6 THERMOCHEMISTRY

When chemical reactions take place heat is either absorbed or evolved. As the term '*heat content of a substance*' implies, different forms of matter have various amounts of energy associated with them; when transformation from one form of matter to another form takes place, as in a chemical reaction, the energy of the products may not be exactly equal to the energy of the reactants. Hence energy will either be absorbed or evolved depending on whether the products have more or less energy than the reactants. If the energies are exactly equal no change in the heat content will be manifest. In chemical reactions the heat changes involved are due to conversion of chemical energy into heat energy and such heat changes are termed heats of reaction. Thermochemistry is that branch of thermodynamics which deals with the heat changes accompanying chemical reactions. Heat changes are usually measured in open vessels at 1.0 atmosphere pressure. As we have seen, heat change at constant pressure is known as ***enthalpy change,*** (ΔH). The laws of thermo-chemistry, however, were established long before the general application of thermodynamics was recognized. As will be seen, the laws of thermochemistry are based mainly on the first law of thermodynamics.

6.1 Heat of Reaction or Enthalpy of Reaction

The enthalpy of reaction is ordinarily defined as the amount of heat evolved or absorbed when the reaction has taken place at constant pressure between the number of moles of the reactants as shown in the balanced equation. If heat is evolved the reaction is said to be ***exothermic*** and when heat is absorbed the reaction is an ***endothermic*** one. *Heat of reaction may also be defined as the difference in enthalpy or heat content,* ΔH, *between the products and the reactants.* The amount of heat change is expressed in kilojoules (kJ).

The following examples will, perhaps, clarify the definition.

$$(a)\ C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta H^\circ = -393.5 \text{ kJ}$$
$$(b)\ 2C(s) + 2H_2(g) \rightarrow C_2H_4(g); \quad \Delta H^\circ = +52.3 \text{ kJ}$$

(a) When one mole (12 g) of graphite reacts with one mole (32 g) of gaseous oxygen to produce one mole (44 g) of gaseous carbon dioxide, the heat of reaction or the change in heat content is −393.5 kJ. Here the heat content of $CO_2(g)$ is less than the sum of the heat contents of $C(s)$ and $O_2(g)$ and heat is evolved; the reaction is exothermic and the heat of reaction, ΔH°, is negative.

(b) In this reaction two moles (24 g) of graphite combine with two moles (4 g) of hydrogen to form one mole (28 g) of ethylene and the heat of reaction is + 52.3 kJ. The heat content of one mole of $C_2H_4\ (g)$ is more than the sum of the heat contents of 2 moles of $C(s)$ and 2 moles of $H_2\ (g)$ and heat is absorbed; the reaction is endothermic and the heat of reaction, ΔH°_r is positive.

6.2 Conventions

(a) Changes of state are accompanied by evolution or absorption of the latent heat. The heat of reaction should depend on the states of the substances involved in the reaction. Thus in the formation of water

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

if the H_2O is in the liquid state the heat of reaction will differ from that observed if the H_2O is vapour. In writing appropriate equations in thermochemistry the state of the substance, i.e. whether it is gaseous, liquid, solid or in solution, is mentioned by writing the symbols (*g*), (*l*), (*s*) or (*aq*) respectively for the states after the chemical formula of the substance. Further, the heat of reaction depends on which crystalline form participates in the reaction.

For these reasons ΔH° values are expressed with reference to reactions with the compounds in certain standard states. The states which by convention have been agreed upon as reference states in tabulating heats of reaction are summarized in Table 6.1.

Table 6.1 Standard States of Substances

Standard state of solid	:	The most stable state at 1 atmosphere pressure and the specified temperature.
Standard state of liquid	:	The most stable form at 1 atmosphere pressure and the specified temperature.
Standard state of gas	:	1 atmosphere pressure and the specified temperature.
Standard state of carbon	:	Graphite*
Standard temperature	:	25°C*

*Other standard states are also in use, e.g., diamond as the standard state of carbon and 18°C as the standard temperature.

Again the heat of reaction will depend on the pressure of the gases involved. The symbol ΔH indicates that the reaction takes place at constant pressure. The value at constant pressure is mentioned in most cases because the reactions are ordinarily carried out in open containers under atmospheric pressure. If the reaction would have been carried out under constant volume conditions the heat of reaction would be different in those cases involving gases where there is a difference in the number of moles of reactants and products.

Heats of reaction have been given special names in some cases depending on the type of the reaction. For example, reaction (a) shown in *Section 6.1* above is a *combustion*

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reaction as carbon burns in oxygen to form carbon dioxide. The heat content change in this reaction is termed the *heat of combustion* (ΔH_C). This is also termed the *heat of formation* (ΔH_F) of carbon dioxide. There are heats of atomization, heats of dissociation, heats of precipitation, heats of neutralization, heats of hydrogenation etc. These are all heats of reaction.

6.3 Heat of Reaction at Constant Pressure and at Constant Volume

When a reaction is carried out at constant volume as in a bomb calorimeter, the pressure within the calorimeter may change but no work is done. The heats of reaction in such cases correspond to ΔU. Ordinarily, reactions are carried out in open vessels under constant pressure conditions. ΔH and ΔU are, however, related by the equation

$$\begin{aligned}\Delta H &= \Delta U + P(V_2 - V_1)\\ &= \Delta U + P\Delta V \qquad (6.1)\end{aligned}$$

It is clear from the above relation that ΔH and ΔU are equal if ΔV is zero, i.e., if there is no change in volume as a result of the reaction, but may differ if there is volume change. For reactions in which the reactants and products are either liquid or solid no appreciable change in volume takes place as a result of the reaction so that ΔH and ΔU are practically the same. This may not be so in the case of reactions involving gases.

The change in volume in a reaction is due to the change in the number of moles of gas during the reaction as can be seen from the following:

For an ideal gas $PV = nRT$. If there are n_1 moles of gaseous reactants and n_2 moles of gaseous products we have

$$P\Delta V = PV_2 - PV_1 = n_2RT - n_1RT = (n_2 - n_1)RT = \Delta n(RT) \qquad (6.2)$$

where $\Delta n = n_2 - n_1$. Equation (6.1) may then be written as

$$\Delta H = \Delta U + \Delta n\, RT \qquad (6.3)$$

If $n_2 > n_1$, $\Delta H > \Delta U$, while if $n_2 < n_1$, Δn is negative and $\Delta H < \Delta U$.

Example 6.1: The heat of combustion at constant pressure of benzoic acid is – 3227.5 kJ mol^{-1} at 25°C. What is the heat of combustion at constant volume?

Solution: The combustion reaction is

$$C_6H_5\,COOH\,(s) + 7\tfrac{1}{2}\,O_2\,(g) \rightarrow 7CO_2\,(g) + 3H_2O\,(l)$$

As the gaseous substances in this reaction are oxygen and carbon dioxide, Δn for this reaction is $(7 - 7\tfrac{1}{2})$ or $-\tfrac{1}{2}$. Substituting in equation (6.3) we get,

$$\begin{aligned}\Delta H &= -3227.5 = \Delta U - (\tfrac{1}{2})(8.314)(298)/1000\\ \Delta U &= -\ 3227.5 + 1.2\ \text{kJ}\\ &= -\ 3226.3\ \text{kJ}\end{aligned}$$

If in a reaction ΔV is positive, work is to be done by the system if it is a constant pressure process. More heat is consequently required making ΔH different from ΔU. When ΔV is negative in a constant pressure process, work is done on the system as the system contracts and heat is given out, again making ΔH and ΔU different.

6.4 The Determination of Heats of Reaction: Calorimetry

Enthalpy changes in chemical reactions are usually measured with the help of calorimeters. A calorimeter is a simple device used for measuring the heat of chemical reactions or physical changes as well as heat capacity. In its simplest form, a calorimeter consists of a vessel or a beaker fitted with a thermometer and a stirrer. The temperature of the reaction mixture water is measured with a thermometer before and after the reaction The total heat capacity of the calorimeter and water multiplied by the change in temperature gives a measure of the heat evolved or absorbed from which the enthalpy of reaction may be calculated. The temperature change is related to energy unit as

$$\textit{Energy unit (kJ)} = \textit{specific heat capacity of water } (kJ\ kg^{-1}\ K^{-1}) \times \textit{mass heated (kg)} \times \textit{change in temperature (K)} = c \times m \times \Delta T \tag{6.4}$$

This amount gives the heat absorbed or evolved for the quantity of reactants used in the experiment. Enthalpy change per mole of the reactant can be calculated from these data.

For good results the reaction should be rapid and should go to completion. The reaction mixture in the calorimeter should be stirred so that the change in temperature is uniform. Loss of heat due to radiation should be minimized as far as possible and a radiation correction introduced. The latter can be done by plotting the temperature of the calorimeter against time and extrapolating the curve to the time at which the reaction started. The corrected rise or fall in temperature is the difference between the extrapolated temperature and the initial temperature.

Adiabatic calorimetry makes the correction for loss due to radiation and conduction almost unnecessary. This method is particularly useful in measuring very small values of heats of reaction. Dewar flasks, i.e., vacuum walled vessels are used to minimize heat losses. In some types the outer jacket is electrically heated at a controlled rate such that the jacket is always kept at the same temperature as the calorimeter.

Example 6.2: Calculate the amount of heat required to raise the temperature of 500 g of water by 5.0 K. The specific heat capacity of water is 4.18 J g^{-1} K^{-1}.

Solution: Heat absorbed $(q) = c \times m \times \Delta T = 4.18 \times 500 \times 5.0 \quad = 10,450$ J

6.5 Enthalpy of Combustion: Bomb Calorimeter

The standard enthalpy of combustion of a compound or an element is defined as the heat evolved when one mole of the substance is burnt completely in oxygen at 25°C temperature and 1 atmosphere pressure. Let us consider the following reaction:

$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+H_2O(l); \qquad \Delta H^{\circ}_{298} = -890.3 \text{ kJ}$$

This means that when 1 mole of methane is burnt completely in oxygen to form gaseous carbon dioxide and liquid water at 298 K and 1 atmosphere pressure 890.3 kJ of heat is evolved. Enthalpies of combustion of substances are usually measured in Berthelot's Bomb calorimeter. The apparatus is shown in Figure 6.1 in sketch.

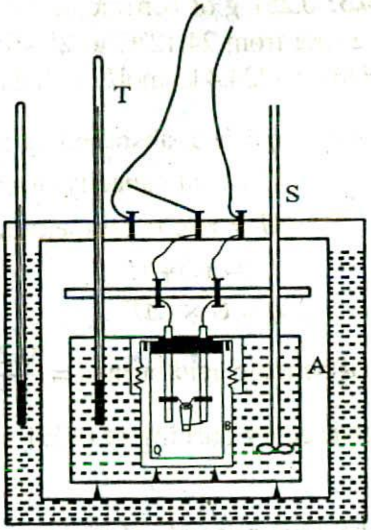


Figure 5.6 Bomb calorimeter

It consists of a strong vessel, B, called the bomb, fitted with a lid which can be screwed on to the bomb. The vessel is made of steel, nickelled on the outside and the inside being coated with some non-oxidizable material such as platinum, gold or enamel. Through the lid there is an inlet tube and valve, through which oxygen can be introduced. The bomb is placed in a bucket which contains a known quantity of water. The temperature of the water is recorded with a sensitive thermometer, T; the stirrer, S, renders the temperature of the water uniform. The bucket, in turn, is surrounded by an insulating air space, A, and the whole thing is placed in a metallic container with an inner lining of some heat insulating material, such as felt or cotton.

The arrangement is such that two pieces of insulated platinum wire can pass right through the outer cover into the bomb. Before assembling the apparatus a weighed quantity of the substance is placed in the cup, Q. The sample is placed in contact with a spiral of thin iron wire which is connected to the platinum wires. If the sample is solid it is compressed into a cylindrical shape before being placed in Q; if liquid, it is placed in a platinum capsule. Oxygen is introduced into the bomb through the tube on the lid and when the pressure inside is about 25 atmosphere the valve screw is tightened. This is then placed in the bucket, B. The temperature of the water is noted and electric current is passed through the platinum wires. The spiral of iron wire burns out and the heat ignites the sample which burns completely in oxygen. From the rise in temperature of the water and the heat capacity of the instruments, i.e., the bucket, thermometer, stirrer, the bomb etc., the quantity of heat evolved may be calculated. The heat of combustion is then obtained, after giving due allowance to the heat developed by the burning of iron wire. In practice the heat capacity of the components of the instruments is determined by burning in the same calorimeter a known quantity of a substance whose heat of combustion is accurately known.

Since this procedure uses a closed bomb, it would give the heat of reaction at constant volume, ΔE. From this value the enthalpy of reaction at constant pressure, ΔH, can be easily calculated. The values are then converted to the standard heats of combustion.

Example 6.3: 0.251 g of benzoic acid (C_6H_5COOH) was burned in a bomb calorimeter. The temperature rose from 24.12°C to 25.46°C. The heat released by benzoic acid was accurately determined to be 3224.4 kJ mol^{-1}. Calculate the heat capacity of the calorimeter.

Solution: Let q = heat absorbed by the calorimeter

C = heat capacity of the calorimeter

ΔT = rise in temperature of water in the calorimeter = 25.46 – 24.12°C = 1.34°C

Then $q = C \times \Delta T$

$$\text{Moles of benzoic acid burned} = \frac{0.251}{122} = 2.06 \times 10^{-3}$$

$$\text{Heat released by burning of 0.251 g of benzoic acid} = 2.06 \times 10^{-3} \times 3224.4 \text{ kJ} = 6.63 \text{ kJ}$$

$$\text{Hence heat capacity of calorimeter} = C = \frac{q}{\Delta T} = \frac{6.63}{1.34} = 4.95 \text{ kJ K}^{-1}$$

The halogen-containing compounds do not always give reproducible values as the products formed are not always definite. The standard enthalpies of combustion of a number of substances are given in Table 6.2.

Table 6.2 Heats of combustion of some substances at 25°C in kJ mol^{-1}

Substance	ΔH_C^0	Substance	ΔH_C^0
$H_2 (g)$	– 285.7	$C_6H_6(l)$	– 3268.0
$CH_4 (g)$	– 890.3	$C_6H_5CH_3 (1)$	– 3910.0
$C_2H_6 (g)$	– 1560.0	$H_3CC_6H_4CH_3 (l)$	– 4552.2
$C_3H_8 (g)$	– 2220.0	$C_{10}H_8 (s)$	– 5138.0
$n\text{-}C_4H_{10} (g)$	– 2878.2	$C_{12}H_{22}O_{11} (s)$	– 5643.8
$n\text{-}C_5H_{12} (g)$	– 3509.1	$H_2NCONH_2 (s)$	– 633.9
$n\text{-} C_6H_{14} (g)$	– 4163.0	$C_6H_5NH_2 (1)$	– 3397.0
$C_2H_4 (g)$	– 1410.0	$CH_3COOH (1)$	– 874.5
$CH_3OH(l)$	– 726.3	$CH_3COOC_2H_5 (1)$	– 2251.0
$C_2H_5OH(l)$	– 1367.0	$C_6H_5COOH(s)$	– 3224.4

Heats of combustion data are useful in the calculations of heats of reaction and formation which cannot be measured directly (*Section 6.6.2*). The calorific values (heating value) of fuel and various foods are their important properties.

