Chemistry by Ira N. Levine, McGraw-Hill Education

(c) Physical Chemistry by P. C. Rakshit, Sarat Book House, Kolkata, India

(d) A Textbook of Physical Chemistry Vol. III by K. L. Kapoor, Macmillan Publishers India

Unit - 2 ❑ Application of Thermodynamics – II

2.1 Objective

On completion of the study of this unit, the learner will be able to

- Discuss the concept of colligative properties
- Describe the effects of solute concentration on the vapor pressure, boiling point, freezing point, and osmotic pressure of a solution.
- Calculate the boiling point, freezing point and osmotic pressure of a solution containing a non-volatile solute in a volatile solvent
- Determine the concentration and molar mass of a non-volatile non-electrolyte from the change in boiling point, freezing point or osmotic pressure of solution
- Explain the magnitude of changes caused by electrolytes compared to those caused by nonelectrolytes and be able to use the van't Hoff factor
- Identify and understand the principles of thermodynamics to solve multiphase equilibrium
- Analyze the conditions associated with ideal and non-ideal vapour-liquid systems at equilibrium through the construction and interpretation of phase diagrams.
- Evaluate thermodynamic quantities that relate to the vapour-liquid or liquid-liquid equilibria of ideal and non-ideal chemical mixtures.

- Explain the concept of fractional distillation and azeotropes through liquid-vapour phase diagrams

2.2 Introduction

In the discussion of thermodynamics, we have learned about properties of isolated and closed systems in the beginning and in unit 1 we have learned about open systems. In all the cases, we have dealt with extensive and intensive properties and their behaviour under different conditions. We have learned about thermal and material equilibrium. In fact the thermodynamic equations we are familiar with were studied preliminarily under material equilibrium, and then in open system, we introduced material exchange. In this unit we will learn mainly two new topics. The first one is on a unique property of the solution known as colligative property. We will discover their formulation, thermodynamic nature and application and find out how these properties affect our everyday natural phenomenon. In the second part we will be introduced to phase equilibrium. Phase equilibrium is the study of the equilibrium which exists between or within different states of matter namely solid, liquid and gas. Phase equilibria is the application of the principles of thermodynamics to the study of equilibrium relationships within or between phases, corresponding to homogeneous and heterogeneous phases.The study of phase equilibria is firmly rooted in thermodynamics as formulated by J.W. Gibbs in the late 19th century. The span of phase equilibrium is vast. It is applicable in chemistry, biology, geology, physics, material science and many interdisciplinary subjects. Here we get a basic understanding of the topic.

2.3 Colligative Properties

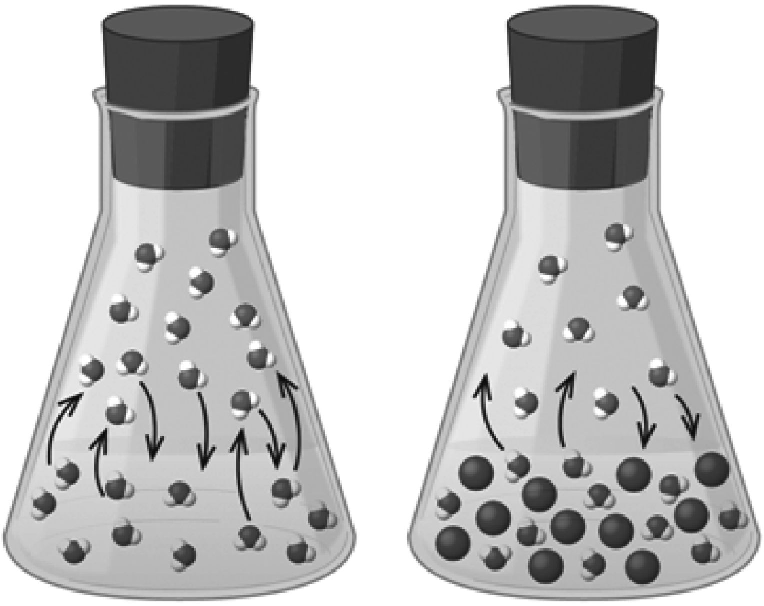
Physical properties can be divided into two categories. Extensive properties (such as mass and volume) which depend on the size of the sample, and intensive properties (such as density and concentration) that are characteristic properties of the substance and do not depend on the size of the sample being studied. This section introduces a category that belongs to the intensive properties of a system. This category, known as colligative properties, can only be applied to solutions. By definition, one of the properties of a solution is a colligative property if it depends only on the ratio of the number of particles of solute and solvent in the solution, not the identity of the solute. Colligative properties of solutions differ significantly from those of pure substances. Such differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol ("antifreeze") to the water in an automobile (car) radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode. Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Thus, such properties of solutions are called colligative properties (from the Latin colligatus, meaning "bound together" as in a quantity). As we will see, the vapour pressure and osmotic pressure of solutions are also colligative properties. We will discuss these four colligative properties in this unit.

2.3.1 Relative Lowering of Vapour Pressure : Raoult's Law

A vapour a is substance in gas phase at a temperature lower than its critical temperature which means the vapour can be condensed to liquids by applying pressure only. The equilibrium vapour pressure of a liquid is the pressure exerted by its gaseous phase when vapourisation and condensation are occurring at equal rates:

$$\text{Liquid} \rightleftharpoons \text{Gas}$$

Dissolving a nonvolatile substance in a volatile liquid results in lowering of the liquid's vapour pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vapourization and condensation processes. To vapourize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vapourization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vapourization-condensation equilibrium is achieved with fewer solvent molecules in the vapour phase (i.e. at a lower vapour pressure) (Figure 2.1). While this interpretation is useful, it does not account for several important aspects of the colligative nature of vapour pressure lowering. A more rigorous explanation involves the property of entropy. For understanding the lowering of a liquid's vapour pressure, it is sufficient to note that the more dispersed nature of matter in a solution, compared to separate solvent and solute phases, serves to effectively stabilize the solvent molecules and hinder their vapourization.



(a) Pue water (b) Aqueous solution

Figure 2.1 : The presence of nonvolatile solutes lowers the vapour pressure of a solution by reducing the evaporation of solvent molecules. This diagram is available under Creative Commons Attribution 4.0 International License from https://openstax.org/

It has been known for many years that when a nonvolatile solute is dissolved in a liquid the vapour pressure of the latter is lowered. The quantitative connection between the lowering of the vapour pressure and the composition of the solution was discovered by F. M. Raoult (1887) as the result of a large number of experiments with a variety of solutions.If P° is the vapour pressure of the pure solvent at a particular temperature, and P is the vapour pressure of the solution at the same temperature, the difference $P^\circ - P$ is the lowering of the vapour pressure; if this is divided by P° the result, $\frac{P^\circ - P}{P^\circ}$ is known as the **relative lowering of the vapour pressure** for the given solution. The **Raoult's law** states that

"*The partial pressure exerted by any component of an ideal solution is equal to the vapour pressure of the pure component multiplied by its mole fraction in the solution.*"

In mathematical form,

$$P_i = x_i\, P_i^o \quad \ldots\ldots (2.1)$$

where P_i is the partial pressure exerted by component i in the solution, P_i^o is the vapour pressure of pure i, and x_i is the mole fraction of A in the solution. A nonvolatile substance is one whose vapour pressure is negligible ($P^o \approx 0$), and so the vapour pressure above a solution containing only nonvolatile solutes is due only to the solvent. So for a nonvolatile substance dissolved in a solvent we can write

$$P_{solution} = x_{solvent} P^o_{solvent} \quad \ldots\ldots (2.2)$$

Please note if n_1 and n_2 are the numbers of moles of solvent and solute respectively, then in accordance with the definition of mole fraction $x_{solvent} = \frac{n_1}{n_1 + n_2}$. In more general terms, the mole fraction of ith component of a solution is expressed as $x_i = \frac{n_i}{\Sigma_i n_i}$. As we can see, an ideal solution has been mentioned in the statement of Raoult's law. In fact, Raoult's Law only works for ideal solutions. In practice, there is no such entity as an ideal solution. However, very dilute solutions obey Raoult's Law to a close approximation. In an ideal solution, it takes exactly the same amount of energy for a solvent molecule to break away from the surface of the solution as it did in the pure solvent. The forces of attraction between solvent and solute are exactly the same as between the original solvent molecules which is not very likely. In any real solution, e.g. salt in water, there are strong attractions between the water molecules and the ions. That would tend to slow down the loss of water molecules from the surface. However, if the solution is sufficiently dilute, there will be good-sized regions on the surface where you may have only water molecules. The solution will then approach ideal behaviour. Now according to Raoult's law, we can express the relative lowering of vapour pressure of a solution as

$$\frac{P^o_{solvent} - P_{solution}}{P^o_{solvent}} = \frac{P^o_{solvent} - x_{solvent} P^o_{solvent}}{P^o_{solvent}} = 1 - x_{solvent} = x_{solute} \quad \ldots\ldots (2.3)$$

The nature of the solute

One must to be careful while doing any calculation using Raoult's Law. What matters is not actually the number of moles of substance that you put into the solution, but the number of moles of particles formed. For each mole of sodium chloride dissolved, we get 1 mole of sodium ions and 1 mole of chloride ions – in other words, we get twice the number of moles of particles as of original salt. $NaCl$ (solid) + H_2O = Na^+ (aq) + Cl^-(aq). So, if we added 0.1 moles of sodium chloride, there would actually be 0.2 moles of particles in the solution – that is the figure we would have to use in the mole fraction calculation. Technically, Raoult's Law only works for solutes which do not change their nature when they dissolve. For example, they must not ionize, associate or dissociate. If either of these things happen, we have to take them into account in our calculation.

Volatile Solutes

Volatile solutes are solutes that have vapour pressure. These are typically miscible liquids that form solutions of any proportion in a solvent, and so it is not always useful to distinguish one as the solvent and the other as the solute. The vapour pressure above the solution is the sum of the vapour pressure of each component within the solution, where the vapour pressure of each component is determined by Raoult's Law. In this case, we need to use equation 2.1 for each of the components. This is actually the general case of Raoult's law. Suppose we have a mixture of 2 moles of methanol and 1 mole of ethanol at a particular temperature. The vapour pressure of pure methanol at this temperature is 81 kPa, and the vapour pressure of pure ethanol is 45 kPa. There are 3 moles in the mixture in total.2 of these are methanol. The mole fraction of methanol is 2/3. Similarly, the mole fraction of ethanol is 1/3. Assuming that a mixture of methanol and ethanol is ideal, we can calculate the vapour pressure of methanol and ethanol as

$$P_{methanol} = x_{methanol}P^{o}_{methanol} = \frac{2}{3} \times 81 kPa = 54 kPa$$

$$P_{ethanol} = x_{ethanol}P^{o}_{ethanol} = \frac{1}{3} \times 45 kPa = 15 kPa$$

We get the total vapour pressure of the liquid mixture by adding these together

$$P_{total} = P_{methanol} + P_{ethanol} = 54 \text{ kPa} + 15 \text{ kPa} = 69 \text{ kPa}$$

Vapour pressure - Composition diagrams

Suppose we have an ideal mixture of two liquids A and B. Each of A and B makes its own contribution to the overall vapour pressure of the mixture - as we've seen above. Let's focus on one of these liquids - A. Suppose we double the mole fraction of A in the mixture (keeping the temperature constant). According to Raoult's Law, this will double its partial vapour pressure. If we triple the mole fraction, its partial vapour pressure will be three times the original value - and so on. In other words, the partial vapour pressure of A at a particular temperature is proportional to its mole fraction. So, if we plot a graph of the partial vapour pressure of A against its mole fraction, you will get a straight line (figure 2.2). Now we'll do the same thing for B - except that we will plot it on the same set of axes. The mole fraction of B falls as A increases so the line will slope downwards rather than up (figure 2.2). As the mole fraction of B falls, its vapour pressure will fall at the same rate. Notice that the vapour pressure of pure B is higher than that of pure A. That means that molecules must break away more easily from the surface of B than of A. B is the more volatile liquid. To get the total vapour pressure of the mixture, we need to add the values for A and B together at each composition. The net effect of that is a straight line. The whole situation is shown in figure 2.2. Some of the binary mixtures that obeys Raoult's law for the entire composition range are (i) ethylene bromide and ethylene chloride (ii) n-hexane and n-heptane (iii) benzene and toluene (iv) carbon tertrachloride and silicone tetrachloride, etc.

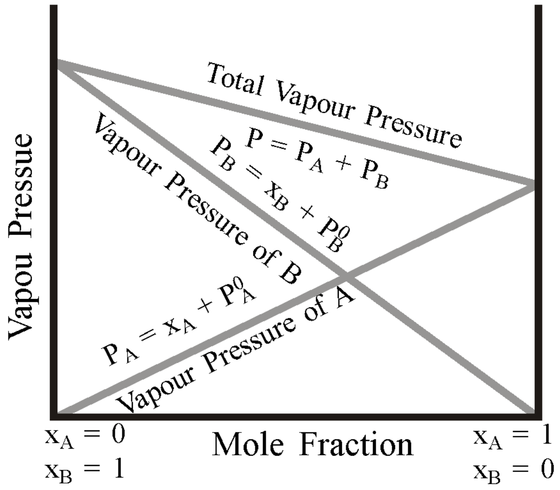


Figure 2.2 : Vapour pressure vs composition diagram for an ideal liquid mixture of A and B

2.3.2 Elevation of the Boiling Point

The next colligative property we are going to discuss is the elevation of boiling point. The boiling point of a liquid is the temperature at which its vapour pressure is equal to 1 atm. Since the vapour pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Vapour pressure increases with temperature, and so a solution will require a higher temperature than the pure solvent to achieve any given vapour pressure, including one identical to that of the surrounding atmosphere.This can be readily seen from the curves in Fig. 2.3, which represent the variation of vapour pressure with temperature of pure solvent and a solution and as we have seen the latter always below the former.

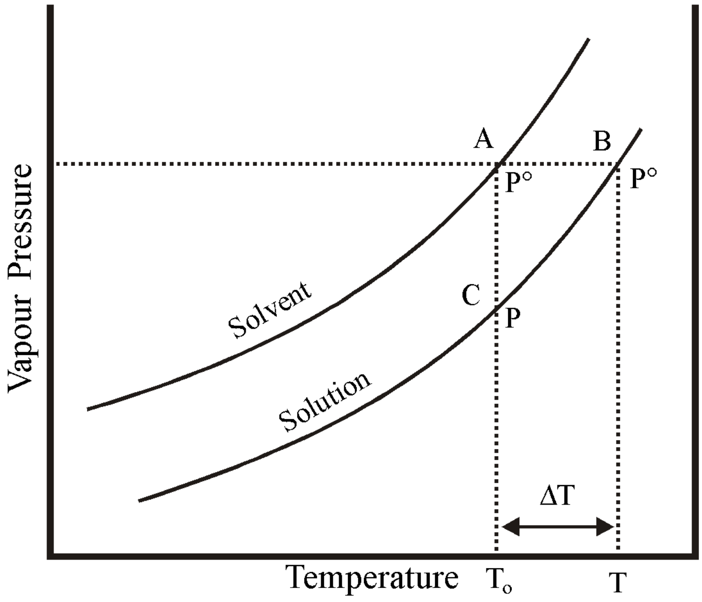


Figure 2.3 : Rise of boiling point of solution

The boiling point of the solvent is T_0 and that of the solution is T. The boiling point is thus raised by the amount $T - T_0 = \Delta T$. This quantity is known as the boiling point elevation, and it is represented by the distance AB in the diagram.Point A gives the vapour pressure P° of the solvent, i.e., 1 atm, while C is the same for the solution, both at the temperature T_0. Hence the distance AC is equivalent to $P° - P$. Since P° is a constant quantity, so it follows that AC is proportional to the relative lowering of vapour pressure, i.e., $\frac{P° - P}{P°}$ .If the vapour pressure curves for a series of solutions are almost parallel in the region of the boiling point, as is probably true for dilute solutions, the ratio of the distances AB to AC will be constant for these solutions. In other words, the boiling point elevation AB will be proportional to the relative lowering of the vapour pressure AC. Further, since the relative lowering isequal to x_2, the mole fraction of the solute, then by Raoult's law it follows that

$$\Delta T = k_b x_2 \text{ ...... } (2.4)$$

Here we have assumed that the mole fraction of the solute is x_2 and the same for the solvent is x_1.

Now we can give an explanation for the phenomenon in terms of chemical potential also. At the boiling point, the liquid phase and the vapour phase have the same chemical potential (or vapour pressure) meaning that they are energetically equivalent. The chemical potential is dependent on the temperature, and at other temperatures either the liquid or the gas phase has a lower chemical potential and is more energetically favorable than the other phase. This means that when a nonvolatile solute is added, the chemical potential of the solvent in the liquid phase is decreased by dilution, but the chemical potential of the solvent in the vapour phase is not affected. This means in turn that the equilibrium between the liquid and vapour phase is established at another temperature for a solution than a pure liquid, i.e., the boiling point is elevated.

The result of equation 2.4 may be derived in a more precise manner which gives the value of the constant k_b in terms of properties of the solvent. We need to use the Clapeyron-Clausius equation for this purpose. This equation has been described in details later in this unit. For now, let us write from figure 2.3, the vapour pressure of the solution at temperature T_0 and T are P and P° respectively and therefore

$$\ell n \frac{P}{P^\circ} = -\frac{\Delta H_{vap}}{R}\left(\frac{T - T_0}{T_0 T}\right) \text{ ...... } (2.5)$$

In this equation ΔH_{vap} is the molar heat (enthalpy) of vapourization. The temperature difference $T - T_o$ is the rise of boiling point ΔT, and since, for a dilute solution, T and T_o are not very different, T_oT may be replaced by T_o^2. Furthermore, according to Raoult's law equation 2.1 $P_1 = x_1P_1^o$ which means $\frac{P_1}{P_1^o} = x_1 = 1 - x_2$. Remember that mole fraction of the solute is x_2 and the same for the solvent is x_1. So equation 2.5 is modified to

$$\ell n(1-x_2) = -\frac{\Delta H_{vap}}{R}\left(\frac{\Delta T}{T_o^2}\right) \quad .... (2.6)$$

The term ln $(1 - x_2)$ can be replaced by the power series expression and since x_2 is small for a dilute solution, ln $(1 - x_2) = - x_2$, Substituting this in equation 2.6 we get

$$x_2 = \frac{\Delta H_{vap}}{R}\left(\frac{\Delta T}{T_o^2}\right)$$

$$\therefore \Delta T = \frac{RT_o^2}{\Delta H_{vap}} x_2 \quad .... (2.7)$$

which is identical in form with equation 2.4. The most important application of these equations is for the determination of molecular weights of dissolved substances, and for this purpose an alternative form is more useful. Since the solutions are dilute, the mole fraction x_2 may be replaced by $\frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} = \frac{w_2}{w_1}.\frac{M_1}{M_2}$. Here n_1 and n_2 are the mole numbers of the solvent and the solute, w_1 and w_2 are their respective weight/mass; and M_1 and M_2 are the molecular weight of solvent and solute. Hence equation 2.7 becomes

$$\Delta T = \frac{RT_o^2}{\Delta H_{vap}}.\frac{w_2}{w_1}.\frac{M_1}{M_2} = \frac{RT_o^2}{l_v}.\frac{w_2}{M_2 w_1} \quad .... (2.8)$$

where $l_v = \frac{\Delta H_{vap}}{M_1}$ is the heat of vapourization per gram of solvent.In study of dilute solutions, it has been found convenient to express the concentration of a solution in terms of its molality that is the number of moles of solute dissolved in 1000 grams of solvent. In the solution under consideration $\frac{w_2}{M_2}$ moles of solute are dissolved in w_1 grams of solvent, and so the molality m is given by

$$m = \frac{w_2}{M_2 w_1} \times 1000 \quad \ldots\ldots (2.9)$$

So, in terms of molality equation 2.8 becomes

$$\Delta T = \frac{RT_o^2}{1000 l_v} \cdot m = K_b . m \quad \ldots\ldots (2.10)$$

where K_b is a constant for each solvent, defined by $K_b = \frac{RT_o^2}{1000 l_v}$. According to equation (2.10), the elevation of the boiling point of a solution is proportional to its molality, provided it is dilute and obeys Raoult's law. This theoretical deduction has been confirmed experimentally for a number of solvents and solutes. Strict proportionality between the molality and boiling point elevation holds only in extremely dilute solutions, but there is an approximate proportionality even in solutions of moderate concentration. Such deviations as are observed is partly due to the solutions not being dilute enough for the approximations made in the derivation of equation (2.10) to be justifiable, and partly because of deviations from Raoult's law due to nonideal behavior.

The constant K_b is called the **molal elevation constant or ebullioscopic** constant. It can be seen from equation (2.10) that it is physically equivalent to the rise of boiling point for a solution of unit molality, i.e., m = 1. Actually, a solution with a molality of unity would not be sufficiently dilute for equation (2.10) to be valid, and so K_b may be regarded as the boiling point elevation for a unit molal solution, if the values were proportional to that for a dilute solution. The values of K_b for some solvents are given in the table 2.1.

Table 2.1 – Ebullioscopic constant of some solvents

Solvent	**K_b (in K· kg/mol)**
Acetic acid	3.08
Benzene	2.53
Camphor	5.95
Carbon disulfide	2.34
Carbon tetrachloride	5.03
Chloroform	3.63
Cyclohexane	2.79
Diethyl ether	2.02
Ethanol	1.07
Water	0.512

Molecular Weight from Boiling Point Elevation

Since the molality of a solution is related to the molecular weight of the solute, according to equation 2.10, measurements of the boiling point elevation can be used to determine molecular weights of dissolved substances. For this purpose, combination of equation 2.10 with 2.9 gives

$$M_2 = K_b \cdot \frac{1000w_2}{Tw_1} \quad \text{.......} \ (2.11)$$

In order to apply this result, it is necessary to know the value of K_b. This may be obtained in two ways. First, from the boiling point and heat of vapourization of the solvent, and second, by measuring the boiling point elevation experimentally for a solution containing a solute of known molecular weight and applying equation 2.11. The results obtained by the two methods are generally in excellent agreement, provided the solutions are dilute, thus supplying confirmation of the theoretical arguments presented above.

2.3.3 Depression of The Freezing Point

Freezing point depression is the phenomenon that describes why adding a solute to a solvent result in the lowering of the freezing point of the solvent. When a substance starts to freeze, the molecules slow down due to the decreases in temperature, and the intermolecular forces start to take over. The molecules will then arrange themselves in a pattern, and thus turn into a solid. For example, as water is cooled to the freezing point, its molecules become slower and hydrogen bonds begin to "stick" more, eventually creating a solid. If salt is added to the water, the Na^+ and Cl^- ions attract the water molecules and interfere with the formation of the large network solid known as ice. In order to achieve a solid, the solution must be cooled to an even lower temperature. Depression of freezing point has applications in real life too. For example, ethylene glycol is added in high concentrations to water to produce antifreeze in a car. Antifreeze lowers the freezing point and increases the boiling point thus preventing your engine from boiling over or freezing in extremely cold places. Salt is placed on roads to decrease the freezing point of water preventing formation of ice in cold weather. Some insects make their own antifreeze, glycol. Although temperatures may be freezing where these insects reside during the winter, their cells do not freeze. Scientists have found a particular moth's eggs that can withstand temperatures down to -45°C. Certain parts of the ocean are below 0°C. The solutes in the water cause freezing point depression preventing the ocean to freeze in polar regions.

The relationship between the freezing point of the pure solvent and that of a solution may be seen with the aid of the vapour pressure curves in Fig-2.4. These curves show the temperature variation of the vapour pressure of the solvent over the pure solvent (e.g., water), the solution, and the solid solvent (e.g., ice), respectively.

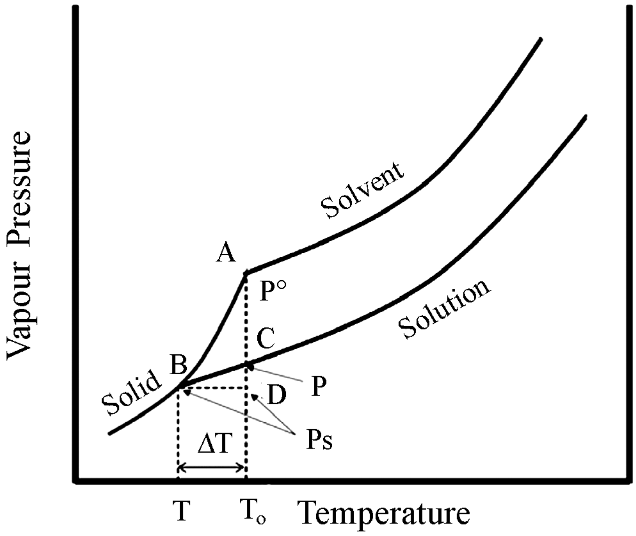


Figure 2.4: Lowering of freezing point of a solution

In the figure, A is the freezing point of the solvent, temperature T_o. Similarly, B, temperature T, is the freezing point of the solution, where the solution is in equilibrium with solid.The freezing point of the solution is obviously lower than that of the solvent, and the freezing point depression ΔT is equal to T – T_o. The distance AC is equivalent to P°– P at the freezing point of the solvent. Since P° at this temperature is a constant, similar to the arguments given in case of boiling point elevation, that AC is proportional to the to the relative lowering of the vapour pressure $\frac{P^\circ - P}{P^\circ}$. If, as in case of boiling point elevation, the vapour pressure curves for a number of dilute solutions are almost parallel straight lines in the vicinity of the freezing point, the ratio AC/BC will be constant. For such solutions, therefore, the depression of the freezing point ΔT will be proportional to the relative vapour pressure lowering, and hence to the mole fraction x_2 of the solute. Let us use the Clausius-Clapeyron equation (discussed later in this unit) again to write the relation between the vapour pressure of the solution P at T_0 and P_s at T.

$$\ell n\frac{P_S}{P} = -\frac{\Delta H_{vap}}{R}\left(\frac{T_0 - T}{T_0 T}\right) \quad .... (2.12)$$

As we can see from figure 2.4, there is one more equilibrium between the solid and the vapour. For the solid, the vapour pressures are P° and P_s, at the temperatures T_0 and T, respectively. Now the transformation of solid directly to vapour is known as **sublimation**. So for this transformation the Clausius-Clapeyron equation will be

$$\ell n\frac{P_S}{P^\circ} = -\frac{\Delta H_{sub}}{R}\left(\frac{T - T_0}{T_0 T}\right) \quad .... (2.13)$$

In this equation ΔH_{sub} is the molar heat (enthalpy) of sublimation. Upon subtracting equation 2.12 from 2.13, replacing T_o – T by –ΔT (the lowering of freezing point), and T_oT by T_o^2 since T_o and T are not very different for a dilute solution, and utilizing the fact that the molar heat of fusion $\Delta H_{fusion} = \Delta H_{sub} - \Delta H_{vap}$, we get

$$\ell n\frac{P}{P^\circ} = \frac{\Delta H_{fusion}}{RT_0^2}\Delta T \quad .... (2.14)$$

Using Raoult's law for the solute and performing the transformations exactly like in the case of boiling point elevation. we get

$$\Delta T = -\frac{RT_0^2}{\Delta H_{fusion}} x_2 \quad .... (2.15)$$

This equation is equivalent to 2.7 except that the molar heat of fusion now replaces the heatof vapourization. By using arguments exactly similar to those employed previously, it is found that for dilute solutions

$$\Delta T = - K_f.m \quad .... (2.16)$$

where K_f is the **molal depression constant or the cryoscopic constant** and is given as $K_f = \frac{RT_0^2}{\Delta H_{fusion}}$. m is the molality of the solution. Remember that $\Delta T = T - T_o$ where T_0 is the freezing point of the pure solvent and T is the freezing point of the solution. The values of K_f for some solvents are given in the table 2.2. Experimental determinations of freezing point depressions are in general agreement with this conclusion; with relatively concentrated solutions deviations from equation 2.16 are observed, as is to be expected. Same as before, this equation can be used estimate the molecular weight of the solute

Table 2.2 –Cryoscopic constant of some solvents

Solvent	**K_f(in K· kg/mol)**
Acetic acid	3.90
Benzene	5.12
Camphor	39.7
Carbon disulfide	3.8
Carbon tetrachloride	30
Chloroform	4.68
Cyclohexane	20.2
Diethyl ether	1.79
Ethanol	1.99
Water	1.86

2.3.4 Osmosis and Osmotic Pressure

A number of natural and synthetic materials exhibit selective permeation, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth, are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature, while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to **as semipermeable membranes**. Consider the apparatus illustrated in Figure 2.5, in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of solvent is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as osmosis. The definition of osmosis is given as

"*The spontaneous flow of solvent into a solution or from a more dilute to a more concentrated solution, when the two liquids are separated from each other by a suitable membrane.*"

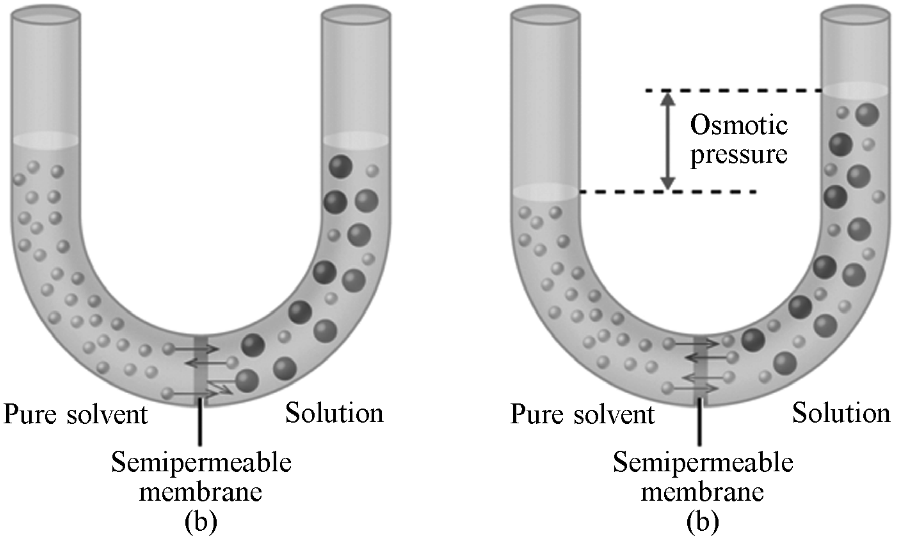


Figure 2.5 : (a) A solution and pure solvent are initially separated by a semipermeable membrane. (b) Net transfer of solvent molecules to the solution occurs until its osmotic pressure makes equal rates of transfer in both directions. This Diagram is available under Creative Commons Attribution 4.0 International License from https://openstax.org/

In figure 2.5, the level of the liquid will rise in the tube until the hydrostatic pressure so produced is sufficient to stop the flow of water. As a result of osmosis, a pressure is developed which opposes the tendency for the solvent to pass through the semipermeable membrane into the solution. This pressure is called the osmotic pressure of the solution.It is defined as the excess pressure which must be applied to a solution to prevent the passage into it of solvent when the two liquids are separated by a perfectly semipermeable membrane. In more perfect term, osmotic pressure should be applied to make the rate of transfer of solvent molecule in both directions through the membrane exactly equal. Osmotic pressure is not the pressure produced by the solution. The osmotic pressure comes to existence only when the solution is separated from the solvent by a semipermeable membrane. The resulting osmosis, or tendency for osmosis to occur, then produces an excess pressure in the solution. When this excess pressure attains the value of the osmotic pressure, the tendency for solvent to enter the solution is exactly compensated by the reverse tendency and a condition of equilibrium occurs.

Examples of osmosis are many biological systems because cells are surrounded by semipermeable membranes. When dried raisins (kismis) are placed in water, they swell up because of osmosis. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solutes in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be isotonic with blood serum. If a less concentrated solution, a hypertonic solution, is injected in sufficient quantity to dilute the blood serum.Water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called hemolysis. When a more concentrated solution, a hypertonic solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called crenation.

Osmotic Pressure Relationship

The first quantitative measurements of osmosis were made by W. F. P. Pfeffer (1877). It was shown by J. H. van't Hoff (1887) that Pfeffer's measurements of osmotic pressure indicated a parallelism between the properties of solution and gases. He showed that it is possible to write $\frac{\Pi}{c}$ = constant at a constant temperature where Π is the osmotic pressure and c is the concentration of the solution. Not only that, the proportionality between osmotic pressure and the absolute temperature, at a given concentration shows that a law equivalent to Gay-Lussac's law for gases applies to solutions i.e. $\frac{\Pi}{T}$ = constant for a solution of a definite concentration. Combining these equations we can write

$$\Pi = cRT \text{ ...... } (2.17)$$

The constant R in this equation can be taken as the gas constant. If the osmotic pressure is known, the molar concentration of the solution can be evaluated. This result can be utilized to determine the molecular weight of the solute, provided the weight concentration is known

2.3.5 Thermodynamic Derivation Using Chemical Potential

In this section we will try to find the thermodynamic relation in terms of amount of solute using the chemical potential. For that purpose, we will use the concepts and relations developed in unit 1 For all the cases, we will assume a binary solution i.e. a solution made up of one solute and one solvent. In all the discussion, the mole fraction of the solvent is x_1 and the solute is x_2. In all the derivations, the subscript 1 shall denote the solvent and 2 shall denote solute.

Vapour Pressure Lowering

We will begin by explaining the first colligative property discussed. Let us first write the Gibbs-Duhem equation for the binary mixture.

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \text{ ...... } (2.18)$$

Since $\frac{n_1}{n_2} = \frac{x_1}{x_2}$, we can write equation 2.18 after rearranging as

$$d\mu_2 = -\frac{x_1}{x_2}, d\mu_1 \text{ ...... } (2.19)$$

The chemical potential of the solvent in the solution is written as

$$\mu_1 = \mu_1^* + RT \ell n x_1$$

$$\therefore d\mu_1 = \frac{RT}{x_1} dx_1 \quad .... (2.20)$$

Using equation 2.20 in equation 2.19 we get

$$d\mu_2 = -\frac{x_1}{x_2} \cdot \frac{RT}{x_1} dx_1 = -RT\frac{dx_1}{x_2} \quad .... (2.21)$$

We know that $x_1 + x_2 = 1$; so $dx_1 + dx_2 = 0$; and $dx_1 = -dx_2$. So equation 2.21 becomes

$$d\mu_2 = RT\frac{dx_2}{x_2} \quad .... (2.22)$$

Integration of equation 2.22 yields

$$\mu_2 = \mu_2^* + RT \ln x_2 \quad .... (2.23)$$

where μ_2^* is the chemical potential of the pure solute. As we can see that the equation for the solute is similar to that of the solvent.

Boiling Point Elevation

The quantitative relation between the elevation of boiling point and the concentration of the solution can be derived using chemical potential. Consider a solution which is in equilibrium with the vapour of the pure solvent. Basically, we have the following equilibrium at the boiling point of the solution. Solvent in solution $\rightleftharpoons$ Vapour of pure solvent. The thermodynamic condition of equilibrium is

$$\mu_{1(sol)}(T, P) = \mu_{1(v)}^*(T, P) \quad .... (2.24)$$

In this equation the subscript 1(sol) indicates chemical potential of the solvent in the solution and subscript 1(l) indicates chemical potential of the pure solvent in the vapour form. T is the boiling point of the solution. At constant pressure, this temperature is a function of mole fraction of the solvent. For an ideal solution, we have $\mu_{(1(sol)} = \mu_{(1(l)}^* + RT \ln x_1$. So using equation 2.24 we can write

$$\ell n\, x_1 = \frac{\mu_{1(v)}^* - \mu_{1(l)}^*}{RT} = \frac{\Delta_{vap}\mu_1^*}{RT} \quad .... (2.25)$$

In this equation, $\Delta_{vap}\mu_1^*$ is the molar free energy of evapouration of the pure solvent at temperature T and pressure P. Equation 2.25 is the required relation between the composition of the solution and the boiling point. We can use the Gibbs-Helmholtz equation to derive in terms of molar enthalpy of vapourisation. So differentiating equation 2.25 with respect to x_1 at constant P, we get

$$\frac{1}{x}=\frac{1}{R}\left\{\left[\frac{\partial\left(\frac{\Delta_{vap}\mu_1^*}{T}\right)}{\partial T}\right]_P\right\}\left(\frac{\partial T}{\partial x_1}\right)=-\frac{\Delta H_{vap}}{RT^2}\left(\frac{\partial T}{\partial x_1}\right)_P$$

$$\therefore \frac{dx_1}{x_1}=-\frac{\Delta H_{vap}}{RT^2}dT \quad \text{......} \ (2.26)$$

We can now perform integration of equation 2.26 to get

$$\frac{1}{T}=\frac{1}{T_o}+\frac{R\,\ell n\,x_1}{\Delta H_{vap}} \quad \text{......} \ (2.27)$$

Here, T_o is the boiling point of the pure solvent. This equation is another version of equation 2.6 which we have discussed earlier. So we can replace the mole fraction of the solute in equation 2.27 and do the approximations as discussed in section 2.3.2 to arrive at equation 2.10.

Freezing Point Depression

The quantitative relation between the depression of freezing point and the concentration of the solution can be derived thermodynamically following the sequence of steps adopted in the derivation of expression for the elevation of boiling point. Basically, at the freezing point of the solution, we have the equilibrium. Solvent in solution $\rightleftharpoons$ Solid solvent. The condition of equilibrium is

$$\mu_{1(sol)}\ (T,\ P) = \mu_{1(s)}^*\ (T,\ P) \quad \text{......} \ (2.28)$$

This time the subscript (s) denotes solid. We can follow the exact derivation as above to get

$$\ell n\, x_1 = \frac{\Delta_{fus}\mu_1^*}{RT} \quad .... (2.29)$$

Here, $\Delta_{fus}\mu_1^*$ is the molar free energy of fusion of the pure solvent at temperature T and pressure P. Using Gibbs-Helmholtz equation we can arrive at the relation

$$\frac{1}{T} = \frac{1}{T_0} + \frac{R\,\ell n\, x_1}{\Delta H_{fus}} \quad .... (2.30)$$

Equation 2.30 can be used to compute the freezing point of a solution in which the amount fraction of solvent is x_1. Replacing the mole fraction of the solute and rearranging we can arrive at equation 2.15.

Osmotic Pressure Relationship

Now we are going to discuss the thermodynamic derivation of osmotic pressure law. We have a solution in equilibrium with its vapour at a constant temperature T. Suppose the external pressure on the solution is increased by a small amount from P to dP and the equilibrium vapour pressure is consequently changed from P_v to P_v + dP_v. The corresponding chemical potential changes at constant temperature are given by

$$d\mu_l = \bar{V}_l dP_v$$

$$d\mu_v = \bar{V}_v dP_v$$

Here the subscript l refers to the liquid (solution) phase and v to the vapour.The quantity $\bar{V}_l$ is the partial molar volume of the solvent constituent in the solution. Similarly, $\bar{V}_v$ is the partial molal volume of the solvent in the vapour.But since the latter does not contain any solute, this is the same as the actual molar volume, $V_{m(v)}$. For the system to remain in equilibrium after the pressure changes, the partial molal free energy (or chemical potential) changes must be the same for solution and vapour. Hence, at a given temperature,

$$\bar{V}_l dP = V_{m(v)} dP_v \quad .... (2.31)$$

At low vapour pressures the vapour may be supposed to obey the ideal gas laws, so that $V_{m(v)}$, may be replaced by $\frac{RT}{P_v}$; hence

$$V_l dP = \frac{RT}{P_v} \cdot dP_v \quad \text{.......} \ (2.32)$$

when the external pressure is changed from P° to P, where P – P° is equal to the osmotic pressure of the solution, the vapour pressure is increased from P_v to P_v^o; consequently, the left-hand side of equation 2.32 must be integrated between the limits of P° to P, and the right-hand side from P_v to P_v^o.

$$\int_{P^o}^{P} \bar{V}_l dP = RT \int_{P^o}^{P_v^o} \frac{dP_v}{P_v} \quad \text{.......} \ (2.33)$$

In a dilute solution, partial molar volume of the solvent in the solution is the same as thatof the pure solvent. So using $\bar{V}_l = \bar{V}_1$ and integrating equation 2.33 we get

$$\bar{V}_l (P - P^o) = RT\, \ell n \frac{P_v^o}{P_v} \quad \text{.......} \ (2.34)$$

Since P – P° is equal to Π, the osmotic pressure of the solution, it follows that

$$\Pi \bar{V}_l = RT\, \ell n \frac{P_v^o}{P_v} \quad \text{.......} \ (2.35)$$

This relationship between osmotic pressure and vapour pressure can be obtained thermodynamically in several different ways. It is independent of any theory or mechanism of osmotic pressure. Now using Raoult's law and implementing assumptions made for dilute solutions, we can write

$$\Pi \bar{V}_l = RTx_2 \ \text{.......} \ (2.36)$$

Since $x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$, according to the definitions of the quantities, equation 2.36 can be written as

$$\Pi \frac{V}{n_1} = RT \frac{n_2}{n_1}$$

$$\therefore \Pi = \frac{n_2}{V}RT = cRT \text{ ...... } (2.37)$$

Here c is the concentration of the solution. Equation 2.37 is our familiar equation of osmotic pressure.

2.3.6 Abnormal colligative properties

Abnormal colligative properties, which are also called anomalous colligative properties, are those which deviate from the norm. Chemist Jacobus van't Hoff was the first to describe anomalous colligative properties, but it was Svante Arrhenius who succeeded in explaining anomalous values of colligative properties. We learned that colligative properties are the properties of solutions that rely only on the number (concentration) of the solute particles, and not on the identity/type of solute particles, in an ideal solution. So let us take an example depression of freezing point. Suppose we have solution in water whose molality is 0.01 m. So according to the derivation of the colligative properties, irrespective of the solute used, the depression in freezing point should be

$$\Delta T = -K_f.m = 1.86° \text{ Cm}^{-1} \times 0.01 \text{ m} = -0.0186° \text{ C}$$

The expected freezing point for this solution would be –0.0186° C Let us say that this solution was that of urea, the measured freezing point is close to –0.0186° C. If it were to be a solution of NaCl, then the measured freezing point would then be –0.0361 C. This type of deviation i.e. departure from ideal behaviour, which is of great chemical significance, has been observed with aqueous solutions of strong acids and bases, of salts, and, in general, with solutions capable of conducting an electric current.

The colligative properties of an electrolytic solution can be expressed in terms of those of a nonelectrolytic solution by use of the **van't Hoff factor**. It is defined as the ratio of colligative effect produced by a given concentration of an electrolytic solution and of a nonelectrolytic solution of the same concentration, i.e.

$$i = \frac{\text{Colligative effect prouced by a given concentration of an electolytic solution}}{\text{Colligative effect prouced by the same concentration of an electolytic solution}}$$

The van't Hoff factor is really just a mathematical factor that scales the mixed or label concentration of a solute so that it matches the actual or total concentration of all species generated by that solute after dissolution. The van't Hoff factor is actually a measured quantity. The most straightforward way to measure it is to measure a colligative property of the solution such as freezing point depression, boiling point elevation, or osmotic pressure. Each of these colligative properties of a solution will reveal a true total concentration of all species. This measured concentration is often referred to as the effective concentration. The ratio between this effective concentration and the stated concentration is the van't Hoff factor. So in our above example, for the solute urea i = 1. For a strong electrolyte like NaCl that produces 2 moles of ions in a solution/ mole of solute dissolved, the effect on the freezing point depression would be expected to be twice as much as that for a nonelectrolyte. The expected i = 2. This leads the colligative properties to be rewritten as demonstrated in the table below.

Original	Rewritten
$\Delta T = K_b.m$	$\Delta T = iK_b.m$
$\Delta T= -K_f.m$	$\Delta T = -iK_f.m$
$\Pi = cRT$	$\Pi = icRT$

Dissociated solutes

The degree of dissociation is the fraction of the original solute molecules that have dissociated. It is usually indicated by the Greek symbol α. There is a simple relationship between this parameter and the Van't Hoff factor. If a fraction of the solute dissociates into n ions, then

$$i = 1 + \alpha(n-1) \text{ .... } (2.38)$$

For example, the dissociation :- $KCl \rightleftharpoons K^+ + Cl^-$ yields n = 2 ions, so that i =

1 + α. For dissociation in the absence of association, the van't Hoff factor is i > 1

Associated solutes

Similarly, if a fraction aof n moles of solute associate to form one mole of a dimer, trimer, etc., then

$$i = 1 - \alpha\left(1 - \frac{1}{n}\right) \quad \ldots\ldots \ (2.39)$$

For the dimerisation of acetic acid in benzene, $2CH_3COOH \rightleftharpoons (CH_3COOH)_2$. 2 moles of acetic acid associate to form 1 mole of dimer, so that $i = 1 - \frac{\alpha}{2}$. For association in the absence of dissociation, the van't Hoff factor is $i < 1$.

So, from all the discussion we can write

- ☐ When solute particles associate in solution, i is less than 1. For example, carboxylic acids such as acetic acid (ethanoic acid) or benzoic acid form dimers in benzene, so that the number of solute particles is half the number of acid molecules.
- ☐ When solute particles dissociate in solution, i is greater than 1 (e.g. sodium chloride in water, potassium chloride in water, magnesium chloride in water).
- ☐ When solute particles neither dissociate nor associate in solution, i equals 1 (e.g. glucose in water).

2.4 Phase Equilibrium and Phase Diagram

Phase diagrams are one of the most important sources of information concerning the behaviour of elements, compounds and solutions. They provide us with the knowledge of phase composition and phase stability as a function of temperature (T), pressure (P) and composition (C). Furthermore, they permit us to study and control important processes such as phase separation, solidification, sintering, purification, growth and doping of single crystals for technological and other applications. Although phase diagrams provide information about systems at equilibrium, they can also assist in predicting phase relations, compositional changes and structures in systems not at equilibrium.

2.4.1 Definitions of Phase, Component and Degrees of Freedom

Before we can start our discussion about phase equilibrium it is necessary to define the important terms involved.

Phase (P)

A phase is defined as "any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces." Ice, liquid water and water vapour are three phases of H_2O which are widely known. Each of the phases is physically distinct and homogeneous, and there are definite boundaries between them. An ice water mixture has two phases, as do systems containing ice-and-vapour, and water-and-vapour. We know that several solids may exist for a substance and each of the solid forms is also called a phase. Diamond and graphite are most common examples (both are solid carbon). One liquid layer constitutes one phase, whether it is a pure substance or a mixture. Two liquid layers in contact represent two phases. A gas or a mixture of gases always constitutes one phase as the system is homogeneous and there is no bounding surface between the different gases that may be present.

Components (C)

"The minimum number of independently variable constituents in terms of which the composition of each phase of a heterogeneous system can be expressed directly or in the form of a chemical equation are called the components of system."

For example, a system consisting of a solution of sugar in water (solution phase) is a two-component system because the solution phase present in the system consists of two constituents—water and sugar. The water system, for example, consists of one component.The composition of each of the three phases solid, liquid and vapour, can be expressed in terms of the component H_2O. Any system consisting of a single chemical individual is always a one-component system.A salt and water solution, to quote a simple case, forms a familiar type of two-component system. For example, the saturated solution of sodium chloride consists of three phases - solid sodium chloride, salt solution and water vapour in equilibrium. The chemical composition of each phase of the system can be expressed if we consider two chemical constituents NaCl and water. Hence, it is a two-component system.

Degrees of Freedom or Variance (F)

"The number of degrees of freedom or variance of a system is the number of variable factors, such as temperature, pressure and concentration, which need to be fixed in order that the condition of a system at equilibrium may be completely defined." In other words, "The smallest number of independently variable factors

such as temperature, pressure and concentration which must be required in order to define the system completely are called the degree of freedom or variance."

When a system has no degree of freedom **(F = 0)** then it is called **non-variant system** or **invariant system**. When a system has only one degree of freedom (F = 1) it is called a **univariant** or a **monovariant system**. Similarly, a system having two degrees of freedom (F = 2) is a **bivariant system**.

The system ice $\leftrightharpoons$ water $\leftrightharpoons$ vapour has no degree of freedom (i.e., F = 0). The three phases of water i.e. ice, liquid water and vapour can exist together in equilibrium only at a particular-temperature and pressure (corresponding to the freezing point) and no factor is necessary to be specified to define the system. Hence, a system consisting of ice, water and vapour in equilibrium has no degree of freedom i.e. it is a non-variant system. The concept of degrees of freedom will be more clear through the following discussions.

2.4.2 Phase rule and its derivations

The general conditions of equilibrium between phases can be summarized in the form of a simple generalization known as the phase rule. This rule was deduced theoretically by J. Willard Gibbs (1876). Provided the equilibrium between the phases is not influenced by gravity, by electrical or magnetic forces, or by surface action, and only by temperature, pressure and concentration, then the phase rule states that the number of degrees of freedom (F) of the system is related to the number of components (C) and number of phases (P) present at equilibrium by the equation

$$F = C - P + 2 \quad \ldots\ldots \quad (2.40)$$

The Gibb's phase rule can be derived on the basis of thermodynamic principle

Let us consider a heterogeneous system consisting of P number of phasesand C number of components in equilibrium. Let us assume that the system is non-reacting that is the transfer of a component from one phase to another does not involve any chemical reaction. When the system is in equilibrium it can be explained completely by specifying the following variables : (i) Pressure, (ii) Temperature (iii) Composition of each phase. So

(a) Total number of variables required specifying the state of system :

(i) Temperature (same for all phases)

(ii) Pressure (same for all phases)

(iii) Concentration

Independent concentration variables for one phase with respect to the C components = C – 1 [Conc. of last component is independent]

Independent concentration variables for P phases with respect to the C components = P(C – 1)

Total number of variables = P(C – 1) + 2

The various phases present in the system can remain in equilibrium only when the chemical potential (μ) of each component is the same in each phases i.e.

$$\mu_{1(a)} = \mu_{1(b)} = \cdots\cdots\cdots = \mu_{1(P)} \text{ For component 1}$$

$$\mu_{2(a)} = \mu_{2(b)} = \cdots\cdots\cdots = \mu_{2(P)} \text{ For component 2}$$

$$\vdots$$

$$\mu_{C(a)} = \mu_{C(b)} = \cdots\cdots\cdots = \mu_{C(P)} \text{ For component C}$$

For each component the no of equilibria for P phases = (P – 1). (b) For C component the no of equilibria for P phases = C (P – 1). Total no. of equilibria involved (E) = C (P – 1).

So the number of variables remaining undetermined for the system at equilibrium is the degrees of freedom

$$F = [P(C - 1) + 2] - C(P - 1) = C - P + 2$$

This is the Gibbs phase rule.

2.4.3 Phase diagram for water

A diagram that depicts existence of different phases of a system under equilibrium is termed as **phase diagram**. It is a graphical representation giving the conditions of pressure and temperature under which various phases exist and transform. It is actually a collection of solubility limit curves. It is also known as equilibrium or constitutional diagram. Phase diagrams are classified according to the number of component present in a particular system.

If a system consists of just one component (e.g.: water), equilibrium of phases exist is depicted by **unary phase diagram**. For one component system, the least number of phases possible in any system is one. So according to Gibb's phase rule

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

Hence, a one-component system requires maximum of two variables to be fixed in order to define the system completely. The two variables are temperature and pressure. There are points, lines and areas in a phase diagram as we will see in the following section. In case of a one component phase diagram, point on a phase diagram represents a non-variant system; area represents a bivariant system and curve or a line represents a univariant system.

Water is a one component system which is chemically a single compound. The three possible phases in this system are: ice (solid phase), water (liquid phase) and vapour (gaseous phase). Hence, water constitutes a three-phase, one-component system. Since water is a three-phase system, it can have the following equilibria: ice $\leftrightharpoons$ water, ice $\leftrightharpoons$ vapour, water $\leftrightharpoons$ vapour. The phase diagram of water has been shown in figure 2.6.

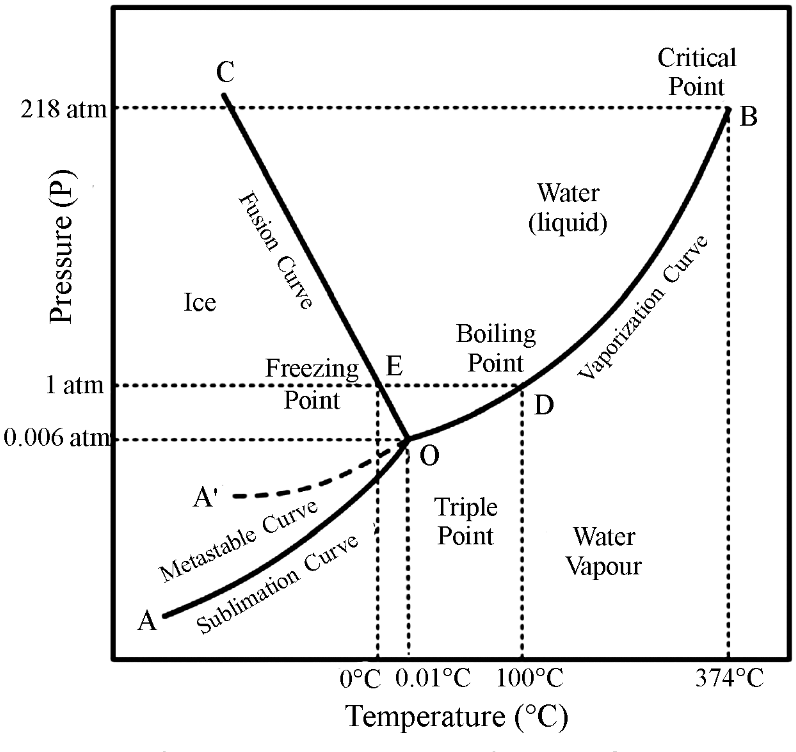


Figure 2.6 : The Phase Diagram of Water

The explanation for different curves, lines and areas under the diagram is as follows.

(a) Areas : There are three distinct areas in the phase diagram of water. **Area AOC** which is the ice phase; **Area COB** which is the liquid water phase and **Area below BOA** which is the water vapour area. Every area contains one component C = 1 and one phase P = 1. So, F = 2. Hence, each area is a bivariant system. So, it becomes necessary to specify both the temperature and the pressure to define a one phase-system.

(b) Curves : The phase diagram of the water system consists of three stable curves and one metastable curve.

Curve OB : The curve OB is known as vapour pressure curve or the vapourization curve of water and tells about the vapour pressure of water at different temperatures. Along this curve, the two phases—water and vapour exist together in equilibrium.At point D, the vapour pressure of water become equal to the atmospheric pressure that is 1 atm and the corresponding temperature 100°C represents the boiling point of water. The curve OB finishes at point B (temp. 374°C and pressure 218 atm) where the liquid water and vapour are indistinguishable and the system has only one phase. This point is called the **critical point**. So a critical point in a phase diagram is the point at which the substance is indistinguishable between liquid and gaseous states.

Curve OA : It is the **sublimation curve**. Along this curve, solid ice is in equilibrium with its vapour. Curve OA starts from the temperature 0.01°C above which solid water i.e., ice cannot exist. The curve ends at A. It is in absolute zero (– 273°C). At this temperature, no vapour can exist and, hence only the solid water(ice) is present. At the other points of the curve OB, ice is in equilibrium with vapour. Hence, there are two phases. According to phase rule, F = C – P + 2 = 1 – 2 + 2 =1.Hence, the system is univariant.

Curve OC : It is the melting point curve or fusion curve. Along this curve two phases, ice and water are in equilibrium. The inclination of OC line towards the pressure axis indicates that the melting point of ice is slightly lowered by increase of pressure. Le Chatelier's principle states that "Increase in pressure causes the water - ice equilibrium to shift in such a direction that there is a decrease in volume". So when water forms ice, the density increases. This is actually an exception. For many other phase diagrams, the fusion curve leans towards right. The curve OC starts from point O but there is no limit for this curve. It goes upto a point corresponding to 2000 atm. According to phase rule, $F = C - P + 2 = 1 - 2 + 2 = 1$ (univariant). The normal freezing point or the melting point of water is point E which corresponds to pressure 1.00 atm and temperature 0°C.

Curve OA' : It is called **"metastable curve"**. When water is cooled below its freezing point without separation of ice then the water is said to be "super cooled water". The vapourpressure curve of liquid water AO extends below O as shown by the dotted curve OA'. Along curve OA' liquid water coexists with vapour. The vapour pressures are different than over the solid. This equilibrium is called **"metastable equilibrium"** as slight disturbance brings the system to the stable region OB of the phase diagram.

(C) Triple Point O

The point O at which the curves AO, BO and CO meet is called the "Triple point". At this point all the three phases viz, ice, water and vapour co-exist. Thus, $P = 3$. $F = C - P + 2 = 1 - 3 + 2$, So $F = 0$. It indicates that there is only one set of variables P and T at which all the three phases coexist. If any of the variables is changed, then the number of phases decreases. If the temperature is raised, the heat melts the soild ice.There is no change in temperature or pressure of the system occurs till the entire solid has completely converted into liquid. If ithappens the system becomes a two-phase system ($P = 2$). In case of water the triple point O occurs at 0.006 atm and 0.01°C.

2.4.4 Phase Diagram of CO_2

The phase diagram of CO_2 is also a one component phase diagram like water. So it contains all the features of the curve, area and points like the water phase diagram. Obviously, the positions of the curves are different. We will point out only the specialties of the carbon dioxide phase diagram here. The calculations of degrees of freedom and rest of the features are similar to that of water. The phase diagram is given in figure 2.7. The first difference with the water phase diagram is the slope of the fusion curve. It is leaning right in this case. In fact this is considered "normal" and the case of water is considered anomalous. The reason is, in case of CO_2 the right leaning fusion curve indicates that when solid melts into liquid, it expands in volume. This is not the case with water but most of the materials follows this trend. The triple point of CO_2 is located at 5.11 atm and -56.4°C which means below this pressure solid CO_2 does not melt into liquid. As seen clearly from the sublimation curve, At 1 atm, solid CO_2 does not melt at any temperature. Instead, it sublimes to form CO_2 vapour. That is why solid CO_2 is known as “dry ice”. Dry ice remains as a solid below –78°C and changes to gas above –78°C. It is used in water or liquid free refrigeration.

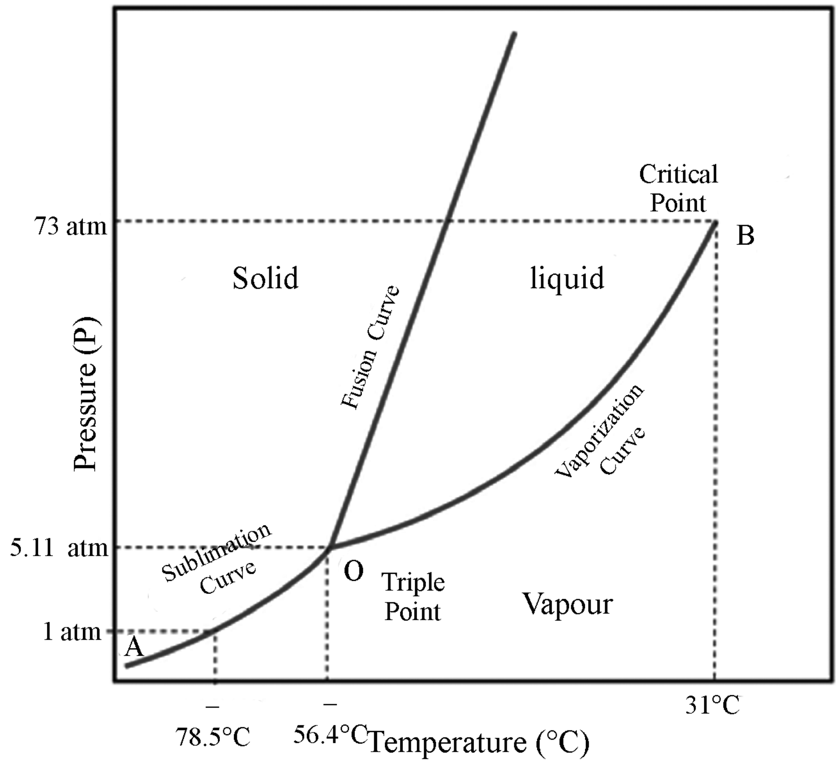


Figure 2.7 : Phase diagram of carbon dioxide

2.4.5 Phase Diagram of Sulfur

The sulfur phase diagram which is also a one component system is a little more complicated. This substance exists in two crystalline forms, namely, rhombic and **monoclinic** sulfur. At a specified pressure, there is a definite temperature, called the **transition point**, at which one form changes reversibly into the other. The stable form of sulfur at ordinary temperatures is the rhombic system, but if heated to 95.6°C, i.e., the transition point at 1 atm pressure, the rhombic crystals change to the monoclinic form.On cooling from above 95.6°, the monoclinic crystals change back to rhombic at this temperature. Crystalline forms that can undergo reversible changes of this type at the transition temperature are said to be **enantiotropic**, the phenomenon being referred to as enantiotropy (Greek : opposite change).

The phase diagram of sulfur is given in figure 2.8. AB is the vapour pressure curve of the rhombic crystals, and BC is that of the monoclinic form.The point B is the transition temperature under a pressure equal to the vapour pressure at thattemperature. The melting points of the two forms are at E (113°C) and C (119°C), respectively and the E point can be achieved only if sulfur is heated rapidly, so that the transition to the monoclinic form does not occur at B. The curves BF and CF give the conditions of equilibrium of the rhombic and monoclinic forms (along BF), and of the monoclinic solid and liquid (along CF). It will be observed that both curves slope to the right so that the transition point and the melting point of monoclinic sulfur increase with increasing pressure. However, because the former happens to change more rapidly than the latter the two curves meet at the point F.

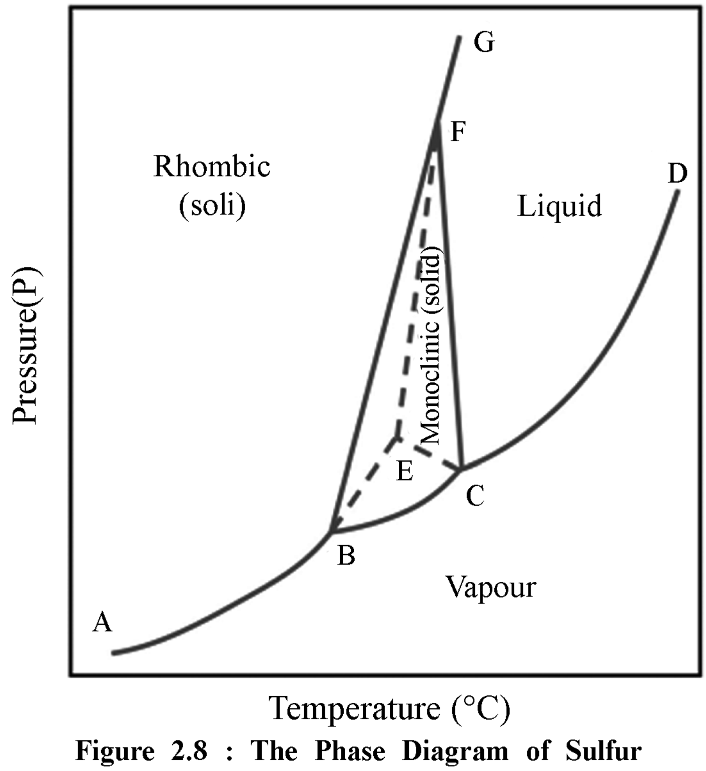


Figure 2.8 : The Phase Diagram of Sulfur

The dashed curves BE, EC and EF represent metastable equilibria; BE is the **metastable vapour pressure** curve for the **rhombic system** which can be achieved if this substance is heated rapidly past the transition point. The system then continues along ABE, without a break, instead of passing on to the stable curve BC. At E, the metastable melting point, the sulfur liquefies, and EC is the metastable vapour pressure curve of the liquid; this is continuous with the stable vapour pressure curve CD for the liquid form. The influence of pressure on the melting point of the rhombic solid is indicated by EFG, and the portion EF gives the conditions of the metastable equilibrium between rhombic sulfur and the liquid form. The curve FG, which is a continuation of EF, represents stable equilibrium between these two phases of sulfur. The sulfur system has **four** observable **triple points** at each of which three phases are in equilibrium. the four points and the corresponding phases are as follows :

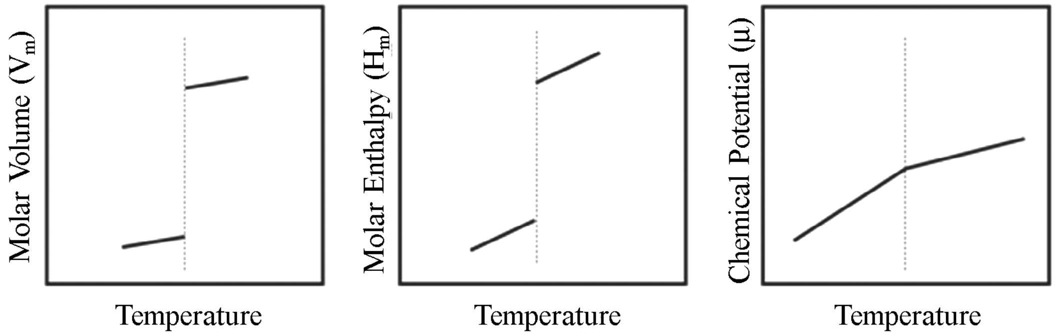
- ☐ B - Rhombic, monoclinic, vapour
- ☐ C - Monoclinic, liquid, vapour
- ☐ E - Rhombic, liquid, vapour
- ☐ F - Rhombic, monoclinic, liquid

For these points, $C = 1$, $P = 3$, and so, by the phase rule, $F = 0$. They are, therefore, all invariant points, with no degrees of freedom. The diagram also shows six curves representing the conditions of equilibrium of two phases; these are : AB(E)-Rhombic, vapour; BC - Monoclinic, vapour; (E)CD - Liquid, vapour; BF - Rhombic, monoclinic; (E)FG - Rhombic, liquid; CF - Monoclinic, liquid.Since $P = 2$, the phase rule requires that $F = 1 - 2 + 2 = 1$; there are thus six kinds of univariant system. The four single phases of sulfur, namely rhombic solid, monoclinic solid, liquid and vapour, each occupy a region of the equilibrium diagram.

2.4.6 First Order Phase Transition and Clapeyron equation

Phase transitions are classified into two types – first order and second order. First-order phase transitions are those that involve a latent heat. During such a transition, a system either absorbs or releases a fixed amount of energy per volume. During this process, the temperature of the system will stay constant as heat is added or withdrawn from the system. Familiar examples are the melting of ice or the boiling of water. The phase transition is possible only if a fixed amount of latent heat is added to the system at 100°C and 1 atm. Thus, the main characteristics of first-order transitions are : (1) The chemical potential is a continuous function of temperature. (2) The derivatives of chemical potential are discontinuous. Second-order phase transitions are also called "continuous phase transitions". Examples of second-order phase transitions are the ferromagnetic transition, superconducting transition etc. In a second-order phase transition of a substance, the chemical potential and its derivatives are continuous functions of temperature whereas the second derivatives are discontinuous.

First Order Phase Transition



Second Order Phase Transition

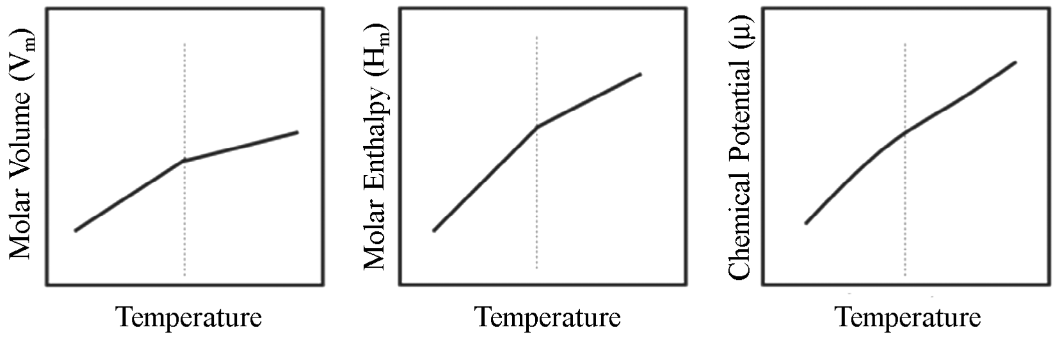


Figure 2.9 : Variation of thermodynamic quantities in different phase transitions

Clapeyron equation

Let us consider a system in which a pure substance i is present in two phases α and β. The two phases may be either solid and liquid, or solid and vapour, or liquid and vapour. At equilibrium, we will have

$$\mu_i^{\alpha} = \mu_i^{\beta} \quad \text{......} \quad (2.41)$$

Equation 2.41 is the condition of phase equilibrium. It means that when two phases are at equilibrium, chemical potential of a specific component must be equal in both the phases. Now let the temperature of the system be changed by an infinitesimal amount. When the equilibrium is re-established, the pressure also undergoes a change by an infinitesimal amount. Under these conditions, the chemical potentials μ_i^{α} and μ_i^{β} also change by infinitesimal amounts $d\mu_i^{\alpha}$ and $d\mu_i^{\beta}$ respectively. Since the system is again in equilibrium, it follows that

$$\mu_i^{\alpha} + d\mu_i^{\alpha} = \mu_i^{\beta} + d\mu_i^{\beta}$$

$$\therefore\ d\mu_i^{\alpha} = d\mu_i^{\beta} \quad \text{......} \quad (2.42)$$

We have used equation 2.41 here. We can write the chemical potential changes in terms of molar volume and molar entropy as

$$d\mu_i^{\alpha} = V_{m,i}^{\alpha}dP - S_{m,i}^{\alpha}dT \quad \text{......} \quad (2.43)$$

$$d\mu_i^{\beta} = V_{m,i}^{\beta}dP - S_{m,i}^{\beta}dT \quad \text{......} \quad (2.44)$$

Here, $V_{m,i}^{\alpha}$ and $V_{m,i}^{\beta}$ are the molar volume of the component in phase α and β. $S_{m,i}^{\alpha}$ and $S_{m,i}^{\beta}$ are the molar entropy in phase α and β. So substituting equation 2.43 and 2.44 in equation 2.42 we get

$$V_{m,i}^{\alpha}dP - S_{m,i}^{\alpha}dT = V_{m,i}^{\beta}dP - S_{m,i}^{\beta}dT$$

$$\therefore\ \frac{dP}{dT} = \frac{S_{m,i}^{\beta} - S_{m,i}^{\alpha}}{V_{m,i}^{\beta} - V_{m,i}^{\alpha}} = \frac{\Delta_{trs}S_m}{\Delta_{trs}V_m} \quad \text{......} \quad (2.45)$$

where $\Delta_{trs}S_m$ and $\Delta_{trs}V_m$ are the respective changes in entropy and volume of the system when 1 mol of pure substance B is transferred from the phase to the phase.

Equation 2.45 is known as the **Clapeyron equation**. Now in case of a solid-liquid phase transition if 1 mole of substance is transferred from the solid phase to the liquid phase, then we can write $\Delta_{trs}S_m$ and $\Delta_{trs}V_m$ as the changes in molar entropy and molar volume of fusion i.e. $\Delta_{fus}S_m$ and $\Delta_{fus}V_m$. At the equilibrium temperature, the transformation of the substance from solid to liquid is reversible, hence

$$\Delta_{fus}S_m = \frac{\Delta_{fus}H_m}{T} \quad \ldots\ldots (2.46)$$

$\Delta_{fus}H_m$ is the molar enthalpy of fusion or the latent heat of fusion. So the Clapeyron equation may be written as

$$\frac{dP}{dT} = \frac{\Delta_{fus}H_m}{T\Delta_{fus}V_m} \quad \ldots\ldots (2.47)$$

The transformation of solid to liquid is always an endothermic process and $\Delta_{fus}H_m$ is positive. Integration of equation 2.47 will give us

$$\Delta P = \frac{\Delta_{fus}H_m}{\Delta_{fus}V_m} \cdot \frac{\Delta T}{T} \quad \ldots\ldots (2.48)$$

Equation 2.48 describes variation in the melting point of a substance with the change in external pressure.

2.4.7 The Clausius-Clapeyron equation

While deriving the integration form of the Clapeyron equation, we have assumed that $\Delta_{fus}V_m$ is constant over the temperature and pressure range of the integration. This is true because for condensed phases (solid and liquid) the compressibility factor is small. However, if we want to derive the same for the liquid vapour equilibrium, the same cannot be held true. The molar volumes of gases are constant as they are for condensed phases. So, to derive the relation, an assumption was made by Clausius for simplification. Now for liquid vapour equilibrium we can write equation 2.47 as

$$\frac{dP}{dT} = \frac{\Delta_{vap}H_m}{T\Delta_{vap}V_m} = \frac{\Delta_{vap}H_m}{T\left[V_m^{vapour} - V_m^{liquid}\right]} \quad \ldots\ldots (2.49)$$

Here, $\Delta_{vap}H_m$ is the molar enthalpy of vapourisation. The molar volume of the vapour is very large compared to that of the liquid i.e. $V_m^{vapour} \gg V_m^{liquid}$. So Clausius stated that we can write $V_m^{vapour} - V_m^{liquid} \approx V_m^{vapour}$. Furthermore, if the vapour is considered an ideal gas, then $V_m^{vapour} = \frac{RT}{P}$ So under these assumptions equation 2.49 is modified to

$$\frac{dP}{P} = \frac{\Delta_{vap}H_m}{RT^2}dT \quad .... (2.50)$$

Equation 2.50 is known as the Clausius-Clapeyron equation. We can further work out the integration and find the how the equilibrium vapour pressure changes with temperature :

$$\ell n\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad .... (2.51)$$

Equation 2.51 is the more familiar form of the Clausius-Clapeyron equation which we have encountered while discussing colligative properties.

Application

The vapour pressures of all substances increase with increasing temperature, and the variation is always represented by a curve of the type shown infigure 2.17.The highest temperature at which vapour pressure can be measured isthe critical point, since liquids cannot exist above this temperature. Provided supercooling does not occur, the lower limit is the triple point, i.e., the freezing point of the liquid under its own vapour.

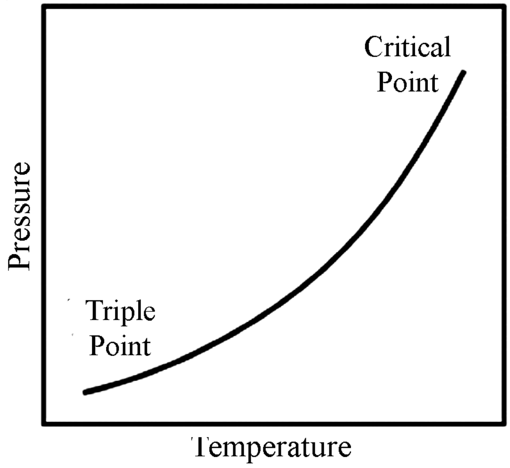


Figure 2.10: Vapour Pressure - Temperature Diagram

Thus, equation 2.51 gives the slope, at any temperature T, of the plot of vapour pressure against the absolute temperature. The Clapeyron-Clausius equation is of value in a number of ways.For example, if the rate of change of the vapour pressure with temperature is known, it is possible to calculate the heat of vapourization of the liquid at that temperature. Alternatively, if the latent heat is known, the rate of change of vapour pressure with temperature or, in other words, the change of boiling point with pressure can be determined.

2.5 Solutions of Gases in Liquids : Henry's Law

A solution of a gas in a liquid is a simple example of a two-component system. The gas dissolves in the liquid and a state of equilibrium is reached when the liquid is saturated with gas. Since there are two components (C = 2) and two phases, i.e., P = 2 (liquid and gas), the phase rule says that F = 2 – 2 + 2 = 2. There are thus two degrees of freedom, namely, temperature and pressure. So the composition of the saturated solution, i.e., the solubility of the gas depends on the temperature and pressure, as well as on the nature of the gas and the liquid solvent.

Since the solubility of a gas is usually determined by measuring the volume, rather than the weight, that has dissolved, the **absorption coefficient** of R. Bunsen (1857) is frequently used. At a given temperature, this coefficient is defined as *"The volume of gas, reduced to STP (0 °C and 1 atm pressure), that has been dissolved by unit volume of solvent under a partial pressure of 1 atm of the gas."*

If v_0 isthe volume of gas dissolved, reduced to STP, by the volume V of the solvent under the partial pressure P_{gas} of the gas, the absorption coefficient is given by

$$\alpha = \frac{v_0 P_{gas}}{V} \quad \ldots\ldots \ (2.52)$$

Effect of Pressure : Henry's Law

The influence of pressure on the solubility of a gas was expressed by W. Henry (1803). His conclusions, generally known as Henry's law, may be stated in the following form: *"the mass of gas dissolved by a given volume of solvent at constant* *temperature is proportional to the pressure of the gas in equilibrium with the solution."* If m is the mass of the gas dissolved by unit volume of solvent at equilibrium pressure P_{gas}, then according to Henry's law, we have

$$m = kP_{gas} \text{ ...... } (2.53)$$

where k is a proportionality constant. If a gas obeys equation 2.53, the plot of the solubility against the pressure should give a straight line passing through the origin. Provided the pressures are not too high or the temperatures too low, most gases obey Henry's law, especially if they are not very soluble. When any chemical reaction takes place between the gas and the solvent, e.g., hydrogen chloride, ammonia or carbon dioxide in water, Henry's law fails to hold if the total solubility is considered.

In equation 2.53 the quantity m is the mass of gas dissolved in unit volume, and hence it may be taken as equal to the concentration of gas molecules in the saturated solution. If this solution is moderately dilute, the concentration is proportional to the mole fraction of the dissolved substance, and so it is possible to write the Henry's law equation as

$$C = kP_{gas} \text{ ...... } (2.54)$$

where C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L); k is Henry's law constant (often in units of M/atm); P_{gas} is the partial pressure of the gas (expressed in units of atm). It can also be expressed as

$$P_{gas} = k_H x_2 \text{ ...... } (2.55)$$

where x_2 is the mole fraction of the solute and k_H is the Henry's law constant expressed in the unit of pressure i.e. atm or bar etc.

Table 2.3 k_H values of some gases in water at 298 K

Gas	k_H (k bar)	Gas	k_H (k bar)
H_2	71.18	CH_4	41.85
N_2	86.78	CO_2	1.67
O_2	44.0	HCHO	1.83×10^{-5}
Ar	40.3	$CH_2 = CHCl$	0.611

Correspondence between Henry's Law and Raoult's Law

In a special case where Henry's law is applicable over the entire range of concentration starting from $x_2 = 0$ (infinitely dilute solution, i.e. pure solvent) to $x_2 = 1$ (pure liquid solute). So for $x_2 = 1$, $k_H = P^*$ where P^* is the vapour pressure of pure liquid solute. So equation 2.55 can be written as

$$P_{gas} = x_2 P^* \quad \text{.......} \quad (2.56)$$

Equation 2.56 is the statement of Raoult's law when applied to a volatile solute. Hence it may be concluded that Raoult's law is a special case of Henry's law. All systems which obey Raoult's law must satisfy Henry's law, but the reverse is not true unless Henry's law is applicable over the entire range of concentrations.

2.6 The Duhem–Margules Equation

The Duhem–Margules equation, named for Pierre Duhem and Max Margules, is a thermodynamic statement of the relationship between the two components of a binary liquid mixture where the vapour mixture is regarded as an ideal gas.

$$\frac{d\,\ell n(P_A)}{d\,\ell n\, x_A} = \frac{d\,\ell n(P_B)}{d\,\ell n\, x_B} \quad \text{.......} \quad (2.57)$$

where P_A and P_B are the partial vapour pressures of the two constituents A and B of the binary liquid mixture and x_A and x_B are their corresponding mole fractions.

2.6.1 Thermodynamic Derivation

Let us consider a binary liquid mixture of two components A and B in equilibrium with their vapours at constant temperature and pressure. Then from Gibbs–Duhem equation is

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \text{......} \quad (2.58)$$

where n_A and n_B are number of moles of the component A and B while μ_A and μ_B are their chemical potential. Dividing equation 2.58 by $n_A + n_B$, we get

$$x_A d\mu_A + x_B d\mu_B = 0 \quad \text{......} \quad (2.59)$$

where x_A and x_B are the mole fractions of component A and B in the liquid mixture. Divining equation 2.59 by dx_A and rearranging

$$x_A \frac{d\mu_A}{dx_A} = -x_B \frac{d\mu_B}{dx_A} \quad \ldots\ldots (2.60)$$

Since $x_A + x_B = 1$; so $dx_A + dx_B = 0$ and $dx_A = -dx_B$. So equation 2.60 is written as

$$x_A \frac{d\mu_A}{dx_A} = x_B \frac{d\mu_B}{dx_B} \quad \ldots\ldots (2.61)$$

The chemical potential of any constituent of a liquid mixture is given by $\mu_i = \mu_i^* + RT \ln\left(\frac{P}{P^\circ}\right)$ where P is the partial vapour pressure of that constituent. In deriving the above expression, it is assumed that the vapour behaves as an ideal gas. For the component A, the above equation on differentiating with respect to x_A at constant temperature and total pressure gives

$$\frac{d\mu_A}{dx_A} = RT \frac{d\ell n\left(\frac{P_A}{P^\circ}\right)}{dx_A} \quad \ldots\ldots (2.62)$$

Similarly for component B

$$\frac{d\mu_B}{dx_B} = RT \frac{d\ell n\left(\frac{P_B}{P^\circ}\right)}{dx_B} \quad \ldots\ldots (2.63)$$

Substituting equation 2.62 and 2.63 in equation 2.61 we get

$$x_A RT \frac{d\ell n\left(\frac{P_A}{P^\circ}\right)}{dx_A} = x_B RT \frac{d\ell n\left(\frac{P_B}{P^\circ}\right)}{dx_B}$$

$$\frac{d\ell n\left(\frac{P_A}{P^\circ}\right)}{d\ell n\, x_A} = \frac{d\ell n\left(\frac{P_B}{P^\circ}\right)}{d\ell n\, x_B} \quad \ldots\ldots (2.64)$$

Equation 2.64 is the Duhem–Margules equation. Since $P^\circ = 1$ atm, sometimes it is written in the form of equation 2.57.

2.6.2 Application of Duhem – Margules Equation

The most important conclusion that can be drawn from the Duhem–Margules equation are : (i) If one component behaves in an ideal manner, the other one will also behave ideally and (ii) if one component shows positive (or negative) deviation from ideality so also must the other.

When One component behaves ideally : Let this component be A. Then, according to Raoult's law, we have $P_A = x_A P_A^*$ and therefore

$$d\ell n\left(\frac{P_A}{P^o}\right) = d\left\{\ell n\frac{x_A P_A^*}{P^o}\right\} = d\ell n\frac{P_A^*}{P^o} + d\ell n x_A = d\ell n x_A \quad \text{......} \quad (2.65)$$

$d \ln\frac{P_A^*}{P^o} = 0$ since $\frac{P_A^*}{P^o}$ is constant. So $\frac{d\ell n\left(\frac{P_A}{P^o}\right)}{d\ell n x_A} = 1$. According to Duhem–Margules equation $\frac{d\ell n\left(\frac{P_B}{P^o}\right)}{d\ell n x_B} = 1$ which upon integration leads to $P_B = x_B P_B^*$ i.e. the B component also follows Raoult's law meaning it is also ideal.

When one component exhibits positive deviation : Let this component be A. Obviously, we have $P_{A(real)} > P_{A(ideal)} = x_A P_A^*$. So following the same procedure we can write

$$\frac{d\ell n\left(\frac{P_{A(real)}}{P^o}\right)}{d\ell n x_A} > 1 \quad \text{......} \quad (2.66)$$

Thus, according to the Duhem-Margules equation, we must also have

$$\frac{d\ell n\left(\frac{P_{B(real)}}{P^o}\right)}{d\ell n x_B} > 1 \quad \text{......} \quad (2.67)$$

So component B must also be a real liquid.

2.6.3 Konowaloff's Rule

A general conclusion regarding the composition of the vapour phase in equilibrium with any particular solution (ideal or nonideal) can be obtained theoretically through the Duhem-Margules equation. Equation 2.57 can be written as

$$\frac{x_A}{P_A}\cdot\frac{dP_A}{dx_A}-\frac{x_B}{P_B}\cdot\frac{dP_B}{dx_B}=0 \quad ...... (2.68)$$

It can also be written under the condition $dx_A = -dx_B$ as

$$\frac{x_A}{P_A}\cdot\frac{dP_A}{dx_A}+\frac{x_B}{P_B}\cdot\frac{dP_B}{dx_A}=0 \quad ...... (2.69)$$

Since total pressure of the system $P = P_A + P_B$; so, we can write

$$\frac{dP}{dx_A}=\frac{dP_A}{dx_A}+\frac{dP_B}{dx_A}=\frac{dP_B}{dx_A}\left[1-\frac{x_BP_A}{x_AP_B}\right] \quad ...... (2.70)$$

Here we have substituted the value of $\frac{dP_A}{dx_A}$ from equation 2.69. The addition of either of the components causes an increase in the corresponding partial vapour pressure. Hence, the derivative $\frac{dP_B}{dx_A}=-\frac{dP_B}{dx_B}$ must be **negative**. The change in the total vapour pressure with theaddition of dx_A can be either positive or negative depending upon the sign of the expression within brackets in the equation 2.70. Thus, we have two alternatives

(i) $x_BP_A > x_AP_B$. In this case $\frac{dP}{dx_A}$ is positive since $\frac{dP_B}{dx_A}$ is negative. So, the condition is written as

$$\frac{P_A}{P_B}>\frac{x_A}{x_B} \quad ...... (2.71)$$

Now using Dalton's law of partial pressures, we have

$$\frac{y_A}{y_B}>\frac{x_A}{x_B} \quad ...... (2.72)$$

where y_A and y_B are the mole fraction of the components in the vapour phase.

So, the ratio of amount fractions of A and B in the vapour phase is greater than the corresponding ratio in the liquid phase. This means that the vapour is relatively richer in A than is the liquid from which it vapourizes. Thus, the vapour is richer in the component (here A) whose addition to the liquid mixture results in an increase in total vapour pressure

(ii) $x_B P_A < x_A P_B$. In this case $\frac{dP}{dx_A}$ is negative since $\frac{dP_B}{dx_A}$ is negative. So, a similar approach as before yields

$$\frac{y_A}{y_B} < \frac{x_A}{x_B}$$

$$\text{or} \quad \frac{y_B}{y_A} > \frac{x_B}{x_A} \quad \ldots\ldots \ (2.73)$$

that is, the ratio of amount fractions of B and A in the vapour phase is greater than the corresponding ratio in the liquid phase. This means that the vapour phase is relatively richer in B than is the liquid from which it vapourizes.Thus, the vapour is richer in the component (here B) whose addition to the liquid mixture results in an increase in total vapour pressure. Hence we have a general conclusion that

"The vapour phase is richer in the component whose addition to the liquid mixture results in an increase in total vapour pressure, or alternatively, the liquid phase is richer in the component whose addition to the liquid mixture results in a decrease in total vapour pressure."