Example 6.4: A sample of 1.210 g of naphthalene, $C_{10}H_8$, was burned in oxygen in a bomb calorimeter placed in a thermostat at 25°C. A total of 48.32 kJ heat was released as a result of complete combustion of the sample. Calculate the enthalpy of combustion per mole of naphthalene.

Solution: The combustion reaction is

$$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O\,(l)$$

$$\text{RMM of naphthalene} = 128$$

$$\text{Moles of naphthalene} = \frac{1.210}{128} = 9.45 \times 10^{-3}$$

Since the combustion was carried out in a bomb calorimeter, the heat released is ΔU.

So, $$\Delta U = \frac{-48.32}{9.45\times10^{-3}} = -5111.5 \text{ kJ mol}^{-1}$$

Here, $\Delta n = 10 - 12 = -2$, and let us assume that the gases behave ideally.

Now $$\Delta H = \Delta U + RT\Delta n \quad \text{(equation 6.3)}$$

$$= (-5111.5) + \frac{8.314\times298\times(-2)}{1000}$$

$$= -5111.5 - 4.96$$

$$\Delta H = -5116.5 \text{ kJ}$$

6.6 Laws of Thermochemistry

Two laws of thermochemistry are very important in thermochemical calculations. Both the laws preceded the *first law of thermodynamics* (1850). It will, however be shown that the *laws of thermochemistry* are direct consequence of the *first law of thermodynamics*.

6.6.1 Lavoisier and Laplace's law (1782)

This law may be stated in the general form as : *the heat change accompanying a chemical reaction in one direction is exactly equal in magnitude, but opposite in sign, to that associated with the same reaction in the reverse direction.*

This is evident from the following two reactions:

(a) $CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) \qquad \Delta H° = -890.3 \text{ kJ mol}^{-1}$

(b) $CO_2\,(g) + 2H_2O\,(l) \rightarrow CH_4\,(g) + 2O_2\,(g) \qquad \Delta H° = +890.3 \text{ kJ mol}^{-1}$

Thus, it can be concluded that, $\Delta H_{\text{forward reaction}} = -\Delta H_{\text{reverse reaction}}$

A chemical equation when written along with enthalpy change for the reaction is termed a ***thermochemical equation***. The two equations are examples of thermochemical equations. Laplace's law allows us to use thermochemical equations as algebraic equations.

6.6.2 Hess's law (1840)

This law was enunciated by G. H. Hess in 1840, and is also known as the *law of constant heat summation*. The law may be stated in different forms. The following statement of the law is used most often.

If a chemical reaction or physical change can be brought about in more than one ways, the oveall enthalpy change is the same provided the initial and final states are the same.

This means that if a reaction, in theory, can be carried out in a number of steps the enthalpy change for the overall reaction is the sum of the enthalpy changes for all the steps. Since H is a thermodynamic state function, ΔH for a reaction is merely the difference between the value of H in the final state (i.e. products) and the initial state (i.e. reactants).

The law can be illustrated by the following example:

When C (graphite) is burned in oxygen $CO_2\ (g)$ can be produced in one step. The same reaction can be carried out in two steps: in the first step C (graphite) is converted to $CO\ (g)$ by reaction with $O_2\ (g)$ and in the second step $CO\ (g)$ is burned to $CO_2\ (g)$ by reaction with more $O_2\ (g)$. The reactions are shown below:

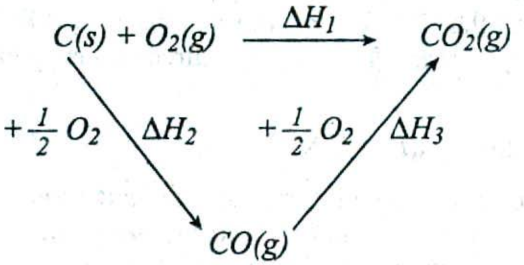
One step reaction: $C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)$; heat change = ΔH_1

Two steps: (i) step 1: $C\ (graphite) + \frac{1}{2}O_2\ (g) \rightarrow CO\ (g)$; heat change = ΔH_2

(ii) step 2: $CO\ (g) + \frac{1}{2}O_2\ (g) \rightarrow CO_2\ (g)$; heat change = ΔH_3

According to Hess's law $\Delta H_1 = \Delta H_2 + \Delta H_3$

since in the two routes the final state and the initial state are the same as can be seen by adding the components in steps (i) and (ii). This can be shown schematically as follows:

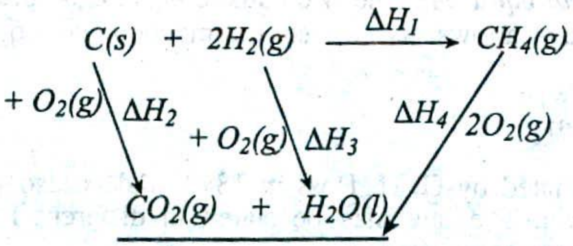


Use can be made of Laplace's law and Hess's law to obtain enthalpy changes for reactions which can not be carried out or is difficult to carry out experimentally.

Consider the reaction

$$C\ (s) + 2H_2\ (g) \rightarrow CH_4\ (g)$$

This reaction does not take place at all. The enthalpy change for this reaction can, however, be calculated by use of Hess's law as shown below.



This shows that in one route starting from $C(s) + 2H_2(g)$ we can get $CO_2(g) + 2H_2O(l)$ by directly burning them in oxygen and in a different route we can first make $CH_4(g)$ and the burn it in oxygen to get the same product. According to Hess's law the enthalpy change for the two routes should be the same. It follows that

$$\Delta H_1 + \Delta H_4 = \Delta H_2 + \Delta H_3$$

All three quantities ΔH_2, ΔH_3 and ΔH_4 can be experimentally determined. The above relation derived by Hess's law can be used to calculate the value of ΔH_1.

The use of Hess's law by using algebraic method is illustrated below:

Let us again consider the reaction between graphite and oxygen to form carbon monoxide.

$$C(s, graphite) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H_R^0 = ? \tag{6.5}$$

The enthalpy change for this reaction, ΔH_R^0, is difficulat to measure experimentally, but can be obtained by use of the two laws of thermochemistry. We can consider the following two reactions for which ΔH_R^0 are accurately known.

$$C(s, graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_1^0 = -393.5\,kJ \tag{6.6}$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H_2^0 = -283.0\,kJ \tag{6.7}$$

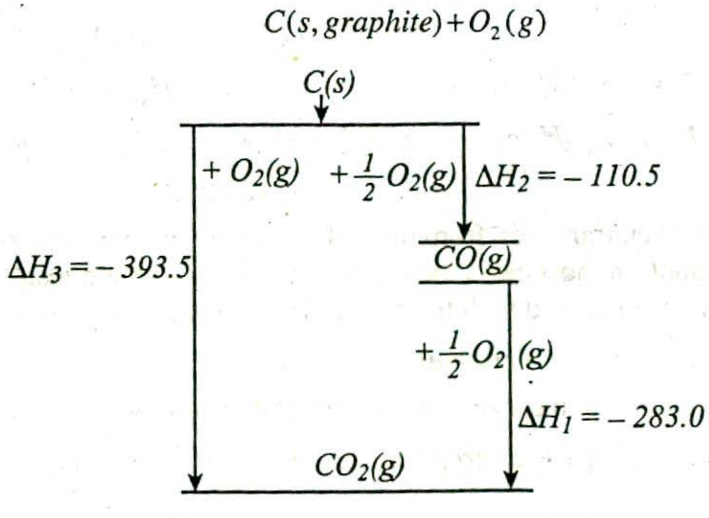
These enthalpy changes can be used to determine the enthalpy change for reaction (6.5). We can reverse reaction (6.7) to get equation (6.8).

$$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) \qquad \Delta H_2^0 = +283.0\,kJ \tag{6.8}$$

Equation (6.8) can be added to equation (6.6) to obtain equation (6.5). From Hess's law

$$\Delta H^0 = \Delta H_1^0 + \Delta H_2^0 = -393.5 + 283.0$$
$$= -110.5 \text{ kJ}$$

The above calculation may also be shown graphically by means of energy diagram.



In the above example $CO_2(g)$ can be prepared in two different ways. But the enthalpy changes are same. This method of adding or subtracting several thermochemical reactions is often used to obtain the heat of reactions that have not yet been measured or cannot be measured by direct experimental methods. The calculation of the heat of reaction when sulphuric acid is formed from its elements will illustrate this aspect since sulphuric acid cannot be prepared by simply mixing sulphur, oxygen and hydrogen. The following four reactions, all easily carried out in a calorimeter, will yield the necessary data for the calculation.

$$
\begin{array}{ll}
S(s) + O_2(g) \rightarrow SO_2(g); & \Delta H^0 = -296.9 \text{ kJ} \\
SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow SO_3(g); & \Delta H^0 = -98.3 \text{ kJ} \\
SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l); & \Delta H^0 = -130.3 \text{ kJ} \\
H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l); & \Delta H^0 = -285.9 \text{ kJ} \\
\hline
S(s) + H_2(g) + 2O_2(g) \rightarrow H_2SO_4(l); & \Delta H^0 = -811.4 \text{ kJ}
\end{array}
$$

Example 6.5: Ethene and ethane are by-products from cracking of crude oil. The enthalpy change at 25°C for the reaction of graphite and hydrogen gas to form ethene is 52.3 kJ mol^{-1} and to form ethane is – 84.7 kJ mol^{-1} respectively. Calculate the ΔH^0_R for the hydrogenation of ethene to give ethane.

Solution: The reaction of interest is, $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$; $\Delta H^0_R = ?$

Given that:

$$2C(graphite) + 2H_2(g) \rightarrow C_2H_4(g); \quad \Delta H^0_{R(A)} = +52.3 \; kJ\,mol^{-1} \quad (A)$$

$$2C(graphite) + 3H_2(g) \rightarrow C_2H_6(g); \quad \Delta H^0_{R(B)} = -84.7 \; kJ\,mol^{-1} \quad (B)$$

If we subtract reaction (A) from (B),

$$\{2C(graphite) + 3H_2(g)\} - \{2C(graphite) + 2H_2(g)\}$$

$$\rightarrow \{C_2H_6(g) - C_2H_4(g)\}$$

$$\text{Or, } \{H_2(g) \rightarrow C_2H_6(g) - C_2H_2(g; \quad \Delta H^0_R = \Delta H^0_{R(B)} - \Delta H^0_{R(A)}$$

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g); \quad \Delta H^0_R = -84.7 - (+52.3) \; kJ\,mol^{-1}$$

$$= -137.0 \; kJ\,mol^{-1}$$

The heat evolved when transition from one solid form to another takes place, i.e., the heat of transition, cannot, in most cases, be measured directly as the transitions are slow processes. These can be calculated with the help of Hess's law. Consider the transition

$$C(diamond) \rightarrow C(graphite)$$

For the decomposition of carbon dioxide to form graphite and oxygen we have :

$$CO_2(g) \rightarrow O_2(g) + C(graphite, s); \quad \Delta H° = 393.5 \text{ kJ}$$

The heat of combustion of diamond is obtained from

$$C(diamond) + O_2(g) \rightarrow CO_2(g); \qquad \Delta H° = -395.4 \text{ kJ}$$

For the transition, diamond → graphite, it follows that

$$C(diamond) \rightarrow C(graphite); \qquad \Delta H° = -1.89 \text{ kJ}$$

6.7 Heat of Formation

'The standard heat of formation of a compound is defined as *the change in heat content, ΔH, when one mole of the substance is formed from its elements in their most stable form in their standard states'.*

In calculating heats of formation the enthalpies of the elements in their standard states are arbitrarily taken as zero. For example, in the reaction

$$C(graphite) + O_2(g) \rightarrow CO_2(g); \qquad \Delta H° = -393.5 \text{ kJ}$$

it is implied that the heat of formation of carbon dioxide is – 393.5 kJ, because 393.5 kJ of heat is evolved when one mole of carbon dioxide gas is formed at 1 atmosphere pressure and 25°C from carbon (graphite) and oxygen under the same conditions. As the heat of formation of a compound is the difference between the heat content of the compound and that of its elements and since the heat of its element (graphite and oxygen in the above example) is taken as zero by convention, it follows that the heat of formation of the compound is equal to its heat content.

The standard heats of formation of many organic and inorganic compounds have been compiled. A few of them are given in Table 6.3.

Table 6.3 Heat of formation of some compounds at 25°C in kJ mol^{-1}

Substance	$\Delta H°_F$	Substance	$\Delta H°_F$
$H_2O(g)$	– 241.8	$AgBr(s)$	– 99.5
$H_2O(l)$	– 285.9	$NaCl(s)$	– 411.0
$HF(g)$	– 269.9	$CH_4(g)$	– 74.9
$HCl(g)$	– 92.3	$C_2H_6(g)$	– 84.7
$HBr(g)$	– 36.2	$C_3H_8(g)$	– 104.1
$HI(g)$	+ 25.9	$n\text{-}C_4H_{10}(g)$	– 124.7
$H_2S(g)$	– 20.2	$iso\text{-}C_4H_{10}(g)$	– 131.6
$SO_2(g)$	– 297.5	$n\text{-}C_5H_{12}(g)$	– 148.4
$SO_3(g)$	– 395.2	$n\text{-}C_6H_{14}(g)$	– 167.2
$C_2H_4(g)$	+51.9	$C_2H_2(g)$	+ 227.0
$NH_3(g)$	– 46.2	$C_6H_6(g)$	+ 82.9
$CO(g)$	– 110.5	$C_6H_6(l)$	+ 49.0
$CO_2(g)$	– 393.5	$CH_3OH(l)$	– 238.6
$Fe_2O_3(s)$	– 824.2	$C_2H_5OH(l)$	– 277.7
$Al_2O_3(s)$	– 1669.8	$HCOOH(l)$	– 409.2
$AgCl(s)$	– 127.0	$CH_3COOH(l)$	– 487.0

The heats of formation data are very useful in calculating enthalpy changes of reactions which are difficult to measure directly. The change in enthalpy ΔH of a given reaction may be obtained by subtracting the heats of formation, ΔH°_{F}, of the reactant from those of the products.

$$\Delta H^{\circ}_{reaction} = \Sigma(\Delta H^{\circ}_{F})_{products} - \Sigma(\Delta H^{\circ}_{F})_{reactants} \qquad (6.10)$$

In using this formula the number of moles of each of the reactants and products in the balanced equation for the reaction has to be considered.

***Example 6.6*:** Use the heats of formation data for compounds from Table 6.3 to calculate the enthalpy of combustion of *n*-butane.

Solution: The combustion reaction for *n* - butane is as follows:

$$C_4H_{10}(g) + 6\tfrac{1}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O\,(l)$$

n-butane

The heat of formation (using data in Table 6.3) of the reactants = $(-124.7 + 6\tfrac{1}{2}\times 0)$

$$= -124.7 \text{ kJ.}$$

The heats of formation of the products = $4 \times (-393.5) + 5 \times (-285.9)$

$$= -3003.5 \text{ kJ.}$$

The heat of the above combustion reaction, i.e., the heat of combustion of *n*-butane, is

$$\Delta H^{\circ}_{comb} = \Sigma(\Delta H^{\circ}_{F})_{products} - \Sigma(\Delta H^{\circ}_{F})_{reactants}$$

$$= -3003.5 - (-124.7) \text{ kJ}$$

$$= -2878.8 \text{ kJ}$$

Heat of formation of a compound may likewise be derived from heat of reaction, provided the heats of formation of all the other substances involved in the reaction are known. The following example will illustrate the point.

Example 6.7: When cane sugar is burnt in oxygen carbon dioxide and water are formed. The thermochemical equation is shown below:

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O\,(l)$$

$$\Delta H^{\circ}_{comb} = -5690.2 \text{ kJ}$$

Calculate the heat of formation of cane sugar.

Solution: The sum of the heats of formation of the products

$$= 12 \times (-393.5) + 11 \times (-285.9) = -7866.9 \text{ kJ}$$

$$\Delta H^{\circ}_{comb.} = \Sigma\, \Delta H^{o}_{F}(products) - \Sigma\, \Delta H^{o}_{F}(reactants)$$

As the heat of formation of oxygen is taken as zero by convention we can use equation (6.10) to write

$$-5690.2 = -7866.9 - \Delta H^{\circ}_{F}\text{ (sucrose)}$$

or $\quad \Delta H^{\circ}_{F}\text{ (sucrose)} = -2176.7 \text{ kJ mol}^{-1}$

6.8 Effect of Temperature on Heat of Reaction: The Kirchhoff Equation

The heat change accompanying chemical or physical processes generally depends on the temperature at which the process takes place. This dependence is mathematically expressed in the form of what is known as Kirchhoff equation after G. R. Kirchhoff (1858) who first developed this equation. The equation may easily be derived with the help of the first law of thermodynamics.

Consider the process in which the reactants in state A at temperature T_1 are converted into products in state B at temperature T_2. Assume that all operations are carried out at constant pressure. The conversion may be carried out in two ways, but according to Hess's law the total heat change must be the same in both cases.

(1) The reactants in state A at temperature T_1 are heated to a temperature T_2. The heat absorbed is $(\Delta T)(C_p)_A$, where $\Delta T = T_2 - T_1$ and $(C_p)_A$ is the heat capacity of the reactants in the state A. The reaction is now allowed to take place at this temperature and the heat change for the process is $(H_B - H_A)_2 = \Delta H_2$.

The total heat change for the process $= (\Delta T)(C_p)_A + \Delta H_2$.

(2) The reactants in state A at temperature T_1 are converted to products in state B at the same temperature. The heat content change $= (H_B - H_A)_1 = \Delta H_1$. The temperature of the products is then raised from T_1 to T_2 and the heat absorbed is $(\Delta T)(C_p)_B$, where $(C_p)_B$ is the heat capacity of the products.
The total heat change for the process $= (\Delta T)(C_p)_B + \Delta H_1$.
From Hess's law

$$(\Delta T)(C_p)_A + \Delta H_2 = (\Delta T)(C_p)_B + \Delta H_1$$

or

$$\Delta H_2 - \Delta H_1 = [(C_p)_B - (C_p)_A] \times \Delta T$$

$$= (\Delta C_p)(\Delta T) \tag{6.11}$$

where $\Delta C_p = (C_p)_B - (C_p)_A$

or

$$\frac{\Delta H_2 - \Delta H_1}{\Delta T} = \Delta C_p \tag{6.12}$$

For an infinitesimally small change in temperature one can write

$$\left[\frac{d(\Delta H)}{dT}\right] = \Delta C_p \tag{6.13}$$

Similarly, it may be shown that if the process is carried out at constant volume the relationship is

$$\left[\frac{d(\Delta U)}{dT}\right] = \Delta C_v \tag{6.14}$$

The relationships (6.13) and (6.14) are different forms of the Kirchhoff equation. The equations are useful for calculating the heat of reaction at a given temperature when the value is known at another temperature provided the heat capacities of the reactants and products are also known.

Example 6.8: Calculate the heat of formation of $H_2O(l)$ at 60°C if the heat of formation at 25°C is −285906 J mol^{-1}

The reaction is $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

Solution: The values of the heat capacities as obtained from Table 2.8 are

$$C_p(H_2) = 28.84 \text{ J mol}^{-1} \text{ deg}^{-1}$$
$$C_p(O_2) = 29.47 \text{ J mol}^{-1} \text{ deg}^{-1}$$
$$C_p(H_2O) = 75.24 \text{ J mol}^{-1} \text{ deg}^{-1}$$

Substituting in equation (6.11),

$$\begin{aligned} \Delta H^\circ_{60} &= \Delta H^\circ_{25} + \Delta C_p (333.16 - 298.16) \\ &= -285906 + 35 (75.24 - 28.84 - \tfrac{1}{2} \times 29.47) \\ &= -284.8 \text{ kJ mol}^{-1} \end{aligned}$$

In the Kirchhoff's equations heat capacities have been taken to be independent of temperature. This is not true when the temperature range is large, particularly at low temperature. Refinements to these equations may be made by using relationships which give the variation of heat capacity of a substance with temperature, viz.

$$C_p = a' + b'T + c''T^2 + \ldots\ldots \tag{6.15}$$

where a', b', c' etc. are constants. There should not be any change of state as a result of the change in temperature. Using similar expressions for reactants and products one may obtain

$$\Delta C_p = a + bT + cT^2 + \ldots\ldots. \tag{6.16}$$

This value of ΔC_p may be substituted in equation (6.15) and the resulting equation integrated to obtain the expression

$$\Delta H_2 - \Delta H_1 = a (T_2 - T_1) + \tfrac{1}{2} b(T_2^2 - T_1^2) + \tfrac{1}{3} c(T_2^3 - T_1^3) + \ldots\ldots \tag{6.17}$$

If ΔH^0 is the heat change at absolute zero of temperature $T_1 = 0$ then from the above expression we can write $\Delta H_1 = \Delta H^0$ and equation (6.17) can be written as

$$\Delta H = \Delta H^0 + aT + \tfrac{1}{2} bT^2 + \tfrac{1}{3} cT^3 + \tag{6.18}$$

A similar expression may be derived for heat of reaction at constant volume.

6.9 Enthalpy of Solution

If some ammonium chloride or glucose is added to water in a test tube the tube becomes cooler. On the other hand if some solid NaOH is added to the test tube the water becomes quite warm. These are examples of a common experience that when solids are dissolved in water heat is either absorbed or evolved. In most cases heat is absorbed so that the solution is cooler than what the solvent was before the addition of the solid. Like other enthalpy changes heat change for the solution process is defined as

'The enthalpy change when 1 mole of substance is completely dissolved in water'. Two examples are given below:

$$Na^+OH^-(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) \quad \Delta H = -40 \text{ kJ mol}^{-1}$$

$$NH_4^+NO_3^-(s) + H_2O(l) \rightarrow NH_4^+(aq) + NO_3^-(aq) \quad \Delta H = +26 \text{ kJ mol}^{-1}$$

Heat of solution, however, depends on the concentration of the resulting solution. For example, the heat of solution of 1.0 mole of $NaOH$ in 5 moles of water and in 200 moles of water are respectively – 37.8 and – 42.3 kJ. The heat of solution is, therefore, *more correctly* defined as

'The change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent'.

The enthalpy change in this case is termed as *integral heat of solution.* Another enthalpy term used is *differential enthalpy of solution.* The distinction between the two quantities can be shown by the following example.

Suppose we make up a solution of 5 moles of KNO_3 in 1000 *g* of water. This can be carried out in two ways. In the first process 5 moles of the salt is added to 1000 *g* of water and the heat change is measured. If we divide the heat change by 5 we obtain the heat change for solution of 1.0 mole of the salt in 1000 *g* of water. This quantity is named the *integral heat of solution.* In the second process 1.0 mole of the salt is added to 1000 *g* of water and the heat change is measured. Next another mole of the salt is added to this solution and the heat change is measured. In the third step another mole of the salt is added to the solution just prepared and the heat measured. This is continued until the remaining 2 moles are added, one mole at a time and the heat change measured after each addition of one mole. The sum of the heat changes of the 5 steps in the second process would be the same as for the first process, as the initial and final states are the same in both the cases. The 5 heat changes for the 5 steps would, however, be different. If the number of steps is very large then the heat change for each step is called the *differential heat of solution.* The differential heat of solution is a partial molar quantity. Hence,

'When one mole of a substance is dissolved in a specified quantity of solvent in a large number of steps ***the enthalpy change per mole of solid for each step*** *is called the differential heat of solution'.*

Sometimes it is desirable to define another enthalpy term known as *enthalpy of dilution.* The heat of dilution is the difference between two integral heats of solutions. Considering the previous example of a solution of $NaOH$ in water, the heat of solution of 1.0 mole of $NaOH$ in 5 moles of water and in 200 moles of water are respectively – 37.8 and – 42.3 kJ. Thus, in the above example of enthalpy of solution of $NaOH$ the difference between the two values, – 4.5 kJ, would be the enthalpy of dilution.

On many occasions it is essential to know the enthalpy of solution at infinite dilution. If we keep on diluting a solution by gradual addition of the solvent there will be heat change at each dilution. Finally a stage will come when any further dilution produces no thermal change. This stage is called the state of infinite dilution. The enthalpy of solution at infinite dilution is defined as

'The enthalpy change when one mole of a substance is dissolved in such a large volume of solvent so that any further dilution produces no thermal effect'.

The integral heat of solution reaches a limiting value at infinite dilution. Thus if 1.0 mole of HCl is dissolved in a large volume of water so that no heat change is observed when more water is added one can write

$$HCl(g) + aq \rightarrow HCl(aq) \qquad \Delta H^\circ = -75.1 \text{ kJ}$$

In recording heat of solution data the total heat content change, ΔH, for dissolving 1 mole completely (i.e., when the solution is complete) in a given quantity of solvent is given. Heats of solution of some common compounds are given in Table 6.4.

Table 6.4 Integral heats of solution of some compounds at 298 K

Compound	ΔH° (kJ mol^{-1})
$LiCl$	-17.1
$NaCl$	4.0
KCl	17.2
$CaCl_2$	-82.8
NH_4Cl	15.2
NH_4NO_3	26.2
KNO_3	27.5

6.10 Heat of Neutralization

'The heat evolved when one mole of water is formed by complete neutralization of an acid with a base is called the heat of neutralization'. Heat of neutralization of strong acids by strong bases is approximately constant and is equal to about –57 kJ mol^{-1}.The constancy of the heat of neutralization of strong acids and bases may be simply explained if one recalls that the acid-base neutralization reaction in all cases is a combination of hydrogen ions and hydroxyl ions to form undissociated water, i.e.,

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

According to the theory of electrolytes all strong acids and strong bases are completely ionized in solution. Consider the following neutralization reactions in aqueous solutions:

(a) $Na^+(aq) + OH^-(aq) + H^+(aq) + Cl^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$

(b) $K^+(aq) + OH^-(aq) + H^+(aq) + NO_3^-(aq) \rightarrow K^+(aq) + NO_3^-(aq) + H_2O(l)$

(c) $Na^+(aq) + OH^-(aq) + H^+(aq) + ClO_4^-(aq) \rightarrow Na^+(aq) + ClO_4^-(aq) + H_2O(l)$

In all these cases the net ionic equation for the reactions is

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

One mole of $H^+(aq)$ ions react with one mole of $OH^-(aq)$ ions to form one mol of $H_2O(l)$. Hence the heat of neutralization is the same, i.e., – 57 kJ mol^{-1} of water formed.

If, however, either the acid or the base or both are weak, the heat of neutralization will not be equal to –57 kJ mol^{-1}. This is because of incomplete dissociation of the electrolyte. For example the heat of neutralization of acetic acid by $NaOH$ is – 55 kJ mol^{-1}. This is because part of the heat evolved during neutralization is used up in bringing about dissociation of the weak acid (this is an endothermic process) so that one mole of water is formed Also, since the salt formed will be that of a weak acid or base, hydrolysis will be a complicating factor. Sometimes the heat of ionization may be estimated from the observed heat of neutralization.

Example 6.9 : Estimate the heat of ionization of NH_4OH, given that heat of neutralization of $NH_4OH(aq)$ with $HCl(aq)$ is –51 kJ mol^{-1} of water and heat of neutralization of $NaOH(aq)$ with $HCl(aq)$ is –57 kJ mol^{-1} of water formed.

Solution: When ammonia is neutralized by hydrochloric acid the reaction may be written as

(a) $NH_4OH(aq) + H^+(aq) + Cl^-(aq) \rightarrow NH_4^+(aq) + Cl^-(aq) + H_2O(l);$

$\Delta H_{neut} = -51$ kJ mol^{-1} of water.

since ammonia is only very slightly ionized. The above reaction is really a combination of two reactions, *viz.*,

(b) $NH_4OH(aq) \rightarrow NH_4^+(aq) + OH^-(aq);$ ΔH_i = heat of ionization

(c) $Na^+(aq) + OH^-(aq) + H^+(aq) + Cl^-(aq) \rightarrow Na^+(aq) + Cl^-(aq)\ H_2O(l);$

$\Delta H_{neut} = -57$ kJ mol^{-1} of water

Adding equations (b) and (c) one obtains equation (a)

Hence from Hess's law, $-51 = \Delta H_i - 57$

i.e., $\Delta H_i = -51 + 57 = +6$ kJmol^{-1}

The heat absorbed when 1.0 mole of ammonium hydroxide is dissociated into ions is 6 kJ.

The question of the heat of neutralization of a weak acid by a strong base has another aspect which is worth noting. Acetic acid is only 1 to 2% ionized at room temperature. A lot of energy should be required to bring about complete ionization of one mole of the acid so that one mole of water can be formed by neutralization by the strong base which is already completely ionized in aqueous solution. Therefore, the heat of neutralization of acetic acid by sodium hydroxide should have been much more negative than – 55 kJ mol^{-1} of water. The answer lies in the high enthalpy of hydration of the H^+ ion as soon as it is formed. The hydration process being exothermic the heat absorbed due to ionization of the weak acid is largely compensated and the result is a value which is not much different from the heat of neutralization of a strong acid with a strong base.

6.11 Enthalpy Change during Phase Change

The change from one physical state to another of a substance is associated with energy changes. For examples, melting (or fusion) of a solid, vaporization of a liquid, condensation of vapour, sublimation of solids and freezing of a substance – all involve energy changes. The enthalpy change per mole in each case is given a name.

For example, *the enthalpy change when one mole of a solid is converted into its liquid form at the same temperature is called the enthalpy of melting or enthalpy of fusion. It should be noted that enthalpy of melting is the same as the latent heat of fusion per mole*

Similar definitions are given for *enthalpy of vaporization (latent heat of vaporization per mole), enthalpy of condensation, enthalpy of sublimation* and *enthalpy of freezing.*

6.11.1 Enthalpy of atomization

The conversion of a substance to its gaseous atoms is called atomization.

The standard enthalpy of atomization of an element is the enthalpy change when one mole of isolated gaseous atoms is formed from its element in its standard state at 298K. Enthalpy of atomization is always an endothermic process.