This rule was stated empirically by D. P. Konowaloff on the basis of his systematical measurements of total vapour pressure of homogeneous liquid systems and is, therefore, known as **Konowaloff's rule**. Since the boiling point of a solution is inversely related to its vapour pressure (higher vapour pressure means lower boiling point and vice versa), we can state Konowaloff's rule in terms of boiling point of the mixture as

"The vapour phase is richer in the component whose addition to the liquid mixture causes a decrease in its boiling point, or alternatively, the liquid phase is richer in the component whose addition to the liquid mixture causes an increase in its boiling point."

2.7 Nonideal Mixtures of Miscible Liquids

If the two components A and B of a liquid mixture are different in character, the molecular forces between the A molecules will differ from those acting between the B molecules. The result will be that the presence of B will affect the escaping tendency of the A molecules, and vice versa. Raoult's law will then not be applicable. A mixture of two dissimilar liquids would thus be expected to behave in a nonideal manner, and this has been found to be the case. If the attraction between the B molecules is much stronger than that between the A molecules, the effect is to force the latter out of the liquid into the vapour.In other words, the escaping tendency of the A molecules will be increased by the presence of B. The partial vapour pressure of A will consequently be greater than is to be expected from Raoult's law. Such behaviour is known as **positive deviation** from the ideal law. We have already discussed that if one component of the mixture shows positive deviation; the other component must also show the same i.e. the overall mixture will show positive deviation. The type of vapour pressure curves obtained at a given temperature for mixtures of this kind is shown in Fig. 2.11, where the dotted lines indicate ideal behaviour.

If the two liquids constituting the mixture are both **nonpolar**, e.g., carbon tetrachloride and heptane, or if both are moderately polar, e.g., ether and acetone, the positive deviations from ideal behavior are not large. On the other hand, if one component is slightly polar while the other is highly polar or, the mixture consists of a polar and a nonpolar compound, e.g., an alcohol and a hydrocarbon, considerable positive deviations may occur. Such large deviations may lead to the liquids becoming partially **immiscible**.

If the two constituents of a mixture are such that the molecules of A and B attract one another strongly, and particularly if a compound between A and B is formed to some extent in the liquid, the vapour pressure of each constituent will be less than that required by the Raoult equation. This type of non-ideal behaviour is described as **negative deviation** from Raoult's law. The vapour pressure curves at constant temperature are then of the form shown in Fig. 2.11, where, as before, the dotted lines indicate ideal behaviour. Systems exhibiting negative deviations from Raoult's law are pyridine and acetic acid, chloroform and ethyl ether, and the halogen acids and water. In every case the molecules of the two components attract one another strongly, even to the extent of interaction or partial compound formation in the liquid state.

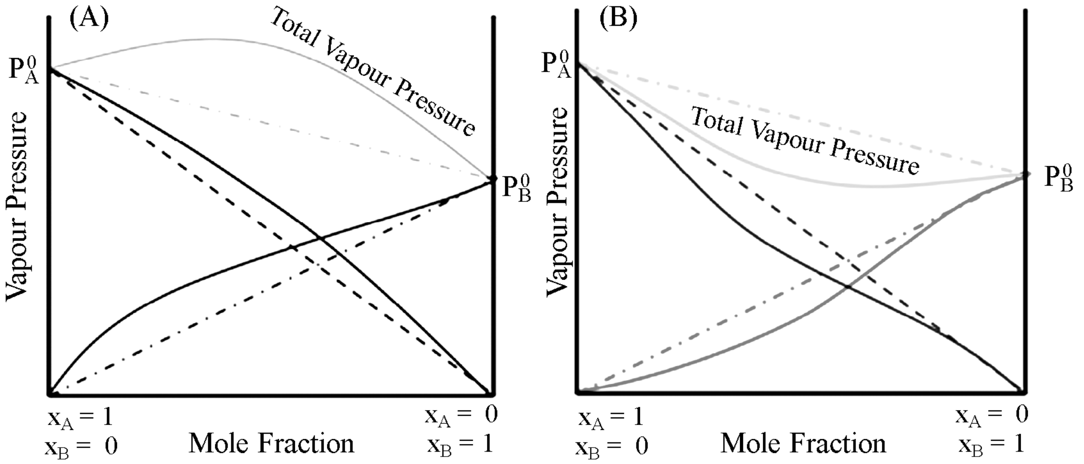


Figure 2.11 : Vapour pressure at constant temperature in a system exhibiting (A) positive deviations (B) negative deviations from Raoult's law

2.8 Composition of Liquid and Vapour

In section 2.6.3 we have discussed the composition of the vapour and liquid phase in case of liquid mixture in equilibrium with the vapour phase. Now we will consider only the ideal behaviour and discuss the plot of the of such phase equilibrium. For that purpose, we can plot both the mole fraction in the liquid phase and the vapour phase in the same plot. This is shownin Fig. 2.12. The upper curve is called the **liquidus** curve since this represents the line above which only **liquid phase** exists. A point anywhere on this line represents the two phases, liquid and vapour, in equilibrium with each other. Similarly, the lower curve is called the **vapourous** curve since it represents the curve **below** which **only vapour** exists. Along this line also the two phases, liquidand vapour, are in equilibrium with each other. A point anywhere in the region between the two curves represents the system in which both liquid and vapour coexist in equilibrium with each other. It is for this reason this region is known as the liquid-vapour region. For a given composition, the points on the liquidus and vapourous curves represent, respectively, the maximum and the minimum pressures within which the two phases can exist in equilibrium with each other.

The region between the liquidus and vapourous curves of Fig. 2.12 represents a region where both the phases exist in equilibrium with each other. For this region, P = 2 and thus F = 2. Since the temperature is fixed, one other variable (any one of x_A, y_A, P) is sufficient to describe the system completely. For instance, if P is chosen, then the amount fractions of the component A in the liquid and vapour phases are represented by the intersection points of a horizontal line, known as the **tie line**, drawn from the given P with those of liquidus and vapourous curves, respectively. If x_A is chosen as the describing variable, then the intersection of a vertical line from x_A with the liquidus curve yields the value of p and a horizontal line from P cutting the vapourous curve gives the vapour composition y_A.

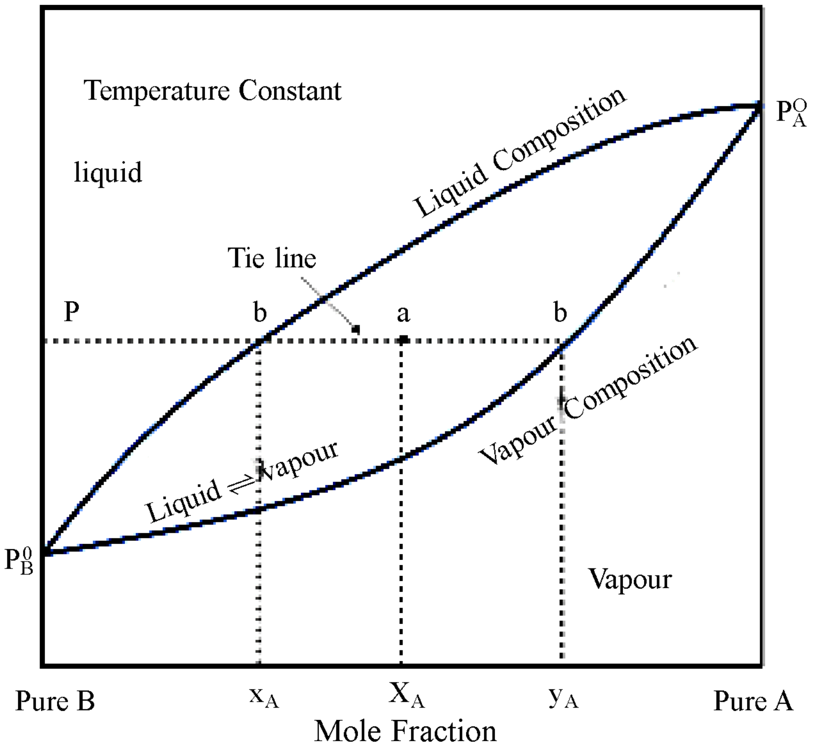


Figure 2.12 : Liquid vapour equilibrium

The Lever Rule

A point within the liquid and vapour curves represents two phases, liquid and vapour, in equilibrium with each other. For the point a shown in Fig. 2.12, the amount fraction of the constituent A in the liquid phase is given by the pointb (i.e. x_A) and that in the vapour phase is given by the point c (i.e. y_A). In fact, any point a on the tie line bc represents the same compositions of liquid and vapour phases, namely, x_A and y_A, respectively. The only difference that exists from point to point is the relative amounts of the two phases. The amount fraction X_A corresponding to the point a represents the amount fraction of the component A in the entiresystem consisting of liquid and vapour phases.

$$X_A = \frac{n_A(l)+n_A(v)}{n_A(l)+n_A(v)+n_B(l)+n_B(v)} \quad \ldots\ldots (2.74)$$

From the figure

$$(ab) = X_A - x_A = \frac{n_A(l)+n_A(v)}{n_A(l)+n_A(v)+n_B(l)+n_B(v)} - \frac{n_A(l)}{n_A(l)+n_B(l)} \quad \ldots\ldots (2.75)$$

$$(ac) = y_A - X_A = \frac{n_A(v)}{n_A(v)+n_B(v)} - \frac{n_A(l)+n_A(v)}{n_A(l)+n_A(v)+n_B(l)+n_B(v)} \quad \ldots\ldots (2.76)$$

We can calculate the ration of ab and ac by simplifying equation 2.75 and 2.76.

$$\left(\frac{ab}{ac}\right) = \frac{n_A(v)+n_B(v)}{n_A(l)+n_B(l)} = \frac{\text{Amount in the vapour phase}}{\text{Amount in the liquid phase}} \quad \ldots\ldots (2.77)$$

This is known as the lever rule.

2.9 Principle of fractional distillation

Now we will discuss the principle of fractional distillation. In a simple distillation the vapour is withdrawn and condensed. If the vapour is completely withdrawn and condensed the first drop gives a liquid of composition which is richer in the more volatile component, A, than the original liquid. But a simple distillation is unable separate the completely. In fractional distillation, the boiling and condensation cycle is repeated successively. Generally if the boiling points of the components of the liquid mixture differ by less than 50°C, fractional distillation is necessary. For this purpose of understanding, we will look at the boiling point diagram which is nothing but a modified version of the diagram depicted in figure 2.12.

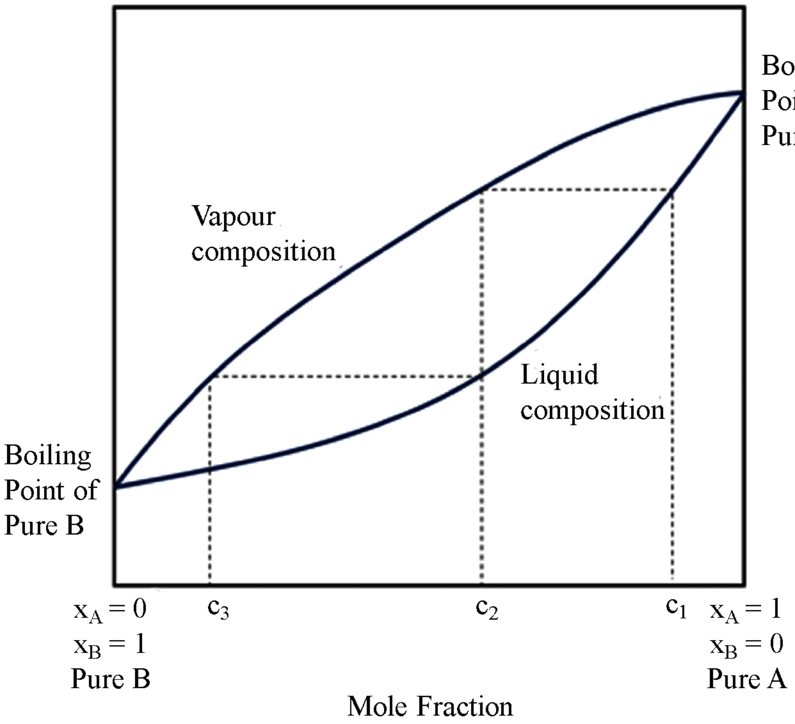


Figure 2.13 : Principle of fractional distillation

According to this diagram, if you boil a liquid mixture C_1, you will get a vapour with composition C_2, which you can condense to give a liquid of that same composition. If you reboil that liquid C_2, it will give a vapour with composition C_3. Again you can condense that to give a liquid of the same new composition. Reboiling the liquid C_3 will give a vapour still richer in the more volatile component B. We can see that if we were to do this once or twice more, we would be able to collect a liquid which was virtually pure B. The secret of getting the more volatile component from a mixture of liquids is obviously to do a succession of boiling-condensing-reboiling operations.

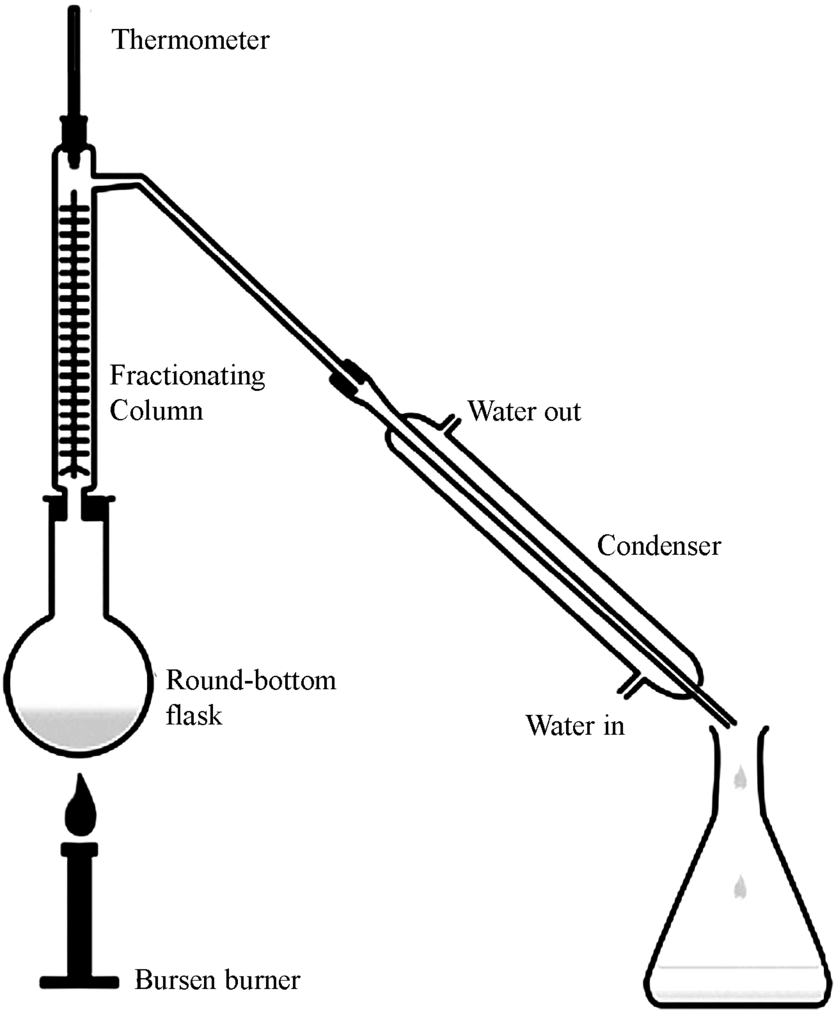


Figure 2.14 : Fractional distillation apparatus. Source : Original : Theresa knott, Derivative work: John Kershaw-, CC BY-SA 3.0, https://commons.wikimedia.org/w/ind

Figure 2.14 depicts a typical laboratory apparatus used for fractional distillation. In a fractional distillation, a mixture of liquids is boiled and the resulting vapours travel up a glass tube called a **"fractionating column"** and separate. The fractionating column is placed between the flask containing the mixture and the "Y" adaptor and improves the separation between the liquids being distilled. Fractional distillation leads to a better separation than simple distillation because the glass beads in the fractionating column provide "theoretical plates" on which the vapours can condense and then re-evaporate, and re-condense, essentially distilling the compound many times over. **One theoretical plate** is equivalent to one **vapourization-condensation cycle**, which is equivalent to one simple distillation. The more volatile liquids will gradually move towards the top of the fractionating column, while higher boiling liquids will stay towards the bottom, giving a better separation between the liquids. The vapour eventually reaches the condenser, where it is cooled and then drips in to the collection vessel. So according to our figure 2.13, suppose we boil a mixture with composition C_1. The vapour over the top of the boiling liquid will be richer in the more volatile component, and will have the composition C_2. Thatvapour now starts to travel up the fractionating column. Eventually it will reach a height in the column where the temperature is low enough that it will condense to give a liquid. The composition of that liquid will, of course, still be C_2. Some of the liquid of composition C_2 will boil to give a vapour of composition C_3 and so on.

2.10 Azeotropic solution

Azeotropic solutions or simply azeotropes are mixtures of at least two different liquids. Their mixture can either have a higher boiling point than either of the components or they can have a lower boiling point. Azeotropes occur when fraction of the liquids cannot be altered by distillation. Azeotropes fail to conform to the idea ideal liquid mixture because, when boiling, the component ratio of unvapourized solution is equal to that of the vapourized solution. So an azeotrope can be defined as a solution whose vapour has the same composition its liquid. As you can imagine, it is extremely difficult to distil this type of substance. In fact, the most concentrated form of ethanol, an azeotrope, is around 95.6% ethanol by weight which boils at 78.2 °C, because pure ethanol is basically nonexistent. In general, a **positive azeotrope** boils at a lower temperature than any other ratio of its constituents. Positive azeotropes are also called **minimum boiling mixtures or pressure maximum** azeotropes. **A negative azeotrope** boils at a higher temperature than any other ratio of its constituents. Negative azeotropes are also called **maximum boiling mixtures** or **pressure minimum azeotropes.** An example of a negative azeotrope is hydrochloric acid at a concentration of 20.2% and 79.8% water (by mass). Hydrogen chloride boils at –84 °C and water at 100 °C, but the azeotrope boils at 110 °C, which is higher than either of its constituents. Some other examples of such mixtures are sulfuric acid (98.3%) / water, boils at 338 °C; nitric acid (68%) / water, boils at 120.2 °C at 1 atm, perchloric acid (71.6%) / water, boils at 203 °C, hydrofluoric acid (35.6%) / water, boils at 111.35 °C. In the following table some examples of azeotropes are given for water and other solvent mixtures

Component A	Component B	Boiling Point A	Boiling Point B	Azeotrope Boiling Point	Azeotrope Wt.% A
Water	Ethanol	100 °C	78.3 °C	78.2 °C	4 %
Water	Isopropanol	100 °C	82.3 °C	80.3 °C	12.6 %
Water	Acetonitrile	100 °C	81.6 °C	76.1 °C	16%
Water	Ethyl Acetate	100 °C	77.2 °C	70.3 °C	8.5 %
Water	THF (tetrahydrofuran)	100 °C	66 °C	65 °C	5%
Water	Dichloromethane	100 °C	40 °C	38.1 °C	1.5%

Positive Deviation from Raoult's Law

A large positive deviation from Raoult's Law produces a vapour pressure curve with a maximum value at some composition other than pure A or B. If a mixture has a high vapour pressure it means that it will have a low boiling point. The molecules are escaping easily and we won't have to heat the mixture much to overcome the intermolecular attractions completely. The implication of this is that the boiling point / composition curve will have a minimum value lower than the boiling points of either A or B. In the case of mixtures of ethanol and water, this minimum occurs with 95.6% by mass of ethanol in the mixture. The boiling point of this mixture is 78.2°C, compared with the boiling point of pure ethanol at 78.5°C, and water at 100°C. One might think that this 0.3°C doesn't matter much, but it has huge implications for the separation of ethanol / water mixtures. The diagram in figure 2.15 shows the boiling point / composition curve for ethanol / water mixtures.

Suppose we are going to distil a mixture of ethanol and water with composition C1 as shown on the diagram. It will boil at a temperature given by the liquid curve and produce a vapour with composition C_2. When that vapour condenses it will, of course, still have the composition C_2. If we boil that, it will produce a new vapour with composition C_3. If we carried on with this boiling-condensing-reboiling sequence, we would eventually end up with a vapour with a composition of 95.6% ethanol. If we condense that we will get a liquid with 95.6% ethanol. The liquid curve and the vapour curve meet at that point. The vapour produced will have that same composition of 95.6% ethanol. If we condense it again, it will still have that same composition. It is impossible to get pure ethanol by distilling any mixture of ethanol and water containing less than 95.6% of ethanol. This particular mixture of ethanol and water boils as if it were a pure liquid. It has a constant boiling point, and the vapour composition is exactly the same as the liquid. It is known as a constant boiling mixture or an azeotropic mixture or an azeotrope.

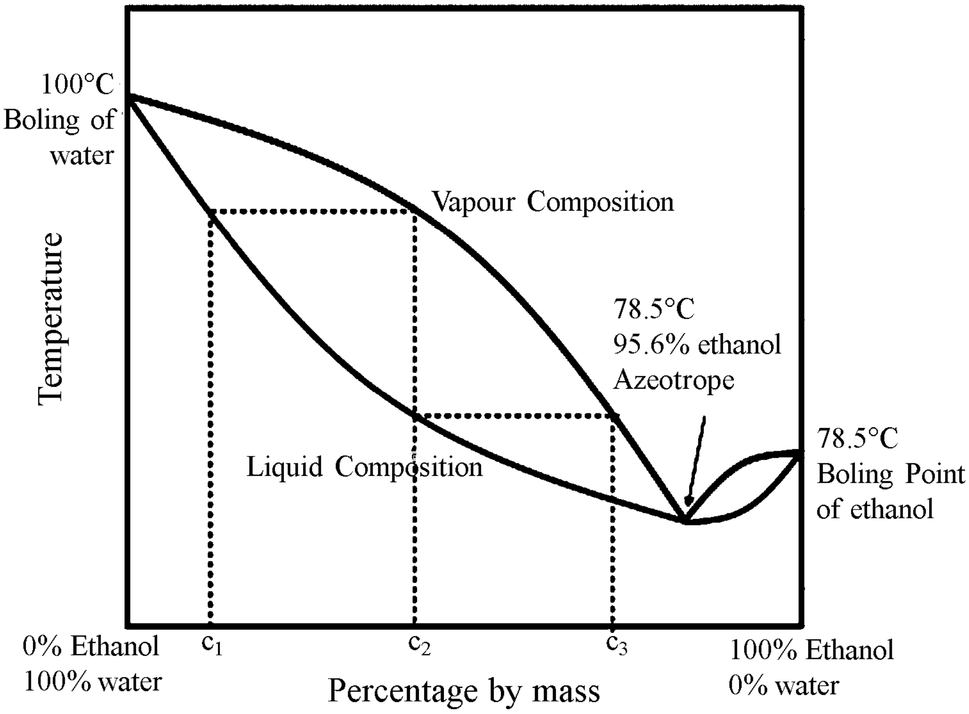


Figure 2.15 : Vapourliquid diagram of ethanol-water system

The implications of this for fractional distillation of dilute solutions of ethanol are obvious. The liquid collected by condensing the vapour from the top of the fractionating column cannot be pure ethanol. The best we can produce by simple fractional distillation is 95.6% ethanol. What we can get from the mixture is pure water. As ethanol rich vapour is given off from the liquid boiling in the distillation flask, it will eventually lose all the ethanol to leave just water.

Negative Deviation from Raoult's Law

Nitric acid and water form mixtures in which particles break away to form the vapour with much more difficulty than in either of the pure liquids. That means that mixtures of nitric acid and water can have boiling points higher than either of the pure liquids because it needs extra heat to break the stronger attractions in the mixture.In the case of mixtures of nitric acid and water, there is a maximum boiling point of 120.5°C when the mixture contains 68% by mass of nitric acid. That compares with the boiling point of pure nitric acid at 86°C, and water at 100°C.

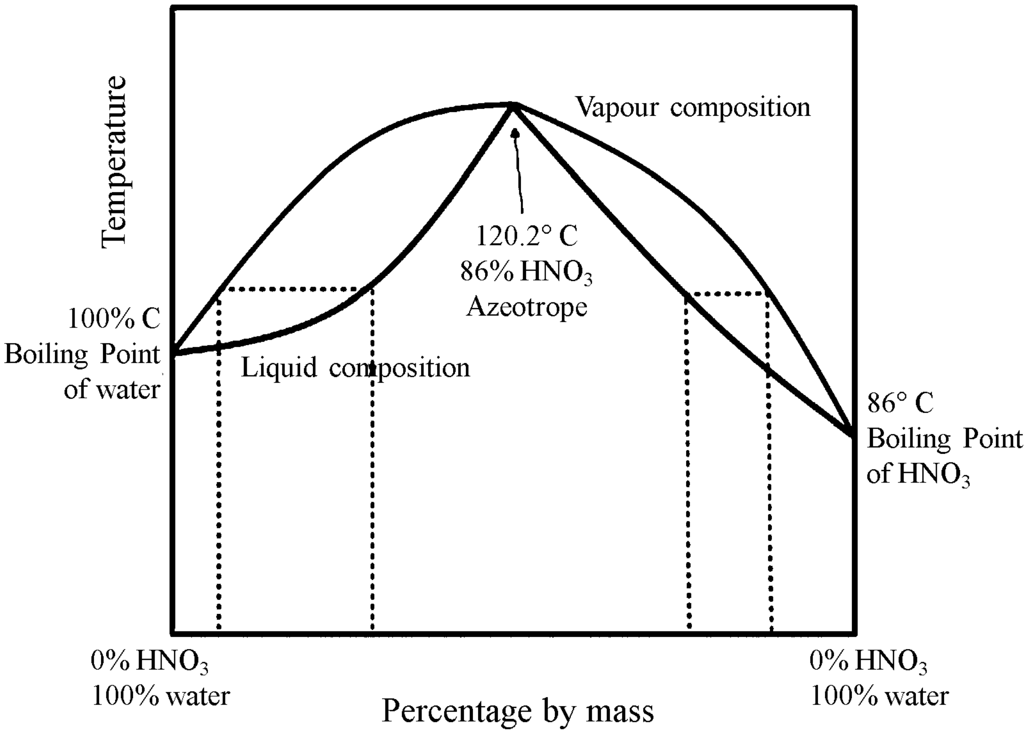


Figure 2.16 : Vapour liquid composition diagram of water-HNO_3 system

Distilling dilute nitric acid : Let us start with a dilute solution of nitric acid with a composition of C_1. The vapour produced is richer in water than the original acid. If we condense the vapour and reboil it, the new vapour is even richer in water. Fractional distillation of dilute nitric acid will enable you to collect pure water from the top of the fractionating column. As the acid loses water, it becomes more concentrated. Its concentration gradually increases until it gets to 68% by mass of nitric acid. At that point, the vapour produced has exactly the same concentration as the liquid, because the two curves meet. We produced a constant boiling mixture (or azeotropic mixture or azeotrope) and if we distil dilute nitric acid, that's what we will eventually be left with in the distillation flask. We cannot produce pure nitric acid from the dilute acid (< 68%) by distilling it.

Distilling nitric acid more concentrated than 68% by mass : This time let us start with a concentration C_2 to the right of the azeotropic mixture.The vapour formed is richer in nitric acid. If we condense and reboil this, we will get a still richer vapour. If we continue to do this all the way up the fractionating column, we can get pure nitric acid out of the top. As far as the liquid in the distillation flask is concerned, it is gradually losing nitric acid. Its concentration drifts down towards the azeotropic composition. Once it reaches that, there cannot be any further change, because it then boils to give a vapour with the same composition as the liquid. Distilling a nitric acid / water mixture containing more than 68% by mass of nitric acid gives us pure nitric acid from the top of the fractionating column and the azeotropic mixture left in the distillation flask.

2.11 Partially Miscible Liquids : The Phenol-Water System

When two liquids are so markedly different in nature that the system exhibits large positive deviations from ideal behavior, there occurs the phenomenon of **partial miscibility**, that is, limited solubility of each liquid in the other. If alcohol is added to acetic acid or to water, or vice versa, there is no limit to the proportion of one liquid that can be added to the other without the formation of two separate layers. Such liquids are said to be completely miscible. On the other hand, if a small quantity of phenol, ether or aniline is added to water, the substance will at first dissolve completely, but if the addition is continued, a condition is reached when no further solution occurs, and two liquid layers are formed. The two liquids are then only partially miscible with one another. Among other pairs of liquids that are partially miscible at ordinary temperatures are aniline and hexane, carbon disulfide and methyl alcohol, and water and butyl alcohol. When the relative quantities of the two components A and B are such that two liquid layers coexist, one of the layers is a saturated solution of A in B while the other is a saturated solution of B in A, e.g., aniline in water and water in aniline. The two liquid layers or phases in equilibrium are called conjugate solutions. Since the **conjugate solutions** are in equilibrium, they will have the same vapour pressures.

We will mainly discuss the phenol-water system. The phenol-water system is a well-studied example of partially miscible liquids. The extent of miscibility is determined by temperature, as can be seen from the graph in figure 2.17. The inverted U-shaped AB curve can be regarded as made up of two halves, the one to the left being the solubility curve of phenol in water and the other the solubility curve of water in phenol. The curves meet at the temperature 66°C where the saturated solutions of water in phenol, and phenol in water, have the same composition. At this temperature the two layers have become identical in composition; they are, in fact, one layer the composition of which is represented by the point C, the maximum of the curve. The temperature tcis known as the **critical solution temperature** or as the (upper) **consolute temperature** of the system. Above this temperature the two liquids, which had previously been partially miscible, become completely miscible in all proportions, and only one liquid layer is then possible.

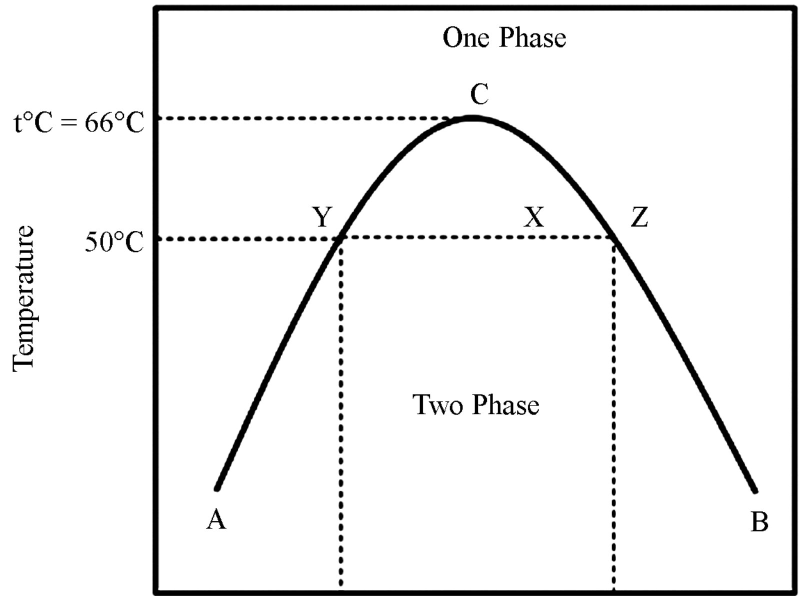


Figure 2.17 : The phenol water system liquid liquid phase diagram

The line of the **umbrella** curve shows the variation in composition of saturated solutions – phenol in water and water in phenol – with temperature. The area to the **left** of the curve represents unsaturated solutions of phenol in water and the area to the **right** represents unsaturated solutions of water in phenol, while the area above the curve represents solutions of phenol and water that are **fully miscible** i.e. miscible in all proportions. In the region inside the curve, the system exhibits its most striking characteristic – it divides into two coexistent phases, the upper phase being a saturated solution of phenol in water and the lower phase a saturated solution of water in phenol. The curious feature of these phases is that for a given temperature their composition is fixed even though the total amounts of phenol and water composing them may vary.

To analyze it, let us consider a dotted line on the diagram, which represents the composition of the phenol-water system at 50°C. Starting with a system which consists of water only we gradually dissolve phenol in it, maintaining the temperature at 50°C, until we reach the point Y on the curve at which the phenol-in-water solution becomes saturated. Now imagine adding to the saturated solution a small additional amount of phenol. It cannot dissolve in the solution and therefore creates a separate coexistent phase. Since this newly-formed phenol phase contains no water, the chemical potential of water in the solution provides the driving force for water to pass from the aqueous phase into the phenol phase. This cannot happen on its own, since water passing out of a phenol-saturated solution would cause the solution to become supersaturated. This would constitute change from a stable state to an unstable state which cannot occur spontaneously. So the movement of water from the solution into the phenol phase simultaneously lowers the chemical potential of phenol in that coexistent phase, allowing phenol to move with the water in such proportion that the phenol-in-water phase remains saturated – as it must do since the temperature remains constant. In other words, saturated solution passes spontaneously from the aqueous phase into the phenol phase, diminishing the amount of the former and increasing the amount of the latter. Because water is the major component of the phenol-in-water phase, this bulk movement will continuously increase the proportion of water in the coexistent water-in-phenol phase until it reaches the saturation point whose composition is given by point Z on the mutual solubility curve. The line YZ is called a **tie-line**. Applying the rule to the one Phase region of the phenol-water system, $F = 2 - 1 + 2 = 3$ where the system variables are temperature, pressure and composition. So for a chosen temperature and pressure, e.g. atmospheric pressure, the composition of the phase can also be varied. In the two phase region of the phenol-water system, $F = 2 - 2 + 2 = 2$. So, for a chosen temperature and pressure, e.g. atmospheric pressure, the compositions of the two phases are invariant.

2.12 Three component systems

The expression of the degrees of freedom of a three-component system as given by the phase rule is F = C – P + 2 = 3 – P + 2 = 5 – P. In case of system of one phase F = 4 – 1 = 3, and therefore, the values of three variables have to be stated in order to define the system completely. These are temperature andthe amount fractions of any of the two components. In case of system of two phases, here F = 4 – 2 = 2, and thus the values of two variables have to be specified in order to define the system completely. These are temperature and the amount fraction of any one component in either of the two phases. These two phases will be in equilibrium with each other and thus the amount fraction of the stated component in the second phase will have a definite value. In case of system of three phases, F = 4 – 3 = 1, and this degree of freedom is the temperature of thes ystem. All the three phases will have definite compositions at a given temperature.

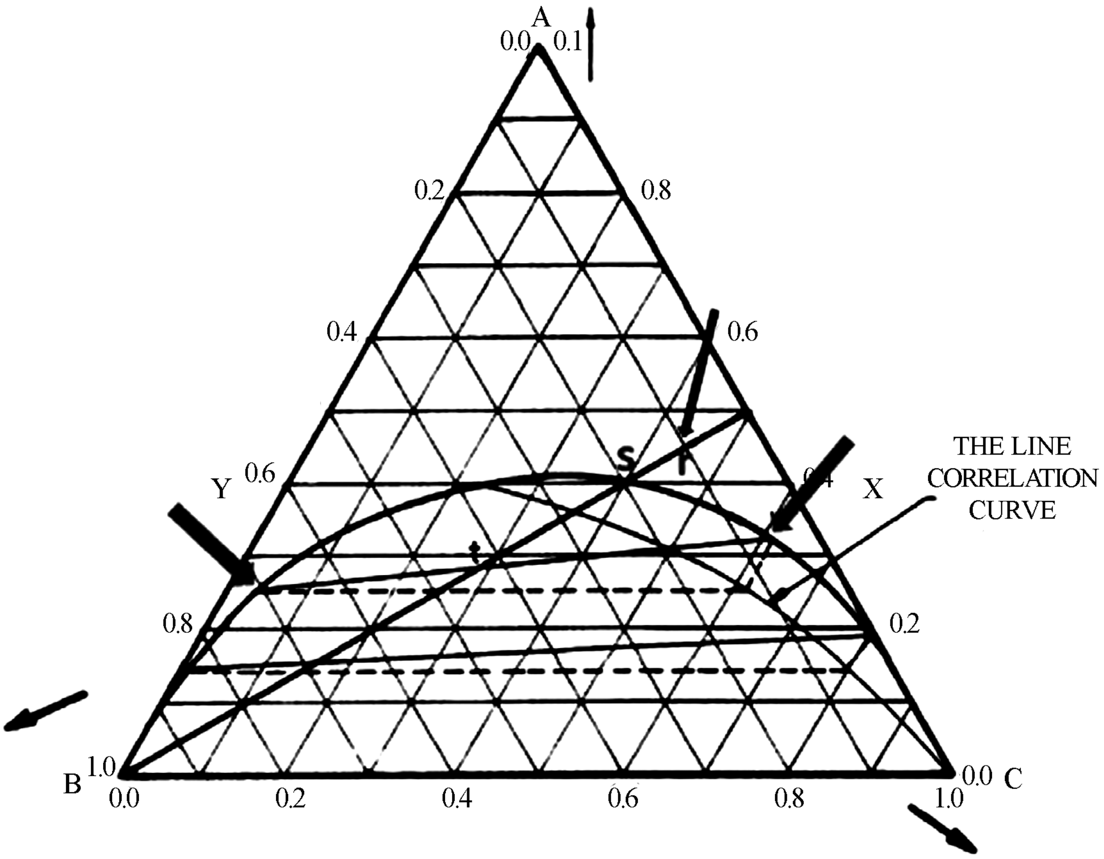


Figure 2.18 : Ternery phase diagram

The solubility of such system can be represented as 'Triangular ternary diagram'. It represents the equilibrium between the various phases that are formed between the three components as a function of temperature. Normally, pressure is not a viable variable in ternary phase diagram construction, and is therefore held constant at 1 atm. As is depicted on the Figure 2.18 the pure components (A, B, C) are located in the respective corners of the triangle. The side AB represents mixture of A and B. For example the mid-point of the side AB corresponds to a mixture of 50% of A and 50% of B by weight. The concentration of each of the three components can be expressed as either 'wt. %' or 'mol-fraction'. Sum of the concentration of the three components must add up to 100% or 1.

Consider the point 'q' (right side on the AC line) representing a 50% of solution A in C (see Fig.2.18). This is homogenous since A and C are completely miscible. Now, let a small amount of B be added to this solution to form a three-component mixture whose composition will be represented inside the triangle. Since the scales are liner this mixture will be represented by a point on the line qB. Let ussay at 'r' such that the ratio of :

$$\frac{\text{Amount of B in Mixture}}{\text{Amount of q in mixture}} = \frac{\text{Length of Line qr}}{\text{Length of Line Br}}$$

Point 'r' will represent a mixture made up of one part of pure B and nine parts of a solution of 50 % A in C, and will result in a solution containing 0.45 mass fraction of A, 0.45 mass fraction of C and 0.1 mass fraction of B as can be read from Figure 2.18. The above equation is known as the **'Lever Rule'** and applies to all analyses involving triangular diagrams.

When a small amount of component B is added to the solution 'q' it will dissolve to from a three-component solution and its composition will be represented by a point on the line qB. As the amount of B added is increased, this point will move away from 'q' to 'B', but because of the limited solubility of component B a point will be reached where the solution becomes saturated in B. Further additions of B will yield a turbid mixture if the liquids are agitated and two liquid layers will separate when the mixture is allowed to stand. Let this point be 's' on Fig.2.18. It represents the mutual solubility of the three components, and if the above procedure is repeated, starting with different binary mixtures of A and C, the **"mutual solubility curve -binodal curve"** (or mutual saturation curve) will be obtained. From the above, it is evident that the area within the triangle and above the curve correspond to homogeneous mixtures of A, B and C completely miscible in one another. Below the curve the limits of solubility will have been exceeded and two phases will be formed. In fact, if the solution 'q' is mixed with a known quantity of the solvent B such that the heterogeneous mixture formed will be of composition 't', two liquid layers will be formed when the disturbance is stopped; one composition 'y' and another composition 'x'. Both 'x' and 'y' will be clear saturated solutions and the straight line joining their compositions on Fig. 2.18 will pass through point 't'. This line is known as "tie line", and is by definition the straight line joining an extract and in equilibrium with one another. There will be an infinite number of tie lines describing the equilibrium of a partially miscible three component system and it is impossible to determine all experimentally. Therefore, in practice a small number, never less than five, are determined experimentally and these are correlated by constructing a "tie line correlation curve" as shown for two tie lines in Fig.2.18. That is, a horizontal line is drawn from extract composition point to intersect an inclined line, parallel to side AB of the triangle, from the corresponding pure composition point to give the coordinates is obviously the tie line correlation curve and its intersection with the saturation curve gives the "plait point". At this point, the last of the tie lines, the mass fraction of A in C in the mixture is identical with the mass fraction of A and B in the extract.

2.13 Solid-liquid phase diagram

If a liquid mixture of two similar components A and B is cooled, solid will commence to separate at a definite temperature, namely the freezing point. The actual value of the freezing point will depend on the composition of the liquid mixture, and if the results for a series of such mixtures of components varying from pure A to pure B are plotted against the corresponding compositions, two curves, like AC and BC in Fig. 2.19, are obtained.The points A and B are the freezing points of the pure components; the addition of B to A lowers the freezing point along AC, and similarly A added to B lowers the freezing point of the latter along BC. If the freezing point and composition of a given mixture are such as to fall on the curve AC, the solid which separates is pure A; on the other hand, if the freezing system is represented by a point on BC, pure solid B will separate from the liquid. The curves AC and BC* may be regarded as representing the conditions of temperature under which liquid phases of various compositions are in equilibrium with the solid phase A or the solid phase B, respectively. Since it gives the conditions of equilibrium of different phases, Fig. 2.19 is an example of a two-component phase diagram.

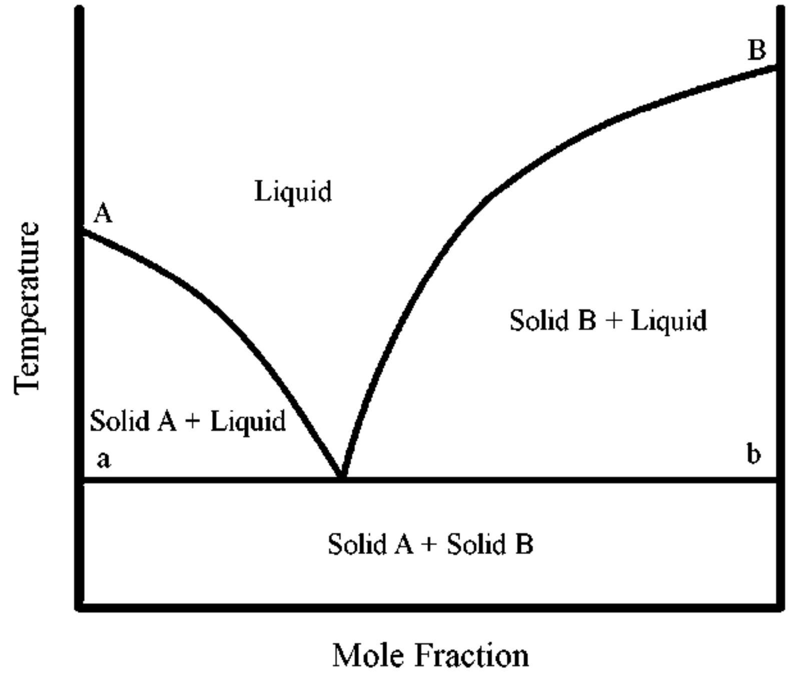


Figure 2.19 : Solid liquid phase equilibria

At the point C, where the curves AC and BC meet, both solids A and B are in equilibrium with the liquid phase. There are consequently three phases present, and since the system involves two components, there can be only one degree of freedom, according to the phase rule; thus P = 3, C = 2, and hence, F = 2 – 3 + 2=1. Since the pressure is arbitrarily fixed at 1 atm,this represents the one degree of freedom. The system has thus effectively no degrees of freedom, that is to say, it is then an invariant condensed system. This means that the mere fact of the existence of the two solid phases A and B in equilibrium with the liquid, at 1 atm pressure, completely defines the point C.There is thus only one temperature where this equilibrium is possible, as the phase diagram actually indicates. The point C, where the freezing point curves AC and BC meet, is the lowest temperature at which any liquid mixture can be in equilibrium with solid A or B. Consequently, it is the lowest temperature at which any mixture of solid A and B will melt. For this reason, C has been called the eutectic point (Greek : easily melting). It is the lowest temperature at which the existence of liquid phase for the given system is possible at the arbitrarily fixed pressure, viz., 1 atm.In general, the term liquidus curve is given to the curve representing thecomposition of the liquid phase in equilibrium with solid. Correspondingly, the composition of the latter is indicated on the solidus curve. Thus, in Fig. 2.19, the liquidus curves are AC and BC, and the corresponding solidus curves are AaC and BbC respectively.