For example, $C(s) \rightarrow C(g) \quad \Delta H° = 715 \text{ kJ mol}^{-1}$

$$\frac{1}{2} I_2(s) \rightarrow I(g) \quad \Delta H° = 74.5 \text{ kJ mol}^{-1}$$

$$\frac{1}{2} Br_2(l) \rightarrow Br(g) \quad \Delta H° = 95.0 \text{ kJ mol}^{-1}$$

Note that in the case of iodine and bromine the atomization enthalpies are not the same as bond enthalpy (*Section 6.12*).

6.12 Calculation of Heat of Reaction: Bond Energy

Reactions between covalent compounds actually involve bond breaking and bond forming. The process of breaking bonds between two atoms to form atoms, molecules or free radicals is endothermic. When the same bond is formed from the species obtained in the breaking process, the same amount of energy will be given out according to the law of Lavoisier and Laplace. If the energies for breaking of covalent bonds between different atoms are known, then these values can be used to calculate the enthalpies of reactions. For this purpose a quantity named bond enthalpy is defined as below:

Bond enthalpy, also called bond dissociation energy, or bond energy, is defined as the energy necessary to break one mole of bonds between two atoms in a gaseous substance to form gaseous atoms or species.

Bond breaking is an endothermic process while bond forming is an exothermic process.

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Bond enthalpy is usually for breaking bonds and is, therefore, positive and expressed in units of kJ mol^{-1}. When the values are stated for 298 K these are referred to as standard bond enthalpy.

Every bond between atoms has its own unique strength or bond enthalpy.

For example, $H_2(g) \rightarrow 2H(g) \quad \Delta H^\circ = 436.0 \text{ kJ mol}^{-1}$

$$N_2(g) \rightarrow 2N(g) \quad \Delta H^\circ = 945 \text{ kJ mol}^{-1}$$

$$O_2(g) \rightarrow 2O(g) \quad \Delta H^\circ = 489.5 \text{ kJ mol}^{-1}$$

An example of a different situation is the breaking four $C-H$ bonds in methane, CH_4. One may consider the breaking of the four $C-H$ bonds one at a time. Enthalpy changes per mole for the four steps are shown below:

$$CH_4(g) \rightarrow CH_3(g) + H(g); \quad \Delta H^\circ = +425 \text{ kJ mol}^{-1}$$

$$CH_3(g) \rightarrow CH_2(g) + H(g); \quad \Delta H^\circ = +470 \text{ kJ mol}^{-1}$$

$$CH_2(g) \rightarrow CH(g) + H(g); \quad \Delta H^\circ = +416 \text{ kJ mol}^{-1}$$

$$CH(g) \rightarrow C(g) + H(g); \quad \Delta H^\circ = +335 \text{ kJ mol}^{-1}$$

Again the enthalpy change for breaking of the first $C-H$ bond in ethane, C_2H_6, is 410 kJ mol^{-1}. For use of bond enthalpy values in enthalpy calculations the average of the bond dissociation enthalpies under different environments are used.

Bond energies have been calculated from information of the heats of dissociation in the case of elements like, hydrogen, oxygen, nitrogen etc. These values are available from a study of the spectra of these compounds. Bond energies may also be calculated from appropriate data obtained from calorimetric and other measurements and use of Hess's law. For example let us calculate the $C-H$ bond energy. The enthalpy change for the following reaction would be the energy necessary to break four $C-H$ bonds.

$$CH_4(g) \rightarrow C(g) + 4H(g)$$

The steps below show how the ΔH for this reaction may be calculated.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \quad \Delta H^\circ = -890.3 \text{ kJ mol}^{-1}$$

$$CO_2(g) \rightarrow C(s) + O_2(g); \quad \Delta H^\circ = +393.5 \text{ kJ mol}^{-1}$$

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g); \quad \Delta H^\circ = +571.8 \text{ kJ mol}^{-1}$$

$$2H_2(g) \rightarrow 4H(g); \quad \Delta H^\circ = +872.0 \text{ kJ mol}^{-1}$$

$$C(s) \rightarrow C(g); \quad \Delta H^\circ = +715.0 \text{ kJ mol}^{-1}$$

$$\text{Add: } CH_4(g) \rightarrow C(g) + 4H(g); \quad \Delta H^\circ = 1662 \text{ kJ mol}^{-1}$$

Hence $C-H$ bond enthalpy = 1662/4 = 415.5 kJ mol^{-1}

Bond enthalpy data for some bonds are given in Table 6.5

Table 6.5 Standard bond enthalpies in kJ mol^{-1}

Bond	Energy	Bond	Energy
$H-H$	436.0	$C-O$	330.5
$C-C$	336.8	$C-Cl$	326.4
$C=O$	724.0	$C-Br$	276.0
$C=C$	606.7	$O=O$	489.5
$C\equiv C$	828.4	$O-H$	460.2
$C-H$	415.5	$N-H$	385.8
$Cl-Cl$	243.0	$Br-Br$	190.0
$H-Cl$	431.0	$H-Br$	368.0

Applications of bond enthalpy data will be discussed in *Section 6.12.1.*

6.12.1 Standard enthalpy of reaction from average standard bond enthalpies

The average standard bond enthalpy data are useful in calculating the standard enthalpy of reactions. As stated earlier, in reactions involving covalent compounds bonds are broken and new bonds are formed. The standard enthalpy of reactions will, therefore, be the difference between the sum of the average standard bond enthalpies of bonds broken and the sum of the standard bond enthalpies of the bonds formed. Mathematically,

$$\Delta H_R^0 = \sum(\text{standard bond enthalpies of bonds broken}) - \sum(\text{standard bond enthalpies of bonds formed}) \qquad (6.19)$$

The calculations of standard enthalpy of reactions from standard bond enthalpy data require two restrictions:

- The method applies only for covalent bonds
- All species must be in the gas phase

Example 6.10: Calculate the ΔH_R^0 when one mole of hydrogen reacts with chlorine to produce hydrogen chloride in the gas phase. Use bond enthalpy from Table 6.5.

Solution: The reaction in question is first written using structural formula,

$$H-H(g) + Cl-Cl(g) \rightarrow 2\,H-Cl(g)$$

Bonds broken		Energy /kJ	Bonds formed		Energy/kJ
$H-H$	1 mole	436.0	$H-Cl$	2 moles	431.0×2
$Cl-Cl$	1 mole	243.0			

So from equation (6.19) we get,

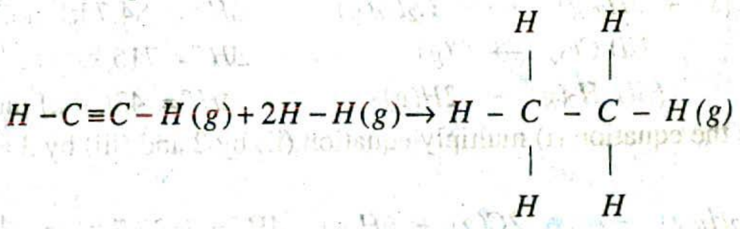
$$\Delta H_R^0 = \Sigma \text{ (standard bond enthalpies of bonds broken)}$$
$$- \Sigma \text{ (standard bond enthalpies of bonds formed)}$$
$$\Delta H_R^0 = (436.0 + 243.0) - (431.0 \times 2)$$
$$= -183.0 \text{ kJ}$$

Example 6.11: Use bond enthalpy data from Table 6.5 to calculate the ΔH_R^0 of the following reaction:

$$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$$

and compare the result with that calculated using ΔH_F^0 from Table 6.3.

Solution: The reaction equation is written below showing all the bonds,



$$H-C\equiv C-H\,(g) + 2H-H\,(g) \rightarrow H-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-H\,(g)$$

Bonds broken		Energy/kJ	Bonds formed		Energy/kJ
$C-H$	2 moles	415.5×2	$C-C$	1 mole	336.8
$C\equiv C$	1 mole	828.4	$C-H$	6 moles	415.5×6
$H-H$	2 moles	436.0×2			

$$\Delta H_R^0 = \Sigma \text{ (standard bond enthalpies of bonds broken)}$$
$$- \Sigma \text{ (standard bond enthalpies of bonds formed)}$$
$$\Delta H_R^0 = (415.5 \times 2 + 828.4 + 436.0 \times 2) - (336.8 + 415.5 \times 6)$$
$$= -298.4 \text{ kJ}$$

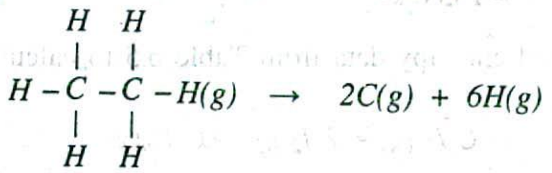
Again ΔH_R^0 can be calculated from ΔH_F^0 values given in Table 6.3. Substituting the appropriate ΔH_F^0 values from equation (6.10) we get,

$$\Delta H_R^0 = \Delta H_F^0\,[C_2H_6(g)] - (\Delta H_F^0\,[C_2H_2(g)] + 2\,\Delta H_F^0\,[H_2(g)])$$
$$= -84.7 - 226.7 - 2(0)$$
$$= -311.4 \text{ kJ.}$$

Note that there is about 3% difference between these two values. The difference arises because in the first case average bond enthalpies have been used. These values may not necessarily be applicable in this example. Calculations using enthalpies of formation are more reliable as these are based on experimental data.

Example 6.12: Calculate the $C-C$ bond enthalpy in ethane, given that
enthalpy of formation of ethane is -84.7 kJ mol^{-1},
enthalpy of sublimation of carbon is $+715.0$ kJ mol^{-1},
enthalpy of dissociation of hydrogen is $+436.0$ kJ mol^{-1},
mean bond enthalpy of $C-H$ bond is $+415.5$ kJ mol^{-1}.

Solution: First we find the enthalpy change for the process



$$H_3C-CH_3(g) \rightarrow 2C(g) + 6H(g)$$

In this process six C – H bonds and one C – C bond have been broken.
From the data given

$$(i)\ 2C(s) + 3H_2(g) \rightarrow C_2H_6(g) \qquad \Delta H^\circ = 84.7 \text{ kJ mol}^{-1}$$

$$(ii)\ C(s) \rightarrow C(g) \qquad \Delta H^\circ = 715 \text{ kJ mol}^{-1}$$

$$(iii)\ H_2(g) \rightarrow 2H(g) \qquad \Delta H^\circ = 436.0 \text{ kJ mol}^{-1}$$

If we reverse the equation (i) multiply equation (ii) by 2 and (iii) by 3 and then add all of them, we get,

$$C_2H_6(g) \rightarrow 2C(g) + 6H(g) \quad \Delta H^\circ = 2822.7 \text{ kJ mol}^{-1}$$

From this enthalpy change we can find $C-C$ bond enthalpy. The energy necessary to break six moles of $C-H$ bonds is 6×415.5 kJ = 2493.0 kJ. Hence the $C-C$ bond energy = 2822.7 – 2493.0 = 329.7 kJ mol^{-1}

6.13 Enthalpy of Ionization or Ionization energy

When an electron is removed from an atom a cation is formed. In this process energy will be absorbed. From an atom the electrons can be removed one by one and each step will be accompanied by absorption of energy. The successive ionization energies are called the first ionization energy, second ionization energy etc. For comparing ionization energies of different elements the following definition is given:

The first ionization energy of an element is the energy required to remove one electron from each of one mole of gaseous atoms to form one mole of unipositively charged gaseous cations. The equation for the process is

$$X(g) \rightarrow X^+(g) + e \qquad \Delta H^\circ = \text{First ionization energy}$$

For elements from left to right in a Period (in the Periodic Table), say from Na to Ar in the third Period, there is an increasing trend of the first ionization energy as the attraction for the outer electron by the nucleus increases. Down a Group the first ionization energy decreases as the outer electrons get farther away from the nucleus of the atom and their attraction by the nucleus decreases due to increasing shielding. The successive ionization energies for a particular element, however, increase as the electrons are removed one by one.

6.14 Electron Affinity

When a neutral atom in the gaseous phase acquires an electron to form a stable anion energy is released. For example

$$Cl\,(g) + e \rightarrow Cl^-\,(g) \qquad \Delta H° = -\text{ve}$$

This happens because an atom like chlorine can attain a stable noble gas configuration by acquiring an electron. To describe this phenomenon a term electron affinity is defined as below:

The first electron affinity of an element is the enthalpy change when each of one mole of atoms of an element in the gaseous phase acquire one electron to form one mole of uninegatively charged gaseous anions. As mentioned this process is exothermic. For oxygen the equation is written as

$$O\,(g) + e \rightarrow O^-\,(g) \qquad \Delta H° = -141 \text{ kJ mol}^{-1}$$

When a second electron is to be acquired by a uninegatively charged anion energy has to be added because the second electron is to be pushed against the repulsion of the already present extra electron in the atom. The second electron affinity of an element is, therefore, endothermic.

$$O^-\,(g) + e \rightarrow O^{2-}\,(g) \qquad \Delta H° = +710 \text{ kJ mol}^{-1}$$

6.14 The Lattice Enthalpy (L.E.)

In an ionic compound the oppositely charged ions are held together by electrostatic forces of attraction. A quantitative measure of the stability of any ionic solid is given by its *lattice energy* or *lattice enthalpy (L.E.)*. The *lattice enthalpy* is defined *as the energy released when 1 mole of ionic crystal is formed from its gaseous ions.*

For an ionic compound *MX* the lattice enthalpy is the energy change in the following reaction:

$$M^{n+}(g) + X^{n-}(g) \rightarrow MX(s) \tag{6.20}$$

It is an exothermic reaction. If, however, we consider the opposite reaction,

$$MX(s) \rightarrow M^{n+}(g) + X^{n-}(g) \tag{6.21}$$

the energy change is termed the *lattice dissociation enthalpy* which is defined as *the energy required to completely separate one mole of a solid ionic crystal into its gaseous ions.*

Lattice dissociation enthalpy (and hence lattice enthalpy) will depend on the attraction between the ions in the ionic crystal. The force of attraction between ions is directly proportional to the product of the charges on the ions and inversely proportional to the square of the distance between the centres of the two ions when they are closest to each other. If Q_1 and Q_2 are the charges and r is the distance apart then

$$\text{The force of attraction} \quad \propto \frac{Q_1 Q_2}{r^2} \qquad (6.22)$$

By applying Coulomb's law it is possible to calculate the lattice enthalpy of simple ionic compounds. Direct experimental measurement of lattice enthalpy is difficult. It is also possible to calculate lattice enthalpies from a thermochemical **'cycle'** known as *Born-Haber Cycle* after two German scientists Max Born and Fritz Haber who developed this cycle. The cycle is based on Hess's law of constant heat summation.

To obtain the lattice enthalpy of $RbCl$ one might think of two routes. One route would be to heat Rb and Cl_2 gas together to prepare one mole of $RbCl$. Enthalpy change for the process would be the enthalpy of formation, ΔH_F, of $RbCl$ which has a value of -431 kJ mol^{-1}. The other route consists of several steps:

B. Conversion of solid rubidium directly into vapour.

C. Dissociation of ½ mole of Cl_2(g) into 1.0 mole of separate gaseous Cl atoms.

D. Ionization of 1.0 mole of gaseous Rb atoms

E. Addition of 1.0 mole of electrons to 1.0 mole of Cl atoms.

F. Combination of 1.0 mole of gaseous Rb^+ ions with 1.0 mole of gaseous Cl^- ions to form 1.0 mole of solid $RbCl$.

Step A. It is the *sublimation* of rubidium. The ΔH_1^0 of sublimation of rubidium is $+86$ kJ mol^{-1}.

Step B. It is the *enthalpy of atomization* of chlorine and is equal to half of $Cl-Cl$ bond energy. The value is + 244/2, or + 122 kJ energy, e.g. $\Delta H_2^0 = +122$ kJ

Step C. Represents the *first ionization energy* of rubidium. The ΔH_3^0 for ionization is $+408$ kJ mol^{-1}.

Step D. It is the *electron affinity* of chlorine and ΔH_4^0 is -349 kJ mol^{-1}.

Step E. This is the *lattice enthalpy* of RbCl. Let the value be *L.E.*

From Hess's law $\quad \Delta H_F = \Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0 + \Delta H_4^0 + L.E.$

Substituting values $\quad -431 = 86 + 122 + 408 - 349 + L.E.$

Hence $\quad L.E. = -431 - 86 - 122 - 408 + 349$

$$= -698 \text{ kJ mol}^{-1}.$$

This can be summed up in schematic form as shown in Figure 6.2 for $RbCl$.

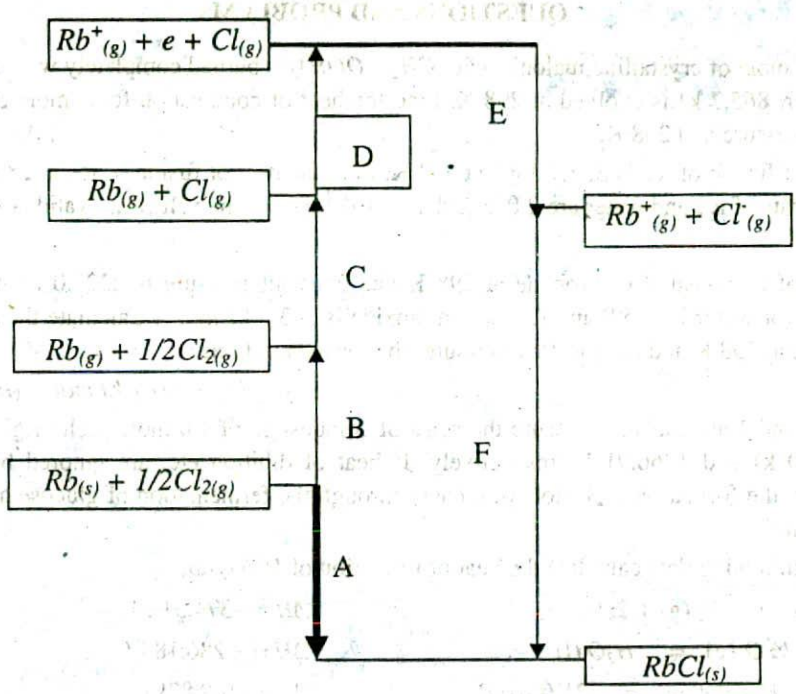


Figure 6.2 Born-Haber Cycle for $RbCl$

The lattice enthalpies of several ionic compounds are given in Table 6.6

Table 6.6 Lattice enthalpies of several ionic compounds

Compound	Lattice enthalpy/kJ mol^{-1} (Born-Haber Cycle)
$NaCl$	–771
$NaBr$	–719
NaI	–699
NaF	–918
KCl	–718
KBr	–656
KI	–615
NaF	–918
CsF	–747
MgO	–3791
BaO	–3054
$AgCl$	–921
$AgBr$	–876

QUESTIONS AND PROBLEMS

1. When one mole of crystalline malonic acid, $CH_2(COOH)_2$ is burned completely with oxygen in a bomb calorimeter, 865.7 kJ is evolved at 298 K. Find the heat of combustion for 1 mole of malonic acid at constant pressure and 298 K. *[Ans. –863.5 kJ mol^{-1}]*
2. The heat of fusion of ice is 333.1 J g^{-1} at 273 K. Find the heat of fusion of ice at 283 K if the average specific heats of ice and water are 2.066 and 4.22 J K^{-1} g^{-1}; all the values are valid at 1 atmosphere. *[Ans. –311.5 J]*
3. The heat of combustion of propane at 298 K and constant pressure is 2220.0 kJ mol^{-1}; the heat of formation for water is 285.9 and for carbon dioxide is 393.5 kJ mol^{-1}. Calculate the heat of formation of propane at 298 K and (a) constant pressure, (b) constant volume. *[Ans. (a) – 104.1 kJ mol^{-1}; (b) – 94.2 kJ mol^{-1}]*
4. At 291 K and 1 atmosphere pressure the heats of combustion of 1.0 mole each of glucose and ethanol are 2820.0 kJ and 1366.91 kJ respectively. If heat of dilution etc. are ignored how much heat is evolved by the formation of 1 mole of ethanol through the fermentation of glucose at this temperature and pressure? *[Ans. 43.09 kJ]*
5. From the following data calculate the heat of formation of $HNO_2\ aq$.

   $NH_4NO_2\,(s) = N_2\,(g) + 2H_2O\,(l)$ $\Delta H = -374.51$ kJ

   $H_2\,(g) + \tfrac{1}{2}\,O_2(g) = H_2O\,(l)$ $\Delta H = -\ 286.18$ kJ

   $N_2\,(g) + 3H_2\,(g) + aq = 2NH_3\,(aq)$ $\Delta H = -169.87$ kJ

   $NH_3\,(aq) + HNO_2\,(aq) = NH_4NO_2\,(aq)$ $\Delta H = -\ 38.07$ kJ

   $NH_4NO_2 + aq = NH_4NO_2\,(aq)$ $\Delta H = +\ 20.08$ kJ *[Ans. – 54.2 kJ]*
6. The heats of solution of Na_2SO_4; $Na_2SO_4.\ H_2O$ and $Na_2SO_4.10\ H_2O$ are respectively –1924.64, 7949.6 and 78491.84 Joules. Calculate the heats of hydration of Na_2SO_4 to (a) monohydrate and (b) decahydrate. *[Ans. (a) – 9.87 kJ, (b) –80.43 kJ]*
7. The heat of combustion of naphthalene (molar mass 128) is –5138.8 kJ mol^{-1}. When 0.250 g of naphthalene is burnt in the calorimeter the temperature rises by 1274.95 K. What is the total heat capacity of the calorimeter? *[Ans. 5141.2 J K^{-1}]*
8. The standard heat of hydrogenation of gaseous propylene to propane is –123.84 J and the standard heat of combustion of propane is –2218.0 kJ at 298K. Calculate (a) the standard heat of formation and (b) standard heat of combustion of propylene if the standard heats of formation of CO_2 (g) and $H_2O\ (l)$ are respectively –393.5 kJ and –285.9 kJ mol^{-1}. *[Ans. (a) – 19.74 kJ; (b) – 2057.9 kJ]*
9. The heats of formation of $SO_2\ (g)$ and $H_2O\ (l)$ are –297.5 kJ and –285.9 kJ mol^{-1} respectively and the heat of combustion of H_2S is –571.9 kJ mol^{-1}. Calculate the heat of formation of H_2S. *[Ans. –11.50 kJ]*
10. Calculate the standard enthalpy of reaction for the formation of one mole of dichloroethane from a reaction between ethylene and chlorine, when all species are in the gas phase. *[Ans. – 151 kJ]*
11. Calculate the molar heat of combustion when benzoic acid $(C_6H_5CO_2H)$ was found to release 3225.60 kJ mol^{-1} of heat after complete combustion in a bomb calorimeter.

    (Hint: Use $\Delta H = \Delta U + \Delta nRT$, assume ideal behaviour). [Ans. – 3226.8 kJ mol^{-1}]
12. Calculate the enthalpy of formation of CO from the following data:

    $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -\ 393$ kJ

    $CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H = -\ 283$ kJ [Ans. – 110 kJ]

13. Using bond enthalpy data calculate the enthalpy of reaction when one mole of ethanol reacts with oxygen to form acetic acid and water at 298 K. [Ans. – 492 kJ]

14. Use the bond enthalpy data to calculate the amount of heat released per mole of acetylene in a torch where acetylene is burned in oxygen to form carbon dioxide and water. [Ans. – 897 kJ mol^{-1}]

15. Calculate the standard enthalpy change for the gas phase reaction between hydrogen and iodine at 298 K, given that the standard enthalpy of formation of HI(g) and standard enthalpy of sublimation of $I_2(s)$ are 26.48 and 62.44 kJmol^{-1} respectively. [Ans. – 9.48 kJ mol^{-1}]

16. Calculate the standard enthalpy of the reaction, $3C_2H_2(g) \rightarrow C_6H_6(g)$ from the standard enthalpy of formations of $C_2H_2(g)$ and $C_6H_6(g)$. [Ans. – 597.20 kJ mol^{-1}]

17. Calculate the standard enthalpy of the following reaction:

$$3Fe_2O_3(s)+2NH_3(g)\rightarrow 6FeO(s)+H_2O(l)+N_2(g)$$

The enthalpy of formations of Fe_2O_3 (s), NH_3 (g), FeO (s) and $H_2O(l)$ are – 824.2, – 46.1, –266.3 and –285.9 kJ mol^{-1} respectively. [Ans. +109.6 kJ mol^{-1}]

18. Calculate ΔH for the following reaction:

$$N_2O(g)+NO_2(g)\rightarrow 3NO(g)$$

Use the enthalpies reactions listed below:

$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$ $\quad \Delta H = -56.6$ kJ

$N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g)$ $\quad \Delta H = -81.6$ kJ

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$ $\quad \Delta H = +90.4$ kJ [Ans. + 155.8 kJ]

19. Using bond enthalpy values from Table–

    (a) calculate the enthalpy change for the reaction

    $2C(g) + 2H_2(g) + Br_2(g) \rightarrow CH_2BrCH_2Br(g)$

    (b) The standard enthalpy change for this reaction is –37.8 kJ. Explain the difference

20. (a) Define the term Lattice Enthalpy.

    (b) State two properties of ions which affect the values of lattice enthalpy of ionic compounds.

    (c) Calculate the lattice enthalpy of $LiCl(s)$ from the following data:

	kJ mol^{-1}
Enthalpy of formation of $LiCl(s)$	– 409
Enthalpy of atomization of $Li(s)$	+ 161
Enthalpy atomization of $Cl(g)$	+ 122
1st ionization of $Li(s)$	+ 519
Electron affinity of $Cl(g)$	– 349

[Ans. 852 kJ mol^{-1}]

Explain whether the enthalpy of atomization of potassium would be greater or less than that of lithium.

    (d) The calculated lattice enthalpy of $AgCl$ is –833 kJ mol^{-1} whereas the experimental value is –905 kJ mol^{-1} . Explain the difference.

21. Consider the reaction

$CH_3CH_2COOH(g) + C_2H_5OH(g) \rightarrow CH_3CH_2COOC_2H_5(g) + H_2O(g)$

Using bond enthalpies C – O = 358 kJ mol $^{-1}$ and O – H = 464 kJ mol $^{-1}$ show that $\Delta H = 0$ for the reaction.

22. Buta – 1,3 – diene reacts with hydrogen as follows:

$CH_2 = CH– CH = CH_2(g) + H_2(g) \rightarrow CH_3\,CH_2\,CH_2\,CH_3(g)\,;\ \Delta H = -237$ kJ mol^{-1}

(a) Use bond enthalpies from the Table6.5 to calculate C – C bond enthalpy.

[Ans. C – C bond enthalpy = 320.2 kJ mol^{-1}]

(b) Explain why this value is different from the average bond enthalpy = +330.6 kJ mol^{-1}

23. The standard enthalpy of neutralization (kJ mol^{-1}) of some acids with sodium hydroxide is tabulated below:

Propionic acid CH_3CH_2COOH	-51
Hydrocyanic acid, HCN	-12
Hydrochloric acid, HCl	-57
Nitric acid, HNO_3	-57

(a) Why are the values the same for HCl and HNO_3

(a) Why is the value for HCN so very different ?

24. (a) Define enthalpy of atomization.

(b) Draw a Born Haber cycle for the formation of $MgO(s)$.

(c) Calculate the lattice enthalpy of MgO using the following data and the Born Haber cycle.

$\Delta H_{formation}$ of $MgO = -602$ kJ mol^{-1}

$\Delta H_{sublimation}$ of $Mg = +150$ kJ mol^{-1}

$\Delta H_{atomization}$ of $Oxygen = +249$ kJ mol^{-1}

1st and 2nd Ionization Energy of $Mg = +2186$ kJ mol^{-1}

1st and 2nd Electron Affinity of $O = +657$ kJ mol^{-1} [Ans. $L.E.$ = – 3844 kJ mol^{-1}]

25. Draw a Born –Haber cycle for the formation of $SrCl_2(s)$ to determine the lattice enthalpy of the compound using the following data:

$\Delta H_{formation}$ of $SrCl_2 = -829$ kJ mol^{-1}

$\Delta H_{sublimation}$ of $Sr = +164$ kJ mol^{-1}

$\Delta H_{atomization}$ of $Cl = +122$ kJ mol^{-1}

1st Ionization Energy of $Sr = +550$ kJ mol^{-1}

2nd Ionization Energy of $Sr = +1064$ kJ mol^{-1}

Electron Affinity of C l= -349 kJ mol^{-1} [Ans. – 2153 kJ mol^{-1}]

7

THERMODYNAMICS II : SECOND AND THIRD LAWS

7.1 Necessity of the Second Law

The first law of thermodynamics treats the universe as a closed system and states that the amount of matter and energy in the universe is constant. It also states that different forms of energies are interconvertible and establishes an exact relationship between heat and work. The law states that heat and mechanical work both are interconvertible. The law, however, does not give us any idea about the *conditions under which this conversion is possible*, and *the limitations associated with this conversion*. Thus, the first law of thermodynamics does not tell us *how much heat energy is converted into work* and also the *direction* and *extent* of energy transformation.

The second law of thermodynamics, among other things, gives information as to the conditions under which heat can be converted to other forms of energy or work and the limitations that govern such conversions.

Experience shows that there is a difference between heat energy and other forms of energy. All other forms of energy can be converted entirely into heat , but heat cannot be converted completely into other forms of energy.

7.2 Spontaneous and Non- spontaneous Processes

Spontaneous process: A process that takes place without any outside influence is called a spontaneous process. All natural processes are spontaneous. Rivers run from the mountains to the sea; water freezes at or below 0°C; trees bear fruit and then die; heat flows from a hot body to a cooler body; a dissolved solute diffuses from a region of high concentration to a region of low concentration; a gas expands from high pressure to a low pressure. All these are examples of spontaneous processes that take place in nature without any outside influence.

The spontaneous natural processes are used by man to obtain useful work. Thus, in a hydroelectric project the falling water turns the blades of the generator which produces electricity; an expanding gas pushes the piston in a motor car or a steam engine. Spontaneous processes are abundant in nature. It may be observed that as a result of a spontaneous process a system loses its ability to do work. Hence although the total energy of the universe remains constant its availability diminishes.