A	Melting Point	B	Melting Point	Eutectic
Antimony	630°C	Lead	326°C	246°C
Bismuth	268°C	Cadmium	317°C	146°C
Silicon	1412°C	Aluminium	657°C	578°C
Potassium chloride	790°C	Silver Chloride	451°C	306°C
o-Nitrophenol	44.1°C	p-Toluidine	43.3°C	15.6°C
Benzene	5.4°C	Methyl Chloride	–63.5°C	–79°C

2.14 Summary

In this unit we first learned about four colligative properties namely relative lowering of vapour pressure, (ii) elevation of boiling point, (iii) depression of freezing point, (iv) osmotic pressure. We saw that these properties in ideal case do not depend on the nature of the solute. We also learned their thermodynamic derivations and relation with molality. Then we learned about the vant' Hoff factor which takes care of the electrolytic dissociation in solution. Next we discussed phase equilibrium. We discussed Gibbs phase rule and its origin. Then we studied phase diagram of water, carbon dioxide and sulfur. We then related equilibrium vapour pressure with temperature using the Clausius Clapeyron equation. We also discussed first and second order phase transitions. We extended the ideas to solvent mixtures both ideal and non-ideal cases and learned about separation of mixtures. The two and three component partially miscible liquid diagrams also showed us how to experimentally estimate the composition.

2.15 Self-Assessment Questions

1. On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid? (i) Sugar crystals in cold water. (ii) Sugar crystals in hot water. (iii) Powdered sugar in cold water. (iv) Powdered sugar in hot water.
2. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law? (i) Methanol and acetone. (ii) Chloroform and acetone. (iii) Nitric acid and water. (iv) Phenol and aniline.
3. What is the unit of ebulioscopic constant?
4. What are the values of van't Hoff factors for KCl, NaCl and K_2SO_4?
5. We have three aqueous solutions of NaCl labelled as 'A', 'B' and 'C' with concentrations 0.1 M, 0.01 M and 0.001 M, respectively. What is the value of van't Hoff factor for these three solutions?
6. Which factor (s) affect the solubility of a gaseous solute in the fixed volume of liquid solvent?
7. Explain why on addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.
8. What is the significance of Henry's Law constant k_H?
9. Why soda water bottle kept at room temperature fizzes on opening?
10. What is "semi permeable membrane"?
11. An aqueous sucrose ($C_{12}H_{22}O_{11}$) solution of unknown concentration is found to have a freezing point of $-0.912°C$. What is the normal boiling point and the partial pressure (in torr) of water at 25°C of this solution. Sucrose is a non-volatile, non-electrolyte.

12. What is the freezing point of a 2M solution of $CaCl_2$ in water ? Kf (water) = 1.853°C. kg/mol

13. Calculate molarity of a sugar solution in water (300 K) has osmotic pressure of 3.00 atm.

14. Calculate osmotic pressure for 0.10 MNa_3PO_4 aqueous solution at 20°C.

15. Hemoglobin is a large molecule that carries oxygen in human blood. A water solution that contains 0.263 g of hemoglobin (Hb) in 10.0 mL of solution has an osmotic pressure of 7.51 torr at 25°C. What is the molar mass of the hemoglobin?

16. Saturated liquid or saturated vapour can be found (a) Along the liquid and vapour equilibrium curve (b) Along the liquid and solid equilibrium curve (c) Along the solid and vapour equilibrium curve (d) None of the mentioned

17. What is the name of the phase transition that occurs when a solid is converted directly into a gas (without going through the liquid phase)?

18. Show that the maximum number of phases that can co-exist at equilibrium for a single component system is P = 3.

19. The vapor pressure of a liquid triples when the temperature is increased from 25°C to 45 °C. What is the enthalpy of vaporization for the liquid?

20. In which equilibrium either P or T can be changed independently?

21. What is degree of freedom when two phases coexist?

22. Air consists of 78.06 per cent by volume of nitrogen and 21.00 per cent of oxygen, the remainder being inert gases. Utilizing the absorption coefficients 0.0150 and 0.0280 for N_2 and O_2 calculate the molar composition of the gas dissolved in water saturated with air at 20°C, assuming ideal behavior of the oxygen and nitrogen. (The solubility of the inert gases is small and may be ignored.)

23. What is Henry's constant for neon dissolved in water given : C_{Ne} = 23.5mL/Lsolution and STP (22,414 mL/mole gas) and pressure (1 atm)?

24. Calculate the solubility of gaseous oxygen in water at a temperature of 293 K when the partial pressure exerted by O_2 is 1 bar. (Given : k for O_2 34840 bar. L. mol)

25. The value of k for carbon dioxide at a temperature of 293 K is $1.6*10^3$ atm. L.mol. At what partial pressure would the gas have a solubility (in water) of $2*10^{-5}$ M?

26. If pure ethanol has a boiling point of 78.3 °C and its azeotrope has a boiling point of 78.174 °C, what would its graph look like?

27. The vapor pressures of pure CCl_4 and SiCl at 25°C are 114.9 mm and 238.3 mm, respectively. Assuming ideal behavior, calculate the total vapor pressure of a mixture of equal weights of the two liquids.

2.16 Answers of Self-Assessment Questions

1. (iv) 2. (i)

4. 2, 2 and 3

5. same

6. nature of solute, temperature and pressure

7. NaCl is a non volatile solute, therefore, addition of NaCl to water lowers the vapour pressure of water. As a result boiling point of water increases. Methyl alcohol on the other hand is more volatile than water, therefore its addition increases, the total vapour pressure over the solution and a decrease in boiling point of water results.

8. Higher the value of Henry's law constant K_H, the lower is the solubility of the gas in the liquid.

11. First find out the molality of the solution from freezing point depression and then calculation the boiling point elevation. BP = 100.25°C; P_{H_2O} = 23.59 torr

12. First, we need to calculate the molality because that is what we use in our equation for freezing point depression. We can get that from the molarity without knowing exactly how many liters or grams we have. We just have to know what we have one mole per liter. The weight of water is one kilogram per liter, so this allows us to make this conversion.

(2mol/1L)* (1L/)1kg = 2mol/1kg = 2m

The molality is 2m. The van't Hoff factor is 3, as we get one calcium ion and two chloride ions per molecule during dissociation.

$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$

We can now plug the values into the equation for freezing point depression.

$T_F = (1.853)(2)(3)$

$T_F = 11.12°C$

This gives us our depression of 11.12°C. The normal freezing point of pure water is 0°C, which means our new freezing point is −11.12°C.

13. Since it is sugar, we know it doesn't dissociate in water, soiis 1.

    M = RT = 3.00 atm.(0.0821 atm.L/mol.K)(300K) = 0.122M

14. Since Na_3PO_4 ionizes into four particles the ni = 4.

    = iMRT = (0.40)(0.0821)(293) = 9.6 atm

15. 6.51×10^4g/mol

16. (a) Saturated liquid or saturated vapour can be found along the liquid and vapour equilibrium curve.

18. The maximum number of components will occur when the number of degrees of freedom is zero. F = 0 = 2 + 1 –P. P = 3.Note : This shows that there can never be a "quadruple point" for a single component system!

19. Solve using Clausius-Clapeyron equation. 43.28 kJmol

20. Univariant

21. F = C + 1 – P => F = 3 – P (C = 2) => F = 3 – 2 = 1.

22. If the gases behave ideally, their partial pressures are proportional to the number of moles of each, and hence to the volume composition.If the total pressure of the air is 1 atm, the partial pressure of the nitrogen is consequently 0.7806 atm, whereas that of the oxygen is 0.2100 atm. The absorption coefficients are 0.0150 and 0.0280, respectively.The solubilities are therefore in the ratio of 0.7806 x 0.0150 volumes (or moles) of nitrogen to 0.2100

x 0.0280 volumes (or moles) of oxygen, i.e., 0.0117 to 0.00588. Neglecting the inert gases, the mole per cent of nitrogen in the dissolved gas is 66.6 moles of nitrogen to 33.4 moles of oxygen

23. $C = kP_{Ne}$

    To use C we must convert 23.5 mL/L solution to molarity. Since Ne is a gas, we can use our standard molar volume. Thus giving us:

    (23.5 mL/L soln)/(1 mole Ne/22,414 mL) = 0.00105M. Now we have solved for the solubility of Ne in the solution. C = 0.00105M and we know the pressure at STP is 1 atm, so we can now use our rearranged equation : $k = CP_{Ne}$ where C = 0.00105M, P_{Ne} = 1 atm, thus giving us k = 0.00105 M/atm

24. As per Henry's law, P = k *C Substituting, k = 34840 bar.L.mol and P = 1 bar, the equation becomes C = 1/34840 mol.L = $2.87*10^{-5}$ mol/L Therefore, the solubility of oxygen in water under the given conditions is 2.87*10-5 M.

27. 173.5 mm

2.17 Suggested Readings

(a) Physical Chemistry by Peter Atkins and Julio De Paula, Oxford University Press

(b) Physical Chemistry by Ira N. Levine, McGraw-Hill Education

(c) Physical Chemistry by P. C. Rakshit,Sarat Book HouseIndia

(d) A Textbook of Physical Chemistry Vol.- III by K. L. Kapoor, Macmillan Publishers India

Unit - 3 ❑ Foundation of Quantum Mechanics

3.1 Objective

On completion of study of this unit, the learner will be able to

- Comprehend the fundamental philosophy behind quantum mechanics.
- Understand the concept of wave particle duality and dual nature of light as well as fundamental particles such as electrons.
- Explain de Broglie hypothesis and Heisenberg uncertainty principle.
- Gain significant knowledge of wavefunction, its acceptability and probabilistic nature along with Schrödinger wave equation.

- Interpret operators, eigenfunctions and eigenvalues; linear operators, properties of operators, Hermitian operators.
- Define the postulates of quantum mechanics and explain them
- Set up and solve the Schrödinger equation for a particle in a one-dimensional box and compare it with free particle eigenfunctions and eigenvalues.
- Understand the properties of particle in a box wavefunctions (normalization, orthogonality, probability distribution)
- Compute the expectation values of x, x^2, p_x and p_x^2 and their significance in relation to the uncertainty principle
- Extend of the problem to two and three dimensions and build the concept of degenerate energy levels.

3.2 Introduction

The fundamental principles of quantum mechanics are the basis of understanding the structure, character, bonding, and properties of molecules and atoms. Prediction of physical and chemical properties of materials and molecules using quantum mechanics is of uttermost importance in science and engineering. Thus, a separate branch of chemistry named quantum chemistry has been born. The importance of this field in solving scientific, medical, and humanitarian problems is such that the newly invented Google quantum computer "Sycamore" is being used to solve quantum chemistry problems.

Historically, by the late nineteenth century, the laws of classical physics were fully established. Atoms were considered to be the basic constituents of matter and we did not have any knowledge about sub-atomic particles. At this time, the scientific world was thought to be deterministic i.e. the properties and movement of the objects and molecules can be predicted exactly following a set of laws. These laws include Newton's laws of motion, the laws of thermodynamics and Maxwell's concept of light as a pure electromagnetic wave. However, there were some experiments which could not be explained by the existing classical laws of physics. Examples of such phenomenon are blackbody radiation, photoelectric effect, the discreet lines in the atomic spectra and discovery of the electron. To explain such events, at the beginning of 20th century (year

1900 onwards) a new branch of science was born, pioneered by Max Planck, Albert Einstein and Niels Bohr. This new theory considered a universe having probabilistic existence and a "micro" world where Newton's laws of physics do not apply. It was named "Quantum Mechanics" by scientist Max Born in 1924. In subsequent years, the subject was enriched via new discoveries from physicists and chemists like Max Born, Paul Dirac, Werner Heisenberg, Wolfgang Pauli, Erwin Schrödinger, Robert S. Mulliken, J. Robert Oppenheimer, Linus Pauling, Erich Hückel, Douglas Hartree to name a few.

In this unit we are going to discuss the basic principles of quantum mechanics and how they were established. These report early progress in the field and sometimes it is called "Quantum Theory" instead of quantum mechanics. You have been already exposed to some of it before, for example black body radiation, Rutherford and Bohr's model of atoms, the Sommerfield's correction etc. In this unit, we will start from duality in nature and will try to develop a deeper understanding of the principles of quantum mechanics.

3.3 Wave Particle Duality

In our everyday life, we encounter waves and particles always and as a matter of fact there is nothing mysterious or ambiguous about them. When we throw a stone in a pond, a ripple effect is generated and it stretches outward from a centre point. This "wave" is generated by upward-downward motion of the water molecules and the wave carries energy with it. By definition, the wave is a propagation of oscillation of one or more quantities from their equilibrium position. On the other hand, a particle is a small object which has certain physical and chemical properties. Particles can range in size from sub-atomic (e.g. electrons, protons, neutrons) to microscopic (e.g. atoms, molecules) to macroscopic (e.g. powders, granules etc.). In the perceivable world in which we live, particles and waves are treated as separate entities. We do not to confuse mechanical properties of particles with specific properties of waves. However, everything is made up of atoms and molecules and in the "atomic" world, the concepts of particles and waves are interlinked. In terms of quantum mechanics, an entity can be described as a particle and a wave simultaneously. In other words, a single entity can exhibit properties of a particle as well as a wave! Two important points in this regard are

(i) In quantum theory, the properties of an entity like light, electron, proton or even atom cannot be solely described by either particle nature or wave nature of it. Instead, both the concepts are required to completely explain its properties

(ii) Wave-particle duality is an unexpected phenomenon but it only happens in the microscopic world and does not hamper our understanding of the macroscopic world.

Now let us consider the example of light and its dual character. In fact, the concept of duality originated to explain experimental results related to light. We are familiar with the concept of wave nature of light. We are familiar with reflection and refraction of light which are common phenomena of waves. Robert Hooke, Christiaan Huygens and Augustin-Jean Fresnel mathematically described the wave nature of light and said that light travels at different speeds in different media which explains the refraction of light. Apart from these two properties, waves also show interference and diffraction.

3.4 Light as a Particle

The discussion in the previous section describes the dual nature of light. The particle nature of light was established using two experiments and their explanations. These two phenomena were the photoelectric effect and the Compton effect. In this section, we will describe them one by one.

3.4.1 The Photoelectric Effect

Photoelectric effect is the phenomenon of emission of electrons from a metal surface exposed to electromagnetic radiation above a certain frequency (or below a certain wavelength) known as **threshold frequency**. These ejected electrons are known as **photoelectrons**. Photoelectric effect has been described as the experiment that opened the gateway of quantum mechanics in the late 19th century and the early 20th century. The history of photoelectric effect from its discovery to explanation stretches over a period of 30 years and it was one of science's most discussed and debated topic at the time.

The first experimental observation of the phenomenon came from German scientist Heinrich Rudolf Hertz in 1886-87. Hertz was trying to prove Maxwell's theory that electromagnetic radiation travels at the speed of light using a device called "spark gap oscillator", a primitive radio broadcasting device. He discovered a "side-effect" of his experiment: in the presence of light, especially ultraviolet light, the "spark" produced in the receiver is stronger. He did not offer any theoretical explanation of the phenomenon. In 1888, the German physicist Wilhelm Hallwachs performed a simpler version of the experiment. He showed that when exposed to ultraviolet (UV) light, negatively charged Zn plates loose charge fast, neutral Zn plates became positive and positive Zn plates looses charge very slowly. This embodiment of the photoelectric effect is known as the Hallwachs effect. In 1899, J.J. Thompson proved that the spark ejected from the metal surface is similar to cathode ray and it is composed of electrons.

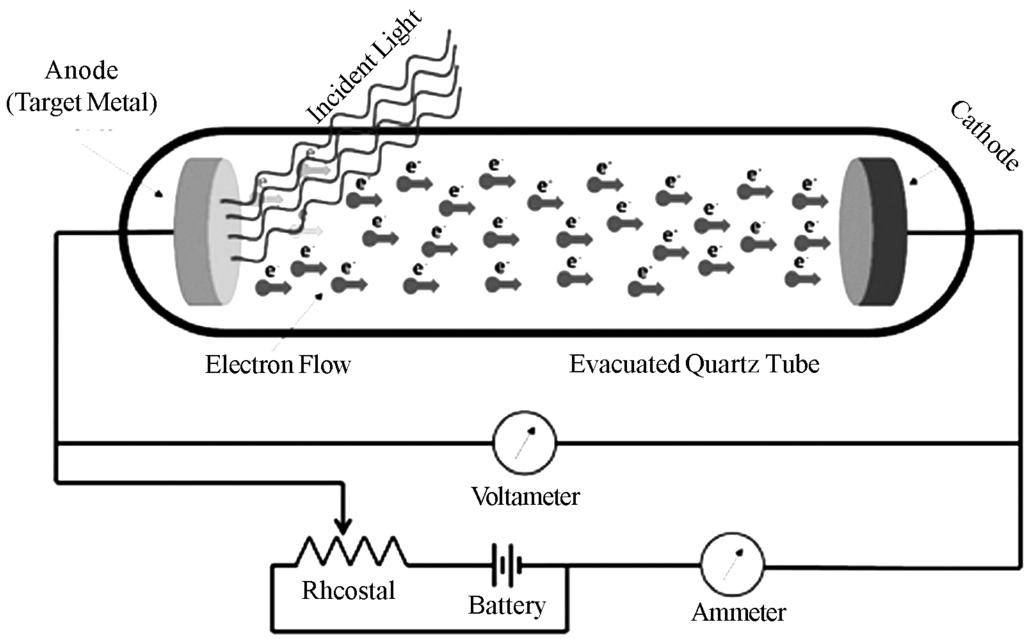


Figure 3.1 : Schematic representation of experimental setup for Photoelectric Effect

A more critical experiment was performed by Phillip von Lenard and later by Robert Millikan. A simple representation of the experiment which is still used today has been provided in figure 3.1. Two electrodes, i.e. cathode and anode, are placed within a vacuum quartz (or glass) tube. Both the electrodes are made of metals but the anode serves as the one which is going to be illuminated by light and it is therefore called the photoelectrode. As depicted in the diagram, when the photoelectrode is illuminated, electrons are emitted from it. These electrons are collected by the cathode which has a higher potential than the anode. The potential difference between the two electrodes can be regulated by the rheostat or other electrical circuits. The vacuum tube is used so that the ejected electrons do not lose any kinetic energy by collision with air molecules. When no light is present, the overall circuit is broken i.e. no current flow is registered by the ammeter. However, when the anode is irradiated with light of certain frequency, ejected photoelectrons complete the circuit and current flows. This is known as **photocurrent**. It is to be noted that the current flow also depends on the potential difference between the electrodes. Suppose we change the polarity of the electrodes by changing the potential difference between them so that the target electrode become positively charged, and then increase the potential difference between the two, then at a certain voltage the photoelectron flow will stop. This voltage at which the photocurrent stops is known as the **stopping potential**. Here, three very important characteristics of this experiment need to be discussed before we proceed further.

(i) There is no time lag for ejection of photoelectrons. It means that when the radiation hits the target material, the electrons are ejected instantaneously, even at a very low intensity of radiation.

(ii) The kinetic energy of photoelectrons : When the photoelectrons leave the surface of the metal, each of them carries some kinetic energy which it acquires from the light. If the stopping potential is V_s then the electrical work done in the process is eV_s where e is the charge of an electron. The largest kinetic energy (Kmax) that an electron can have is equal to the electrical work. So we can say

$$K_{max} = eV_s \text{ ...... } (3.1)$$

Now, it is important to note that the maximum kinetic energy of the photoelectron does not depend on the intensity of the incident radiation (refer to figure 3.2A) which is contrary to the conventional idea of physics available at that time.

(iii) The threshold frequency : For every metal there exists a minimum frequency of incident radiation below which no photoelectron is ejected. This particular frequency of light is known as the threshold frequency or cut-off frequency for that metal (figure 3.2B) and it has different values for different metals. This threshold frequency is also independent of the intensity of the electromagnetic radiation.

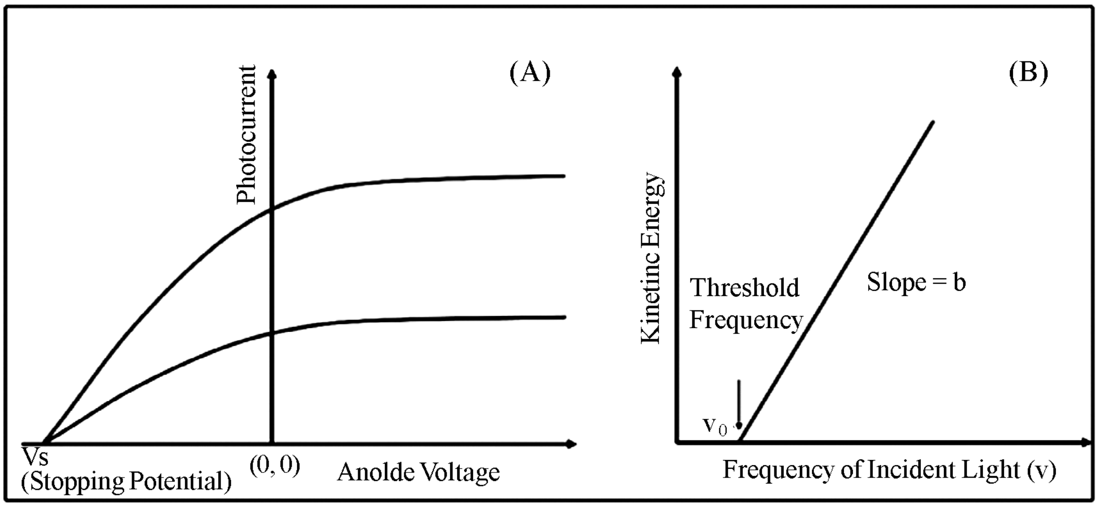


Figure 3.2 : (A) Measured photocurrent with respect to applied anode voltage for two different intensities of light (B) Kinetic energy of photoelectrons measured at the surface of the electrode versus the frequency of incident light

Einstein's Explanation of Photoelectric Effect

The photoelectric effect was explained in 1905 by Albert Einstein employing Planck's idea of quantization of energy. Einstein hypothesised that electromagnetic radiation consists of energy quanta. It means a monochromatic light of a fixed frequency is made of particles of light of certain energy known as **photons**. Each photon moves at the speed of light and has an energy $E = h\upsilon$. h is known as the **Planck's constant** and has a value of **6.626×10^{-34}J.s**. In photoelectric effect, photons arrive at the metal surface and each photon gives away all of its energy to only one electron on the metal surface. It should be noted that either each of the photon transfers all its energy to the electron and ceases to exist or there is not energy transfer at all. This is known as the **quantum phenomenon**. So, if we use a light of frequency υ for the photoelectric effect, the threshold frequency of the metal is υ_0 and the photoelectron having mass m is ejected with the velocity v. Hence, we can write

$$h\upsilon = \frac{1}{2}mv^2 + h\upsilon_0 \text{ ...... } (3.2)$$

It is clear from equation 3.2 that if we use a light of frequency below the threshold frequency υ_0, then no electron will be ejected. The energy associated with this threshold frequency is known as the **work function** of the metal and is designated as $\varphi = h\upsilon_0$ and it is an internal property of the metal.

3.4.2 Compton Effect

The second experiment which sealed the concept of light as a particle is Compton effect. This experiment was performed by Arthur Compton and his colleagues. Compton explained the phenomenon in 1923 and hence the name. By definition Compton effect is the scattering of X-ray or gamma-ray by a small particle accompanied by the recoil of the particle. The unusual thing about the process is that the scattered light has different wavelength than the incident light. It cannot be explained by classical physics and Compton used Einstein's idea of photons to explain the process. We can best describe it using a schematic diagram as given in figure 3.3.

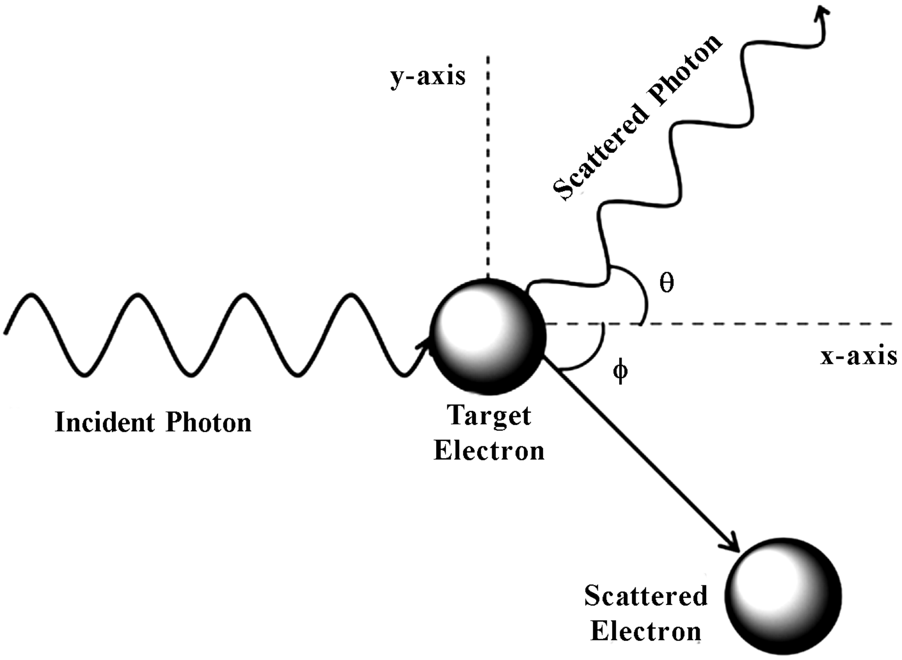


Figure 3.3 : Schematic representation of the Compton effect showing the collision between a photon and an electron

Figure 3.3 is the simplest representation of the collision of a photon with an electron. Suppose the incident photon is of an X-ray light with wavelength. For more simplicity, we will assume that the electron is at rest at the beginning and the incident light travels in the x-axis direction. Now, according to Compton's experiment, the wavelength (and the frequency) of the incident light changes after the collision. Let us say that the transformed wavelength is and after the collision the photon is travelling at an angle with the x-axis. Due to this collision, the electron will also recoil and let the direction of recoil makes an angle f with x-axis with a velocity v. The energy of the electron before collision is only rest mass energy, m_0c^2 (m_0 is the rest **mass of electron = 9.109 × 10^{-31}kg**, c is the **speed of light** = 3 × 10^8 m/s) and after collision it changes to mc^2 (m is the mass at velocity). Now, Compton scattering can be explained using the conservation of energy and momentum in the x and y direction. To make understanding easy, a table is provided below listing all the components of energy and momentum.

	Energy		Momentum			
			x-component		y-component	
	Before	After	Before	After	Before	After
Electron	m_0c^2	mc^2	0	$mv\cos\varphi$	0	$mv\sin\varphi$
Photon	$\frac{hc}{\lambda}$	$\frac{hc}{\lambda'}$	$\frac{hc}{\lambda}$	$\frac{hc}{\lambda'}\cos\theta$	0	$\frac{h}{\lambda'}\sin\theta$

From energy conservation we can write,

$$\frac{hc}{\lambda}+m_0c^2=\frac{hc}{\lambda'}+mc^2 \quad \text{......} \quad (3.3)$$

From momentum conservation we can write by eliminating φ,

$$m^2v^2=\frac{h^2}{\lambda'^2}+\frac{h^2}{\lambda^2}-\frac{2h^2}{\lambda\lambda'}\cos\theta \quad \text{......} \quad (3.4)$$

Einstein prescribed the relativistic dependence of mass as

$$m=\frac{m_0}{1-\frac{v^2}{c^2}} \quad \text{......} \quad (3.5)$$

From equation 3.3, 3.4 and 3.5 we can perform few eliminations and rearrangements to derive

$$\Delta\lambda=\lambda'-\lambda=\frac{h(1-\cos\theta)}{m_0c}=\lambda_0(1-\cos\theta) \quad \text{......} \quad (3.6)$$

$\lambda_0 = \frac{h}{m_0c} = 2.426 \times 10^{-12}$ m = 2.426 pm (picometer) is called the Compton wavelength. Thus, this experiment proved that Einstein's proposition of light as a particle was indeed correct.

3.5 Electrons as Waves : The de-Broglie Hypothesis

3.5.1 The Hypothesis of de Broglie

We have learned so far that by 1920's scientists understood that waves especially electromagnetic radiation can have dual character and energy can be transferred in a quantised manner. We also know how matter behaves in a macroscopic world from our basic understanding of science. Waves show interference patterns in the macro world which is not shown by any particle. However, as new evidence was gathered on the dual nature of light, a young French scientist named Louis de Broglie asked if electromagnetic radiation can have particle-like character, can electrons and other sub-microscopic particles exhibit wavelike character? In 1924, in his doctoral thesis de Broglie proposed the idea that electrons can have dual character i.e. they can be particle and wave just like light. This revolutionary idea brought him the 1929 Noble prize in Physics. According to de Broglie, the dual nature is general and can be applied to both light i.e. photon as well as for material particles like electrons. He said that each matter particle has a wave character associated with it which is known as the matter wave. The relation between the wavelength of this matter wave with the momentum of the particle is given by the equation

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad ...... (3.7)$$

In equation 3.7, h is Planck's constant, p is the particle's momentum, m is mass of the particle and v is the velocity of the particle. This is the **de Broglie hypothesis** and λ is called the **de Broglie wavelength**. It is extremely important to understand that matter wave is a characteristic of particles and other bodies. So λ is the wavelength of the matter wave, not of the electromagnetic radiation. The equation involves velocity, not frequency. The significance of de Broglie hypothesis is that it showed that wave-particle duality was not merely an aberrant behaviour of light, but rather was a fundamental principle exhibited by both radiation and matter. As such, it becomes possible to use wave equations to describe material behaviour, so long as one properly applies the de Broglie wavelength. This would prove crucial to the development of quantum mechanics. It is now an integral part of the theory of atomic structure and particle physics.

3.5.2 Derivation of de Broglie Wavelength

The argument for de Broglie relation comes from Einstein's equations. Einstein's famous equation relates mass (m) and energy (E) as

$$E = mc^2 \text{ ...... } (3.8)$$

In the above equation c is velocity of light. On the other hand, Planck's equation describes energy as quantized as

$$E = \frac{hc}{\lambda} \text{ ...... } (3.9)$$

In the above equation, h is Planck's constant. de Broglie stated that particle and wave are characteristics of same entity, so we can say

$$mc^2 = \frac{hc}{\lambda}$$

$$\lambda = \frac{h}{mc} \text{ ...... } (3.10)$$

Since real particles do not travel at the speed of light, de Broglie argued that the velocity of light should be replaced by velocity of the matter wave which transformed the equation to

$$\lambda = \frac{h}{mv} \text{ ...... } (3.11)$$

3.5.3 Dual Nature of Electrons and Bohr's Model of Atom

We are familiar with the Bohr's model of atoms which was the first model to successfully explain the stability of atoms and the line spectrum of H-atom by using quantization of energy and angular momentum. However, Bohr's model does not provide any justification as to why angular momentum of an electron is quantized in an atom. It merely assumes integral values for the orbits. But in 1924, de Broglie provided an explanation for it based on the dual nature of electrons. He said the quantization of angular momentum is a natural manifestation of wave nature of electrons. de Broglie realized that if you use the wavelength associated with the electron, and assume that an integral number of wavelengths must fit in the circumference of an orbit, you get the same quantized angular momenta that Bohr did. So, if an electron wave moves around the nucleus, then it should happen in a way that after each cycle the wave is superimposed on the previous one or in other words there must be constructive interference. If after each cycle, the waves are not superimposed onto one another, then there will be destructive interference and the orbit will not be stable. This condition is similar to a standing wave situation and has been clearly illustrated in figure 3.4.

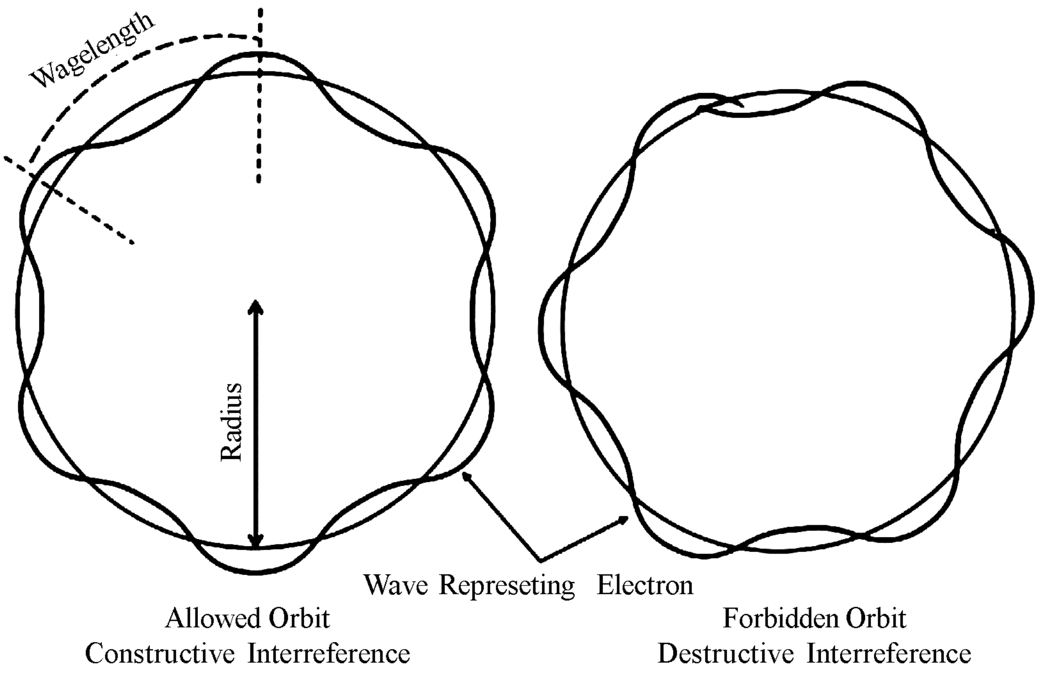


Figure 3.4 : Electrons in an atom as de Broglie waves : allowed and forbidden orbits

Mathematically, for a circular orbit of radius r we can say

$$2\pi r = n\lambda \ ; \ n = 1, 2, 3 \ldots \text{(integers)} \quad \ldots\ldots \quad (3.12)$$

The stable orbits are those for which n is an integer. Any non-integer or fractional value of n will lead to forbidden orbits. Taking the wavelength to be the de Broglie wavelength and using equation 3.11,

$$2\pi r = \frac{nh}{mv} \quad \ldots\ldots \ (3.13)$$

Rearranging,

$$mvr = \frac{nh}{2\pi} \quad \ldots\ldots \ (3.14)$$

Equation 3.14 is Bohr's equation of atom.

3.5.4 Experimental Evidence of de Broglie Waves

In 1927, physicists Clinton Davisson and Lester Germer of Bell Labs performed an experiment where they fired electrons at a crystalline nickel target. The resulting diffraction pattern matched the predictions of the de Broglie wavelength. Davisson and Germer jointly won the Nobel Prize in 1937 for the experimental discovery of electron diffraction (and thus the proof of de Broglie's hypothesis). Further experiments have held de Broglie's hypothesis to be true, including the quantum variants of the double slit experiment. Diffraction experiments in 1999 confirmed the de Broglie wavelength for the behaviour of molecules as large as buckyballs, which are complex molecules made up of 60 or more carbon atoms.

3.6 The Uncertainty Principle

3.6.1 An Imaginary Experiment

We learned that electron has wave nature. We also know that electron has finite mass and particle character. The amazing thing about this is one cannot design an experiment where one observes both simultaneously. It can be understood by conducting a thought experiment. Suppose you have a microscope. This microscope has a high resolution and you are measuring the position and momentum of electrons by using a light of wavelength. From theory, the resolving power of the microscope can be expressed in terms of distance between the two points which is the uncertainty in the measurement of position. So the uncertainty in measurement of position of the electron (Δx) is

$$\Delta x \approx \frac{\lambda}{2\sin\theta} \quad \ldots\ldots \ (3.15)$$

Now, process of "seeing" a particle through a microscope means striking the object with photons and observing the reflected photons through our eyes or via instruments. However, we have learned in the Compton effect that photons can transfer their energy to the electrons and get scattered. It means if you want to observe an electron, the light photons will transfer their energy to the electron and will change the scattered light wavelength. The electrons will also gain energy and recoil which means they will gain some extra momentum from the incident light photons. So, our experiment will be incorrect because we cannot stop the Compton effect in the entire process. Whatever momentum you will measure, there will always be an "uncertainty". In fact, we can express the uncertainty in measurement of momentum via the following equation

$$\Delta p \approx \frac{h \sin\theta}{\lambda} \quad \ldots\ldots \ (3.16)$$

So, the overall uncertainty of the measurement can be expressed by combining equation 3.15 and 3.16

$$\Delta x \Delta p \approx h \ \ldots\ldots \ (3.17)$$

In fact, this is the minimum uncertainty. The actual uncertainty in measurement will be greater.

3.6.2 Heisenberg's Uncertainty Principle

In 1927, a young German scientist named Werner Heisenberg realised that

(i) In the world of very small particles, one cannot measure any property of a particle without interacting with it in some way.

(ii) This introduces an unavoidable uncertainty into the measurement.

(iii) One can never measure all the properties exactly.

Essentially, he realised that we cannot know the future because we cannot know the present. The credit of Heisenberg is that he determined the fundamental limit to how accurately we can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. Heisenberg stated that *it is fundamentally impossible to know both the exact position and exact momentum of a microscopic particle at the same time*. For a particle of mass m moving in the x direction with a velocity v_x and a momentum p_x; the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δp_x must be greater than or equal to

$$\Delta x \Delta p_x \geq \frac{h}{4\pi} \quad ...... \ (3.18)$$

Assuming that the mass remains constant during the experiment, and using $p_x = mv_x$

$$\Delta x \Delta v_x \geq \frac{h}{4\pi m} \quad ...... \ (3.19)$$

This is **Heisenberg's uncertainty principle**. It is important to note that this equation can be employed in three-dimension with each dimension following equation 3.18. This principle is also applicable for all matter waves. Moreover, Heisenberg's uncertainty relation is not limited to position and momentum. It can be extended to the conjugate pairs or mathematically non-commutating operators. Energy and time are two such quantities. So, the uncertainty in energy and time for a measurement can be expressed as

$$\Delta E \Delta t \geq \frac{h}{4\pi} \quad ...... \ (3.20)$$

Heisenberg's uncertainty relation may appear as a problem in measurement but in reality, it is completely the opposite. It is one the most important and useful theory in quantum mechanics. Heisenberg was successfully able to differentiate the quantum world from the classical world and thus he was awarded the 1932 Noble Prize in Physics. In subsequent units and in other courses we will know more about this principle.

3.7 Concept of Operators

3.7.1 Elementary Concept of Operators

Before proceeding further, we need to understand the basic concept of operators. Operators are extremely important in quantum mechanics since all the physical properties are represented by operators. In the subsequent sections we will represent the equations using operators and therefore it is good to develop a basic understanding of it in this section. The definition of the operator is

*"An **operator** is a rule that transforms one function to another"*

In other words, an operator instructs us to do something (operation). By this definition, addition, subtraction, multiplication and division (+, –, ×, ÷) are operators because they instruct you to perform a mathematical operation. In a similar way **square, square root, cube, cube root, exponent (power), differentiation, integration** etc. are also operators since they transform functions. We denote an operator by a capital letter O with a carat over it like in the following equation.

$$\hat{O}f(x) = g(x) \ldots\ldots \ (3.21)$$

In this equation, $\hat{O}$ is an operator which transforms function f(x) to g(x). The list of operators and operations is endless. However, to understand the concept, here few examples are provided following equation 3.21 in form of a table.

Operator $\hat{O}$	**Function f(x)**	**Result g(x)**	**Operator $\hat{O}$**	**Function f(x)**	**Result g(x)**
Square $(\ )^2$	x	x^2	Exponent n	x^2	x^{2n}
Square Root $\sqrt{\quad}$	x^2	x	Absolute Value	–x	x
Differentiation $\frac{d}{dx}$	x^2	2x	Partial Differentiation $\frac{\partial}{\partial x}$	xy	y
Integration $\int$	x	$\frac{x^2}{2}$	Second Derivatived $\frac{d^2}{dx^2}$	x^2	2

It is important to remember that combination of one or more operator can act as a new operator. For example, combining of second derivation and first derivative operator, we can generate new operators like the following

$$\hat{O}=\frac{d^2}{dx^2}+\frac{d}{dx};$$

$$\hat{O}=\frac{d^2}{dx^2}+\frac{d}{dy};$$

$$\hat{O}=\frac{d^2}{dx^2}+5\frac{d}{dx}+10\ ;$$

$$\hat{O}=\frac{\partial}{\partial x}+\frac{\partial}{\partial y}+\frac{\partial}{\partial z}$$

Again, this list is practically extremely long. However, all the operators share some common properties. Although these properties may seem obvious because we have encountered them before in different forms in basic mathematics but it is a good practice to list them here.

(i) Sum of two operators $\hat{A}$ and $\hat{B}$ is given as [f denotes function]

$$(\hat{A}+\hat{B})f = \hat{A}f+\hat{B}f \quad ...... (3.22)$$

(ii) Difference of two operators $\hat{A}$ and $\hat{B}$ is given as

$$(\hat{A}-\hat{B})f = \hat{A}f-\hat{B}f \quad ...... (3.23)$$

(iii) To get the product of two operators on a function, first one operation is performed and then the other operation is performed on the resulting function of the first operation.

$$\hat{A}\hat{B}f = \hat{A}[\hat{B}f] \quad ...... (3.24)$$

(iv) Two operators are equal if for all functions of f

$$\hat{A}f=\hat{B}f \quad ...... (3.25)$$

3.7.2 Eigenfunctions and Eigenvalues

Now, we will learn about a special type of mathematical operation. If an operator acts on a function and we get back the same function multiplied by a constant then the function is called an eigenfunction of that operator and the constant is called an eigenvalue. Suppose $\hat{A}$ is an operator applied on a function f. Due to this operation, we get back the function f multiplied by a constant a.

$$\hat{A} f = af \quad ...... (3.26)$$

In this case, the function f is an eigenfunction of the operator $\hat{A}$ and the constant a is called an eigenvalue. In quantum mechanics, we have a lot of eigenvalue problems i.e. given an operator we are required to find the eigenfunctions and eigenvalues. In the following units we will encounter a lot of such type of equations. For example, the function e^{ax} is an eigenfunction of the operator $\frac{d}{dx}$ because when we operate $\frac{d}{dx}$ on the said function we get the function back with the eigenvalue a.

$$\frac{d}{dx}(e^{ax}) = ae^{ax} \quad ...... (3.27)$$

Another such example is the operator $\frac{d^2}{dx^2}$ which has a set of eigenfunctions in the form of cos kx and as sin kx where k is a real number. Both these functions have same eigenvalues $-k^2$.

$$\frac{d^2}{dx^2}(\cos kx) = \frac{d}{dx}[-k \sin kx] = -k^2 \cos kx \quad ...... (3.28)$$

$$\frac{d^2}{dx^2}(\sin kx) = \frac{d}{dx}[-k \cos kx] = -k^2 \sin kx \quad ...... (3.29)$$

3.7.3. Linear Operators

In most cases, the operators used in quantum chemistry are linear operators. A linear operator is an operator which satisfies the following two conditions.

$$\hat{A}(f+g) = \hat{A} f + \hat{A} g \quad ...... (3.30)$$

$$\hat{A}(cf) = c\hat{A} f \quad ...... (3.31)$$

Here, $\hat{A}$ is the linear operator, f and g are two functions and c is a constant. Any operator which does not satisfy these two rules is called a non-linear operator. For example, we will check the two operators $\frac{d}{dx}$ and $()^2$. For the first one

$$\frac{d}{dx}[f(x) + g(x)] = \frac{d}{dx}f(x) + \frac{d}{dx}g(x) \quad ...... (3.32)$$

$$\frac{d}{dx}[cf(x)] = c\frac{d}{x}f(x) \;\; \text{......} \;\; (3.33)$$

However, for the square operator

$$[f(x) + g(x)]^2 \neq [f(x)]^2 + [g(x)]^2 \;\; \text{......} \;\; (3.34)$$

So, the operator $\frac{d}{dx}$ is called a linear operator and the square operator $()^2$ is called a non-linear operator. Similarly integration operator is linear operator while the square root is a non-linear operator.