Spontaneous processes are not reversible as at no stage of the process equilibrium is obtaining except at the final stage; in other words natural processes are irreversible. In a reversible process the system is at equilibrium at all stages so that an infinitesimal increase in the tendency opposing the process will bring about its reversal.

Non-spontaneous process : Non-spontaneous processes are those that do not take place by themselves. Examples are the reverse of spontaneous processes: water does not flow from a lower level to a higher level; heat does not flow from a cold body to a hot body; solute particles in a solution do not gather together in one part of the solution etc. Non-spontaneous processes can be carried out by supplying work or heat. For example water can be lifted from a lower level to a higher level by people or by mechanical means; in a refrigerator heat is transferred from the cold area inside it to the hot area outside it; gases can be compressed to smaller volume etc. As pointed out all these are performed by external help. Discussion of the second law of thermodynamics will lead to the understanding of the spontaneous and non-spontaneous processes.

7.3 Heat Engine

Heat engine is a machine which converts *thermal energy into work.* The discovery of heat engine played a crucial role in many technological developments that include, among others, automobile engines and steam turbines to run generators to produce electricity. A schematic diagram of a heat engine is shown in Figure 7.1.

In a heat engine heat energy q_2 is absorbed from a hot reservoir at temperature T_2. The engine does work w (w is negative as work is done by the engine or the system) and discards the remaining heat q_1 (q_1 is negative as heat is given out) to the cold reservoir at temperature T_1. In thermodynamic terms, the hot reservoir is called a *'Source'* and the cold reservoir is called a *'Sink'*. To repeat the process, the engine must be returned to the initial temperature T_2, and the steps followed in sequence, and we say that it completes a *'cycle'*. However, in order to evaluate the usefulness of a heat engine a quantity, known as *'Efficiency'* (E) of the engine, is defined. The efficiency is defined as,

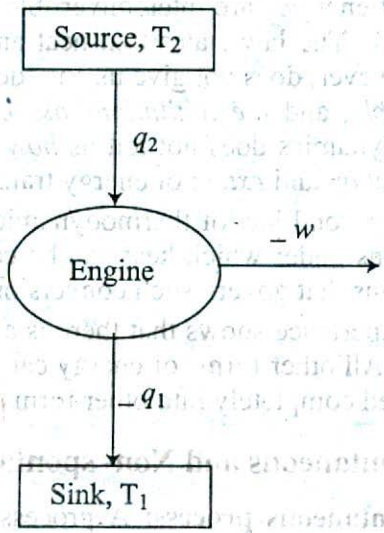


Figure 7.1 Schematic diagram of a heat engine

'The ratio of work done to the quantity of energy supplied'.

Mathematically,

$$E = \frac{Energy\ out}{Energy\ in} = \frac{Work\ done}{Energy\ supplied} = \frac{Heat\ input - Heat\ discharged}{Heat\ supplied} \qquad (7.1)$$

$$E = \frac{q_{T_2} - q_{T_1}}{q_{T_2}} \qquad (7.2)$$

From detailed analysis of the reversible Carnot cycle (*Section7.5*) Lord Kelvin later concluded that the quantities of heat for a reversible Carnot engine are proportional to absolute temperature. Thus, equation (7.2) can be written as,

$$E = \frac{T_2 - T_1}{T_2} \qquad (7.3)$$

It may, therefore, be concluded that the efficiency of a reversible heat engine is dependent on the temperatures of the *source* and the *sink*. High efficiency is obtained when $T_2 >> T_1$ and 100% efficiency is predicted when $T_1 = 0$. But in practice 100% efficiency can never be obtained, since there is always some unavailable energy.

Example 7.1: What is the efficiency of a reversible cyclic engine operating between temperatures 20^0C and 500^0C?

Solution: $T_2 = 273 + 500 = 773$ and $T_1 = 273 + 20 = 293$

Using equation (7.3) we get,

$$E = \frac{T_2 - T_1}{T_2} = \frac{773 - 293}{773} = 0.620$$

Example 7.2: A steam engine operates between temperature 125^0C and a sink temperature of $T_1{}^0$C. If the efficiency of the engine is 0.239, calculate the temperature of the sink.

Solution: $T_2 = 273 + 125 = 398$

According to equation (7.3), $E = \frac{398 - T_1}{398}$

$$\text{or} \qquad 398 \times E = 398 - T_1$$

$$\text{or} \qquad T_1 = 398 - 398 \times 0.293$$

$$= 281.4 \text{ K}$$

7.4 Statement of the Second Law

The second law has been stated in many ways which may appear to be different. However, these various statements are all rephrasing of the same fundamental concept. The definitions are,

(1) It is impossible to construct a machine functioning in cycles which can convert heat completely into the equivalent amount of work without producing changes elsewhere.

(2) Heat cannot pass from a colder to a hotter body without some other change occurring at the same time.

It must again be pointed out that these statements summarize the experience of many men over a long period of time. Except perhaps in submicroscopic phenomena no exceptions to this law have ever been found. In fact, men have tried, without success, to construct a machine by means of which heat could be completely converted into work. It is not to be concluded that the machine is at fault, or men have not been clever enough to construct a perfect machine of the desired type; rather the conclusion has been reached that owing to some peculiar property of heat energy itself there are certain limitations on the direction of flow or the extent of its convertibility into work. However, the second law provides a quantitative relationship giving the maximum fraction of an amount of heat which can be converted into work. The relationship may be derived with the help of an imaginary process devised by the French engineer S. Carnot (1824) and known as the Carnot cycle.

7.5 The Carnot Cycle

The Carnot cycle represents the operation of an idealized engine in which heat is transferred from a '*source*' at high temperature T_2, partly converted into *work* (w) and partly discarded into a '*sink*' at low temperature T_1. The operation is best illustrated with one mole of ideal gas as the working substance in the engine. The engine works in cycles, and at the end of each cycle the working substance is returned to its original state. The engine would operate by continually repeating this cycle.

As the working substance in the engine is brought back to its original state at the end of each cycle, the change in internal energy of the gas is zero for each cycle. According to the first law, then, the amount of heat absorbed during the cycle is equal to the sum of all the work done. The cycle is considered to consist of four reversible steps in the order stated, namely,

Step 1: Isothermal expansion at temperature T_2
Step 2: Adiabatic expansion to temperature T_1
Step 3: Isothermal compression at temperature T_1 and
Step 4: Adiabatic compression back to the original temperature T_2

Each step is performed reversibly, i.e. the pressure of the gas is only infinitesimally different from the pressure exerted on it and the heat flow is infinitesimally slow. The cycle is represented most conveniently by a pressure–volume diagram, as shown in Figure 7.2.

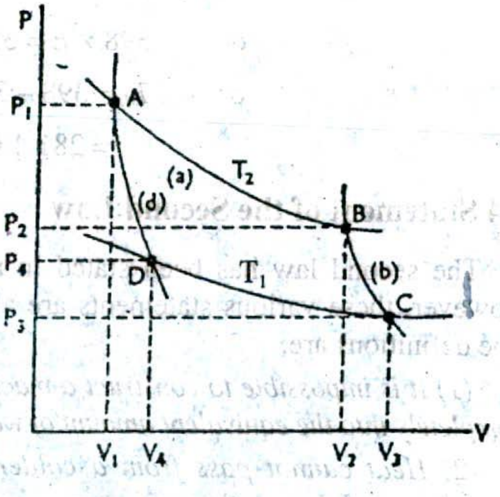


Figure 7.2 The Carnot Cycle on a P-V diagram.

One mole of the gas is placed in a cylinder fitted with a weightless, frictionless piston. The cylinder is a good conductor of heat. Two constant temperature heat reservoirs, one maintained at T_2 and the other at T_1 are provided. A thermally insulated vessel into which the cylinder fits is also provided. At the beginning let the pressure of the gas be P_1, its volume V_1, at the temperature T_2. The cycle is now completed in the following four steps.

Step 1: The cylinder is placed in the heat reservoir at temperature T_2 and the gas allowed to expand isothermally and reversibly until its pressure and volume change from P_1 and V_1 to P_2 and V_2 respectively. The gas absorbs heat from the reservoir and performs work w_1. For this step:

Heat absorbed = q_2, and since the gas is ideal and expands isothermally, $\Delta U = 0$.

$$work = w_1 = -RT_2 \ln \frac{V_2}{V_1} \tag{7.4}$$

Step 2: The cylinder containing the gas at a pressure P_2, volume V_2 and temperature T_2 is now placed in the insulated vessel and further expanded adiabatically to a volume V_3 when the pressure falls to P_3. The temperature of the gas falls to T_1, as the temperature falls during an adiabatic expansion. Let the work done by the gas as a result of this expansion be w_2. Since the cylinder is placed in an insulated vessel no heat is absorbed, i.e. $q = 0$. In this step

$$Work\ done = w_2 = \Delta U = \int_{T_2}^{T_1} C_V\, dT = C_V(T_1 - T_2) \tag{7.5}$$

or,

$$w_2 = C_V(T_1 - T_2) \qquad \text{7.5a)}$$

Step 3: The cylinder is now placed in the heat reservoir at T_1 and the gas is compressed adiabatically and reversibly from volume V_3 to volume V_4, the pressure changing from P_3 to P_4. An amount of work w_3 is done on the gas by the piston, and an amount of heat q_1 is given out by the gas to the reservoir at temperature T_1. In this step

Heat change = q_1 (q_1 is a negative quantity, since heat is given out)

$$w_3 = -RT_1 \ln \frac{V_4}{V_3} \tag{7.6}$$

$\Delta U = 0$, since the process is isothermal

Step 4: The cylinder of gas, now at temperature T_1, is again placed in the insulated vessel. The gas is compressed adiabatically and reversibly from volume V_4 to the original volume V_1; the temperature rises to T_2 and the pressure changes from P_4 to P_1. An amount of work, w_4, is done on the gas and no heat is given out or absorbed, i.e. $q = 0$. Now the gas is in the same state as at the start of *Step 1*. For this step:

Heat change $q = 0$,

$$w_4 = \Delta U = \int_{T_1}^{T_2} C_V\, dT = C_V(T_2 - T_1) \tag{7.7}$$

The cycle is now complete as the gas has returned to its original state. The total work done by the gas during the cycle is

$$W_{total} = w_1 + w_2 + w_3 + w_4 \tag{7.8}$$

Also w_2 and w_4, being numerically equal but opposite in sign, cancel each other. The net work done by the system is, therefore,

$$W_{net} = w_1 + w_3 \tag{7.9}$$

$$= -RT_2 \ln \frac{V_2}{V_1} + \left(-RT_1 \ln \frac{V_4}{V_3}\right)$$

$$= -RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_4}{V_3}$$

$$\text{Or,} \quad -W_{net} = -RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3} \tag{7.10}$$

It can be seen from Figure 7.2 that V_1 and V_4 lie on one adiabatic curve, while V_2 and V_3 lie on another curve. It can be shown by applying temperature-volume relationship for adiabatic processes that,

$$\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1} \text{ and } \left(\frac{V_4}{V_1}\right)^{\gamma-1} = \frac{T_2}{T_1}$$

Combining these two equations we get,

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}, \qquad \text{or} \qquad \frac{V_4}{V_3} = \frac{V_1}{V_2} \tag{7.11}$$

On substitution of equation (7.11) into equation (7.10) and rearranging we get,

$$\text{Or,} \quad -W_{net} = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

$$\text{So,} \quad -W_{net} = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_1}{V_2}$$

$$\text{Or,} \quad -W_{net} = RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_2}{V_1}$$

$$\text{Hence,} \quad -W_{net} = R(T_2 - T_1) \ln \frac{V_2}{V_1} \tag{7.12}$$

Since this is a positive quantity (with the sign convention as given in *Section 5.2.5)*, equation (7.12) gives the net amount of work produced per cycle. In other words heat is being converted into work.

Again, in *Step 1*, the work done is equal to heat absorbed q_2, i.e.,

$$q_2 = RT_2 \ln \frac{V_2}{V_1} \tag{7.13}$$

From equations (7.13) and (7.4) one obtains,

$$\frac{W_{net}}{q_2} = \frac{R(T_2 - T_1) \ln (V_2/V_1)}{RT_2 \ln (V_2/V_1)} = \frac{T_2 - T_1}{T_2} \tag{7.14}$$

As $W_{net} = q_2 + q_1$ the equation (7.14) may also be written as,

$$\frac{q_2 + q_1}{q_2} = \frac{T_2 - T_1}{T_2} \tag{7.15}$$

Equations (7.14) as well as (7.15) give the ***efficiency*** of the Carnot cycle or Carnot engine. Since the operations of the cycle are all reversible, W_{net} is the maximum work obtainable from the cycle. It may he seen from equation (7.15) that the efficiency of the reversible Carnot cycle depends only on the temperature of the *source* and the *sink*. The Carnot cycle efficiency can, therefore, be used to make an estimate of the maximum conversion of heat into work that can be expected for a real engine.

Example 7.3: Calculate the amount of heat supplied to a Carnot reversible cycle working between temperatures 100 ^{0}C and 25 ^{0}C, if the maximum work obtained is 900 joules.

Solution : $T_1 = (25 + 273)\text{ K} = 298\text{ K}$ and $T_2 = (100 + 273)\text{ K} = 373\text{ K}$

$w = 900$ joules

Using equation (7.14),

$$\frac{w}{q} = \frac{T_2 - T_1}{T_2} = \frac{373 - 298}{373} = 0.20$$

Or,

$$q = \frac{900}{0.20} = 4{,}500\text{ J}$$

Example 7.4 : A heat engine operates between temperatures 500 and 200 K. What is the minimum amount of heat that must be withdrawn from the reservoir to obtain 1500 joules of work?

Solution : Given that, $T_1 = = 200$ K, $T_2 = 500$ K and $-w = 1500$ J

Substituting in equation (7.14) we get,

$$\frac{-w}{q} = \frac{500 - 200}{500} = 0.6$$

Or,

$$q = -\frac{1500}{0.6} = -2500\,J$$ [Heat is supplied by the system]

7.6 Entropy – A New Thermodynamic State Function

For a reversible Carnot cycle working between temperature T_1 and T_2 ($T_2 > T_1$) it was shown (equation 7.15) that,

$$\frac{q_2 + q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

The above equation may be written in the form,

$$1-\frac{q_2+q_1}{q_2}=1-\frac{T_2-T_1}{T_2}$$

or

$$-\frac{q_1}{q_2}=\frac{T_1}{T_2}$$

which upon rearrangement gives,

$$\frac{q_2}{T_2}+\frac{q_1}{T_1}=0$$

$$\text{or } \Sigma\frac{q}{T}=0=\oint\frac{q}{T} \qquad (7.16)$$

Equation (7.16) holds for any reversible cycle, although it has been derived for a particular type of cycle described by Carnot. The reversible cycle (Figure 7.3) may be considered to be made up of a large number of Carnot cycles. The outside boundaries of these small cycles, shown as the zig-zag curve, follow closely the path of the general cycle ABA. All steps in the Carnot cycles that fall inside the boundary cancel out, since each is traced once in the forward direction and again in the reverse direction. By making each Carnot cycle smaller and increasing their number the outside boundaries may be made to correspond very closely to ABA. The reversible cycle may, therefore, be regarded as being made up of an infinite number of small Carnot cycles. For each Carnot cycle the relation, $\Sigma\frac{q}{T}=0$, holds. For an infinite number of Carnot cycles (i.e. for any cyclic reversible process performed on an ideal gas) one can, by replacing the summation by an integral, write

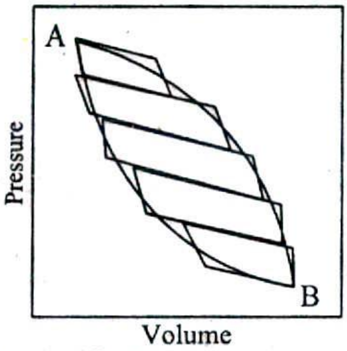


Figure 7.3 P-V changes as a succession of Carnot cycles.

$$\int\frac{dq_{rev}}{T}=0 \qquad (7.17)$$

The subscript on q is introduced to emphasize that this relation holds only when the process is performed reversibly.

The term $\frac{q_{rev}}{T}$ must be an exact differential, because its cyclic integral equals zero. It defines a state function or a thermodynamic property. This state function is given the name ***entropy*** and is usually designated by S. Hence

$$dS=\frac{dq_{rev}}{T} \qquad (7.18)$$

For macroscopic process, we can write,

$$\Delta S = \frac{q_{rev}}{T} \tag{7.19}$$

Integrating equation (7.18) for going from state A to state B,

Or $$S_B - S_A = \Delta S = \int \frac{dq_{rev}}{T} \tag{7.20}$$

Equation (7.20) signifies that in going from state A to state B the change in entropy is the value of the integral on the right hand side of the equation. That *S* is a state function can be easily shown by considering the cycle A→B and then B→A. Since the cycle is performed in two steps, we can write,

$$\oint \frac{dq_{rev}}{T} = \int_A^B \frac{dq_{rev}}{T}(path\, I) + \int_B^A \frac{dq_{rev}}{T}(path\, II) = 0$$

Or, $$\int_A^B \frac{dq_{rev}}{T}(path\, I) = -\int_B^A \frac{dq_{rev}}{T}(path\, II) = \int_A^B \frac{dq_{rev}}{T}(path\, II) \tag{7.21}$$

In other words, the change in entropy in going from state A to state B by one path is numerically the same as in going from state B to state A by a different path. This can only be true if entropy is a property of the state and independent of the way in which that state is reached; that is, entropy is a state function. This is the most important consequence of the second law of thermodynamics.

Unit of entropy : By definition entropy has the dimensions of energy divided by the absolute temperature. The unit of entropy is J K^{-1}. Since entropy depends on the amount of the system it is usually expressed as J K^{-1} mol^{-1}. The entropy unit is also abbreviated as *e.u.* unit.

7.6.1 Entropy change of the system and the surrounding in a reversible process

In a reversible process the net entropy change between the system and the surroundings is zero, provided the process is carried out isothermally. Let us assume that q_{rev} is the heat absorbed by the system reversibly. Then $-q_{rev}$ must be the heat lost by the surrounding. Since the process takes place under isothermal condition at temperature T we can write,

(i) Change of entropy of the system, $$\Delta S_{system} = \frac{q_{rev}}{T} \tag{7.22}$$

(ii) Change of entropy of the surrounding, $$\Delta S_{surrounding} = -\frac{q_{rev}}{T} \tag{7.23}$$

The net entropy change between the system and the surrounding will be,

$$\Delta S_{system} + \Delta S_{surrounding} = \frac{q_{rev}}{T} + \left(-\frac{q_{rev}}{T}\right) = \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0$$

Thus, the net entropy change for the combined system and surrounding is zero.

7.6.2 Entropy change in an irreversible process

Entropy is a state function and ΔS, in going from an initial state A to a final state B, is always the same and is independent of the path followed. It makes no difference whether the path is reversible or irreversible. For a reversible path the entropy change is given by,

$$\Delta S = S_B - S_A = \int_A^B \frac{q_{rev}}{T} \tag{7.24}$$

If the transfer from state A to state B is carried out irreversibly even then the entropy change is given by equation (7.24). *The entropy change in an irreversible process may, therefore, be calculated if one can determine the amount of heat that* ***would be*** *absorbed if the process were carried out reversibly.* For example, a mole of gas at 5 atm pressure and at 25°C may be expanded to a larger volume at 1 atm and at the same temperature by reducing the pressure in a single step. This would be an irreversible process because at no stage of the expansion process equilibrium was maintained. The heat absorbed during this process could not be used for calculating the entropy change. In order to obtain the entropy change for this expansion process one has to carry out the process in a reversible manner and determine the heat absorbed when the process is so conducted.

We know that in a reversible process the work done is maximum (W_{max}); and in going from state A to state B the change in internal energy, ΔU, of the system is the same whether the change is carried out reversibly or irreversibly. From the first law of thermodynamics we know that the heat absorbed in the irreversible path is less than the heat absorbed when the path is reversible. Consequently,

$$\frac{dq_{irev}}{T} < \frac{dq_{rev}}{T} \tag{7.25}$$

Also in an irreversible cyclic process the sum of the dq/T terms is always less than zero:

$$\int \frac{dq_{rev}}{T} < 0 \tag{7.26}$$

This can also be shown from a consideration of the efficiency of cyclic processes. In the reversible cycle the efficiency is maximum. The efficiency of an irreversible cycle must then be less than that of a reversible cycle operating between the same temperatures of the source and the sink. It follows, then, that for an irreversible process,

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2} \tag{7.27}$$

and, therefore,

$$\left(\frac{q_2}{T_2} + \frac{q_1}{T_1}\right) < 0 \tag{7.28}$$

For the inequality to hold it is not necessary for both the stages to be irreversible; the relation is valid even if any one of the stages is irreversible. In general, for any cyclic process, if one or more of the steps of the cycle is irreversible, the sum of the $\frac{q}{T}$ terms will be less than zero.

7.6.3 Total entropy change of a system and its surroundings

A system is that part which is under investigation. The surroundings constitute all other parts which might interact with the system. In most cases the surroundings consist of heat reservoirs that can add heat to or take out heat from the system or of a mechanical device which does work on or accept work from a system.

In a reversible process, when an amount dq_{rev} of heat is absorbed by the system an equal amount is lost by the surroundings. The change in entropy of the system is equal and opposite to the change in entropy of the surroundings, so that the total change in entropy of the system and the surroundings is zero (*Section 7.6*).

Consider now, an irreversible process in which the system absorbs an amount dq_{irrev} of heat and goes from state A to state B. Entropy being a state function, the gain in entropy of the system is given by $S_B - S_A$. This gain in entropy, of course, is calculated from the relation :

$$\Delta S = S_B - S_A = \int_A^B \frac{dq_{rev}}{T} \tag{7.29}$$

where dq_{rev} is the heat that *the system would have absorbed if the process were carried out reversibly*. During the process the surroundings have supplied a quantity of heat $dq_{irrev.}$ Although this heat has been taken up irreversibly by the system, the change in entropy of the surroundings is calculated by supposing that this quantity of heat has been given out reversibly. Hence the decrease in entropy of the surroundings is given by $\int_A^B \frac{dq_{irrev}}{T}$. The total change of entropy of the system and the surroundings when the system goes from state A to state B will be obtained in the following way:

Gain in entropy of the system = $S_B - S_A$

Loss in entropy of the surrounding = $\int_A^B \frac{dq_{irrev}}{T}$

$$\text{Net change in entropy} = (S_B - S_A) - \int_A^B \frac{dq_{irrev}}{T} \tag{7.30}$$

According to the relation (7.25) the value of the integral is always less than $S_B - S_A$, so that the net change in entropy is a positive quantity; that is, as a result of the process there is a gain in entropy of the system and the surroundings taken together. Hence, if any part of a process is irreversible there is an increase in entropy when the system and its surroundings are considered together. Natural processes are spontaneous and, therefore, irreversible. It follows, then, that natural processes are accompanied by an increase in entropy and the sum total of entropy in the universe is increasing. This deduction led Clausius to make his famous statement of the laws of thermodynamics:

"The energy of the universe is constant;
the entropy of the universe tends always towards a maximum."

This conclusion from the second law of thermodynamics has profound philosophical implications.

Considering the system and the surrounding together we can, in summary, write:

$$\begin{aligned} &\Delta S = 0 \quad \text{for a reversible process} \\ \text{and} \quad &\Delta S > 0 \quad \text{for a natural process} \end{aligned} \tag{7.31}$$

7.7 Entropy and equilibrium

A system is said to be in equilibrium when it has no further tendency to change. In a reversible process all stages are at equilibrium position. Since for a reversible process $dS = 0$, this must also be the condition of equilibrium. This implies that when the system is at equilibrium any change in the system will not lead to a change in the entropy of the system as long as the equilibrium condition is maintained. Conversely, if in a process the total change in entropy of the system turns out to be zero, the system is said to be in equilibrium.

The natural tendency of all systems is to approach a state of equilibrium. In mechanical systems the state of equilibrium is the state at which the system has minimum potential energy. The equilibrium conditions in a thermodynamic system may be expressed in terms of entropy. A spontaneous change in a system is accompanied by an increase in entropy. In such a process the entropy will increase until no further spontaneous change can occur. Under this condition the entropy of the system is maximum and a state of equilibrium has been established. This may be described as *thermodynamic equilibrium*. A criterion of such equilibrium is:

In a system at equilibrium the entropy is maximum.

7.8 Entropy Change of an Ideal Gas

We know that entropy is a thermodynamic state function, and its value is dependent on any two of the three variables *T, P and V*. It is, therefore, possible to consider a number of situations.

7.8.1 T and V as variables

For a reversible process for one mole of ideal gas the first law of thermodynamics states that,

$$\begin{aligned} dq &= dU + PdV \\ &= C_V dT + RT\frac{dV}{V} \end{aligned} \tag{7.32}$$

From the definition of entropy,

$$dS = \frac{dq_{rev}}{T} = C_v \frac{dT}{T} + R\frac{dV}{V} \tag{7.33}$$

On integration of equation (7.33) between limits one obtains :

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} C_v \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V} \tag{7.34}$$

At constant volume,

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} C_v \frac{dT}{T} \tag{7.34a}$$

Assuming C_v to be constant over the temperature range T_1 to T_2, we get,

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \tag{7.35}$$

For n mole of gas equation (7.35) can be written as:

$$\Delta S = n\, C_v \ln \frac{T_2}{T_1} + n\, R \ln \frac{V_2}{V_1} \tag{7.35a}$$

7.8.2 P and T as variables

Let us consider that P_1 and V_1 are the initial pressure and volume respectively at temperature T_1, while P_2 and V_2 are the final pressure and volume at temperature T_2. From combined gas laws we get,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{and} \quad \frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}$$

which upon substitution in equation (7.35a) gives,

$$\Delta S = n\, C_v \ln \frac{T_2}{T_1} + n\, R \ln \frac{P_1T_2}{P_2T_1} \tag{7.36}$$

Equation (7.36) can be rearranged into,

$$\Delta S = n\,(C_v + R) \ln \frac{T_2}{T_1} + n\, R \ln \frac{P_1}{P_2} \tag{7.37}$$

Equation (7.37) can be written as,

$$\Delta S = n\, C_p \ln \frac{T_2}{T_1} + n\, R \ln \frac{P_1}{P_2}, \qquad [\text{since } C_p - C_v = R] \tag{7.38}$$

Equations (7.36), (7.37) and (7.28) can be used to calculate ΔS under different conditions. However, few special cases must also be considered.

Case 1: For an isothermal process ($T_1 = T_2$) equations (7.35a) and (7.38) respectively become

$$\Delta S = n\,R\,ln\frac{V_2}{V_1} \tag{7.39}$$

and
$$\Delta S = n\,R\,ln\,\frac{P_1}{P_2} \tag{7.40}$$

It should be noted that for an isothermal expansion of a gas, ΔS is positive ($V_2 > V_1$ and $P_1 > P_2$), while for isothermal compression ΔS is negative ($V_2 < V_1$ and $P_1 < P_2$).

Case 2: For an isobaric process ($P_1 = P_2$) equations (7.38) turns into,

$$\Delta S = n\,C_p\,ln\frac{T_2}{T_1} \tag{7.41}$$

Case 3 : For an isochoric ($V_1 = V_2$) process equation (7.35a) reduces to:

$$\Delta S = n\,C_V\,ln\frac{T_2}{T_1} \tag{7.42}$$

In the integral form we can write

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} C_V\frac{dT}{T} \tag{7.42a}$$

Example 7.5: Calculate the change in entropy of 5 moles of an ideal gas when the gas is expanded reversibly and isothermally from 2 atm to 1 atm at 25°C.

Solution: $\Delta S = n\,R\,ln\frac{P_{initial}}{P_{final}} = (5)(8.314)\ (2.303)\ \log 2 = 29.0\ \mathrm{J\ K^{-1}}$

Example 7.6: Calculate the entropy change when 2 moles of nitrogen are heated from 27°C to 127°C (a) at constant pressure and (b) at constant volume. The values of C_p and C_v, in this temperature range are 29.04 J $\mathrm{mole^{-1}}$ and 20.67 J $\mathrm{mole^{-1}}$ respectively.

Solution : (a) $\Delta S = n\,C_p\,ln\frac{T_2}{T_1} = (2)\ (29.04)\ (2.303)\ \log\frac{400}{300} = 16.59$ e.u.

(b) $\Delta S = n\,C_V\,ln\frac{T_2}{T_1} = (2)\ (20.67)\ (2.303)\ \log\frac{400}{300} = 11.81$ e.u.

7.9 Calculation of ΔS for Physical Processes

In this section we will consider ΔS during physical changes.

7.9.1 Phase change

Phase transitions, e.g., vaporization of liquids, fusion of solids, freezing of liquids etc., at the transition temperature under 1 atmospheric pressure are reversible processes. The temperature does not change as long as both phases are present, although the amount of the phases can be changed by adding or removing heat. The heat required to change one mole of the substance from one phase into another phase is called the enthalpy of transition. The ΔS_{trans} for the process can be calculated from,

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}} \tag{7.43}$$

Example 7.7: Calculate ΔS_{trans} when 1.0 mole of liquid ethanol at its normal boiling temperature of 78.3^0C and at 1 atm changes to vapour at the same temperature. The ΔH_{vap} is 38576 J mol^{-1} at this temperature.

Solution: From equation (7.43) we get,

$$\Delta S_{trans} = \frac{38576}{351.5} = 109.7 \text{ J K}^{-1}$$

Entropy changes during other changes of state may be calculated in a similar manner. Fusion of a solid at its melting point or the evaporation of a liquid at a constant pressure equal to its vapour pressure, or transformation from one crystalline form into another at a given temperature are examples of reversible isothermal processes.

7.9.2 Phase transition under irreversible conditions

It is known that a liquid freezes at a constant temperature below its normal freezing point. For example, supercooled water at – 5°C and at 1.0 atm pressure changes to ice if disturbed; but ice at – 5°C and 1.0 atm pressure does not melt spontaneously. So, this is an irreversible process. In order to calculate ΔS for such a process one has to devise a means of carrying out the same overall process by a reversible path. Usually, this will involve two or more reversible paths, and the ΔS for the irreversible path must be equal to that of the reversible path. The following examples will justify the statement.