3.7.4 Commutation of Operators

Before discussing the commutation of operators, we need to know the product of two operators. The product between two operators is defined as the successive operation of the operators, with the one on the right operating first. For example,

$$\left(\hat{x}\frac{d}{dx}\right)f(x) = x\frac{df(x)}{dx} \;\; \text{......} \;\; (3.35)$$

We first apply the operator on the right (in this case "take the derivative of the function"), and then the operator on the left ("multiply by x whatever you got in the first step"). In general, the order of multiplication of operators is important and reversing the order may lead to different results. In the above example, if we reverse the two operators then,

$$\left(\frac{d}{dx}\hat{x}\right)f(x) = \frac{d}{dx}[xf(x)] = f(x) + x\frac{df(x)}{dx} \;\; \text{......} \;\; (3.36)$$

Clearly the result in equation 3.36 is completely different from the result in equation 3.35. So we can say that the order in which we apply these two operators matters. Whether order matters or not has very important consequences in quantum mechanics, so it is useful to define the so-called **commutator** as

$$\left[\hat{A},\hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} \;\; \text{......} \;\; (3.37)$$

For example, the commutator of the operators $\hat{x}$ and $\frac{d}{dx}$ is denoted by $\left[\hat{x},\frac{d}{dx}\right]$ and is by definition

$$\left[\hat{x}, \frac{d}{dx}\right] = \hat{x}\frac{d}{dx} - \frac{d}{dx}\hat{x} \quad \ldots\ldots \ (3.38)$$

Now, two operators are said to commute each other when their commutator is zero i.e. $\left[\widehat{A}, \widehat{B}\right] = \widehat{A}\widehat{B} - \widehat{B}\widehat{A}$ = 0 and they are said to be non-commutating if their commutator is non-zero i.e. $\left[\widehat{A}, \widehat{B}\right] = \widehat{A}\widehat{B} - \widehat{B}\widehat{A} \neq 0$. In these definitions, it is implicit that these operators and commutators operate on a function. From the above discussion it becomes clear that the commutator $\left[\hat{x}, \frac{d}{dx}\right]$ is non-zero since $\hat{x}\frac{d}{dx}[f(x)] \neq \frac{d}{dx}\hat{x}[f(x)]$. So the operators $\hat{x}$ and $\frac{d}{dx}$ are non-commutating. On the other hand, the operators $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$ commute with each other because $\left[\frac{d}{dx}, \frac{d^2}{dx^2}\right] = \frac{d}{dx}, \frac{d^2}{x^2} f(x) - \frac{d^2}{dx^2}, \frac{d}{dx} f(x) = 0$. Similarly, $\left[\hat{x}, \widehat{x^2}\right]$ is also zero and the two operators commute.

An important aspect is that if two operators commute, then there exists a set of functions which are simultaneously eigenfunctions of both the operators. Suppose, ψ is an eigenfunction of operator $\widehat{A}$. Then we can write

$$\widehat{A}\psi = a\psi \quad \ldots\ldots \ (3.39)$$

Let the operator $\widehat{B}$ commute with operator $\widehat{A}$. So we can write

$$\widehat{A}(\widehat{B}\psi) = \widehat{A}\,\widehat{B}\psi = \widehat{B}\,\widehat{A}\psi = \widehat{B}(a\psi) = a(\widehat{B}\psi) \ \ldots\ldots \ (3.40)$$

This means that $\widehat{B}\psi$ is also an eigenfunction of the operator $\widehat{A}$ and its eigenvalue a is the same as that of the function ψ. This is possible only when $\widehat{B}\psi$ is a multiple of ψ, say bψ, where b is a constant.

$$\widehat{B}\psi = b\psi \quad \ldots\ldots \ (3.41)$$

Equation 3.41 implies that ψ is also an eigenfunction of the operator $\widehat{B}$. We can also conclude the converse fact that if there exists a set of functions which are eigenfunctions of two operators, then the two operators commute.

3.7.5 Uncertainty Relation and Commutator

Now we will discuss a key detail about commutators in quantum mechanics. We will learn in later sections that the physical variables are measured using their corresponding operators in quantum mechanics. If an operator and a function satisfy the eigenequation i.e., if the function is an eigenfunction of the operator and the eigenvalue is real number then it implies that the physical quantity for which the operator stands for can be measured experimentally. Thus the physical significance of the commutator can be summarised in the following two points

(i) If the two operators commute, then it is possible to measure simultaneously the precise values of both the physical quantities which the operators stand for.

(ii) If the two operators do not commute, then it is not possible to measure simultaneously the precise values of both the physical quantities which the operators stand for.

We can see that the above statements are in line with the uncertainty principle discussed in the previous section. Accordingly, we can actually arrive at the Heisenberg uncertainty relation from the commutator of position and momentum operator. In this context, let us introduce the position operator $\hat{x}$ = x (multiplication by position) and position operator $\widehat{P_X} = -i\hbar\frac{d}{dx} = -i\frac{h}{2\pi}\frac{d}{x}$ in one dimension. Please note that $\hbar$ is called "h-bar" or "Dirac's h" and is equal to $\frac{h}{2\pi}$. Now we evaluate the commutator

$$[\hat{p}_X, \hat{x}]f = \hat{p}_X\hat{x}f - \hat{x}\hat{p}_X f = -i\frac{h}{2\pi}\frac{d}{dx}(xf) - x\left[-i\frac{h}{2\pi}\frac{df}{dx}\right]$$

$$= -i\frac{h}{2\pi}f - i\frac{h}{2\pi}x\cdot\frac{df}{dx} + i\frac{h}{2\pi}x\cdot\frac{df}{dx} = -i\frac{h}{2\pi}f$$

So we can write $[\hat{p}_X, \hat{x}] = i\frac{h}{2\Pi}.\hat{I}$ ...... (3.42)

Here, $\hat{I}$ is called a unitary operator. To write it simply we can omit the unitary operator and put the functional form as

$$[\hat{p}_X, \hat{x}]f = i\frac{h}{2\pi}.f \quad \text{......} \quad (3.43)$$

Equation 3.43 signifies that $\hat{p}_x$ and $\hat{x}$ do not commute and so the linear momentum of the particle along the x-axis and its position along the x-axis cannot be determined simultaneously.

3.7.6 Expectation Value

In quantum mechanics, the **expectation value** is the probabilistic (expected) value of the result (measurement) of an experiment. In other words, the average value of a large number of observations is given by the expectation value of the operator corresponding to the observable of interest. The expectation value of an operator is defined as

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi d\tau \quad ...... (3.44)$$

Here, ψ is the function that describes a state and ψ^* is the complex conjugate of the function. Also, the integration is over all the space accessible to the particle i.e. $d\tau$ = dxdydz. We will discuss later that ψ is actually the wavefunctions and this definition is valid for the normalised wavefunctions meaning $\int \psi^* \psi d\tau = 1$. If, in general, ψ is an eigenfunction of $\hat{A}$ with the eigenvalue a then

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi d\tau = \int \psi^* a \psi d\tau = a \int \psi^* \psi d\tau = a \quad ...... (3.45)$$

because a is a constant and may be taken outside the integral, and the resulting integral is equal to 1 for a normalized wavefunction. The interpretation of this expression is that, because every observation of the property $\hat{A}$ results in the a value, the mean/average value of all the observations is also a. We will evaluate expectation values of actual quantum mechanical operators in later sections.

3.7.7 Hermitian Operators

A special feature of all the quantum mechanical operators associated with physical observables is that they are all Hermitian operators. A Hermitian operator satisfies the following relation

$$\langle \hat{A} \rangle = \int \psi_j^* \hat{A} \psi_i d\tau = \left\{ \int \psi_i^* \hat{A} \psi_j d\tau \right\}^* = \int \psi_i \left(\hat{A} \psi_j \right)^* d\tau \quad ...... (3.46)$$

Here. ψ_j and ψ_i are two functions and the asterisk means complex conjugate.

Hermitian operators have profound implications in quantum mechanics. We will discuss the hermiticity of position and momentum operator here.

For the position operator $\hat{x}$ is it very easy to prove Hermitian property because the operator is simply a multiplication by x and we are free to alter the positions of the functions.

$$\int_{-\infty}^{+\infty} \psi_i^* \hat{x} \psi_j d\tau = \int_{-\infty}^{+\infty} \psi_i^* x \psi_j d\tau = \int_{-\infty}^{+\infty} \psi_j x \psi_i^* d\tau = \left\{ \int_{-\infty}^{+\infty} \psi_j^* x \psi_i d\tau \right\}^* \text{ ...... (3.47)}$$

The proof for momentum operator $\hat{P}x$ is not so straightforward and involves integration by parts. Since the operator is for one dimension, we will use dx instead of dτ.

$$\int_{-\infty}^{+\infty} \psi_i^* \widehat{Px} \psi_j dx = -i\frac{h}{2\pi} \int_{-\infty}^{+\infty} \psi_i^* \frac{d\psi_j}{dx} dx \text{ ...... (3.48)}$$

Using integration by parts, we can write for two functions, $\int f \frac{dg}{dx} x = fg - \int g \frac{df}{g} dx$.

Taking a similar approach in equation 3.48, we write

$$\int_{-\infty}^{+\infty} \psi_i^* \hat{p}_x \psi_j dx = -i\frac{h}{2\pi} \int_{-\infty}^{+\infty} \psi_i^* \frac{d\psi_j}{dx} dx = -i\frac{h}{2\pi} \left[\psi_i^* \psi_j \right]_{-\infty}^{+\infty} + i\frac{h}{2\pi} \int_{-\infty}^{+\infty} \psi_j \frac{d\psi_i^*}{dx} dx \text{ ..... (3.49)}$$

Here, we need to understand that we use momentum operators on wavefunctions i.e. ψ_j and ψ_i and all the wavefunctions become zero at infinite limit. This means the first part of equation 3.49 $\left[\psi_i^* \psi_j \right]_{-\infty}^{+\infty}$ = 0. So we write,

$$\int_{-\infty}^{+\infty} \psi_i^* p_x \psi_j dx = -\frac{ih}{2\Pi} \int_{-\infty}^{+\infty} \psi_i^* \frac{d\psi_j}{dx} dx = i\frac{h}{2\pi} \int_{-\infty}^{+\infty} \psi_j \frac{d\psi_i^*}{dx} dx = \left\{ -i\frac{h}{2\pi} \int_{-\infty}^{+\infty} \psi_j^* \frac{d\psi_i}{dx} dx \right\}^* \text{ (3.50)}$$

Please note that the complex conjugate of i is –i. Equation 3.50 proves that momentum operator is Hermitian.

The Eigenvalues of a Hermitian operator are real

This is a very important consequence used in quantum mechanics. In quantum mechanics, we find the values of physical observables by operating the system wavefunction with Hermitian operators. The value of the physical observable must be a real quantity. The Hermitian operators satisfy this criterion because the eigenvalues of Hermitian operators are real. It can be proven easily as follows. Suppose, ψ_i is one of the eigenfunctions of the Hermitian operator $\hat{A}$ and a_i is the corresponding eigenvalue.

$$\hat{A}\,\psi_i = a_i\psi_i \text{ ...... } (3.51)$$

Multiplying both sides of the equation with ψ_i^* and integrating

$$\int \psi_i^* \hat{A}\psi_i d\tau = a_i \int \psi_i^* \psi_i d\tau \text{ ...... } (3.52)$$

The complex conjugate of equation 3.52 must be valid. So

$$\left\{\int \psi_i^* \hat{A}\psi_i d\tau\right\}^* = \int \psi_i \hat{A}\psi_i^* = a_i^* \int \psi_i \psi_i^* d\tau \text{ ...... } (3.53)$$

Since the operator is Hermitian, the left side of equation 3.52 and 3.53 are same. So we can write

$$a_i \int \psi_i^* \psi_i d\tau = a_i \int \psi_i \psi_i^* d\tau \text{ ...... } (3.54)$$

Since $\int \psi_i^* \psi_i d\tau$ is a non-zero quantity, it must be

$$a_i = a_i^* \text{ ...... } (3.55)$$

Equation 3.55 is only valid for real numbers. So the eigenfunctions of an Hermitian operator must be real.

3.8 Wave Function and The Schrödinger Equation

The Schrödinger equation is the fundamental principle of Quantum Mechanics. If electrons, atoms, and molecules have wave-like properties, then there must be a mathematical function that is the solution to a differential equation that describes electrons, atoms, and molecules. This differential equation is called the **wave equation**, and the solution is called the **wavefunction**. Such thoughts may have motivated **Erwin Schrödinger** (1887-1961) to argue that the wave equation is a key component of Quantum Mechanics. In January 1926, Schrödinger published the paper "Quantisierung als Eigenwertproblem" (Quantization as an Eigenvalue Problem) on wave mechanics and presented what is now known as the **Schrödinger equation**. In this paper, he gave a derivation of the wave equation for time-independent systems and showed that it gave the correct energy eigenvalues for a hydrogen-like atom. This paper has been universally celebrated as one of the most important achievements of the twentieth century and created a revolution in most areas of quantum mechanics and indeed of all physics and chemistry. A second paper was submitted just four weeks later that solved the quantum harmonic oscillator, rigid rotor, and diatomic molecule problems and gave a new derivation of the Schrödinger equation. In subsequent third and fourth papers Schrödinger established a more general description of the wave mechanics in quantum systems, discussed Stark Effect, perturbation theory and time-dependent Schrödinger equation.

Before going further, we need to understand the term "postulate" in science. A scientific postulate is a generally accepted statement, which is accepted because it is consistent with experimental observations and serves to predict or explain a variety of observations. A postulate cannot be directly proven or derived. However, the postulates are able to explain observations and the conclusions arising from postulates successfully describe the physical systems. Schrödinger equation is one such postulate. It cannot be derived from any common fundamental principles. Schrödinger equation is a differential equation involving one or more derivatives. The solutions to the differential equations are the mathematical functions of the variables. Since some mathematical functions, such as the sine and cosine, go through repeating periodic maxima and minima, they produce graphs that look like waves. Such functions can themselves be thought of as waves and can be calledwavefunctions. Now in case of Schrödinger equation, the solutions are able to describe the wave-like behavior of the system (electrons, atoms etc.) and they contain all the information of the system. The solution to the Schrödinger equation is also called **wavefunction** and the equation is called a **wave equation**.

3.8.1 Classical Wave Equation

The easiest way to find a differential equation that will provide wavefunctions as solutions is to start with a wavefunction and work backwards. Let us consider a sine wave

$$A(x,\ t) = A_0 \sin(kx - \omega t) \ \ldots\ldots\ (3.56)$$

In this equation, A(x, t) is the amplitude of the sin wave at position x and time t; A_0 is the maximum amplitude; k is the wave-vector or angular wavenumber (not to be confused with linear wavenumber) and ω is the angular frequency. If the frequency and the wavelength of the sine wave is υ and λ respectively, then by definition,

$$k = \frac{2\pi}{\lambda} \ \ldots\ldots\ (3.57)$$

$$\omega = 2\pi\upsilon \ \ldots\ldots\ (3.58)$$

Now, let us consider the partial second derivative of equation 3.56 with respect to position and time i.e.x and t.

$$\frac{\partial^2 A(x,t)}{\partial x^2} = -k^2 A_0 \sin(kx - \omega t) = -k^2 A(x,t)$$

Or,
$$A(x,t) = -\frac{1}{k^2}\frac{\partial^2 A(x,t)}{\partial x^2} \ \ldots\ldots\ (3.59)$$

$$\frac{\partial^2 A(x,t)}{\partial t^2} = -\omega^2 A_0 \sin(kx - \omega t) = -\omega^2 A(x,t)$$

Or,
$$A(x,t) = -\frac{1}{\omega^2}\frac{\partial^2 A(x,t)}{\partial t^2} \ \ldots\ldots\ (3.60)$$

Comparing equation 3.59 with 3.60 we can write,

$$-\frac{1}{k^2}\frac{\partial^2 A(x,t)}{\partial x^2} = -\frac{1}{\omega^2}\frac{\partial^2 A(x,t)}{\partial t^2}$$

$$\frac{\partial^2 A(x,t)}{\partial x^2} = \frac{k^2}{\omega^2}\frac{\partial^2 A(x,t)}{\partial t^2} \quad ...... (3.61)$$

The wavelength and the frequency of the wave is related as

$$\lambda\upsilon = v \quad ...... (3.62)$$

Here, v is the velocity of the wave. Using this relation, we can establish the relation between as

$$\omega = 2\pi\upsilon = 2\pi\frac{v}{\lambda} = vk \quad ...... (3.63)$$

$$\therefore \frac{k^2}{\omega^2} = \frac{1}{v^2} \quad ...... (3.64)$$

Using equation 3.64 in equation 3.61 we get

$$\frac{\partial^2 A(x,t)}{\partial x^2} = \frac{1}{v^2}\cdot\frac{\partial^2 A(x,t)}{\partial t^2} \quad ...... (3.65)$$

Equation 3.65 is known as the **classical wave equation in one dimension** and the solution of this differential equation describes all waves in one dimension that move with a constant velocity.

3.8.2 Time Independent Schrödinger Equation

We have already mentioned that the Schrödinger equation cannot be "derived". In chemistry, our goal is to find appropriate wavefunctions for describing atoms, molecules etc. and to do that we need an appropriate wave equation. This is achieved by the Schrödinger equation. Here, we are going to discuss the time independent Schrödinger equation. You will learn about the time dependent Schrödinger equation later in your academics.

It is common in Quantum Mechanics to symbolize the functions that are solutions to Schrödinger's equation as ψ or f and from now on we will denote the wavefunctions as such. A general method for finding solutions to differential equations that depend on more than one variable (x and t in this case) is to separate the variables into different terms. This separation makes it possible to write the solution as a product of two functions, one that depends on x and one that depends on t. This important technique is called the method of separation of variables. This technique is used in most of the applications that we will be considering.

$$\psi(x,\ t) = \psi(x).\psi(t) \ \ldots\ldots\ (3.66)$$

Let us consider the time dependent part of the wavefunction as a cosine function and thus the overall wavefunction becomes

$$\psi(x,\ t) = \psi(x).\cos\omega t \ \ldots\ldots\ (3.67)$$

Now, if we use this wavefunction in the classical wave equation i.e. equation 3.65 then we get

$$\frac{\partial^2\psi(x,t)}{\partial x^2} = \frac{1}{v^2}\cdot\frac{\partial^2\psi(x,t)}{\partial t^2}$$

$\cos\omega t.\dfrac{\partial^2\psi(x)}{\partial x^2} = -\dfrac{\omega^2}{v^2}\cdot\psi(x).\cos\omega t$ [The second derivative of cosωt i.e. $\dfrac{\partial^2 \cos\omega t}{\partial t^2} = -\ \omega\dfrac{\partial \sin\omega t}{\partial t} = -\omega^2\cos\omega t$.]

$$\therefore\ \frac{\partial^2\psi(x)}{\partial x^2} = -\frac{\omega^2}{v^2}\cdot\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{\omega^2}{v^2}\cdot\psi(x) = 0 \ \ldots\ldots\ (3.68)$$

Since we are working out the equation in quantum mechanics, we can use the principles of the subject. Here, we are trying to establish the wave equation of a quantum mechanical entity. From the de Broglie hypothesis, we know that every quantum particle has an associated wave property. We will use it to modify our equation. From de Broglie equation we know $\lambda = \dfrac{h}{mv} = \dfrac{h}{p}$ where p = mv = momentum of the particle. Using this relation along with $\omega = 2\pi\upsilon = 2\pi\dfrac{v}{\lambda}$ we can write

$$\frac{\omega^2}{v^2}=\frac{(2\pi v)^2}{\lambda^2 v^2}=\frac{(2\pi)^2}{\lambda^2}=\frac{(2\pi)^2 p^2}{h^2} \quad \ldots\ldots (3.69)$$

Replacing the value of $\frac{\omega^2}{v^2}$ from equation 3.69 to equation 3.68 we get

$$\frac{\partial^2\psi(x)}{\partial x^2}+\frac{(2\pi)^2 p^2}{h^2}\cdot\psi(x)=0 \ldots\ldots (3.70)$$

Next, we will use the total energy of a particle as the sum of the kinetic energy and potential energy to replace the momentum in the equation.

$$E = K.E. + P.E. = \frac{p^2}{2m} + V(x) \quad \ldots\ldots (3.71)$$

So equation 3.70 is modified as

$$\frac{\partial^2\psi(x)}{\partial x^2}+\frac{(2\pi)^2 p^2}{h^2}\cdot\psi(x)=0$$

$$\frac{\partial^2\psi(x)}{\partial x^2}+\frac{(2\pi)^2}{h^2}\cdot 2m(E-V(x))\psi(x)=0 \ldots\ldots (3.72)$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x) \quad \ldots\ldots (3.73)$$

If we use $\hbar = h/2\pi$ as mentioned in the previous section then we can write equation 3.73 as

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x) \quad \ldots\ldots (3.74)$$

Equation 3.72, 3.73 and 3.74 are essentially the same equation and are known as the Schrödinger's equation for a particle of mass m moving in one dimension (x) in a potential field specified by V(x). Since the equation does not incorporate any time dependence, it is also known as the time independent Schrödinger's equation. As mentioned previously, functions like $\psi(x)$are called wavefunctions because they are solutions to this wave equation. The time independent Schrödinger equation for a particle moving in three dimensions (x, y, z) is obtained simply by adding the other second derivative terms and by including the three-dimensional potential energy function. The wavefunction ψ then depends on the three variables x, y, and z.

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x, y, z) + V(x, y, z\ )\psi(x, y, z) = E\psi(x, y, z) \text{ ...... } (3.75)$$

The three second derivatives in parentheses together are called the Laplacian operator or del-squared,

$$\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \text{ ...... } (3.76)$$

So equation 3.75 is also written as

$$-\frac{\hbar}{2m}\nabla^2\ \psi(x, y, z) + V(x, y, z\ )\psi(x, y, z) = E\psi(x, y, z) \text{ ...... } (3.77)$$

In quantum mechanics, the **Hamiltonian** of a system is an operator corresponding to the total energy of that system, including both kinetic energy and potential energy. The **Hamiltonian operator** is represented as

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) + V(x,y,z) = -\frac{\hbar^2}{2m}\nabla^2 + v(x,y,z) \text{ ...... } (3.78)$$

In one-dimension, the Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \text{ ...... } (3.79)$$

So the time independent Schrödinger's equation is simply written as

$$\hat{H}\psi = E\psi \text{ ...... } (3.80)$$

Equation 3.80 says that the Hamiltonian operator operates on the wavefunction to produce the energy (which is a scalar) times the wavefunction. We have learned that such equations are called eigenvalue equations. So we can say that the wavefunction is the eigenfunction of the Hamiltonian operator and the total energy of the system is its eigenvalue.

3.8.3 Wave Functions and The Born interpretation

The term **wavefunction** is the central idea of quantum mechanics. Wavefunctions are mathematical functions that represent the state of a system. In this case, the system is a quantum system. To understand the wavefunction, let us first think of a simple ripple of water. In the wave formed over water, the quantity that varies periodically is the height of the water surface. As stated in de Broglie hypothesis, in quantum mechanics we are dealing with matter waves. The quantity whose variations make up matter waves is called the wave function which is denoted by Greek letter ψ (psi). However, the wavefunction itself does not have a physical interpretation. The quantity which has a real physical interpretation is the probability density which is expressed as

$$|\psi|^2 = \psi^*\psi \quad ...... \quad (3.81)$$

Probability density is the square of the wavefunction's absolute magnitude evaluated at a particular place at a particular time and is proportional to the probability of finding the particle there at that time. So it must be a real quantity. We can see from equation 3.81 that even if ψ is a complex function, $|\psi|^2$ will be a real quantity as required. Max Born interpreted wavefunctions as

If the wavefunction of a particle has the value ψ *at x, then the probability of finding the particle between x and x + dx is proportional to* $|\psi|^2\, dx$.

For a particle free to move in three dimensions (for example, an electron near a nucleus in an atom), the wavefunction depends on the coordinates x, y, and z and is denoted $\psi(r)$.

If the wavefunction of a particle has the value ψ *at r, then the probability of finding the particle in an infinitesimal volume* $d\tau = dxdydz$ *at that position is proportional to* $|\psi|^2\, dt$.

This is known as the **Born interpretation.**

Normalisation of Wavefunction

A probability is a real number between 0 and 1. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. This means that the particle has to be located somewhere and therefore

$$\int_{-\infty}^{+\infty} |\psi|^2 \, d\tau \neq 1 \quad \ldots\ldots \; (3.82)$$

The integral in equation 3.82 cannot be infinity also because it will also mean the particle does not exist. So it must be a finite value. It is a good practice to equal the integral to the probability density which varies between 0 and 1. This is performed with the help of **normalisation**. Since ψ is a solution of the Schrödinger equation, $N\psi$ is also a solution where N is a constant. This liberty means we can find a constant factor N termed as the **normalisation constant** which will equate the probably density to $|\psi|^2$ in the following manner.

$$\int_{-\infty}^{+\infty} (N\psi)^*(N\psi)d\tau = 1$$

$$\therefore N^2 \int_{-\infty}^{+\infty} \psi^*\psi d\tau = 1 \quad \ldots\ldots \; (3.83)$$

So, the normalisation constant is

$$N = \frac{1}{\left(\int_{-\infty}^{+\infty} \psi^*\psi d\tau\right)^{\frac{1}{2}}} \quad \ldots\ldots \; (3.84)$$

Provided this integral has a finite value (that is, the wavefunction is 'square integrable'), the normalization factor can be found and the wavefunction 'normalized' and specifically 'normalized to 1'.

3.8.4 Acceptable Wavefunction

The Born interpretation puts some restrictions on the wavefunctions. All types of mathematical functions cannot be wavefunctions. For a mathematical function to be a wavefunction, few conditions must be satisfied. These rules have been summarised below-

(i) ψ must be continuous and single-valued everywhere. This means that for all given values of x, $\psi(x)$ must have a unique value. This is a way of guaranteeing that there is only a single value for the probability of the system being in a given state. A non-continuous function means that the derivative of the function may very large at a certain point. Since the momentum of the system is found using the momentum operator, which is a first order derivative, this would imply an infinite momentum, which is not possible in a physically realistic system.

(ii) $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}, \frac{\partial\psi}{\partial z}$ must be continuous and single-valued everywhere. Following the same reasoning as before, a discontinuous first derivative would imply an infinite second derivative, and since the energy of the system is found using the second derivative, a discontinuous first derivative would imply an infinite energy, which again is not physically realistic.

(iii) ψ must be normalizable and finite, which means that ψ must go to 0 as x, y and z go to ∞. This is because the integral of $|\psi|^2$ over all space must be finite. This is another way of saying that it must be possible to use $|\psi|^2$ as a probability density, since any probability density must integrate over all space to give a value of 1, which is clearly not possible if the integral of $|\psi|^2$ is infinite. So ψ must be square integrable.

Let us examine a common mathematical function e^x in the range 0 to ∞. In this range e^x is single valued and continuous for all values of x. However, the function is not finite since $e^{\infty} = \infty$. So e^x is not an acceptable wavefunction. However, in the same limit e^(-x) is an acceptable wavefunction since the function and it's first derivative are both continuous, single valued and the function is finite as $e^{-\infty} = 0$. In the next step, as an exercise, one can try to examine whether e^{-x} is an acceptable wavefunction in the range $-\infty$ to ∞.

3.9 Postulates of Quantum Mechanics

Till now, we have become familiar with several fundamental principles of quantum mechanics. Now it is time to introduce the postulates of quantum mechanics. It has been already mentioned in the previous section that a postulate means something that is generally accepted without proof because the inferences drawn from it can be experimentally proven. Similarly, there are few postulates or axioms in quantum mechanics which we will learn in this section. As we continue our journey through quantum mechanics, we will use these principles in solving problems.

Postulate 1

The state of a quantum mechanical system is completely specified by the function $\psi(x)$ *that depends on the coordinates of the particle x. All possible information about the system can be derived from* $\psi(x)$*. This function is called the wavefunction or state function and has the property that* $\psi(x)^* \psi(x)dx$ *is the probability that the particle lies in the interval dx, located at the position x.*

This is the statement of for a particle in one dimension. In three dimensions, we can say that the particle is described by the wavefunction $\psi(x, y, z)$ and the particle is located within the volume element $d\tau = dxdydz$. This postulate is known as the probabalistic interpretation of the wavefunction.

Postulate 2

To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics.

This postulate comes from the observation that the expectation value of an operator that corresponds to an observable must be real and therefore the operator must be Hermitian. Some examples of linear, Hermitian operators used in quantum mechanics are

Observable	**Classical Symbol**	**Quantum Operator**	**Operation**
Position	x	$\hat{x}$	Multiply by x
	r	$\hat{r}$	Multiply by r
momentum	px	$\hat{p}x$	$-i\hbar\frac{\partial}{\partial x}$
	p	$\hat{p}$	$-i\hbar\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$
kinetic energy	T	$\hat{T}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
potential energy	V(r)	$\widehat{V(r)}$	Multiply by V(r)
total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(r)$
Angular Momentum	lx	$\hat{l}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	ly	$\hat{l}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	lz	$\hat{l}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

Postulate 3

In any measurement of the observable associated with operator $\hat{A}$ *the only values that will ever be observed are the eigenvalues a that satisfy the eigenvalue equation* $\hat{A}\ \psi = a\psi$.

This postulate means that the values of dynamical variables are quantized in quantum mechanics.

Postulate 4

If a system is in a state described by the normalised wavefunction then the average value of the observable corresponding to A is given by

$$\langle \hat{A} \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{A} \psi d\tau \quad ...... (3.85)$$

Postulate 5

The wavefunction or state function of a system evolves in time according to the time-dependent Schrödinger equation.

$$\hat{H}\psi(r,t) = i\hbar \frac{\partial \psi(r,t)}{\partial t} \quad ...... (3.86)$$

3.10 Particle in a Box

In quantum mechanics, the **particle in a box** model (also known as the **infinite potential well** or the **infinite square well**) describes a particle free to move in a small space surrounded by impenetrable barriers. Although mainly studied as a model system, it is one of the few systems in quantum mechanics that can be solved analytically. Particle in a box problem elaborates the difference between classical and the quantum world. In this simplistic problem we get our first glimpse of the quantization of energy. Quantization of energy is at the heart of all the systems studied in quantum mechanics. The simplest form of the problem is particle in a one-dimensional box which we will learn first and then extend the problem to particle in a two and three-dimensional box.

3.10.1 Particle in a One-dimensional Box

Consider a particle of mass m that is allowed to move only along the x-direction and its motion is confined to the region between hard and rigid walls located at x=0 and x=L. Here, the walls are impenetrable but the particle is allowed to move freely within the space. A depiction of the system has been shown in figure 3.5. This physical situation is called the particle in a one-dimensional box or in a infinite square well. The potential inside the well or the box is zero and infinity everywhere else. Due to this infinite potential outside the box, the particle can never escape it.

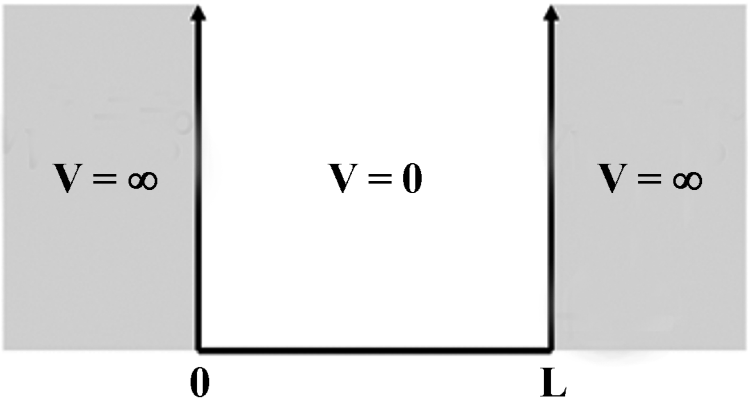


Figure 3.5: Schematic description of the particle confined in a one-dimensional box of length L

This physical situation is expressed in mathematical terms as follows

$$V(x)=\begin{cases} 0 \text{ for } 0 \le x \le L \\ \infty \text{ for } x<0 \text{ and } x>L \end{cases} \quad \ldots\ldots \; (3.87)$$

Now we can formulate the Schrödinger equation for the particle in a one dimensional box. The time independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\cdot\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x) \ldots\ldots \; (3.88)$$

We now impose the condition mentioned in the equation 3.87 onto 3.88 for particle inside the box i.e. $V(x) = 0$ for $0 \le x \le L$. So equation 3.87 reduces to

$$-\frac{\hbar^2}{2m}\cdot\frac{d^2\psi(x)}{dx^2}=E\psi(x) \quad \ldots\ldots \; (3.89)$$

here E is the total energy of the particle and $\psi(x)$ is the wavefunction. The equation can be written as

$$\frac{d^2\psi(x)}{dx^2}+\frac{2mE}{\hbar^2}\psi(x)=0 \quad \ldots\ldots \; (3.90)$$

This equation is similar to differential equation of the form

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \text{ ...... } (3.91)$$

Now the general solution of equation 3.91 is

$$\psi(x) = A \cos kx + B \sin kx \text{ ...... } (3.92)$$

With

$$k^2 = \frac{2mE}{\hbar^2} \text{ ...... } (3.93)$$

Since the walls are rigid and impenetrable, it means that the particle is never found beyond the wall. Mathematically, this means that the solution must vanish at the walls i.e. at $\psi = 0$ at $x = 0$ and $x = L$. So we can write at $x = 0$

$$\psi(0) = A \cos k.0 + B \sin k.0 = 0$$

$$\therefore A = 0 \text{ since } \cos 0 = 1$$

So, the wavefunction must be

$$\psi(x) = B \sin kx \text{ ...... } (3.94)$$

Now we impose the condition $\psi = 0$ at $x = L$ on equation 3.94.

$$\psi(L) = B \sin kL = 0 \text{ ...... } (3.95)$$

The right side of equation 3.95 is 0 which can happen in two ways. The first possibility is that B = 0 which is not possible because in this case the whole wavefunction becomes 0 everywhere meaning the particle does not exist. So sin kL= 0 must be the valid condition. This condition is only satisfied for integer multiples of π.

$$kL = n\pi$$

$$\therefore k = \frac{n\pi}{L} \text{ for } n = 1, 2, 3 \text{ ...... } (3.96)$$

We use equation 3.93 to write $\sqrt{\frac{2mE}{\hbar^2}} = \frac{n\pi}{L}$

$$\therefore E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2\pi^2h^2}{2mL^2(2\pi)^2} = \frac{n^2h^2}{8mL^2} \text{ for } n = 1, 2, 3 \text{ ...... } (3.97)$$

Equation 3.97 gives the energy of the particle inside the box. The most important point to observe here is that n can take only integer values which means the energy of the particle inside the box is not continuous but discrete. So, we can say that the particle bound to a one-dimensional box can only have certain discrete (quantized) values of energy. Further, the particle cannot have a zero kinetic energy as $n \neq 0$ i.e. it is impossible for a particle bound to a box to be "at rest." The index n is called the energy quantum number or principal quantum number or quantum number. The state n = 1 is called the ground state, the state for n = 2 is the first excited state, the state for n = 3 is the second excited state, and so on.

Following this condition, equation 3.94 changes to

$$\psi_n(x) = B\sin\frac{n\pi}{L}x \quad \text{for } n = 1, 2, 3 \; \ldots\ldots \; (3.98)$$

Now to find the complete wavefunction we need to consider normalisation of the wavefunction. We know that an acceptable wavefunction must satisfy the normalisation condition. So equation 3.98 should also satisfy the same.

$$\int_0^L |\psi_n(x)|^2\, dx = 1$$

$$\int_0^L \left(B\sin\frac{n\pi}{L}x\right)^2 dx = \int_0^L B^2 \sin^2\frac{n\pi}{L}x dx = B^2\int_0^L \sin^2\frac{n\pi}{L}x dx = 1$$

We can easily show that the integral $\int_0^L \sin^2\frac{n\pi}{L}x dx = \frac{L}{2}$. So

$$B^2\frac{L}{2} = 1$$

$$B = \sqrt{\frac{2}{L}} \quad \ldots\ldots \; (3.99)$$

So the overall wavefunction becomes

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x \quad \text{for } n = 1, 2, 3 \; \ldots\ldots \; (3.100)$$

In figure 3.6 the wavefunction and the energy levels of a particle in a one-dimensional box have been represented following equations 3.97 and 3.100. The wavefunctions are sometimes referred to as the "states of definite energy." Particles in these states are said to occupy energy levels, which are represented by the horizontal lines in the figure. Energy levels are analogous to a ladder that the particle can "climb" as it gains or loses energy. Please note that quantization energy forbids occupying any in-between energy levels apart from the ones satisfied by equation 3.97. Energy quantization is a consequence of the boundary conditions. If the particle is not confined to a box but wanders freely, the allowed energies are continuous. Conservation of energy demands that if the energy of the system changes, the energy difference is carried in some other form of energy. For the special case of a charged particle confined to a small volume (for example, in an atom), energy changes are often carried away by photons. The frequencies of the emitted photons give us information about the energy differences (spacings) of the system and the volume of containment—the size of the "box". The point where the wavefunction becomes zero is called a node.

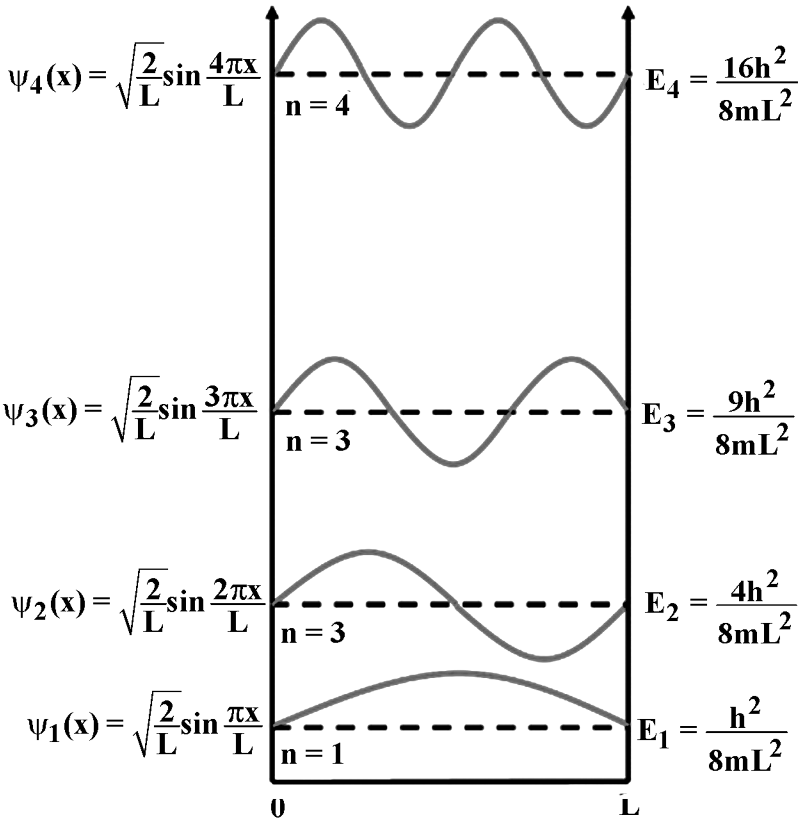


Figure 3.6 : Representation of wavefunctions and energy levels of a particle in one-dimensional box

3.10.2 Orthogonality of Wavefunctions

Orthogonality is an important idea in quantum mechanics. If two wavefunctions are orthogonal it means when you perform a measurement on them, the particle has to be in either one of them, but not in both at the same time. If one state is found, the particle is wholly in that state and not in the other. Two wavefunctions (which are eigenfunctions of the same operator) are said to be orthogonal if

$$\int \psi_m^* \psi_n d\tau = 0 \text{ ...... } (3.101)$$

For particle in a 1-D box, we can verify the orthogonality of the wavefunctions of the different states. Let us work out the same for ψ_1 and ψ_2. We know that $\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} x$ and $\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi}{L} x$. Since both the functions do not have any imaginary part we can write

$$\int_0^L \psi_1 \psi_2 dx = \int_0^L \left(\sqrt{\frac{2}{L}} \sin \frac{\pi}{L} x \right) \left(\sqrt{\frac{2}{L}} \sin \frac{2\pi}{L} x \right) dx = \frac{2}{L} \int_0^L \sin \frac{\pi}{L} x \sin \frac{2\pi}{L} x dx$$

$$= \frac{2}{L} \cdot \frac{1}{2} \int_0^L \left[\cos\left(\frac{\pi x}{2} - \frac{2\pi x}{L} \right) - \cos\left(\frac{\pi x}{L} + \frac{2\pi x}{2} \right) \right] dx = \frac{1}{L} \int_0^L \left[\cos\left(-\frac{\pi x}{L} \right) - \cos\left(\frac{3\pi x}{L} \right) \right] dx$$

$$= \frac{1}{L} \cdot \frac{L}{\pi} \left[\sin \frac{\pi x}{L} \right]_0^L - \frac{1}{L} \cdot \frac{L}{3\pi} \left[\sin \frac{3\pi n}{L} \right]_0^L = 0 \text{ ...... } (3.102)$$

Here, we have used $\sin\alpha \sin\beta = \frac{1}{2} [\cos(\alpha - \beta) - \cos(\alpha + \beta)]$ and $\sin(p\pi) = 0$ for $p = 0, 1, 2\ldots$ Clearly the solutions of particles in a one-dimensional box are orthogonal to each other. We also know that the wavefunctions are normalised which we discussed while solving the Schrödinger equation. So we can say that the wavefunctions are **orthonormal**. Mathematically, the combined orthonormality condition is expressed using the **Kronecker delta function** δ_{mn}. For particle in a one-dimensional box we write

$$\int_0^L \psi_m \psi_n dx = \delta_{mn} \text{ ...... } (3.103)$$

Where $\delta_{mn} = \begin{bmatrix} 1 \text{if } m = n \\ 0 \text{if } m \neq n \end{bmatrix}$

3.10.3 Expectation Values of x, x^2, p and p^2

The expectation value of an operator has already been discussed in section 3.7.6. Now we will find the expectation value of position and momentum for a particle in a one-dimensional box and will also calculate the product of root mean square uncertainties to establish that the Heisenberg uncertainty principle is valid in this case. For this purpose, first we will calculate the expectation value of x in the following way. For all the calculations, equation 3.100 has been used.

$$\langle x \rangle = \int_0^L \psi_n x \psi_n dx = \frac{2}{L}\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right)dx = \frac{2}{L}\int_0^L x\left(\frac{1-\cos\left(\frac{2n\pi x}{L}\right)}{2}\right)dx$$

$$= \frac{1}{L}\left[\int_0^L x dx - \int_0^L x \cos\frac{2n\pi x}{L} dx\right] = \frac{1}{L}\left[\frac{x^2}{2}\right]_0^L - 0 = \frac{1}{L}\cdot\frac{L^2}{2} = \frac{L}{2} \text{ ...... } (3.104)$$

The cosine part of the integral has been evaluated using integration by parts.

$$\int_0^L x\cos\left(\frac{2n\pi x}{L}\right)dx = \left[\frac{xL}{2n\pi}\sin\left(\frac{2n\pi x}{2}\right) + \frac{L^2}{4n^2\pi^2}\cos\left(\frac{2n\pi x}{L}\right)\right]_0^L = 0$$

We have also used the relation $2 \sin^2 \theta = 1 - \cos 2\theta$

In the next step we find the expectation value of x^2.

$$\left\langle x^2 \right\rangle = \int_0^L \psi_n \widehat{x^2} \psi_n dx = \frac{2}{L}\int_0^L x^2 \sin^2\left(\frac{n\pi x}{L}\right)dx = \frac{2}{L}\int_0^L x^2\left\{\frac{1-\cos\left(\frac{2\pi x}{L}\right)}{2}\right\}dx$$

$$= \frac{1}{L}\left[\int_0^L x^2 dx - \int_0^L x^2 \cos\frac{2n\pi x}{L}dx\right] = \frac{1}{L}\left[\frac{x^3}{3}\right]_0^L$$

$$-\left[\frac{L^2}{2n^2\pi^2}\cdot x\cos\frac{2n\pi x}{L} + \frac{\left(\frac{2n\pi x}{L}\right)^2 - 2}{\left(\frac{2n\pi}{L}\right)^3}\cdot \sin\frac{2n\pi x}{L}\right]_0^L$$

$$= \frac{1}{L}\left[\frac{L^3}{3} - \frac{L^3}{2n^2\pi^2}\right] = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} \quad \text{..... (3.105)}$$

Here we have used the integral $\int x^2 \cos ax = \frac{2}{a^2} x\cos ax + \frac{a^2x^2 - 2}{a^2}\sin ax$

Next, we evaluate the expectation value of p_x.

$$\langle \hat{p}_x \rangle = \int_0^L \psi_n \left(-i\hbar\frac{d}{dx}\right)\psi_n dx = -i\hbar\frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(\frac{d}{dx}\right)\sin\left(\frac{n\pi x}{L}\right)dx$$

$$= -i\hbar\frac{2}{L}\cdot\frac{L}{n\pi}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx = -i\hbar\frac{2}{n\pi}\cdot\frac{L}{n\pi}\left[-\frac{1}{2}\cos^2\left(\frac{n\pi x}{L}\right)\right]_0^L = 0 \text{... (3.106)}$$

Lastly, we will evaluate the expectation value of p_x^2.

$$\left\langle \hat{p}_x^2 \right\rangle = \int_0^L \psi_n \left(-i\hbar\frac{d}{dx}\right)^2 \psi_n dx = -\hbar^2\cdot\frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(\frac{d^2}{dx^2}\right)\sin\left(\frac{n\pi x}{L}\right)dx$$

$$= \hbar^2\cdot\frac{2}{L}\cdot\left(\frac{n\pi}{L}\right)^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = \hbar^2\cdot\frac{2}{L}\cdot\left(\frac{n\pi}{L}\right)^2\cdot\frac{L}{2} = \frac{h^2}{4\pi^2}\cdot\frac{n^2\pi^2}{L^2} = \frac{n^2h^2}{4L^2} \quad \text{..... (3.107)}$$

Now,

$$(\Delta x)^2 = \left\langle x^2 \right\rangle - \langle x \rangle^2 = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \left(\frac{L}{2}\right)^2 = \frac{L^2}{12} - \frac{L^2}{2n^2\pi^2} \quad \text{..... (3.108)}$$

$$(\Delta p_x)^2 = \langle p_x^2 \rangle - \langle p_x \rangle^2 = \frac{n^2h^2}{4L^2} 0 = \frac{n^2h^2}{4L^2} \quad \text{..... (3.109)}$$

$$(\Delta x)^2(\Delta p_x)^2 = \left(\frac{L^2}{12} - \frac{L^2}{2n^2\pi^2}\right)\left(\frac{n^2h^2}{4L^2}\right) = \frac{h^2}{16\pi^2}\left(\frac{n^2\pi^2}{3} - 2\right) \quad \text{..... (3.110)}$$

Hence.

$$\Delta x . \Delta p_x = \frac{h}{4\pi}\sqrt{\frac{n^2\pi^2}{3} - 2} > \frac{h}{4\pi} \text{since } \frac{n^2\pi^2}{3} > 2 \text{ always for } n = 1, 2, 3 \quad \text{..... (3.111)}$$

Thus, we arrive at the Heisenberg uncertainty principle in case of a particle in a one-dimensional box.

3.10.4 The Probability Distribution Function

In section 3.8 and 3.9 we have introduced the probability density function. The probability distribution function gives the probability of finding the particle around location x between the walls when the particle is in quantum state ψ_n. In case of particle in a one-dimensional box, the probability density is given by

$$|\psi_n(x)|^2 = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right) \quad \text{..... (3.112)}$$

The plot of equation 3.112 has been given in figure 3.7 for ground state, first and second excited state and a higher excited state that corresponds to a large quantum number. We see from these plots that when a quantum particle is in the ground state, it is most likely to be found around the middle of the box, where the probability distribution has the largest value. This is not so when the particle is in the first excited state because now the probability distribution has the zero value in the middle of the box, so there is no chance of finding the particle there. When a quantum particle is in the first excited state, the probability distribution has two maxima, and the best chance of finding the particle is at positions close to the locations of these maxima. This quantum picture is unlike the classical picture

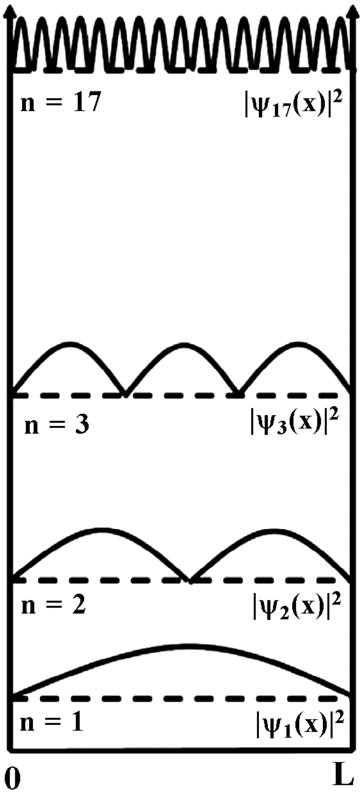


Figure 3.7 : The probability density distribution for a particle in a one-dimensional box

The probability density of finding a classical particle between x and x + dx depends on how much time the particle spends in this region. The probability density of finding the classical particle at x is uniform throughout the box, and there is no preferable location for finding a classical particle. This classical picture is matched in the limit of large quantum numbers. For example, when a quantum particle is in a highly excited state, shown in figure 3.7, the probability density is characterized by rapid fluctuations and the interval becomes very small and therefore a continuum type of situation is observed. So for large quantum numbers, the laws of quantum physics must give identical results as the laws of classical physics. This is known as the **Bohr's correspondence principle**.

3.10.5 Particle in a Two-Dimensional Box

Now we extend the problem for a particle confined in a two-dimensional box. Let us consider a particle confined in a two-dimensional box which has a height a and width

b. It means we can write that the particle is confined in a rectangular area with 0 < x < a and 0 < y < b. The walls have infinite potential. The potential energy of the particle inside this rectangular area is 0. Similar to particle in a one-dimensional box we can write the Schrödinger equation for the particle confined in a two-dimensional box as

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi(x,y)}{\partial x^2}+\frac{\partial^2\psi(x,y)}{\partial y^2}\right]=E\psi(x,y) \quad ..... (3.113)$$

It is important to note that the wavefunction of the particle in this case varies with both x and y and so we have represented it as $\psi(x, y)$. Since the Hamiltonian (i.e. left side of Equation 3.113) is the sum of two terms with independent (separate) variables, we will use a separation of variable approach to solve the equation. The wavefunction $\psi(x,y)$ can be written as the product of two independent one dimensional functions as

$$\psi(x, y) = X(x)Y(y) \quad ..... (3.114)$$

We can separate the Schrödinger equation (3.113) into two independent one dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\cdot\frac{\partial^2 X(x)}{\partial x^2}=\varepsilon_x X(x) \quad ..... (3.115)$$

$$-\frac{\hbar^2}{2m}\cdot\frac{\partial^2 Y(y)}{\partial y^2}=\varepsilon_y Y(y) \quad ..... (3.116)$$

where the total energy of the particle is the sum of the energies from each one-dimensional Schrödinger equation $\varepsilon_x + \varepsilon_y = E$. These two equations can now be solved exactly according to the one-dimensional box equations as discussed in previous section. By doing so we will get the energy values as

$$\varepsilon_{n_x}=\frac{n_x^2 h^2}{8ma^2} \quad ..... (3.117)$$

$$\varepsilon_{n_y}=\frac{n_y^2 h^2}{8mb^2} \quad ..... (3.118)$$

If for simplicity we assume that the box is a square box i.e. a = b = L then we can write $\varepsilon_{n_x} = \frac{n_x^2 h^2}{8mL^2}$ and $\varepsilon_{n_y} = \frac{n_y^2 h^2}{8mL^2}$. The total energy of the particle can be written as

$$E_{n_x} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} \text{ for a rectangular box ..... (3.119)}$$

$$E = \left(n_x^2 + n_y^2\right)\frac{h^2}{8mL^2} \text{ for a square box ..... (3.120)}$$

Similarly, the wavefunction can be written as

$$\psi_{n_x \cdot n_y}(x, y) = \frac{2}{\sqrt{a} \cdot \sqrt{b}} \cdot \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sin\left(\frac{n_y \pi x}{b}\right) \text{ for a rectangular box..... (3.121)}$$

$$\psi_{n_x \cdot n_y}(x, y) = \frac{2}{L} \cdot \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \text{for a square box ..... (3.122)}$$

The wavefunctions given here are normalised. In the case of two-dimensional box, we need two different integers n_x and n_y because the conditions are completely independent and can be satisfied by any two different (or similar) values of these integers. Both these quantum numbers vary as n_x = 1, 2, 3... and n_y = 1, 2, 3...

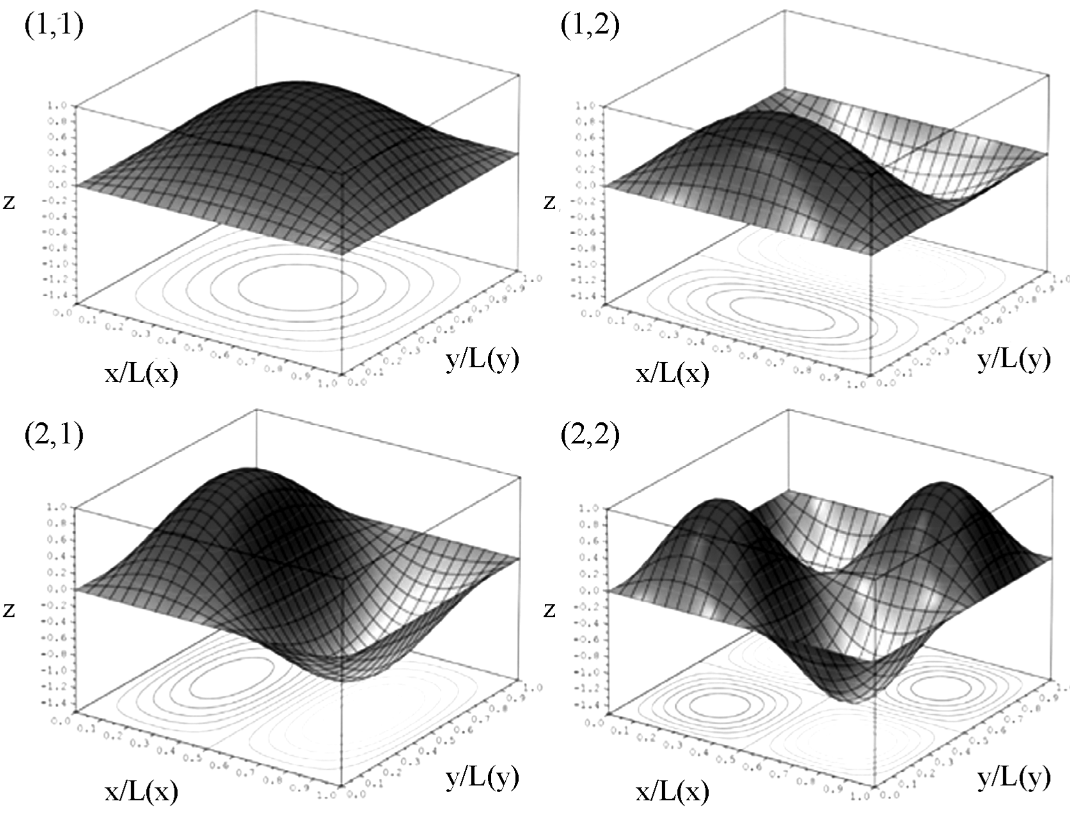


Figure 3.8 : Visualisationof first four wavefunctions of particle in a two-dimensional box. The numbers in the bracket indicate quantum numbers. The plots are available in public domain from commons.wikimedia.org/

The visualisation of wavefunction in this case is not straightforward. A depiction of the first four wavefunctions for a square box has been shown in figure 3.8. Unlike in the one-dimensional analogue, where nodes in the wavefunction are points where wavefunctions are zero, here entire lines can be **nodal lines**.

3.10.6 The Concept of Degeneracy

The particle in a two-dimensional box problem presents us with the concept of degeneracy. Two distinct wavefunctions are said to be degenerate if they correspond to the same energy. For a rectangular box degeneracy will depend on the length and width of the box. But for a square box the concept of degeneracy can be illustrated easily. The energy of the particle in a 2-D square box in the ground state i.e. for $n_x = 1$ and $n_y = 1$ is $E_{1,1} = \frac{2h^2}{8mL^2}$. For the ground state of the particle in a 2D box, there is one wavefunction (and no other) with this specific energy; the ground state and the energy level are said to be **non-degenerate**. However, in the 2-D box potential, the energy of a state depends upon the sum of the squares of the two quantum numbers. The particle having a particular value of energy in the excited state may has several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be degenerate. For the first excited state, the combinations of the quantum numbers are $n_x = 2$ and $n_y = 1$ and $n_x = 1$ and $n_y = 2$. The sum of squares of the quantum numbers in each combination is same (equal to 5). Each wavefunction has same energy $E_{2,1} = E_{1,2} = \frac{5h^2}{8mL^2}$. Corresponding to these combinations three different wavefunctions and two different states are possible. Hence, the first excited state is said to be doubly degenerate. The number of independent wavefunctions for the stationary states with a shared energy is called as the degree of degeneracy of the energy level. The same type of degeneracy will arise for quantum numbers (1, 3) & (3, 1); (2, 3) & (3, 2) etc.

3.10.7 Particle in a Three-Dimensional Box

The quantum particle in the 1D box problem can be expanded to consider a particle within a higher dimension as demonstrated for a quantum particle in a 2D box. Now we continue the expansion into a particle trapped in a 3D box. As always, the potential inside the box is zero and infinity everywhere else. Let us consider that the length, width and height of the box is a,b,c respectively. So the particle is confined in $0 < x < a$, $0 < y < b$ and $0 < x < c$ We can follow the exact procedure as before with extension in the z-direction. So the Schrödinger equation will be

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right]=E\psi(x,y,z) \quad \text{..... (3.123)}$$

The wavefunction can be separated into three independent functions $\psi(x, y) = X(x)Y(y)Z(z)$. We can now solve the Schrödinger equation similar to the 2D box and obtain the wavefunction and the energy as

$$\psi_{n_x,n_y,n_z}(x,y,z)=\sqrt{\frac{2}{a}}\cdot\sqrt{\frac{2}{b}}\cdot\sqrt{\frac{2}{c}}\cdot\sin\left(\frac{n_x\pi x}{a}\right)\cdot\sin\left(\frac{n_y\pi x}{b}\right)\cdot\sin\left(\frac{n_z\pi x}{c}\right) \quad \text{..... (3.124)}$$

$$E_{n_x,n_y,n_z}=\frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right) \quad ..... \ (3.125)$$

The quantum numbers vary as $n_x = 1, 2, 3...$, $n_y = 1, 2, 3...$, $n_z = 1, 2, 3....$ If the particle is trapped in a cubei.e. $a = b = c = L$, then the energy of the particle becomes

$$E=\left(n_x^2+n_y^2+n_z^2\right)\frac{h^2}{8mL^2} \quad ..... \ (3.126)$$

Now we can see that the ground (1, 1, 1) state is non-degenerate. The first excited state is actually three possible combinations of quantum numbers (2, 1, 1), (1, 2, 1), (1, 1, 2). Thus the first excited state is three-fold degenerate.

3.11 Summary

Classical mechanics failed to explain two experimental phenomenon – photoelectric effect and Compton effect. Einstein adopted Planck's idea of blackbody radiation and explained the dual nature of light to successfully explain the photoelectric effect. The quanta of light were termed as photons.

de Broglie gave the concept of matter waves associated with particles and explained how electrons can behave both as a particle and as a wave. His hypothesis gave the formula for the wavelength of the matter waves. Heisenberg prescribed the uncertainty principle which stated that the momentum and position for small particles cannot be measured simultaneously.

The postulates of quantum mechanics describe the wavefunctions. Schrödinger equation is one of such postulates. It is also known as the wave equation. Being a postulate, Schrödinger equation cannot be derived from fundamental principles. However all the quantum mechanical systems follow this equation. Application of the quantum mechanical principles to a particle confined in a potential well shows us that energy of such system is not continuous but quantized.

3.12 Self-Assessment Questions

1. The work function of copper metal is $\varphi = 7.53 \times 10^{-19}$ J. If we shine light with a frequency of 3.0×10^{-16} Hz. on copper metal, will the photoelectric effect be observed?
2. The stopping potential in an experiment of photon is 2eV. what is the maximum kinetic energy of photoelectrons emitted?
3. Calculate the frequency of light required to eject electrons with a kinetic energy of 0.66 eV.
4. An incident 71 pm X-ray is incident on a calcite target. Find the wavelength of the X-ray scattered at a 30° angle.
5. Compton shift depends on which of the following? (a) Incident radiation; (b) Nature of scattering substance (c) Angle of scattering (d) Amplitude of frequency
6. Calculate the de Broglie wavelength of an electron which has been accelerated from rest on application of potential of 400 volts.
7. What is the de Broglie wavelength for a 100 kg car moving at a speed of 100m/s?
8. Dual behaviour of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other types of material. If the velocity of the electron in this microscope is 1.6×10^6 ms^{-1}, calculate de Broglie wavelength associated with this electron.
9. Is the wavelength of electron on different orbits, same or different? If different what is the ratio of the wavelength in first and 4th orbit?
10. (a) The uncertainty in the momentum p of a football of mass 0.4 kg traveling at 40m/s is 1×10^{-6} of its momentum. What is its uncertainty in position x? (b) There is 2 mL of water traveling on the football at the same speed and p. Calculate its x. (c) Calculate its x of an electron travelling at the same speed with the same uncertainty in momentum. Mass of an electron is 9.1×10^{-31} kg.
11. Prove that the momentum operator $-i\hbar\frac{d}{dx}$ is a linear operator.

12. Check whether $e^{3x} + e^{-3x}$ is an eigenfunction of $\frac{d^2}{dx^2}$ and find the eigenvalue.

13. Which operators is Hermitian (a) $\frac{d}{dx}$ (b) $\frac{d^2}{dx^2}$?

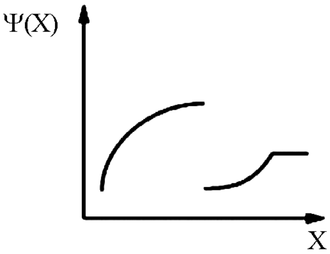
14. Is x^2 a Hermitian operator?

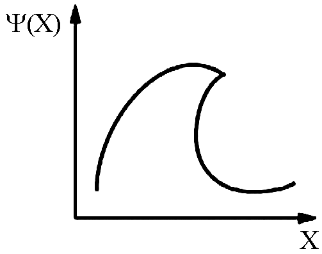
15. Find out the commutator of Hamiltonian and position operator.

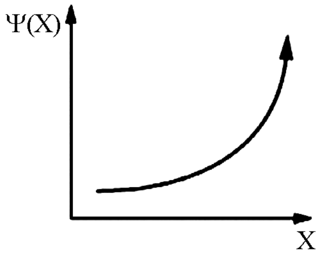
16. Which of the following wave functions are acceptable over the range x = 0 to 2p (a) tan x (b) cosec x (c) cos x + sin x?

17. Among the following functions cot x, sec x and sin x, which one can be an acceptable wave function?

18. Which of the following wave functions is a valid wave-function solution for Schr dinger's equation?





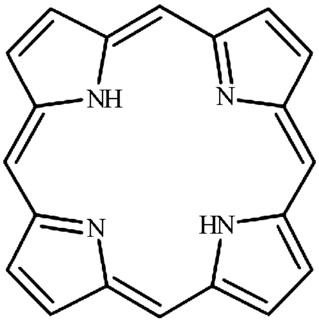


19. When do the eigenfunctions of an operator form an orthonormal basis?

20. Suppose a proton is confined to a box of width L=1.00×10^{-14} m (a typical nuclear radius). What are the energies of the ground and the first excited states? If the proton makes a transition from the first excited state to the ground state, what are the energy and the frequency of the emitted photon?

21. Assuming that a particle is characterized by a standing de Broglie wave, come up with an equation for the allowed energies of a particle in a one-dimensional box.

22. Metal porphyrin molecules are commonly in many proteins and it has the general structure.



This molecule is planar, so we can approximate electrons as being confined inside a square. What are energy levels and corresponding degeneracies of a particle in a square of side m? Porphyrin molecules have 18 electrons. If the length of the molecule is 850 pm, what is the lowest energy absorption of the porphyrin molecules?

23. The particle loses energy when it collides with the wall. (A) True or (B) False
24. Calculate the Zero-point energy for a particle in an infinite potential well for an electron confined to a 1 nm atom.
25. For a particle in a cubic box, what is the degeneracy of a state with $E = \frac{6h^2}{8mL^2}$?

3.13 Answers of Self-Assessment Questions

1. In order to eject electrons, we need the energy of the photons to be greater than the work function of copper. So, $E = h\nu = (6.626 \times 10^{-34}$ J.s). $(3.0 \times 10^{16}$ Hz) $= 2.0 \times 10^{-17}$ J. Since the photon energy is greater than the work function, photoelectric effect will be observed.
2. The relation connecting the stopping potential and maximum kinetic energy $K_{max} = eV_0 = 2$ electron volt. So $K_{max} = 2 \times 1.602 \times 10^{-19}$ Joules $= 3.2 \times 10^{-19}$ Joules.
3. Answer - 1.22×10^{15} Hz
4. To find the wavelength of the scattered X-ray, first we must find the Compton shift for the given scattering angle, $\Delta\lambda = \lambda_0 (1 - \cos\theta) = 2.426$ pm $(1 - \cos 30°) = 0.325$ pm. Then we add this shift to the incident wavelength

to obtain the scattered wavelength. $\Delta\lambda + \lambda = \lambda'$. $\lambda' = 0.325$ pm + 71 pm = 71.325 pm

5. c

6. For a charged particle, E = eV. de Broglie wavelength = $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$ $= \frac{h}{\sqrt{2meV}}$; de Broglie wavelength = $(6.625 \times 10^{-14})/(2 \times 9.11 \times 10^{-31} \times 1.6 \times 10^{-19} \times 400)$; Wavelength = 0.6135 Å.

7. 6.63×10^{-30} m.

8. 4.55×10^{-10} m

9. Assuming the mass of the electron to be the same in all orbits, $\lambda = \frac{h}{mv}$ or $\lambda \alpha \frac{1}{v}$. The velocity of the electron varies in orbits, so the wavelength of the electron in different orbits will not be the same. Atomic number and other constant being same, Velocity of the electron in an atom $v \propto \frac{1}{n}$. So $\lambda \propto n$. Ratio of de Broglie wavelength in first and fourth orbit $\frac{\lambda_1}{\lambda_4} = \frac{n_1}{n_4} = \frac{1}{4}$.

10. (a) p = mv = (0.40 kg) (40 m/s) = 16 kg.m/s. p = p × (1×10^{-6}) = 16 × (1×10^{-6}) = 16×10^{-6} kg.m/s. x = h/4p p = $(6.626 \times 10^{-34}$ Js) 4p 16×10^{-6} kg.m/s) = 3.3×10^{-30} m. (b) 2mL water = 2×10^{-3} kg; x = 6.6×10^{-28} m. (c) = 1.5 m

12. eigen value = 9;

13. (a) not Hermitian (b) Hermitian;

15. $[H, x] = -\frac{i\hbar}{m}\hat{p}$

16. (A) (x) = tan x. Not acceptable wave function in (0, 2) because it becomes discontinuous at x = $\pi/2$ (B) (x) = cosec x. Not acceptable as discontinuous at x = 0 & π (C) since $\psi(x)$ = cosx + sinx is finite everywhere in $(0, 2\pi)$ and continuous and square integrable so this is an acceptable wavefunction in the given range.

17. only sin x

18. The third function since it is continuous

19. The eigenfunctions of a linear Hermitian operator, once normalized, form an orthonormal basis. Thus the eigenfunctions of any operator corresponding to a physical observable form an orthonormal basis set.

20. If we assume that the proton confined in the nucleus can be modeled as a quantum particle in a box, all we need to do is to find its energies E_1 and E_2. The mass of a proton is $m = 1.76 \times 10^{-27}$ kg. The emitted photon carries away the energy difference $E = E_2 - E_1$. The ground state: 3.28×10^{-13} J. The first excited state 13.12×10^{-13} J. The frequency of the emitted photon is 1.49×10^{21} Hz. This is the typical frequency of a gamma ray emitted by a nucleus and this is a simple model of the nucleus.

21. The de Broglie relationship is $\lambda = \frac{h}{p}$. Because the waves are standing waves, an integral number of half wavelengths will fit in the box i.e. $L = \frac{h\lambda}{2} = \frac{nh}{2p}$.

    So $p = \frac{nh}{2L}$. The energy $\therefore E_n = \frac{p^2}{2m} = \frac{n^2h^2}{8mL^2}$ for n = 1, 2, 3..

23. (B) False. The total energy of the particle inside the box remains constant. It does not lose energy when it collides with the wall.

24. Here, $m = 9.1 \times 10^{-31}$ kg, $L = 10^{-9}$ m. So, $E = 5.9 \times 10^{-29}$ J.

25. 6-fold

3.14 Suggested Readings

(a) Physical Chemistry by Peter Atkins and Julio De Paula, Oxford University Press

(b) Physical Chemistry: A Molecular Approach by McQuarrie and Simon; Viva Books

(c) A Textbook of Physical Chemistry Vol.- IV by K. L. Kapoor; Macmillan Publishers India

Unit - 4 ❑ Electrical Properties of Molecules

4.1 Objective

On completion of this unit, the learner will be able to

- Define the chemical potential of an ion in solution
- Comprehend the concept of activity and activity coefficient of ions in solution
- Describe Debye–Hückel limiting law for ions in solution and estimate the activity coefficient of ions
- Understand the applications and limitations of the Debye–Hückel limiting law.
- Understand electrolysis, its importance and describe Faraday's laws of electrolysis
- Explain electrochemical cells, different types of cells, electrodes, cell potential and half cell potential
- Comprehend the electromotive force on a cell and its measurement
- Define and use Nernst law, standard electrode potential
- ApplyEMFmeasurements in determining (i) free energy, enthalpy and entropy of a cell reaction, (ii) equilibrium constants, and (iii) pH values, using hydrogen, quinone-hydroquinone, glass electrodes
- Understand the concept of liquid junction potential and its elimination, concentration cells and their use

- Define polarisation and different type of polarisation for non-polar and polar molecules
- Comprehend Clausius-Mosotti equation and Debye equation and their application

4.2 Introduction

We have introduced the concept of chemical equilibrium and the factors affecting it in previous chapters. The concept has been discussed in general terms involving gases, liquids and solids. In case of solutions, we have mostly dealt with non-electrolytes or non-ionic equilibrium with some concepts about ionic species in solution. In this unit, we will consider ionic equilibriums. The basic concept of ionic equilibrium is already familiar to us. The acid-base equilibrium, salt hydrolysis, buffer solutions, pH etc. are all part of ionic equilibrium and they are described in details in inorganic and physical chemistry texts. So, our discussion for this unit will consist mostly of ionic equilibrium in terms of activity of ions in solution. The chapter is of much significance since ionic equilibrium are vital for understanding reactions in living species, in agriculture and in industrial applications.

In the second part of the unit, we will learn about electrochemistry. Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic gadgets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

4.3 Ionic Equilibrium in Non-Ideal Solutions

4.3.1 Activity and the Activity Coefficient

The concept of activity was first introduced by G. N. Lewis in 1907. It is a widely applicable concept in case of solutions of electrolytes, non-electrolytes and gases. In case of gases, it is known as fugacity which we have learned earlier in this course. We have also introduced activity in previous units but here we will learn it in a more general setup. Activity can be used whenever there is a difference between ideal and observed properties as a function of concentration. For example, in figure 4.1, a measurable property of a solution has been represented as a function of concentration. The dashed line shows the theoretically predicted behavior of a system as a function of concentration according to some simplified/ideal model, while the solid line represents the actual (i.e., observed/ experimental) behavior as the system composition changes. In most cases, the observed and predicted behaviors will approach one another asymptotically at either low concentrations ("infinite dilution") or high concentrations ("pure solute"). In figure 4.1, for example, theory and experiment meet asymptotically at high concentrations. Theoretical constructs that exhibit such behavior are sometimes called limiting laws. The activity of a component in a mixture is a way of describing the actual behavior of the system in terms of its model behavior. It is the "effective concentration" of a component of the system, according to some idealized picture of how the system ought to act.

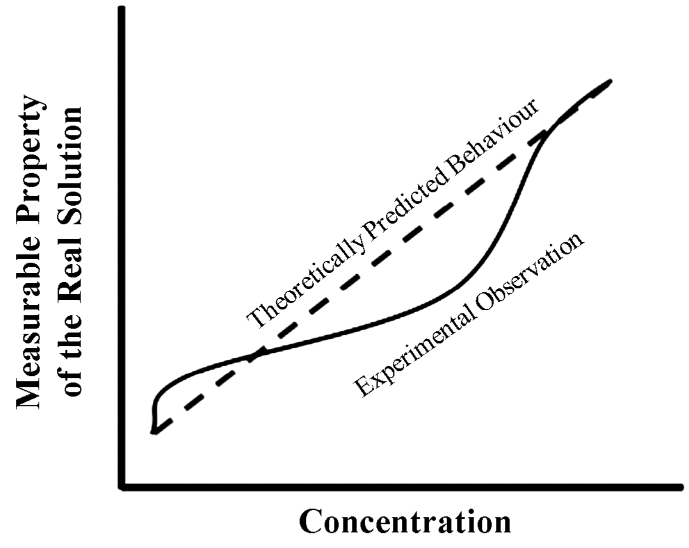


Figure 4.1 : The variation of a property of a real solution as compared to theoretical behaviour

Let us consider Henry's law as an ideal law for the system i.e., our model will be an ideally dilute solution. According to this law, $P_i = K_HC_i$ where P_i is the partial vapor pressure of the solute above the solution, C_i is the concentration of the solute in the solution and K_H is a constant (Henry's constant). Note that Henry's constant is often used to express the solubilities of gases in liquids. In order for a solution to follow Henry's Law, it must possess the following characteristic: the solute is surrounded on all sides by solvent molecules. Most solutions approximate this ideal only at dilute concentrations and hence the name "ideal dilute solutions". An ideal dilute solution of concentration C_i would be expected to exert a vapor pressure as predicted by Henry's Law. In most cases, the observed vapor pressure will be some different value. The difference is due to the departure of the actual solution from the characteristics in an ideal dilute solution.The departure from ideal behaviour can be expressed as the ratio of observed and ideal behaviour. This ratio, γ_i, is the activity coefficient of the solute. Let's imagine that a given solution of concentration C_i exerts a pressure of P_i; an ideal dilute solution of concentration a_i would give the same vapor pressure : In other words, the activity is the concentration of solute that would be needed to exert vapour pressure P_i if the solution possessed the properties of an ideal dilute solution. Another way of looking at it is that the solution of concentration C_i "acts like" an ideal solution of concentration a_i. The activity is the "effective concentration" of the real solution, where the term "effective" refers specifically to the behaviour of some ideal (in this case, a solution that follows Henry's Law). Since Henry's Law is linear with concentration, the activity coefficient is also the ratio of the activity to the actual concentration.

$$\gamma_i = \frac{\text{effective concentration}}{\text{actual concentration}} = \frac{a_i}{C_i} \quad \ldots.. \ (4.1)$$

In other words, the activity can be calculated if the activity coefficient is known. So activity of the solution is given by

$$a_i = \gamma_i C_i \quad \ldots.. \ (4.2)$$

The activity coefficient indicates the extent of the departure of the solute from ideal behaviour. Our model of an ideal solute is one in which every solute molecule is surrounded only by solvent molecules. This picture is more closely approached as the concentration decreases - Henry's Law is a limiting law that is approached asymptotically as the concentration approaches zero. Thus, as $C_i \rightarrow 0$, then $\gamma_i \rightarrow 1$ and $a_i \rightarrow C_i$. So in extension we can say that the standard state of the solution is when $a_i = 1$ M.

4.3.2 Chemical Potential and Activity

For an ideal or ideally dilute liquid or solid solution of nonelectrolytes, the chemical potential of each component is expressed as

$$\mu_i^{ideal} = \mu_i^o + RT \ln x_i \quad ..... \ (4.3)$$

where μ_i^0 is the chemical potential of the component at standard state and x_i is the mole fraction. We can rearrange the equation to express x_i as

$$x_i = \exp\left(\frac{\mu_i^{ideal} - \mu_i^o}{RT}\right) \quad ..... \ (4.4)$$

For a non-ideal solution, we express the effective concentration as activity. Similar to equation 4.4, in case of a non-ideal solution, the activity is defined as

$$a_i = \exp\left(\frac{\mu_i - \mu_i^o}{RT}\right) \quad ..... \ (4.5)$$

μ_i is the chemical potential of the species in any solution. In fact, equation 4.5 is valid in any solution irrespective of whether it is ideal or non-ideal. We can rearrange equation 4.5 to write for any solution,

$$\mu_i = \mu_i^o + RT \ln a_i \quad ..... \ (4.6)$$

Thus, the activity replaces the mole fraction in the expression for a nonideal solution. So the difference between the real solution chemical potential with that of the ideal solution is

$$\mu_i - \mu_i^{ideal} = RT\,\ell n\, a_i - RT\,\ell n\, x_i = RT\,\ell n \frac{a_i}{x_i} = RT\,\ell n\, \gamma_i \quad ..... \ (4.7)$$

The ratio $\frac{a_i}{x_i}$ is thus a measure of the departure from ideal behaviour which we have previously defined as activity coefficient γ_i.

4.3.3 Activity of Electrolyte Solution

We know that an electrolyte is a substance that ionizes (nearly completely) when dissolved in a solution and often the solvent used is water as it is a very good ionizing solvent. The cations and anions formed from the electrolyte interact very strongly according to Coulomb's law. Due to this strong interaction between the solute particles, the solution of electrolytes behaves non-ideally even at a very low concentration. Suppose, the electrolyte is $X_{V+}\ Y_{V-}$ and it dissociates as

$$Xv_+Yv_- = v_+X^{z+} + v_-Y^{z-}$$

So, for H_2SO_4, the values are $v_+ = 2$, $v_- = 1$, $z+ = 1$ and $z- = 2-$ i.e. when dissolved $H_2SO_4 = 2H^+ + SO_4^{2-}$. Similarly, for $CaCl_2$, the values will be $v_+ = 1$, $v_- = 2$, $z+ = 2+$ and $z- = 1-$. So, when an electrolyte $X_{v+}\ Y_{v-}$ dissolves, we get v_+ moles of cation and v_- moles of anions. In an electrolyte solution, the positive and negative ions are difficult to separate. Therefore, we use the **mean ionic chemical potential** for the solute which is defined as

$$\mu = v\mu_\pm = v_+\mu_+ + v_-\mu_- \ ..... \ (4.8)$$

In this equation, μ is the overall chemical potential, $\mu_\pm$ is the mean ionic chemical potential, v is the sum of stoichiometric coefficients of cations and anions i.e. $v = v_+ + v_-$, μ_- and μ_- are the chemical potentials of the cation and the anion respectively. We can see that v is the total number of ions produced by one mole of solute. In this way, the chemical potential of the solute (from both the positive and negative ions) becomes

$$\mu = \mu_\pm^o + RT \ln a = v\,(\mu_\pm^o + RT \ln a_\pm) \ ..... \ (4.9)$$

Here $a_\pm$ is the **mean ionic activity** of the solute. It is related to the activity as $a = a_\pm^v$. On the other hand, if we were able to write the chemical potential separately for the positive and the negative ions, we would have

$$\mu = v_+(\mu_+^0 + RT \ln a_+)\ v_-(\mu_-^0 + RT \ln a_-) \ ..... \ (4.10)$$

$$a_\pm^v = a_+^{v+} + a_-^v \quad ..... \ (4.11)$$

To quantify the concentration of electrolyte solutions, it is often convenient to use the molality instead of mole fraction. The molality m of a solute is defined as the number of moles of the solute n per kilogram of solvent. The nice feature about using the molality todescribe solute concentration instead of the mole fraction or the molarity is that the molality of one solute is independent of all other solutes. In contrast to the molarity, the molality is also independent of temperature or the mixing volume. In the high dilution limit, all three concentration measures are proportional to each other. Using the same approach as above, we can define **mean ionic activity coefficient** $\gamma_\pm$ and **mean ionic molality** $m_\pm$ as

$$\gamma_\pm^v = \gamma_+^{v+} + \gamma_-^{v-} \ ..... \ (4.12)$$

$$m_{\pm}^{v} = m_{+}^{v+} + m_{-}^{v-} \quad ..... (4.13)$$

The corresponding expression for the chemical potential is

$$\mu = v\left(\mu_{\pm}^{0} + RT\,\ell n\,\gamma_{\pm}m_{\pm}\right) \quad ..... (4.14)$$

4.3.4 The Ionic Strength

In order to represent the variation of activity coefficient with concentration, especially in the presence of added electrolytes, a quantity called the **ionic strength** was introduced by G. N. Lewis and M. Randall in 1921. It is a measure of the intensity of the electrical field due to the ions in a solution. The ionic strength is usually represented by the symbol μ or I, and is defined as half the sum of the terms obtained by multiplying the molality (or concentration) of each ion in the solution by the square of its valence. Ionic strength is a unitless quantity.

$$I = \frac{1}{2}\sum_{i} C_i Z_i^2 \quad ..... (4.15)$$

In equation 4.15, C_i is the concentration of the ionic species and Z_i is the charge of the ion. For example, let us determine the ionic strength of a 0.10 M solution of $MgCl_2$ at pH 7.0. The concentrations of each ion in this solution are $[Mg^{2+}] = 0.10$ M; $[Cl^-] = 0.20$ M; $[H^+] = 1.0 \times 10^{-7}$ M; $[OH^-] = 1.0 \times 10^{-7}$ M. Considering the H^+ and OH^- concentrations to be negligible, use the concentrations and charges for Mg^{2+} and Cl^- to calculateionic strength as $I = \frac{1}{2}\{0.1 \times (+2)^2 + 0.2 \times (-1)^2\} = 0.30$. For a 1:1 electrolyte such as 0.1 M $NaClO_4$ or NaCl, the ionic strength is equal to the molarity of the electrolyte. Figure 4.2 depicts a plot of mean ionic activity coefficient with ionic strength. As we can clearly see, the plot is non-linear and each electrolyte has a certain variation.

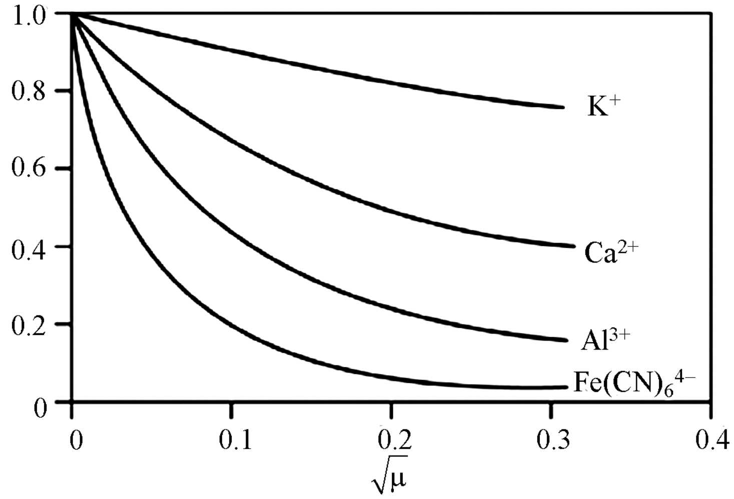


Figure 4.2 : Variation of mean ionic activity with ionic strength of the solution

4.3.5 Debye Hückel Limiting Law

The properties of electrolyte solutions can significantly deviate from the laws used to derive chemical potential of solutions. In nonelectrolyte solutions, the intermolecular forces are mostly comprised of weak Van der Waals interactions. In ionic solutions, however, there are significant electrostatic interactions between solute and solvent as well as solute and solute molecules. Consequently, the behaviour of an electrolyte solution deviates considerably from that an ideal solution. In 1923, Peter Debye and Erich Hückel developed a theory that would allow us to calculate the mean ionic activity coefficient of the solution, and could explain how the behaviour of ions in solution contributes to this constant. Briefly, they combined Poisson's equation of electrostatics with the Boltzmann factor of statistical mechanics to derive a (nonlinear) partial differential equation for the electrostatic potential about a central ion in solution.

The Debye-Hückel theory is based on three assumptions of how ions act in solution :

(i) Electrolytes completely dissociate into ions in solution.

(ii) Solutions of electrolytes are very dilute, on the order of 0.01 M.

(iii) Each ion is surrounded by ions of the opposite charge, on average.

This theory showed that the electrical free energy could be calculated by determining the electrostatic potential of an ion due to its oppositely charged ionic atmosphere and then evaluating the work done in charging the neutral particle to this potential. According to this theory the mean ionic activity coefficient is given by the equation

$$\log \gamma_{\pm} = -\frac{1.824 \times 10^{6}}{(\varepsilon T)^{3/2}} | z_{+} z_{-} | \sqrt{I} \quad ..... (4.16)$$

Here, ε is the dielectric constant, z_+ and z_- are the charges of the cation and anion, respectively and I is the ionic strength of the solution. For a given solvent and temperature, ε and T have definite values which may be inserted. Equation (4.16) then takes the general form

$$\log \gamma_{\pm} = -A | z_{+} z_{-} | \sqrt{I} \quad ..... (4.17)$$

Since most of the electrolyte solutions we study are aqueous (ε = 78.54) and have a temperature of 298 K, the Limiting Law in equation 4.16 reduces to

$$\log \gamma_{+} = -0.509 | z_{+} z_{-} | \sqrt{I} \quad ..... (4.18)$$

These equations represent the Debye-Hückel limiting law. The term "limiting" is used because the derivation is such that the results are applicable only to very dilute solutions approaching the limit of infinite dilution. For an ideal solution the activity coefficient $\gamma_\pm$ is unity, and hence log $\gamma_\pm$ would be zero. The fact that log $\gamma_\pm$ is negative, according to this equation, means that the activity coefficient should be less than unity, as it actually is in dilute solutions of electrolytes. According to equation 4.17 the plot of log $\gamma_\pm$ againstv $\sqrt{I}$ should be a straight line, passing through the origin, with a slope equal to $-A|z_+ z_-|$. The experimental results tend toward the values required by the Debye-Hückel limiting law as infinite dilution is approached. Further, the Debye-Hückel limiting equation contains no reference to the specific nature of the electrolyte, apart from the valence of the ions. Hence, electrolytes of the same valence type should have equal activity coefficients at the same concentration or ionic strength. In general, the Debye-Hückel limiting law holds within the limits of experimental error for ionic strengths up to about 0.01. Beyond this point, the activity coefficient decreases more slowly, passes through a minimum, and then increases as the concentration is increased. Although the valence type is still an important factor, the specific properties of the individual electrolyte now become apparent. This law is used in study of solubility and solubility product, effect of common ions on solubility, complex formation etc. It is also useful in studying kinetic salt effect especially in biological systems.

4.4 Electrochemistry

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic gadgets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes. Either a chemical reaction can generate electricity or electricity can induce chemical changes. Electrochemistry encompasses both these phenomena. We will learn about the basic concepts as well as the applications of electrochemistry in our life.

The connection between chemistry and electricity is a very old one, going back to Allesandro Volta's discovery, in 1793, that electricity could be produced by placing two different metals on opposite sides of a moistened paper. In 1800, Nicholson and Carlisle, using Volta's primitive battery as a source, showed that an electric current could decompose water into oxygen and hydrogen. This was surely one of the most significant experiments in the history of chemistry, for it implied that the atoms of hydrogen and oxygen were associated with positive and negative electric charges, which must be the source of the bonding forces between them. By 1812, the Swedish chemist Berzelius could propose that all atoms are electrified, hydrogen and the metals being positive, the nonmetals negative. In electrolysis, the applied voltage was thought to overpower the attraction between these opposite charges, pulling the electrified atoms apart in the form of ions (named by Berzelius from the Greek for "travellers"). Humphrey Davy prepared the first elemental sodium by electrolysis of a sodium hydroxide melt. Davy's former assistant, Michael Faraday, showed that there is a quantitative relation between the amount of electric charge and the quantity of electrolysis product.

Electricity refers to a number of phenomena associated with the presence and flow of electric charge. Electricity includes lightning, static electricity, the current generated by a battery as it discharges etc. The flow or movement of charge generates an electric current. Electrons or ions may carry the charge. The elementary unit of charge is the charge of a proton, which is equal in magnitude to the charge of an electron. The SI unit of charge is the coulomb (C) and the charge of a proton/electron is 1.602×10^{-19}C. The presence of an electric charge generates an electric field. Electric current is the rate of flow of charge. The SI unit for electrical current is the ampere (A), which is a flow rate of 1 coulomb of charge per second (1 A = 1 C/s). An electric current flow in a path, called an electric circuit. It is necessary to maintain a closed path for current to flow. The flow of charge is generated by an electrical potential difference or potential, between two points in the circuit. Electrical potential is the ability of the electric field to do work on the charge. The SI unit of electrical potential is the volt (V). When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule (J) of energy. Resistance is a measure of the opposition to current flow in an electrical circuit. Resistance is measured in ohms, symbolized by the Greek letter omega (Ω) or English letter R. Matters can be divided into three categories based on their ability to resist the flow of electricity through them. Conductors are the material where electrons flow easily and have low resistance. Semi-conductors allow electron to flow under certain circumstances i.e., they have variable resistance according to formulation and circuit conditions. Insulators have high resistance and electrons can flow through them only with great difficulty. Making electrons flow through a resistance requires an attractive force to pull them. This force, called Electromotive Force or EMF, is measured in volts. So we measure electrical potential and EMF both in volts.

4.4.1 Electroneutrality

Any process which will lead to an excess of positive or negative charges in matter does not occur in nature. Suppose, for example, that we immerse a piece of zinc metal in pure water. A small number of zinc atoms go into solution as Zn^{2+} ions, leaving their electrons behind in the metal : $Zn\ (s) \rightleftharpoons Zn^{2+} + 2e^{-}$. As this process goes on, the electrons which remain in the zinc cause a negative charge to build up which makes it increasingly difficult for additional positive ions to leave the metallic phase. A similar buildup of positive charge in the liquid phase adds to this inhibition. Very soon, therefore, the process comes to a halt, resulting in a solution in which the concentration of Zn^{2+} is so low (around 10^{-10} M) that the water can still be said to be almost pure. The degree of charge unbalance (that is allowed) produces a very tiny difference in electric potential, and corresponds to concentration imbalance of oppositely charged particles that are not even detectable by ordinary chemical means. This is a consequence of the electroneutrality principle, which is a simple consequence of the thermodynamic work required to separate opposite charges, or to bring like charges into closer contact. The additional work raises the free energy G of the process, making it less spontaneous. The only way we can get the above reaction to continue is to couple it with some other process that restores electroneutrality to the two phases. A simple way to accomplish this would be immerse the zinc in a solution of copper sulfate instead of pure water. The reaction is a simple oxidation-reduction process, a transfer of two electrons from the zinc to the copper :

$$\mathrm{Zn\,(s)} \rightarrow \mathrm{Zn^{2+}} + 2e^- \qquad\qquad \mathrm{Cu^{2+}} + 2e- \rightarrow \mathrm{Cu\ (s)}$$

The dissolution of the zinc is no longer inhibited by a buildup of negative charge in the metal, because the excess electrons are removed from the zinc by copper ions that come into contact with it. At the same time, the solution remains electrically neutral, since for each Zn^{2+} introduced to the solution, one Cu^{2+} is removed. The net reaction

$$\mathrm{Zn\,(s)} + \mathrm{Cu^{2+}} \rightarrow \mathrm{Zn^{2+}} + \mathrm{Cu(s)}$$

This discussion forms the basic idea behind electrochemistry.

4.4.2 Electrochemical Cell

Electrochemistry is the study of reactions in which charged particles (ions or electrons) cross the interface between two phases of matter, typically a metallic phase called the electrode and a conductive solution, or electrolyte. A process of this kind is known generally as an electrode process. Please note that electrodes are not limited to metals and as we will learn in the subsequent discussion there can be several different types of electrodes available. Electrode processes are basically redox chemical reactions where electron exchange between the reactants takes place. Electrode processes (reactions) take place at the surface of the electrode, and produce a slight unbalance in the electric charges of the electrode and the solution. The result is an interfacial potential difference which can materially affect the rate and direction of the reaction. The interfacial potential differences which develop in electrode-solution systems are limited to only a few volts at most. This may not seem like very much, but it is important to understand that what is important is the distance over which this potential difference exists. In the case of an electrode immersed in a solution, this distance corresponds to the thin layer of water molecules and ions that attach themselves to the electrode surface which normally only a few atomic diameters. In this way a very small voltage can produce a very large potential gradient. For example, a potential difference of one volt across a thickness of only 10^{-8} cm amounts to a potential gradient of 100 million volts per centimetre i.e. a very significant value.

In any electrochemical process, electrons flow from one chemical substance toanother, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The reductant is the substance that loses electrons and is oxidized in the process. The oxidant is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements. Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two half-reactions, one representing the oxidation processand one the reduction process. We have seen the example of reaction between Zn and Cu^{2+} in the previous section and how it can be described as two half-reactions. Here we will take another such example of the reaction of zinc with bromine. The overall chemical reaction is

$$Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2Br^-(aq)$$

The half-reactions are as follows

reduction half-reaction : $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$

oxidation half-reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Each half-reaction is written to show what is actually occurring in the system; Zn is the reductant in this reaction (it loses electrons), and Br_2 is the oxidant (it gains electrons). Adding the two half-reactions gives the overall chemical reaction. A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. With redox reactions, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work.

An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an electrochemical cell.

There are two types of electrochemical cells: galvanic cells and electrolytic cells.

4.4.2.1 Galvanic Cells (Voltaic Cells)

Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. Galvanic cells, also known as voltaic cells, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit. In addition, a second connection that allows ions to flow between the compartments (shown as a vertical line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current.

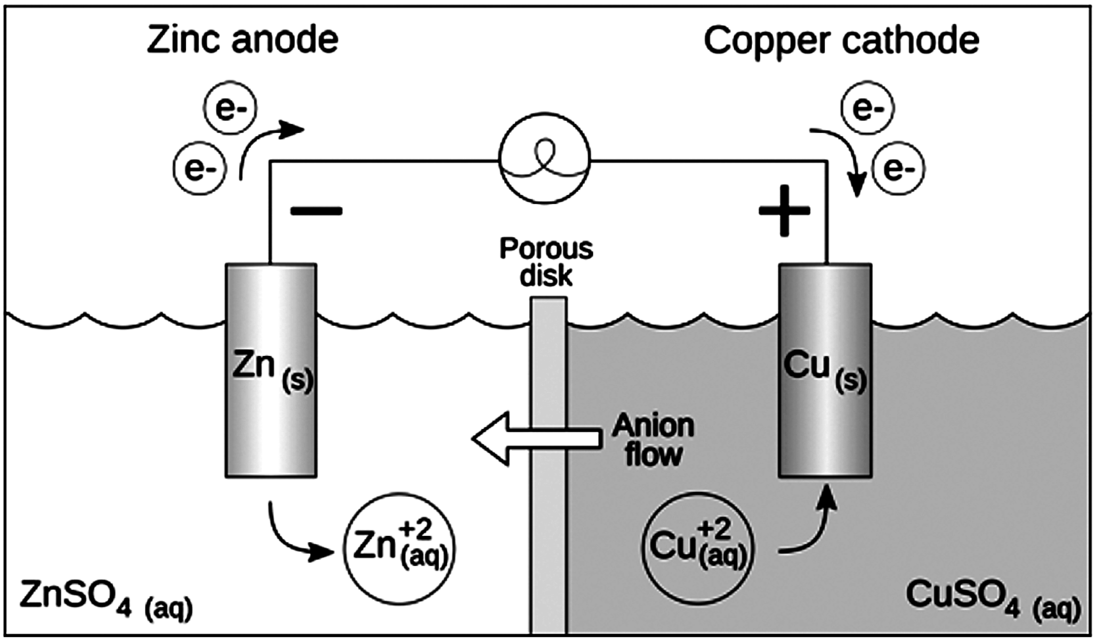


Figure 4.3 : A simple galvanic (voltaic) cell.

Figure 4.3 shows a typical Galvanic cell consisting of two pieces of metal, one zinc and the other copper, each immersed in a separate solution containing a dissolved salt of the corresponding metal. The two solutions are separated by a porous barrier that prevents them from rapidly mixing but allows ions to diffuse through it. If we simply left it at that, no significant amount of reaction would take place. However, if we connect the zinc and copper by means of a metallic conductor, the excess electrons that remain when Zn^{2+} ions go into solution in the left cell would be able to flow through the external circuit and into the right electrode, where they could be delivered to the Cu^{2+} ions which become "discharged", that is, converted into Cu atoms at the surface of the copper electrode. The overall cell reaction is already known to us. Since the half reactions are occurring in the cell, they are also called half-cell reactions. To describe an electrochemical cell, we adopt a specific description. For the cell in the figure 4.3, the notation would be

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

In this notation, the vertical bars indicate phase boundaries. The double vertical bar in the middle denotes the phase boundary between the two solutions. As a matter of convention, the chemical species that undergo reduction when the cell reaction proceeds to the right according to the net equation are shown on the right side, and those that undergo oxidation are shown on the left. Note that this is entirely independent of the physical location of the two electrodes in the actual cell. Electrochemical cells have two conductive electrodes, called the anode and the cathode. The anode is defined as the electrode where oxidation occurs. The cathode is the electrode where reduction takes place. Electrodes can be made from any sufficiently conductive materials, such as metals, semiconductors, graphite, and even conductive polymers. In between these electrodes is the electrolyte, which contains ions that can freely move. For example, for a galvanic cell constructed using metallic Cu and Ag electrode and $CuNO_3$ and $AgNO_3$ the half-cell reactions are

$$\text{oxidation : } Cu(s) \rightarrow Cu^{2+}(aq)+2e^-$$

$$\text{reduction : } 2\times(Ag^+(aq) + e^- \rightarrow Ag(s)) \text{ or } 2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

$$\text{Overall Reaction : } 2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

The Cu electrode is the anode and the Ag electrode is the cathode in this case. The cell notation is $Cu(s) \mid Cu^{2+}(aq) \mid Ag^+(aq) \mid Ag(s)$. The double vertical line indicates salt bridge which is discussed later. If electrons flow from the left electrode to the right electrode (as depicted in the above cell notation) when the cell operates in its spontaneous direction, the potential of the right electrode will be higher than that of the left, and the cell potential will be positive. "Conventional current flow" is flow of positive charge from positive potential to negative, which is opposite to the direction of the electron flow. This means that if the electrons are flowing from the left electrode to the right, a galvanometer placed in the external circuit would indicate a current flow from right to left.

4.4.2.2 Electrolytic Cell

Galvanic cells or Voltaic cells are not the only kind of electrochemical cells. It is possible to construct a cell that does work on a chemical system by driving an electric current through the system. These cells are called **electrolytic cells**. Electrolytic cells, like galvanic cells, are composed of two half-cells: one is a reduction half-cell, the other is an oxidation half-cell. The direction of electron flow in electrolytic cells, however, may be reversed from the direction of spontaneous electron flow in galvanic cells, but the definition of both cathode and anode remains the same, where reduction takes place at the cathode and oxidation occurs at the anode. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed.

To explain what happens in an electrolytic cell, let us examine the decomposition of molten sodium chloride into sodium metal and chlorine gas. The reaction is

$$2NaCl \leftrightharpoons 2Na + Cl_2$$

The forward reaction is non-spontaneous while the backward reaction is spontaneous. If molten NaCl(l) is placed into the container and inert electrodes of C(s) are inserted, attached to the positive and negative terminals of a battery, an electrolytic reaction will occur. The electrolytic cell used for that purpose is shown in figure 4.4. Electrons from the negative terminal travel to the cathode and are used to reduce sodium ions into sodium atoms. The sodium will be deposited onto the cathode as it forms. The sodium ions are migrating towards the cathode. $Na^+ + e^- \leftrightharpoons Na(s)$. The negative chloride ions migrate towards the anode and release electrons as they oxidize to form chlorine atoms. The chlorine atoms will combine together to form chlorine gas which will bubble away. $2Cl^- \leftrightharpoons Cl_2(g)+2e^-$ .Note that the site of oxidation is still the anode and the site of reduction is still the cathode, but the charges on these two electrodes are reversed. Anode is now positively charged and the cathode has a negative charge. The conditions under which the electrolyte cell operates are very important. The substance that is the strongest reducing agent will undergo oxidation. The substance that is the strongest oxidizing agent will be reduced. If an aqueous solution of sodium chloride was used in the above system, hydrogen would undergo reduction instead of sodium, because it is a stronger oxidizing agent than sodium.

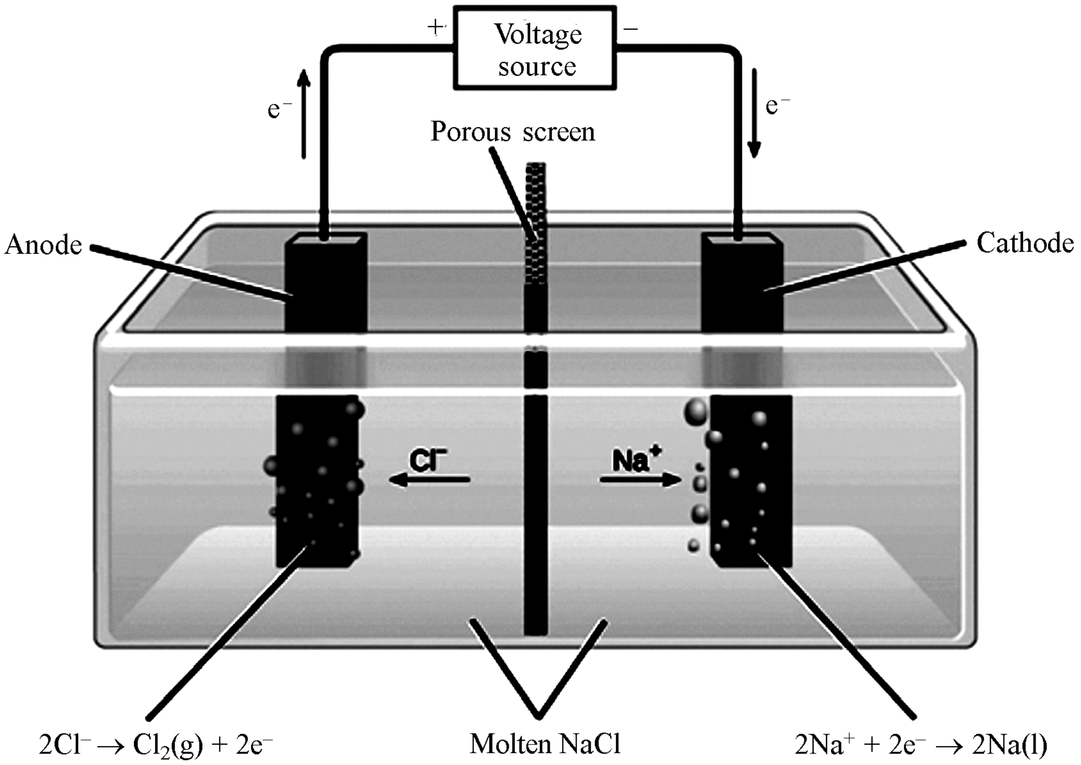


Figure 4.4 : Schematic representation of an electrolytic cell where electrolysis of molten NaCl is being performed

4.4.3. Quantitative Aspects of Electrolysis: Faraday's Laws

Michael Faraday discovered in 1833 that there is always a simple relationship between the amount of substance produced or consumed at an electrode during electrolysis and the quantity of electrical charge Q which passes through the cell. For example, the half-equation $Ag^+ + e^- \rightarrow Ag$ (s) tells us that when 1 mol Ag^+ is plated out as 1 mol Ag, 1 mol e^- must be supplied from the cathode. Based on these observations, Faraday proposed two laws of electrolysis.

Faraday's First Law

When electric current is passed through an electrolyte, the amount of substance deposited in an electrode is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation : $W \propto Q$.

We know that, Q = current in amperes (I) × time in seconds (t). So Faraday's first law is written as

$$W = z \times I \times t \quad ..... (4.19)$$

Here, z is a constant, known as **electrochemical equivalent**, and is characteristic of the substance deposited. So, when a current of one ampere is passed for one second, i.e., one coulomb (Q = 1), then W = z. Thus, electrochemical equivalent can be defined as the mass of the substance deposited by one coulomb of charge or by one ampere of current passed through the solution for one second. For example, when a charge of one coulomb is passed through silver nitrate solution, the amount of silver deposited is 0.001118 g. this is the value of electrochemical equivalent of silver. The unit of electrochemical equivalent will be gram per coulomb.

Faraday's Second Law

When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.

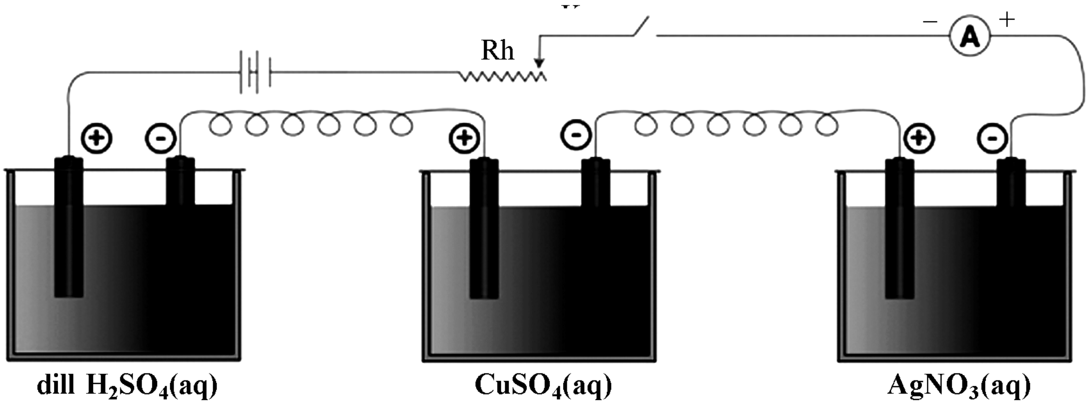


Figure 4.5 : Three electrochemical cells in series

The law can be illustrated by passing same quantity of electric current through three electrochemical cells connected in series containing solutions of H_2SO_4, $CuSO_4$ and $AgNO_3$ respectively as shown in Fig. 4.5. In the first cell, hydrogen and oxygen will be liberated. In the second, copper will be deposited and in the third, silver will be deposited. So according to Faraday's second law,

$$\frac{\text{Mass of hydrogen}}{\text{Mass of copper}} = \frac{\text{Equivalent mass of hydrogen}}{\text{Equivalent mass of copper}}$$

$$\frac{\text{Mass of copper}}{\text{Mass of silver}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

$$\frac{\text{Mass of silver}}{\text{Mass of hydrogen}} = \frac{\text{Equivalent mass of silver}}{\text{Equivalent mass of hydrogen}}$$

It is observed that by passing one coulomb of electric charge, hydrogen evolved = 0.00001036 g, copper deposited = 0.0003292 g and silver deposited = 0.001118 g. These masses are in the ratio of their equivalent masses. From these masses, the amount of electric charge required to deposit one equivalent of hydrogen or copper or silver can be calculated.

For hydrogen = 1/0.0001036 = 96500 coulomb. For copper = 31.78/0.0003292 = 96500 coulomb. For silver = 107.88/0.001118 = 96500 coulomb. This follows that 96500 coulomb at electric charge will deposit one g equivalent of any substance. 96500 coulomb is thus termed as one Faraday and is denoted by F. The precise value of Faraday constant is 96485 coulomb/mol but for the purpose of ease of calculations we can use 96500 coulomb/mol value. Using this value in the first law equation we get, when Q = 96500 coulomb, W becomes gram equivalent mass (E).

$$E = z \times 96500$$

$$\therefore z = \frac{E}{96500} \quad \text{..... (4.20)}$$

$$\frac{z_1}{z_2} = \frac{E_1}{E_2} \quad \text{..... (4.21)}$$

Equation 4.21 is the mathematical version of Faraday's second law. The fundamental unit of charge can be found out from these laws in the following way. As one g-equivalent of an ion is liberated by 96500 coulomb, it follows that charge carried by one g-equivalent of an ion is 96500 coulomb. If the valency of an ion is 'n', then one mole of these ions will carry a charge of nF coulomb. One g-mole of an ion contains 6.023×10^{23} ions. Then, the charge carried by an ion = $nF/(6.023 \times 10^{23})$ coulomb. For $n = 1$, the fundamental unit of charge = $F/(6.023 \times 10^{23}) = 96500/(6.023 \times 10^{23}) = 1.6 \times 10^{-19}$ coulomb or we can say that 1 coulomb = 6.24×10^{18} electrons.

As we learned that Faraday's laws give us the quantification of electrolysis process. Let us take some examples. Suppose we are asked that how much electric charge is required to oxidise (a) 1 mole of H_2O to O_2 and (b) 1 mole of FeO to Fe_2O_3? Solution (a) The oxidation reaction is $H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^-$; $Q = 2 \times F = 2 \times 96500 = 193000$ coulomb (b) The oxidation reaction is $FeO + 1/2\ H_2O \rightarrow Fe_2O_3 + H^+ + e^-$ $Q = F = 96500$ coulomb.

4.4.4 Salt Bridge

A salt bridge is a connection containing a weak electrolyte between the oxidation and reduction half-cells in a galvanic cell. Its purpose is to keep the electrochemical reaction from reaching equilibrium too quickly. If a cell is constructed without a salt bridge, one solution would quickly accumulate positive charge while the other would accumulate negative charge. This would halt the reaction and thus the generation of electricity. We will later know that it happens due to liquid junction potential. Salt bridge is indicated by two vertical lines in the cell notation. An example of a salt bridge is shown in figure

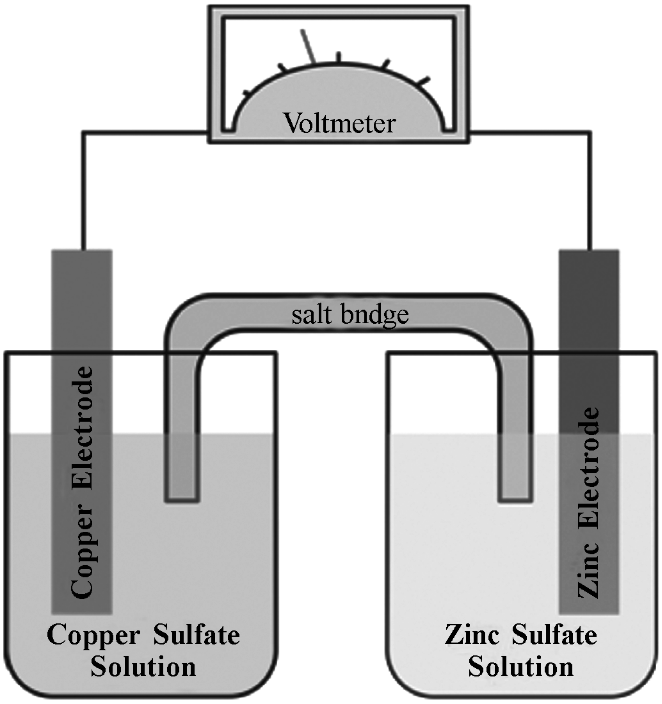


Figure 4.6 : An electrochemical cell (resembling a Daniell cell) with a filter paper salt bridge. The paper has been soaked with a potassium chloride solution.

The two main types of salt bridges are a glass tube and a piece of filter paper :

Glass Tube Bridge : This is a U-shaped glass tube filled with an electrolyte, such as sodium chloride, potassium chloride, or potassium nitrate. The electrolyte needs to be relatively unreactive with other chemicals in the cell and have cations and anions with similar migratory speed (comparable ion charge and molecular weight). Because a salt solution could easy diffuse into the cell, the electrolyte is often held in a gel, such as agar-agar. The concentration of the salt solution is the biggest factor in conductivity. The diameter of the tube also has an effect. Lowering the concentration of the electrolyte or narrowing the glass tube lowers conductivity.

Filter Paper Bridge : Another common type of salt bridge consists of filter paper or another porous material soaked in an electrolyte (usually sodium chloride or potassium chloride). In this bridge, conductivity is affected by electrolyte concentration, porosity of the filter paper, and the roughness of the paper. A smooth, absorbent paper yields higher conductivity than rough paper with low absorbency.

4.4.5 Reversible and Irreversible Cells

The use of thermodynamic principles when applied to a system is subject to one important restriction, namely, that the system must be reversible in nature. This requires that:

(1) the driving and opposing forces be infinitesimally different from each other

(2) it should be possible to reverse any change taking place by applying a force infinitesimally greater than the acting one.

A cell satisfying the above two requirements constitutes a reversible cell. The potential difference of the cell can be substituted into the relevant thermodynamic relations and hence the values of thermodynamic properties such as free energy change, entropy change and enthalpy change of the cell reaction can be determined. When the above conditions are not satisfied, the cell is said to be **irreversible**, and thermodynamic relations do not apply. The difference between reversible and irreversible cells may be illustrated with the following two examples.

Example of Reversible Cell

Consider a cell composed of Zn and Ag-AgCl electrodes dipping into an aqueous solution of zinc chloride. The following reactions take place on connecting the electrodes externally

$$\text{Anode : } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$\text{Cathode : } AgCl\,(s) + e^- \rightarrow Ag\,(s) + Cl^-(aq)$$

$$\text{The net reaction : } Zn(s) + 2AgCl\,(s) \rightarrow Zn^{2+}(aq) + 2Ag\,(s) + 2Cl^-(aq)$$

The above process continues as long as the external opposing potential is infinitesimally smaller than that of the cell. However, if the opposing potential becomes slightly larger than that of the cell, the direction of current flow is reversed, and so is the cell reaction. Now zinc ions are converted to zinc at one electrode, silver chloride is formed from silver and chloride ions at the other, and the overall cell reaction becomes

$$Zn^{2+}(aq) + 2Ag\,(s) + 2Cl^-(aq) \rightarrow Zn(s) + 2AgCl(s)$$

Thus, it is obvious that the second condition of reversibility mentioned above is satisfied. The first condition can be satisfied by drawing from or passing through the cell a very minute current. Hence, the cell is reversible

Example of Irreversible Cell

Consider a cell composed of zinc and silver electrodes immersed in a solution of sulphuric acid. When the two electrodes are short circuited, (i.e. connected externally by a wire) zinc dissolves with the evolution of hydrogen to form zinc sulphate according to the reaction:

$$Zn(s) + H_2SO_4 \rightarrow ZnSO_4 + H_2(g)$$

However, when the cell is connected with an external source of potential slightly greater than its own, silver dissolves at one electrode, hydrogen is evolved at the other, and the cell reaction becomes

$$2Ag(s) + H_2SO_4 \rightarrow Ag_2SO_4 + H_2(g)$$

Thus, it is obvious that though the first condition of reversibility can be satisfied, the second cannot. Hence, the cell is an irreversible cell. The potential of such a cell does not have any definite thermodynamic significance.

4.4.6 Electrodes and Electrodes Reactions

An electrode is a solid electric conductor that carries electric current into non-metallic solids, or liquids, or gases. Electrodes are typically good electric conductors, but they need not be metals. In an electrochemical cell, reduction and oxidation reactions take place at the electrodes. Whether an electrode operates as a cathode or anode depends on the direction the cell is operating in. The electron-transfer step that takes place at each electrode is known as the electrode reaction. The substances that receive and lose electrons are called the electroactive species. There are mainly four types of electrodes: i) Gas electrodes ii) Metal–sparingly soluble metal salt electrodes iii) Metal – metal ion electrodes and iv) Redox electrodes.

Gas Electrodes :

A gas electrode consists of a gas (e.g. H_2, Cl_2, O_2) in contact with a solution containing the ions derivable from the gas e.g. H^+, Cl^-, OH^-. The potential of the gas electrode depends upon the concentration of its ions in the solution and the pressure of a gas. A gas electrode consists of gas, bubbled about inert metal wire (platinized platinum electrode) immersed in a solution containing ions with which gas is irreversible. Platinum is used as conductor and to adsorb the gas. Examples of such electrodes are standard hydrogen electrode, chlorine gas electrode (Pt| $Cl_2(g)$ (1 atm.)| $Cl^-(aq)$ (1 M)) etc.

Metal-Sparingly Soluble Metal Salt Electrode :

Reversible anion electrode is also called as metal-sparingly soluble metal salt electrode. In this electrode, a metal and a sparingly soluble salt of the metal in equilibrium with a solution containing the same anion as the sparingly soluble salt are taken. An example is the calomel electrode.

Metal – Metal Ion Electrodes :

In this case, a metal strip is kept in contact with the solution of a water-soluble salt-containing cation of the same metal, e.g. Zn(s) | $Zn^{++}(aq)$. In the electrochemical cell, the electrode having higher oxidation potential undergoes oxidation and acts as the anode or negative electrode and the electrode having lower oxidation potential undergoes reduction and acts as the cathode or positive electrode.

Redox Electrode :

In these electrodes, an inert metal like Pt is dipped in a solution containing ions of an active metal in two different oxidation states. Pt | Fe^{2+}, Fe^{3+}.

4.4.7 Electromotive Force of a Cell : Standard Potentials

In the Daniell cell, electrons flow from Zn electrode to Cu electrode. This is due to the fact that Zn atom can be more easily oxidized to Zn^{2+} ion than Cu atom to Cu^{2+} ion. On the other side, Cu^{2+} ion can be more easily reduced than the Zn^{2+} ion. Consequently, Zn atom is oxidized to Zn^{2+} ion and the electrons set free at the Zn electrode move towards Cu electrode where Cu^{2+} ion is reduced to Cu atom. Basically, we can say that the flow of electrons is due to the difference between oxidation tendencies of the two atoms, or it is due to the difference of reduction tendencies of the two ions. The relative oxidation tendencies of atoms can be represented by the oxidation potentials. A more easily oxidizable atom will have a larger value of oxidation potential and a less easily oxidizable atom will have a low value of oxidation potential. Thus, Zn atom has a larger oxidation potential than the Cu atom. Electrons in the external circuit flow from the electrode of higher oxidation potential to the electrode of lower oxidation potential. The difference of potential which causes a current to flow from the electrode of higher potential to the lower one is known as the **electromotive force**, abbreviated as EMF of the cell and is expressed in volts. We will represent EMF of a cell by the symbol E_{cell}. Thus

$$E_{cell} = \textit{Higher Reduction Potential} - \textit{Lower Reduction Potential}$$

$$= E_{cathode} - E_{anode} \;\; \ldots\ldots \;\; (4.22)$$

By convention, E_{cell} is expressed in terms of reduction potentials (known as standard potentials) of the two electrodes. The reduction potentials measure the relative reduction tendencies of ions and these values are simply negative of oxidation potentials of the corresponding atoms. where $E_{cathode}$ and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts.

To determine the accurate emf of a cell, direct use of voltmeter cannot be made, since it draws some current from the cell, which will change the emf due to the changes in the concentrations of species caused by the electrode reactions. Again, with appreciable current flow, part of the emf will have to be utilized to overcome the internal resistance of the cell, and hence the potential measured on the voltmeter will not be the accurate cell emf. The precise value of the emf of a cell can be determined by using potentiometric method. In this method, an unknown emf is opposed by another emf until the two are equal. The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** (E^{o}_{cell}), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, 1 atm for gases, and pure solids or pure liquids for other substances) and at a fixed temperature (usually 298K).

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured. (This is analogous to measuring absolute enthalpies or free energies). We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common.

This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential (E°) for the Zn/Cu system is 1.10 V, whereas E° for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V – 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram :

$$Co(s) \mid Co^{2+} (aq, 1\ M) \parallel Cu^{2+} (aq, 1\ M) \parallel Cu\ (s)\ E^\circ = 0.59\ V$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode. All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances. Standard electrode potentials for various reduction reactions are given in Table 4.1. The standard cell potential (E^o_{cell}) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum :

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} \quad ..... \quad (4.23)$$

Here, $E^o_{cathode}$ is the standard reduction potential for the reduction half reaction occurring at the cathode and E^o_{anode} is the standard reduction potential for the oxidation half reaction occurring at the anode.

Table 4.1: Standard Electrode Potentials in Aqueous Solution at 25°C

Cathode (Reduction) Half-Reaction	**Standard Potential E°(volts)**
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.04
$K^+(aq) + e^- \rightarrow K(s)$	–2.92
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	–2.76
$Na^+(aq) + e^- \rightarrow Na(s)$	–2.71
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–2.38
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.66
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–0.83

Cathode (Reduction) Half-Reaction	**Standard Potential E°(volts)**
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.41
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–0.40
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.23
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.14
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.13
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.04
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.16
$ClO_4^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_3^-(aq) + 2OH^-(aq)$	0.17
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.22
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$ClO_3–(aq) + H_2O(l) + 2e^- \rightarrow ClO_2–(aq) + 2OH^-(aq)$	0.35
$IO^-(aq) + H_2O(l) + 2e^- \rightarrow I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightarrow Cu(s)$	0.52
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$ClO_2^-(aq) + H_2O(l) + 2e^- \rightarrow ClO^-(aq) + 2OH^-(aq)$	0.59
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$	0.85

Cathode (Reduction) Half-Reaction	**Standard Potential E°(volts)**
$ClO^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	1.44
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.82
$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$	2.01
$O_3(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + H_2O(l)$	2.07
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode** (SHE) is universally used for this purpose and is assigned a **standard potential of 0 V**. The SHE consists of a platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. The standard potential of the SHE is arbitrarily assigned a value of 0 V. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface as per the following equation

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

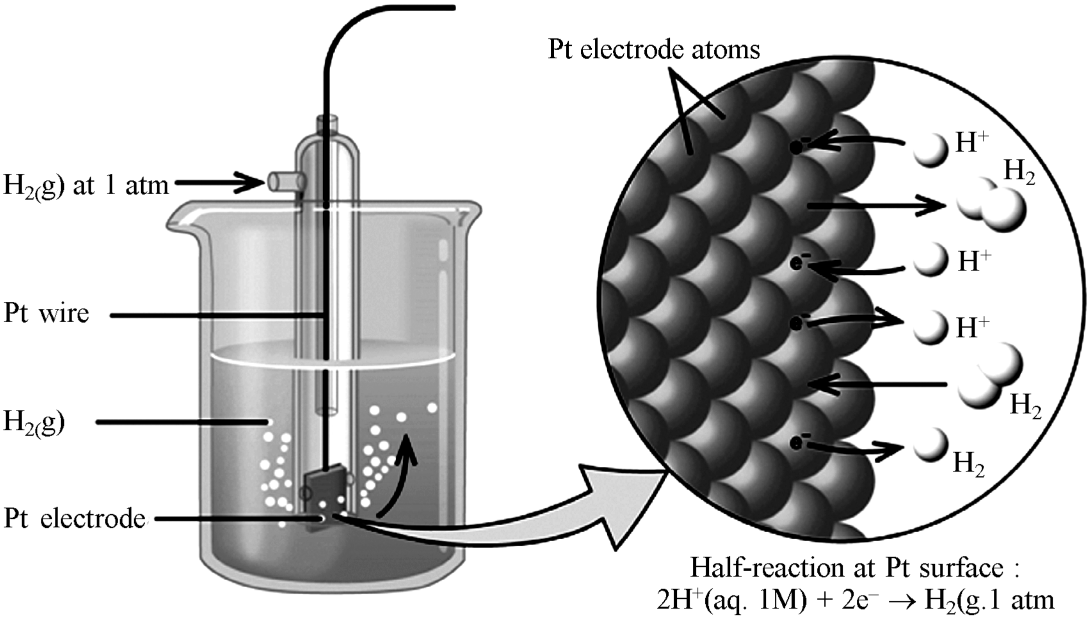


Figure 4.7 : Standard Hydrogen Electrode

To determine a standard electrode potential using a standard hydrogen electrode we need to construct a galvanic cell using them. Consider a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus, the hydrogen electrode is the cathode, and the zinc electrode is the anode. The notation for this galvanic cell is as follows:

$$Zn(s) \mid Zn^{2+}(aq) \parallel H^+(aq, 1\ M) \mid H_2(g, 1\ atm) \mid Pt(s)$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows :

cathode : $2H^+(aq) + 2e^- \rightarrow H_2\ (g)\ E^o_{cathode} = 0\ V$

anode : $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-\ E^o_{anode} = -0.76\ V$

overall : $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2\ (g);\ E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.76V$

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the standard electrode potential for that half-reaction. In this example, the standard reduction potential for the reaction is –0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} **redox couple**, or the Zn/Zn^{2+} couple, is (–0.76 V) = 0.76 V. Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction (E^o_{cell}) is a measure of the tendency of reactants in their standard states to form products in their standard states. Consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram : $Zn(s) \mid Zn^{2+}(aq, 1\ M) \mid Cu^{2+}(aq, 1\ M) \mid Cu(s)$

cathode : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o_{cathode} = 0.34V$

anode : $Zn(s) \rightarrow Zn^{2+}(aq, 1\ M) + 2e^-$ $E^o_{anode} = -0.76V$

overall : $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.34V - (-0.76V) = 1.10V.$

Let us study one more example. A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows :

cathode : $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

anode : $Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, then we can find the potential for the oxidation of Ni to Ni^{2+}.

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$0.27V = E^{o}_{cathode} -(-0.55V)$$

$$E^{o}_{cathode} = -0.28 \text{ V}$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E^{o}_{cathode}$. Thus 0.28 V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

4.4.8 Reference Electrodes

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, **the reference electrode**, must be constant. We are already familiar with one example of a reference electrode : the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half reaction are as follows :

$$Cl^{-}(aq) \mid AgCl(s) \mid Ag(s)$$

$$AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}(aq)$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–

silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$\mathrm{Pt(s)} \mid \mathrm{Hg_2Cl_2(s)} \mid \mathrm{KCl\ (aq,\ sat)}$$

$$\mathrm{Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-\ (aq)}$$

At 25°C, the potential of the SCE is **0.2415 V** versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H+ ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane. The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows

$$E_{glass} = E' - 0.0591\mathrm{V} \times \mathrm{pH} \ \ldots\ldots \ (4.24)$$

The voltage E′ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated. That is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

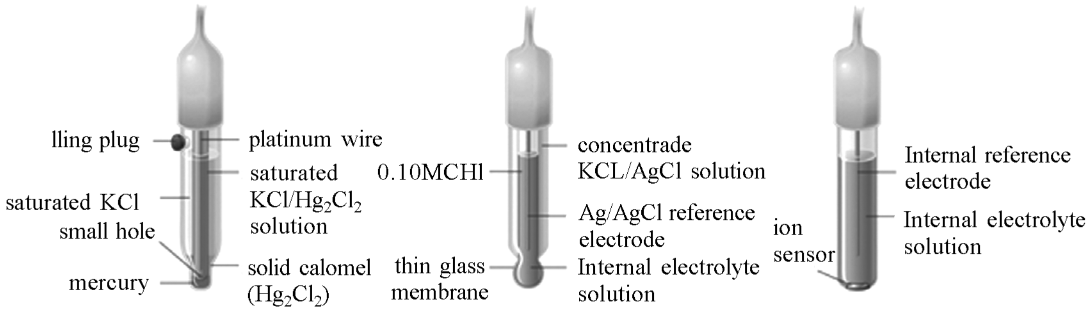


Figure 4.8 : Common reference electrodes

Ion-selective electrodes are used to measure the concentration of a particular species in solution. They are designed so that their potential depends on only the concentration of the desired species. These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution.

4.4.9 Cell Potential and Free Energy

The potential difference between the electrodes of a cell is a measure of the tendency for the cell reaction to take place: the more positive the cell potential, the greater the tendency for the reaction to proceed to the right. But we already know that the standard free energy change expresses the tendency for any kind of process to occur under the conditions of constant temperature and pressure. This and the cell potential are related in a simple way. The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = -\,nFE_{cell} \quad \ldots\ldots \quad (4.25)$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings. The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$).

$$\Delta G = -nF\,E_{cell} \quad ..... \quad (4.26)$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows :

$$\Delta G^\circ = -nF\,E^\circ_{cell} \quad ..... \quad (4.27)$$

The negative sign on the right indicates that a positive cell potential (according to the sign convention) implies a negative free energy change, and thus that the cell reaction will proceed to the right. Electrical work is done when an electric charge q moves through a potential difference ΔV. The right side of Eq. 4.27 refers to the movement of n moles of charge across the cell potential E°, and thus has the dimensions of work. "Useful" work is that which can be extracted from the cell by electrical means to operate a lamp or some other external device. This excludes any P–V work that is simply a consequence of volume change (which could of course conceivably be put to some use!) and which would be performed in any case, even if the reactants were combined directly. This quantity of work $-\Delta G^\circ$ can only be extracted from the system under the limiting conditions of a reversible change, which for an electrochemical cell implies zero current. The more rapidly the cell operates, the less electrical work it can supply. If F is expressed in coulombs per mole, the electrical work is in joules per mole. To relate these units to electrical units, recall that the coulomb is one amp-sec, and that power, which is the rate at which work is done, is measured in watts, which is the product of amps and volts. Thus 1 J = 1 watt-sec = 1 (amp-sec) ×volts.

We can use the relationship between ΔG° and the equilibrium constant K, defined to obtain a relationship between E°_{cell} and K. We know that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free energy change and the equilibrium constant are related by the equation $\Delta G^\circ = RT \ln K$. So we can write

$$E^\circ_{cell} = \frac{RT}{nF}\,\ell n\ K \quad ..... \quad (4.28)$$

4.4.10 The Effect of Concentration on Cell Potential : The Nernst Equation

The equation 4.27 and 4.28 apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations uses the relationship between ΔG and the reaction quotient Q. The actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows

$$\Delta G = \Delta G + RT \ln Q \text{ ..... } (4.29)$$

Substituting equation 4.26 and 4.27 in equation 4.29 and rearranging we can write

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF} \ln Q \text{ ..... } (4.30)$$

Equation 4.30 is called the **Nernst equation** after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), Equation 4.30 reduces to Equation 4.28 because Q = K, and there is no net transfer of electrons (i.e., $E_{cell} = 0$). Substituting the values of the constants into Equation 4.30 with T = 298 K and converting to base-10 logarithms give the relationship of the actual cell potential, the standard cell potential, and the reactant and product concentrations at room temperature :

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log Q \text{ ..... } (4.31)$$

Equation 4.31 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 4.31 that the cell potential changes by 0.0591/ n V for each 10-fold change in the value of Q because log 10 = 1.

Consider the following reaction proceeds spontaneously under standard conditions because $E^{o}_{cell} > 0$ (which you now know means that $\Delta G^{o} < 0$)

$$2Ce^{4+} (aq) + 2Cl^{-} (aq) \rightarrow 2Ce^{3+} (aq) + Cl_2 (g) \quad E^{0}_{cell} = 0.25 \text{ V}$$

Let us calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously : $[Ce^{4+}] = 0.013$ M, $[Ce^{3+}] = 0.60$ M, $[Cl^{-}] = 0.0030$ M, $PCl_2 = 1.0$ atm, and T = 25°C.

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 4.31 instead of 4.30.

The overall reaction involves the net transfer of two electrons. So n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2,

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log Q = 0.25 \text{ volt} - \frac{0.0591}{2} \log\left(\frac{[Ce^{3+}]^2 PCl_2}{[Ce^{4+}][Cl^-]^2}\right) = 0.0 \text{ volt}$$

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and $\Delta G = 0$). The composition specified is that of an equilibrium mixture.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$. The reaction quotient is therefore $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0×10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 4.31.

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log Q = 1.10 \text{ volt} - \frac{0.0591}{2} \log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right) = 1.28 \text{ volt} \;..... \;(4.33)$$

Thus the initial voltage is greater than E° because Q < 1. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio $Q = \left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so Q = 1 and $E_{cell} = E^{o}_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0×10^{-6} M Cu^{2+}), $Q = 1.0 \times 10^{6}$, and the cell potential will be reduced to 0.92 V.

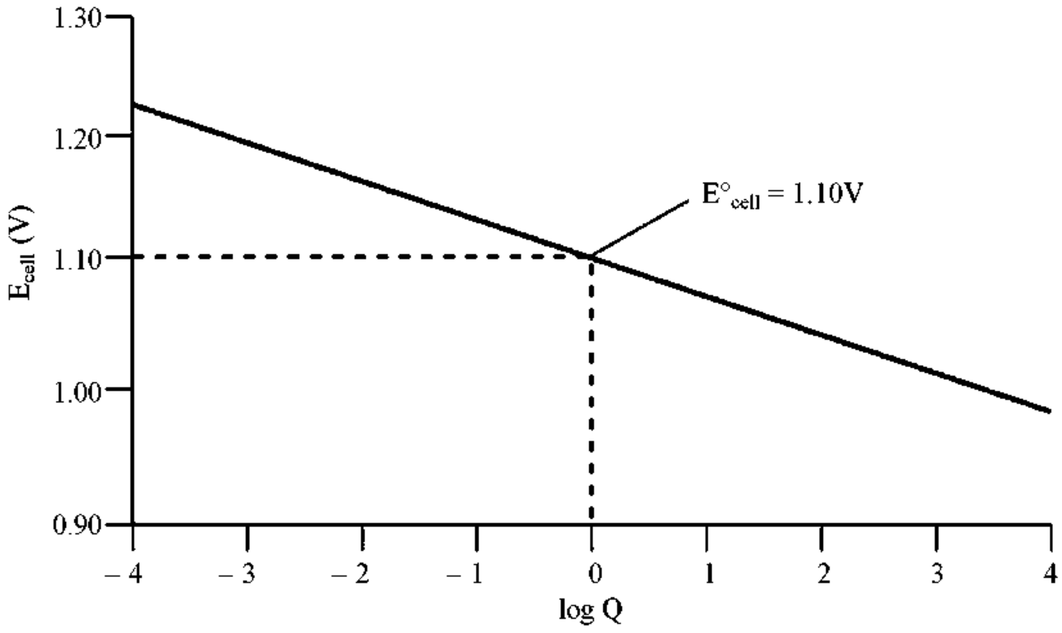


Figure 4.9 : Variation of cell potential with reaction quotient

The variation of E_{cell} with log Q over this range is linear with a slope of $-0.0591/n$, as illustrated in Figure 4.9. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead."

4.4.11 Concentration Cells and Liquid Junction Potential

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows :

$$Ag(s) \mid Ag^+(aq,\ 0.010\ M) \parallel Ag^+(aq,\ 1.0\ M) \mid Ag(s)$$

$$\text{cathode : } Ag^+(aq,\ 1.0\ M) + e^- \rightarrow Ag(s)$$

$$\text{anode : } Ag(s) \rightarrow Ag^+(aq,\ 0.010\ M) + e^-$$

$$\text{overall : } Ag^+(aq,\ 1.0\ M) \rightarrow Ag^+(aq,\ 0.010\ M)$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of Ag(s) in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for E^o_{cell} because $E^o_{cathode} = -E^o_{anode}$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log Q = 0 - \frac{0.0591}{1}\log\frac{0.01}{1}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero, $E_{cell} = 0$. Concentration cells are of two types. (i) **Electrode concentration cell** (amalgam cell, electrodes of different concentration) (ii) (electrolytes of different concentration). Electrolyte concentration cell can be of two types : (i) **Concentration cell without transference** - no direct transference of electrolyte but it occurs due to the result of chemical reaction. Each electrode is reversible with respect to one of the ions of the electrolyte; (ii) **Concentration cell with transference** - there is direct transference with electrolyte. The same electrode is reversible with respect to one of the ions of electrolyte.

Concentration cell without transference

Let us consider a cell having electrodes reversible with respect to H^+ and Cl^- as

$$H_2(1\ \text{atm}) \mid HCl\ (a1),\ AgCl(s) \mid Ag$$

where a_1 = apparent concentrationi.e. activity of HCl. Hydrogen at left hand electrode dissolves to form H^+ ion whereas silver gets deposited at right hand electrode from AgCl.

$$\tfrac{1}{2} H_2\ (1\ \text{atm}) \rightarrow H^+ + e^-$$

$$AgCl\ (s) + e^- \rightarrow Ag + Cl–$$

The net cell reaction is $\tfrac{1}{2} H_2\ (1\ \text{atm}) + AgCl\ (s) \rightarrow HCl\ (a_1) + Ag(s)$

EMF of the cell may be expressed as

$$E_1 = E^0_{cell} - \frac{RT}{F}\ell n\, a_1 \quad ..... (4.34)$$

Another cell with a_2 activity of HCl may be represented by H_2 (1 atm) | HCl (a_2), AgCl (s) | Ag. EMF of this second cell is

$$E_2 = E^0_{cell} - \frac{RT}{F}\ell n\, a_2 \quad ..... (4.35)$$

When the two cells containing HCl of activities a1 and a_2 are connected with EMF E_1 and E_2 opposing each other, the resulting cell may be expressed as

H_2(1atm) | HCl(a_1), AgCl(s) | Ag | AgCl(s), HCl(a_2) | H_2(1 atm)

The EMF of the cell formed

$$E = E_1 - E_2 = \frac{RT}{F}\ell n\frac{a_2}{a_1} \quad ..... (4.36)$$

As $a_2 > a_1$, there is net transfer of electrolyte from concentrated to dilute solution. Since the EMF of the cell without transference depends upon concentration of the solution on both sides so the equation 4.36 may be re-written using concentration in place of activities for dilute solutions and for any concentration cell without transference

$$E_{wot} = \frac{v}{v_\pm z_\pm}\frac{RT}{F}\ell n\frac{c_2}{c_1} \quad ..... (4.37)$$

where and are the number of positive and negative ions and is the total number of ions where z_+ and z_- are valencies (+) ve and (–)ve ions with respect to electrodes with which these are reversible. So for H^+cell in example

$$E_{wot} = 2\frac{RT}{F}\ell n\frac{c_2}{c_1} \quad ..... (4.38)$$

Concentration cell with transference

Let us consider a cell of this type having the liquid junction potential between the junction of two solutions.

H_2(1 atm) | HCl (a_1) HCl (a_2) | H_2(1 atm)

Two solutions of HCl are in contact with each other and the dotted line represents the liquid junction potential. There is a direct transfer of HCl from more concentrated solution (a_2) to the less concentrated one (a_1). The EMF of such cell is

$$E_{wt} = t_a \frac{v}{v_{\pm} z_{\pm}} \frac{RT}{F} \ell n \frac{c_2}{c_1} \quad ..... (4.39)$$

where v is the total number of ions and t_a is the transport number of the anion. In H_2/HCl cell, $v = 2$, $v_{\pm} = 1$, $z_{\pm}$. So

$$E_{wt} = 2t_a \frac{RT}{F} \ell n \frac{c_2}{c_1} \quad ..... (4.40)$$

The difference between the EMF of is known as the **liquid junction potential** i.e,

$$E_{ij} = E_{wt} - E_{wot} = 2(1-t_a) \frac{RT}{F} \ell n \frac{c_2}{c_1} \quad ..... (4.41)$$

Equation 4.41 is valid for H^+ concentration cell but we can easily write a general expression for it.

A **liquid junction potential** is developed when a cell contains two electrolytic solutions of different concentration in contact with one another (development of potential at the junction of the two liquids). The more concentrated solution possesses a tendency to diffuse into the comparatively less concentrated one. Large concentration difference between the liquid phases results in high liquid junction potential. The rate of diffusion of an ion at the junction of the two solutions is proportional to its speed. It may be regarded as a steady state where an effectively time-independent charge separation is developed. It is non-equilibrium potential. The structure of the liquid junction may hardly change as diffusion tends to be a slow process in it.

The introduction of the liquid junction potential interferes with the exact measurement of the potential difference or emf of the cell. In order to eliminate liquid function potential, the following methods are generally employed.

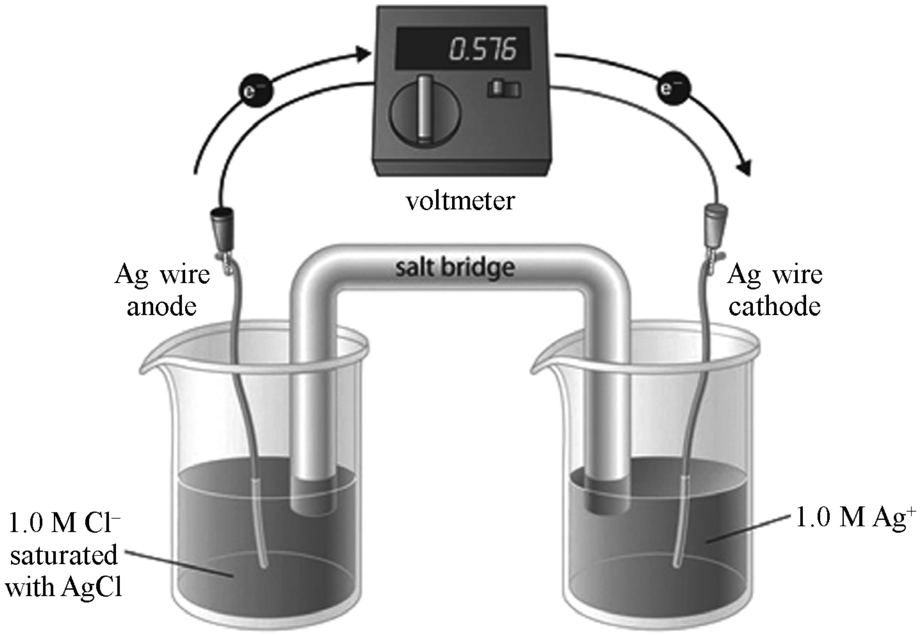
(I) Introduction of salt bridge : It is a general practice to introduce a salt bridge between two salt solutions. The salt bridge is a saturated solution of KCl or NH_4NO_3 in agar-

agar. In most of the cases KCl salt bridge is used. However, in such cases when one of the solutions contains a soluble silver, mercurous or thallous ion, the saturated solution of NH_4NO_3 is used. Solutions of sodium nitrate and lithium acetate have also been suggested for this purpose. For nonaqueous solution, sodium iodate in methyl alcohol and potassium thiocyanate is also used. The principle of using a bridge of a saturated solution to eliminate the liquid junction potential is that the ions of these salts are present in large excess at the junction and they carry almost the whole of the current across the junction. The efficiency of KCl or NH_4NO_3 in its elimination is probably connected with the fact that in these salts, the transport numbers of anion and cation are the same.

(II) Nernst suggested the device of adding an indifferent electrolyte (KCl or KNO_3) at the same concentration to both sides of the cell for eliminating liquid junction potential. If the concentration of the added substance is much greater than that of the electrolyte present, the former will carry almost all the current. Since its concentration is the same on both sides of the boundary of the two half cells, it will produce no potential difference at the junction. This method is, however not used because the addition of an excess of electrolyte will have a marked effect on the activities of the reversible ions. The method is now-a-days modified that a series of cells is set up containing ions in different concentrations. The emf so obtained is extrapolated to zero concentration of the added substance.

4.4.12 Measurement of Solubility Products from Cell Potential

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (Ksp) of sparingly soluble substances. We know that solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.



anode : $Ag(s) \rightarrow AgCl(s) + e^-$ cathode : $Ag^+(aq)+e^- \rightarrow Ag(s)$

Figure 4.10 : A galvanic ("concentration") cell for measuring the solubility product of AgCl

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 4.10, which is designed to measure the solubility product of silver chloride. $K_{sp} = [Ag^+][Cl^-]$. In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+. The other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting :

$$[Ag^+]\frac{K_{sp}}{[Cl^-]} = \frac{K_{sp}}{1.0} = K_{sp} \quad ..... \quad (4.42)$$

The overall cell reaction is as follows : Ag^+(aq, concentrated) → Ag^+ (aq, dilute). Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows :

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log Q = 0 - \frac{0.0591}{1}\log\frac{[Ag^+]_{dilute}}{[Ag^+]_{concentrated}} = -0.0591\,\text{volt}\log K_{sp}$$

By closing the circuit, we can measure the potential caused by the difference in $[Ag^+]$ in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 4.43 for K_{sp}, we get $K_{sp} = 1.5\times10^{-10}$. Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

4.4.13 Electrochemical Measurement of pH

We have learned before that hydrogen ion concentration in a solution can be measured using electrochemical methods. The hydrogen electrode and glass electrode (glass membrane electrode) give response to the H+cation, so they are used for the potentiometric pH measurements.

pH measurement using Hydrogen Electrode

The gas electrode used for the potentiometric pH measurements is the half-cell set consisting of a platinum foil covered with very finely divided platinum (so called platinized platinum), immersed in the measured solution and bubbled around by the hydrogen gas. In principle the electrode is the same as the standard hydrogen electrode, the hydrogen gas is also bubbled under normal barometric pressure, but the measured solutions are of various kinds. The hydrogen gas is adsorbed on the surface of the platinum foil and due to the catalytic effect of the finely divided platinum, the following electrode reaction (half-reaction) occurs on the boundary between the platinum and the solution.

$$\tfrac{1}{2} H_2 \rightarrow H^+ + e-$$

With respect to the stated electrode reaction, the potential of the hydrogen electrode is given by the Nernst equation in the following form for 25° C

$$E_H = -0.0591pH \;.....\; (4.44)$$

The standard potential is identical with the potential of the standard hydrogen electrode, which is assigned as zero. However, the potentiometric measurements cannot be done with a single electrode (half-cell) but an electrochemical cell with two electrodes is necessary. Therefore, we combine the sensing hydrogen electrode with the suitable reference electrode, to set up a complete cell and to measure the cell potential. We use a saturated calomel electrode as the reference and by this way the following complete cell is set up.

Pt, H_2(1 atm) H^+ (measured solution)| KCl (saturated solution) | Hg_2Cl_2 |Hg

In the diagrammed cell, the hydrogen electrode (Pt) is the negative terminal (–) and the calomel electrode (Hg) the positive terminal (+) of the cell, since the potential (Ecal) of the calomel electrode is higher than the potential (EH) of the hydrogen electrode. the measured cell potential is the potential difference between the right hand side electrode (Ecal) and the left hand side electrode (E_H).

$$E = E_{cal} - E_H$$

$$\therefore \text{pH} = \frac{E - E_{cal}}{0.0591} \quad ..... \quad (4.45)$$

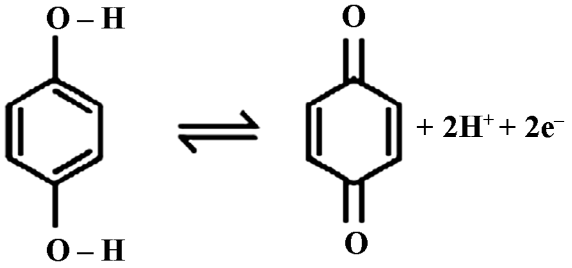
This is valid at 298K. At other temperatures the denominator of the equation will change accordingly. The hydrogen electrode is regarded as a primary standard for the pH measurements, other methods are in fact based on the data measured by the hydrogen electrode. It can measure the whole range of the pH scale, from pH 0 to 14. With special arrangement the hydrogen electrode can measure the hydrogen ion activity even in a broader scale, in the solutions of concentrated strong acids as well as strong alkalis, where other methods fail. The electric resistance of the cell with the hydrogen and calomel electrodes is not too high, so the cell potential (EMF) can be easily measured, also by older compensation potentiometers. On the other hand, there are some severe limitations of the pH measurements with the hydrogen electrode. The hydrogen catalysed by the platinum is highly reactive, it can react with a long list of the oxidizing agents, which must not be present in the measured solutions: salts of heavy metals, peroxides, nitrates, reducible organic compounds, H_2S and sulphides, cyanides, ammonia etc. The tedious maintenance and operation of the hydrogen electrode are also impractical and unsuitable for routine use. The main purpose of the hydrogen electrode is the accurate measurement of the primary pH standards, the buffer solutions by which other pH electrodes, such as glass electrodes, are standardized (calibrated). The more practical and routine methods of pH measurements are thus in fact based on the data measured with the hydrogen electrode.

pH measurement using Quinhydrone Electrode

The quinhydrone electrode is a type of redox electrode which can be used to measure the hydrogen ion concentration (pH) of a solution in a chemical experiment. It provides an alternative to the commonly used glass electrode in a pH-meter. A redox electrode consists of an inert material like platinum or gold dipping into a solution containing a chemical species in two different oxidation states. The transfer of electrons between the species takes place through the inert material. The electrode potential is given by

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ell n\frac{[red]}{[ox]} \quad ..... \; (4.46)$$

Here, [red] and [ox] are the concentrations of the reduced and oxidized species. The quinhydrone electrode consists from a platinum wire dipped into a solution saturated with quinhydrone. Quinhydrone (HQ) is a slightly soluble compound formed by the combination of one mole of quinone (Q) and one mole of hydroquinone (H_2Q).



Quinone is oxidant, and hydroquinone is reductant in this reaction. This electrode is very easy to prepare and handle. Pure solid quinhydrone is dissolved in the solution to be measured until the solution is saturated and excess is present. A platinum wire is dipped in this solution. The electrode potential is given by :

$$\frac{E_{H2Q}}{Q} = \frac{E^0_{HeQ}}{Q} = \frac{RT}{2F}\ell n\frac{[a_{H2Q}]}{[a_Q][a_{H+}]^2} \quad ..... \; (4.47)$$

Quinone (Q) and hydroqu inone (H2Q) are obtained by dissolving quinhydrone in solution, therefore $a_{H2Q} = a_Q$. Applying the following substitution we get

$$\frac{E_{H2Q}}{Q} = \frac{E^0_{H2Q}}{Q} - 2.303\frac{RT}{F}pH \quad ..... \; (4.48)$$

For the potentiometric measurements we combine the quinhydrone electrode with a suitable reference electrode to create an electrochemical cell. We use a saturated calomel electrode as the reference, and the cell is set up :

Hg | $HgCl_2$ | KCl (saturated solution) | H_2Q, Q, H^+ (measurement solution) | Pt

If the potential of this cell is E then the pH of the solution is given by the equation

$$pH = \frac{E^{o}_{\frac{H2Q}{Q}} - E_{cat} - E}{2.303\frac{RT}{F}} \quad ..... (4.49)$$

This is a general equation for pH measurement at any temperature. The quinhydrone electrode cannot be used in solutions that would react with quinone or hydroquinone. Hydroquinone being a weak acid, the electrode cannot be used above pH = 8.5 when the dissociation of hydroquinone becomes appreciable. Another drawback is that quinone is oxidized by air in strongly alkaline medium. In spite of all this, the quinhydrone electrode is frequently used in titration acids with bases since the end point is reached below pH = 8 in most cases.

pH measurement using Glass Electrode

Potentiometric measurement of pH of various solutions by the glass electrode is a practical and often used method of the pH determination. The glass electrode is one of the numerous membrane electrodes or ion-selective electrodes, they are sophisticated electrode systems based on the existence of the membrane potential between the solution and a suitable membrane. The membrane potential is due to elective ion-exchange, that is adsorption and desorption of a certain kind of ions on the membrane surface. Due to the selective ion-exchange the membrane exhibits potential response in the presence of certain ion and the membrane potential can also be expressed by the Nernst equation. Membrane of the glass pH electrode is a thin glass layer, made of special sodium glass, which exhibits selective potential response to the hydrogen ions in the solution. The membrane is shaped as a small glass bulb and inside the bulb is internal solution with the internal reference electrode. The cable outlet (terminal) of the glass electrode is connected just to the internal reference electrode. In the most cases, it is the silver-silver chloride electrode, indeed a silver wire covered by AgCl, and dipped in the internal solution of diluted aqueous HCl. The potential of the sealed internal system of the glass electrode is relatively constant but when the glass bulb is dipped in the various measured solutions, potential of the whole glass electrode changes, according to the activity of hydrogen ions in the measured solution. The sensing glass electrode must be combined with an external reference electrode to set up an electrochemical cell. The external reference electrode may also be the silver-silver chloride electrode or the calomel electrode. Modern combination glass electrodes have the external reference electrode housed together with the glass electrode in one body (shaft), and there is a one co-axial (dual) outlet cable from the two electrodes. In the case of the combination electrode, the liquid junction of the external reference electrode is placed just above the glass bulb of the glass electrode (small greyish spot). Both the glass bulb and the liquid junction must be dipped in the measured solution.

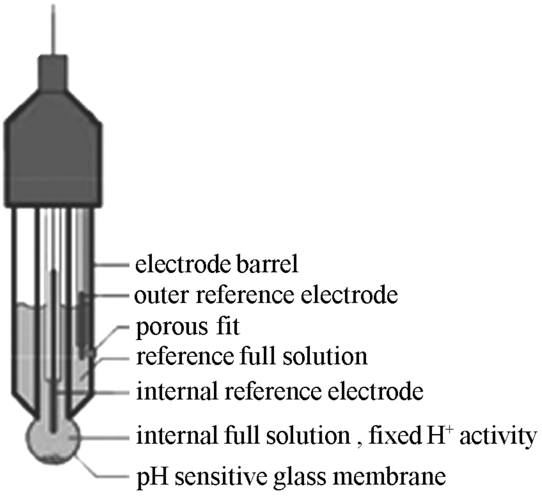


Figure 4.11 : The glass electrode

The complete electrochemical cell necessary for measurements of pH using glass electrode is represented by the following diagram:

Ag | AgCl | internal solution H^+Cl^- |glass| H^+ measured solution |external reference electrode

The relationship between cell potential and pH of the measured solution in case of a glass electrode is

$$E = E_{ref} - E_g^* + 0.0591 \text{ pH} \; ..... \; (4.50)$$

E_g^* is here a sum of several potential contributions, it includes the potential of the internal Ag | AgCl electrode and a so called asymmetrical potential of the glass membrane. One of the disadvantages of the glass electrode is the potential E_g^* is not known beforehand and is only relatively constant. As the glass electrode is ageing, it may change somewhat, mainly due to the time variations of the asymmetrical potential of the glass membrane. Therefore, the glass electrode must be repeatedly standardized (calibrated) by the standard buffer solutionswith known value of pH. At the standardization procedure the electrodes are dipped in a standard buffer solution with known pH_{st} and the corresponding cell potential (EMF) E_{st} is measured. The standard solution is then replaced by the given solution with unknown pH and here thecell potential is E. After inserting into Equation 4.50, the operational expression for the unknown pH of the measured solutions is obtained (25 °C) :

$$pH = pH_{st} + \frac{E - E_{st}}{0.0591} \quad \ldots\ldots \ (4.51)$$

The calculation after Equation 4.51 is done by the used pH-meter (potentiometer) measuring the cell potential in the course of the standardization procedure and the instrument shows the resulting pH value of the measured solution. For high quality pH measurements, the standardization by two (or more) standard buffers is recommended, one buffer with lower pH and one with higher pH than the expected measured value are required. The accuracy of the measured pH always depends on the accuracy of the standardization of the glass electrode and on the quality of the instrumentation, for the high quality measurements it is about 0.01 pH unit.

4.4.14 Potentiometric Titrations

In many situations, accurate determination of an ion concentration by direct measurement of a cell potential is impossible due to the presence of other ions and a lack of information about activity coefficients. In such cases it is often possible to determine the ion indirectly by titration with some other ion. For example, the initial concentration of an ion such as Fe^{2+} can be found by titrating with a strong oxidizing agent such as Ce^{4+}. The titration is carried out in one side of a cell whose other half is a reference electrode :

$$Pt(s) \mid Fe^{2+}, Fe^{3+} \parallel \text{reference electrode}$$

Initially the left cell contains only Fe^{2+}. As the titrant is added, the ferrous ion is oxidized to Fe^{3+} in a reaction that is virtually complete:

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$$

The cell potential is followed as the Fe^{2+} is added in small increments. Once the first drop of titrant has been added, the potential of the left cell is controlled by the ratio of oxidized and reduced iron according to the Nernst equation

$$E = E^\circ = 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad \text{.....} \quad (4.52)$$

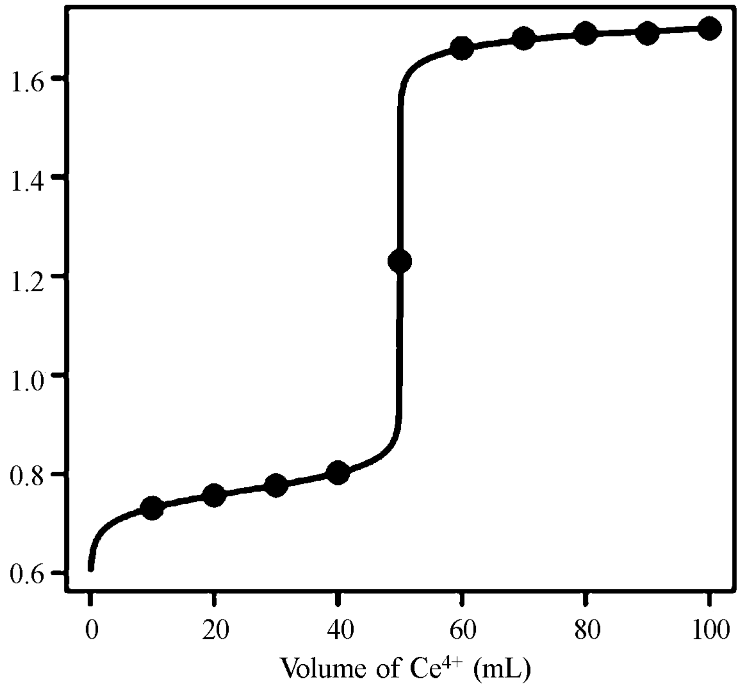


Figure 4.12 : Potentiometric titration curve of Fe^{2+} with Ce^{4+}

When the equivalence point is reached, the Fe^{2+} will have been totally consumed (the large equilibrium constant ensures that this will be so), and the potential will then be controlled by the concentration ratio of Ce^{3+}/Ce^{4+}. The idea is that both species of a redox couple must be present in reasonable amount for the concentration to control the potential of an electrode of this kind. If one works out the actual cell potentials for various concentrations of all these species, the resulting titration curve looks much like the familiar acid-base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

For a general titration, for example, a titration in which a titrand in a reduced state, Ared, reacts with a titrant in an oxidized state, Box

$$A_{red} + B_{ox} \rightleftharpoons B_{red} + A_{ox}$$

where Aox is the titrant's oxidized form, and Bred is the titrant's reduced form. The reaction's potential, E_{rxn}, is the difference between the reduction potentials for each half-reaction.

$$E_{rxn} = E_{\frac{BOX}{Bred}} - E_{\frac{AOX}{Ared}} \quad ..... (4.53)$$

After each addition of titrant the reaction between the titrand and the titrant reaches a state of equilibrium. Because the potential at equilibrium is zero, the titrand's and the titrant's reduction potentials are identical.

$$E_{\frac{Box}{Bred}} = E_{\frac{Aox}{Ared}} \quad ..... (4.54)$$

This is an important observation because we can use either half-reaction to monitor the titration's progress. Before the equivalence point the titration mixture consists of appreciable quantities of the titrand's oxidized and reduced forms. The concentration of theunreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we use the Nernst equation for the titrand's half-reaction.

$$E_{rxn} = E^{o}_{\frac{AOX}{Rred}} - \frac{RT}{nF} \ln \frac{[A_{red}]}{[A_{ox}]} \quad ..... (4.55)$$

After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E_{rxn} = E^{o}_{\frac{BOX}{Bred}} - \frac{RT}{nF} \ln \frac{[B_{red}]}{[B_{ox}]} \quad ..... (4.56)$$

4.5 Dipole moment and Polarizability

Electrical insulator materials which will prevent the flow of current in an electrical circuit are being used since the beginning of the science and technology of electrical phenomena. Dielectrics are insulating materials that exhibit the property of electrical polarization, thereby they modify the dielectric function of the vacuum. Mossotti and Clausius have done a systematic investigation about the dielectric properties of materials. They attempted to correlate the specific inductive capacity, a macroscopic characteristic of the insulator introduced by Faraday which is now popularly termed as dielectric constant, with the microscopic structure of the material. Following Faraday in considering the dielectrics to be composed of conducting spheres in a non-conducting medium, Clausius and Mossotti succeeded in deriving a relation between the real part of the dielectric constant er and the volume fraction occupied by the conducting particles in the dielectric. In the beginning of 20th century, Debye realized that some molecules had permanent electric dipole moments associated with them, and this molecular dipole moment is responsible for the macroscopic dielectric properties of such materials. Debye succeeded in extending the Clausius-Mossotti theory to take into account permanent dipole moments of the molecules, which allowed him and others to calculate the molecular dipole moment from the measurement of dielectric constant. His theory was later extended by Onsager and Kirkwood and is in excellent agreement with experimental results for most of the polar liquids.

4.5.1 Polarization of Molecules in Electric Field : Induced Polarization

A molecule as a whole is neutral, but is composed of positively charged nuclei and negatively charged electrons. When a molecule is put under the influence of an electric field, the positive nuclei will be attracted towards negative plate and electrons towards positive plate. This results in a change in the molecule, causing positive charges at one end and negative charges at the other i.e. formation of electrical dipoles takes place. Such distortion is called distortion polarization or electrical distortion (polarization) of the molecule. Hence electrical polarization is defined as the creation of electrical dipoles in a neutral molecule, under the influence of an electric field. The molecule, even though nonpolar in nature, acquires a dipole moment, when kept in an electric field.

The electrical polarization of molecule is temporary and disappears as soon as the electric field is removed. This type of electrical polarization is called induced polarization and the dipole formed is called **induced dipole**. The dipole moment of this indeed dipole is called induced dipole moment or induced moment denoted by μ_{ind}. Induced moment is directly proportional to the strength of applied electric field and is given by

$$\mu_{ind} = \alpha E \quad ..... \quad (4.57)$$

Here, ais α constant called distortion polarizability and E is the strength of applied electric field. Induced polarization is of two types : (i) **Atomic polarization :** when the nuclei are distorted with respect to each other, it is called atomic polarization, denoted by P_a

and (ii) Electric (electron) polarization: When the electrons are distorted, it is called electric polarization, denoted by P_e

Induced polarization = Atomic polarization + Electric polarization

$$P_i = P_a + P_e \quad ..... \quad (4.58)$$

According to Clausius-Mossotti Equation,

$$\frac{4}{3}\pi N\alpha = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho} \quad ..... \quad (4.59)$$

Here, M = Molecular weight of the substance, ρ = Density of the substance, N = Avogadro's number, α = Distortion polarizability, ε = Dielectric constant of the medium.

The left hand side of the above equation is called **molar polarization of the substance** and is denoted by P and hence

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho} \quad ..... \quad (4.60)$$

In nonpolar molecules, the polarization is all induced. Hence P also stands for induced polarization (P_i) in case of nonpolar molecules only. Induced polarization is the electrical distortion caused in one mole of substance by unit field. For nonpolar molecules

$$P_i = P = \frac{4}{3}\pi N\alpha = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho} \quad ..... \quad (4.61)$$

In this equation N and α are independent of temperature, Hence P_i will also be independent of temperature. Since ε is a dimensionless number, polarization will be expressed in the unit of volume. It is important to note that the substances which do not have permanent dipole moment (i.e., nonpolar substances) the molar polarization is independent of temperature. But the substances which have permanent dipole moment (i.e., polar or partial polar molecules) their molar polarization changes with temperature.

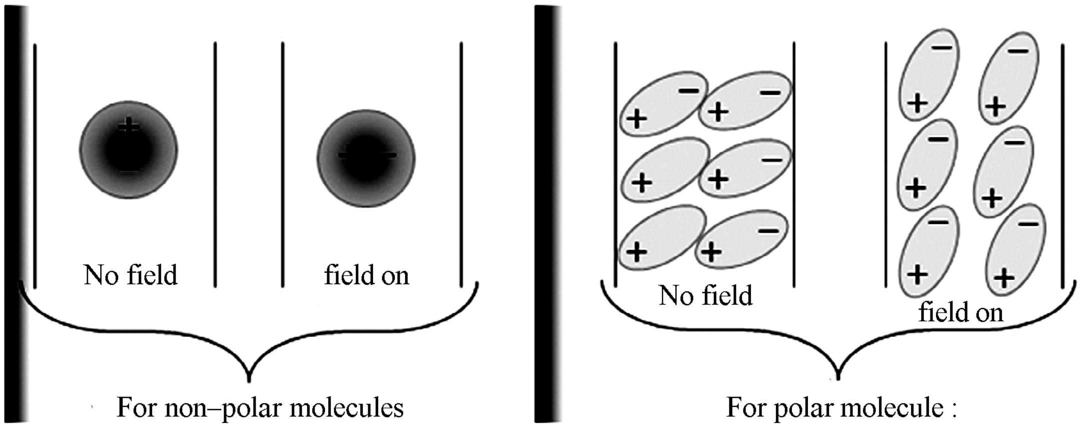


Figure 4.13 : Behaviour of molecules in an electric field

4.5.2 Polarization of Polar Molecules in Electric Field

The induced polarization (P_i) is common to all substances (polar and nonpolar both). Polar molecules, in absence of electric field, are oriented in all directions (as they have dipoles) due to thermal effects. But when such molecules are put in an electric field, two effects will arise :

(i) Induced Polarization (P_i) : Usual distortion of positive and negative charges will take place giving rise to induced polarization

(ii) Orientation Polarization (P_o) : Since the molecules are polar, the electric field tries to orient them in the direction of electric field. But the molecules themselves are constantly moving in all possible directions. This is called thermal agitation. This **thermal agitation** opposes such orientation of molecules. Under such conditions, the molecules would occupy some mean position between the direction of field and their original position. This kind of effect of the electric field on the molecules is called orientation polarization.

Thus for a polar molecule, the molar polarization is given by

Molar polarization = Induced polarization + Orientation polarization

$$P = P_i + P_o$$

From dielectric measurement we know,

$$P = \frac{4}{3}\pi n\alpha + P_0 = \frac{\varepsilon - 1}{\varepsilon + 2}\cdot\frac{M}{\rho} + P_0 \quad ..... (4.62)$$

Debye showed that,

$$P_0 = \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \quad ..... (4.63)$$

where μ is the permanent dipole moment. From equation 4.63, the following conclusions are drawn (a) P_0 is inversely proportional to temperature and (b) for nonpolar molecule $\mu = 0$. Therefore, $P_0 = 0$. That is, there is no orientation polarization. Thus equation 4.62 transforms to

$$P = \frac{4}{3}\pi N\alpha + \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) = \frac{\varepsilon - 1}{\varepsilon + 2}\cdot\frac{M}{\rho} + \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) = A + \frac{B}{T} \quad ..... (4.64)$$

Equation (4.64) represents a straight line. That is the plot of P against $\frac{1}{T}$ will be a straight line with the intercept A = $\frac{4}{3}$ πNa and slope B = $\frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right)$.

4.5.3 Measurement of Dipole Moment

Measurement of dipole moment can be performed in several ways using different techniques. These are as follows.

Temperature Method

If total molar polarization P_1 and P_2 is determined at two temperatures T_1 and T_2 then

$$P_1 = A + \frac{B}{T_1} \quad ..... (4.65)$$

$$P_2 = A + \frac{B}{T_2} \quad ..... (4.66)$$

We can eliminate A from the two equations and using some standard values we can determine the dipole moment from the B value obtained.

Refraction Method

This method involved measurement of dielectric constants in terms of refractive index. Maxwell showed that for the same wavelength of light, the refractive index and the dielectric constant are related as

$$\varepsilon = n^2 \text{ ..... } (4.67)$$

Hence the total molar polarization in terms of refractive index becomes

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} \text{ ..... } (4.68)$$

Since n can change with the wavelength of light, we need to measure it at very high wavelength for precision. A solution of the dipolar compound in a nonpolar solvent e.g. nitrobenzene in benzene– is prepared at various concentrations. The dielectric constant is measured and the apparent molar polarization calculated from equation 4.61. This quantity is made up of the electric polarizations of both solute and solvent plus the orientation polarization of the polar solute. The molar polarizations due to distortion can be set equal to the molar refractions RM, calculated from the refractive indices of the pure liquids. When these RM are subtracted from the total apparent P, the remainder is the apparent molarorientation polarization for the solute alone. This polarization is plotted against the concentration in the solution and extrapolated to zero concentration. A value is obtained in this way from which the effect of dipole interaction has been eliminated.

From eq. 4.64, therefore, it is equal to $\frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right)$ and the dipole moment of the polar solute can be calculated.

4.6 Summary

Real solutions deviate significantly from ideal solutions and to account for that deviation, the concept of activity is introduced. Basically, activity signifies effective concentration. Especially for electrolyte solutions, activity becomes extremely important. A quantitative expression for activity coefficient can be found from Debye Huckel limiting law. Electrolytes are also important for electrochemical cells. Electrochemical cells are used to produce electrical energy from chemical reactions as well as driving non-spontaneous chemical reactions using electrical energy. Electrochemical cells can be of different types and their functionality depend on the electrode potentials. Nernst equation is used to determine the electromotive forces in a cell. Electrochemistry has huge applications. At the last of the chapter the behaviour of non-polar and polar molecules in an electric field has been explained using the concept of polarisation.

4.7 Self-Assessment Questions

1. Calculate the ionic strength of a solution of 0.10 M NaCl. Repeat the calculation for a solution of 0.10 M Na_2SO_4.
2. Calculate the activity coefficients for K^+ and SO_4^{2-} in a 0.020 M solution of K_2SO_4.
3. Using activities, calculate the pH of a 0.10 M aqueous solution of KH_2PO_4.
4. What is the half-reaction that occurs at the anode during the electrolysis of molten sodium bromide?
5. What mass (in grams) of nickel could be electroplated from a solution of nickel(II) chloride by a current of 0.25 amperes flowing for 10 hours?
6. Molten $AlCl_3$ is electrolyzed for 5.0 hours with a current of 0.40 amperes. Metallic aluminum is produced at one electrode and chlorine gas, Cl_2, is produced at the other. How many liters of Cl_2 measured at STP are produced when the electrode efficiency is only 65%?
7. How many faradays are required to reduce 1.00 g of aluminum (III) to the aluminum metal?
8. Which of the following is the strongest oxidizing agent?

   (a) Pb^{2+} (b) I2 (c) Ag+ (d) Pb (e) Cu^{2+}
9. What is E° for the following balanced reaction?

   $Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$

   Half-reaction Standard Reduction Potential

   $Zn(aq) + 2e- \rightarrow Zn(s)$ –0.763

   $Pb^{2+}(aq) + 2e- \rightarrow Pb(s)$ –0.126

10. Given the electrochemical reaction shown, if the standard reduction potential of $Ag^+ \rightarrow Ag$ is + 0.80 V, and the standard reduction potential of $Cu^{2+} \rightarrow Cu$ is + 0.34V, what is E° for the following? Cu / Cu2$^+$(aq) // Ag$^+$(aq) / Ag

11. Given the electrochemical reaction shown, if the standard reduction potential of $Zn^{2+} \rightarrow Zn$ is –0.76 V, what is the standard reduction potential of $Mg^{2+} \rightarrow Mg$? Mg / Mg^{2+}(aq) // Zn^{2+}(aq) / Zn E° = + 1.61 V

12. Which of the following statements accurately describes the Nernst equation shown below?

13. What is the standard cell potential for a voltaic cell using the Pb^{2+}/Pb and Mg^{2+}/Mg half-reactions? Which metal is the cathode?

14. In the standard notation for a voltaic cell, the double vertical line "||" represents:

    (a) a phase boundary (b) gas electrode (c) a wire (metal) connection (d) a salt bridge (e) a standard hydrogen electrode

15. Estimate the equilibrium constant for the system indicated at 25°C.

    $3\ Mg^{2+} + 2Al \rightleftharpoons 3Mg + 2Al^{3+}$

    (a) $\sim 10^{69}$ (b) $\sim 10^{23}$ (c) $\sim 10^{-24}$ (d) $\sim 10^{-36}$ (e) $\sim 10^{-72}$

16. What is ΔG° per mole of dichromate ions for the reduction of dichromate ions, $Cr_2O_7^{2-}$ to Cr^{3+} by bromide ions, Br^-, in acidic solution? (Hint : Use the standard cell potential.)

4.8 Answers to Self-Assessment Questions

1. 0.10 M and 0.30 M
2. $\Delta_{K+} = 10^{-0.101} = 0.79$ and $SO_4 = 10^{-0.463} = 0.344$
4. $2\ Br^- \rightarrow Br_2 + 2e^-$
5. 6 g; 6. 0.55 L; 8. C
10. 0.46 V
11. –2.37V
15 e
16. –145 kJ

4.9 Suggested Readings

(a) Physical Chemistry by Peter Atkins and Julio De Paula, Oxford University Press

(b) Physical Chemistry by Ira N. Levine; McGraw-Hill Education

(c) Physical Chemistry by P. C. Rakshit; Sarat Book House, India

(d) A Textbook of Physical Chemistry Vol.- III by K. L. Kapoor, Macmillan Publishers India

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