Example 7.8: If 1.0 mole of liquid water at – 5°C and 1.0 atm pressure is changed to ice at the same temperature and pressure, calculate the entropy change for the process. (For liquid water $C_{p,m} = 75.3$ J K^{-1} mol^{-1} and for ice $C_{p,m} = 36.8$ J K^{-1} mol^{-1}; heat of fusion of ice = 6008 J mol^{-1}).

Solution : The desired change can be achieved by carrying out the following series of reversible steps:

(i) Heating the liquid to 0°C
(ii) Changing the liquid to a solid at 0°C
(iii) Cooling the solid to – 5 °C.

[*raising or lowering of temperature at constant pressure are reversible processes*]

ΔS values for these three steps are:

(i) ΔS (liquid from – 5° to 0°) $= C_{p,m}\ ln\frac{T_2}{T_1}$

$$= 75.3\ ln\frac{273.16}{268.16}$$

$$= 1.39\ J\ K^{-1}$$

(ii) ΔS (liquid to solid at 0°C) $= \frac{\Delta H_{cryst}}{T} = -\frac{6008}{273.16} = -21.99\ J\ K^{-1}$

(iii) ΔS (cooling solid from 0° to – 5°C) $= C_{p,m}\ ln\frac{T_2}{T_1}$

$$= 36.78\ ln\frac{268.16}{273.16}$$

$$= -0.68\ J\ K^{-1}$$

So, ΔS (Total) $= 1.39 + (-21.99) - 0.680 = -21.28\ J\ K^{-1}$

Example7.9: Calculate ΔS for freezing of 1.0 mole of water at – 10°C. Given that $C_{p,\,m}$(ice) = 36.78 J K^{-1}, $C_{p,\,m}$(water) = 75.31 J K^{-1} and the heat of fusion, $\Delta H = 6008\ J\ mol^{-1}$ at 0°C.

Solution : The following processes must be carried out:

(1) Heat water to 0°C, $\Delta S_{(1)} = 75.31\ ln\frac{273.16}{263.16} = 2.81\ JK^{-1}$

(2) Water is frozen at 0°C, $\Delta S_{(2)} = \frac{-6008}{273.16} = -21.99\ JK^{-1}$

(3) Ice is cooled to – 10°C, $\Delta S_{(3)} = 36.78\ ln\frac{263.16}{273.16} = -1.37\ JK^{-1}$

Therefore, $\Delta S_{Total} = \Delta S_{(1)} + \Delta S_{(2)} + \Delta S_{(3)}$

$$= 2.81 - 21.99 - 1.37 = -20.55\ JK^{-1}$$

7.9.3 *Entropy of mixtures of gases*

When two or more gases are allowed to mix, the total entropy change is the sum of the changes for each individual gas. Let us consider that n_A moles of gas A at a pressure of P_A are allowed to mix isothermally with one or more non-interacting gases, so that the new pressure of A is P'_A. From equation (7.40) we get,

$$\Delta S_A = n_A\ R\ ln\frac{P_A}{P'_A} \tag{7.44}$$

Or, $$\Delta S_A = -n_A\ R\ ln\frac{P'_A}{P_A} \tag{7.44a}$$

Similar expressions can be deduced for all gases.

For a mixture of gases with *i* components equation (7.44a) may be written as

$$\Delta S(for\, n_i) = \sum_i - n_i\, R \quad ln \frac{P'_A}{P_A} \tag{7.45}$$

Equation (7.45) can be further transformed into another form. Thus, if we consider that the gases behave ideally, $P'_A = X_i\, P_A$ (Raoult's Law), it follows that

$$X_i = \frac{P'_A}{P_A}$$

When the X_i values for all components of the mixture are substituted in equation (7.45) we obtain

$$\Delta S = \sum_i \; - n_i\, R\, ln\, X_i \tag{7.46}$$

Example 7.10: What will be the entropy change if 2.0 moles N_2 and 3.0 moles Ar, at constant temperature and pressure, are allowed to mix in a container? Assume ideal behaviour.

Solution: $X_{N_2} = \frac{2}{5}$ *and* $X_{Ar} = \frac{3}{5}$.

Using equation (7.46) we get,

$$\Delta S = \; -8.314\,(2\, ln\, 2/5 + 3\, ln\, 3/5) = 27.98 \;\; J\, K^{-1}$$

7.10 The Third Law of Thermodynamics

The second law of thermodynamics leads to the definition of entropy and calculation of differences of entropy. We have seen that entropy is a measure of chaos in a system. When a system goes from an ordered state to a disordered state the entropy is increased. The converse is also true. But the second law does not allow calculation of absolute value of the entropy of a system. The third law of thermodynamics developed by Ludwig Boltzmann offers a method of calculating the absolute value of entropy.

The law can be stated in different forms:

(1) '*It is impossible to attain the absolute zero of temperature*' (W. Nernst, 1912)

(2) '*The entropy of a solid or liquid chemically homogeneous substance has the value of zero at the absolute zero of temperature*'. (M. Planck, 1912)

An alternative definition of the third law of thermodynamics was given by Gilbert N. Lewis and Merle Randall in 1923.

> '*Every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of a perfectly crystalline substance*'.

The third law of thermodynamics gives us an opportunity to calculate the absolute entropy of a system at any specified temperature. Consider that a solid is transformed at constant pressure from 0°C to some temperature, T, below its melting point:

$$\text{Solid } (0°\text{K}) \rightarrow \text{Solid } (\text{T})$$

The entropy change for the transformation is given by equation (7.47)

$$S_T - S_0 = \int_{S=S_0}^{S=S_T} dS = \int_{T=0}^{T=T} C_P \frac{dT}{T} \qquad (7.47)$$

$$\left[\text{ since, } dS = \frac{dq}{dT},\ dq = C_p dT, \text{and so } dS = \frac{C_p dT}{T} \right]$$

According to the third law of thermodynamics, $S_0 = 0$,

Hence, $$S_T = \int_0^T C_P \frac{dT}{T} = \int_0^T C_p \, d \ln T \qquad (7.48)$$

The value of the entropy of an element at any temperature can be obtained from careful measurements of the heat capacity C_P of the element from the desired temperature down to absolute zero. However, since the measurements of heat capacity at very low temperature, e.g. about 15 K or below, do not yield accurate results, use is made of Debye's equation (*Section 4.15*) for specific heat of solids at low temperatures; that is,

$$C_v = aT^3 \qquad (7.49)$$

where 'a' is a constant. At such low temperatures C_p and C_v are not different. Since the constant 'a' may be determined from experiments at the lowest temperature at which accurate measurements are possible Debye's equation is used to evaluate C_p up to the lowest temperature of measurements, say 15 K. The value of $C_v = C_p = aT^3$ is substituted in equation (7.48) to obtain the entropy upto 15 K. When C_p is not constant but is known as a function of temperature the entropy of a substance from 15 K to temperature T is evaluated by plotting either C_p / T against T or C_p against log T. The area under the curve is the value of the integral from 15 K to the temperature T. If there is a phase change in the interval of temperature used the entropy change for the phase change is calculated in the usual manner. The sum of all these values gives the entropy of the substance at temperature T.

It should be mentioned that unlike the other laws of thermodynamics the third law is not based on experiments and is applicable only to special class of compounds, namely pure, crystalline solids. The law has, however, been extremely useful in obtaining absolute values of entropy. The agreement in many cases of such entropy values with those calculated from a totally different concept, namely molecular spectroscopy, lends support to the validity of the law.

7.11 Entropy and Molecular Chaos

It has now been established that spontaneous processes are accompanied by increase of entropy and the entropy of a system at equilibrium is maximum. As a matter of fact the spontaneous processes are associated with an increase in chaos that exists in any molecular system. For example let us consider the diffusion of gases. It can be well imagined that due to diffusion the movement of the molecules has become more chaotic. The increase in chaotic movement of the molecules becomes even more apparent in fusion of solids and evaporation of liquids etc. The consideration of these and similar other processes led to the concept of *entropy as a measure of randomness or chaos. An increase of entropy means an increase of randomness of the system.* These ideas enable us to predict the sign of ΔS^o for a reaction or a physical process even without knowing the values of entropy of substances. The entropy usually increases in the following situations:

1. *When a substance changes from a solid state to a liquid state or from a liquid state to a gaseous state. (Reverse of these processes will be accompanied by decrease of entropy).*
2. *A reaction in which a reactant is broken down into more than one product.*
3. *A reaction in which the number of moles of gas increases.*

The kinetic molecular theory of matter emphasizes the fact that the *macroscopic* or bulk property of matter is a consequence of the motions and positions of the constituent atoms or molecules. There may be a large number of arrangements in respect of position and velocity of the molecules which will give the required macroscopic property. Each arrangement which gives the same bulk property is known as a *microscopic state.* The *microscopic* state of a system changes very rapidly as the molecules are always in motion and, in the gaseous state, are colliding with each other with a high frequency. Since the time of a collision is small, even during the time it takes to measure a macroscopic property of a gas, such as pressure, the microscopic state of the system must change a large number of times. In spite of this rapid change of the microscopic state the bulk properties of a system at equilibrium are constant. The number of microscopic states associated with a particular macroscopic state is defined as *thermodynamic probability*, W, of that state. *This number also represents the number of different ways in which the given state of the system can be realized.* It is assumed that all microscopic states are equally probable. At equilibrium the thermodynamic probability is maximum. Since entropy of a system at equilibrium is maximum, it was thought reasonable to relate thermodynamic probability with entropy by the relation,

$$S = k \ln W \tag{7.50}$$

where k is the Boltzmann constant. That the relationship between S and W is logarithmic may be shown by considering two systems with entropies S_1 and S_2 and thermodynamic probabilities W_1 and W_2 respectively. If the systems are combined the probability of the resulting system will be $W_1 \times W_2$ but the entropy will be $S_1 + S_2$. A relation of the type shown in equation (7.50) will satisfy this condition. It must be understood, however, that this is not a complete proof of the relation between S and W. Equation (7.50) is the basis of statistical thermodynamics and leads to calculation of absolute entropies from molecular constants such as mass, moment of inertia, frequency of vibration of bonds. Such calculations are independent of the third law of thermodynamics.

Example 7.11 : Predict the sign of ΔS^o for each of the following reactions:

(a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(b) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(c) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

(d) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(e) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

Solution : (a) decreases as the number of moles of gas decreases; (b) decreases as gases are converted into a liquid; (c) decreases as gases are converted into a solid; (d) increases as gas is produced from solids; (e) as the number of gas molecules are equal on both sides no prediction can be made.

7.12 The Free Energy and the Work Function

We have already established the criterion of spontaneous processes and equilibrium. Spontaneous processes, whether chemical or physical, often have:

- A negative internal energy change, (release of heat energy, $\Delta U_{S,V} < 0$)
- A negative enthalpy change, (release of heat energy, $\Delta H_{S,P} < 0$)
- An increase in entropy, (increase in disorder, $\Delta S_{U,V} > 0$)

Thus, it appears that spontaneity of a process involve thermodynamic properties – internal energy, enthalpy and entropy. For practical purposes, however, these criteria are generally inconvenient, since it requires knowledge of the properties of the surroundings in addition to those of the substances of primary interest. This inconvenience has been minimized by the introduction of two more thermodynamic functions which are derived from the functions *U*, *H* and *S*. The functions are:

(i) Free Energy or Gibbs Free Energy, G

William Gibbs, an American mathematical physicist, developed an equation in 1870s, combining enthalpy and entropy contributions. This equation provided a means to describe energy content and, therefore, a means to evaluate the spontaneity of a reaction when that energy content changes. The energy content of a substance was termed the *Gibbs Free Energy, G*. In the relation

$$G = H - TS \tag{7.51}$$

H is enthalpy, *S* is entropy and *T* is the temperature in Kelvin

(ii) Work Function or Helmholtz Free Energy, A

In 1882 the German physicist and physiologist Hermann von Helmholtz coined the term 'free energy' for the function *A* which is given by

$$A = U - TS. \tag{7.52}$$

U is the internal energy and the other terms have the same significance as in (i).

The term 'free energy', however, now refers to Gibbs free energy, G. The Helmholtz free energy function, A, is generally used to describe the change in a system at constant temperature and constant volume.

7.12.1 Gibbs free energy function and its significance

For two states of a system equation (7.51) can be written as

Initial state : $G_1 = H_1 - TS_1$ (7.53)

Final state : $G_2 = H_2 - TS_2$ (7.54)

So, the change in free energy, ΔG is equal to,

$$\Delta G = G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1) \tag{7.55}$$

Equation (7.55) can be rearranged to

$$\Delta G = \Delta H - T\Delta S \tag{7.56}$$

From second law of thermodynamics, $\Delta S = \dfrac{q_{rev}}{T}$, or $T\Delta S = q_{rev}$

and at constant pressure $\Delta H = \Delta U + P\Delta V$

Substitution of the expression of ΔH and $T\Delta S$ in equation (7.56) we get,

$$\Delta G = \Delta U + P\Delta V - q_{rev} \tag{7.57}$$

Equation (7.57) can be rewritten as, $\Delta G = (\Delta U - q_{rev}) + P\Delta V$ (7.57a)

According to the First Law of thermodynamics, $q_{rev} = \Delta U + w_{\max}$ which can also be written as $\Delta U - q_{rev} = -w_{\max}$. On substitution of this relationship in equation (7.57a) we get

$$\Delta G = -w_{\max} + P\Delta V,$$

$$\text{or} \quad -\Delta G = w_{\max} - P\Delta V \tag{7.58}$$

Equation (7.58) is a very important relationship. It signifies that *at constant temperature and pressure the decrease in free energy of a system is equal to the net work, i.e., the total work obtainable from the system minus the pressure-volume work. In other words, decrease in free energy of a system is equal to the maximum work available from the system for useful purposes.*

Like standard enthalpy changes of reactions, standard free energy change, ΔG°, of reactions have been defined as the free energy change that occurs when reactants in their standard and most stable states are converted into products in their standard states. Under standard conditions equation (7.56) takes the form

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7.59}$$

It may be recalled that the standard states are: for pure liquids and solids, 1 atm pressure; for gases 1 atm partial pressure; for solutions concentration 1.0 mol L^{-1}. The temperature is 25°C (298 K).

7.12.2 Gibbs free energy, spontaneity and equilibrium

We know that useful work can be obtained from spontaneous natural processes. Since the free energy change is a measure of the useful work that might be obtained from a constant pressure process, one deduces the very important result that the decrease in free energy of a constant pressure process is the measure of the tendency of the process to proceed spontaneously. In other words, spontaneous processes are accompanied by decrease in free energy. Spontaneous processes can continue to occur as long as the free energy of the system can decrease, that is, until the free energy of the system reaches a minimum value. As in the equilibrium state the system has no further tendency to change, the system at equilibrium has a minimum value of the free energy; at equilibrium the system must satisfy the condition

$$dG = 0 \qquad \text{or} \qquad \Delta G = 0 \tag{7.60}$$

If a process tends to be accompanied by an increase in free energy, the process will not proceed spontaneously in the direction considered. For constant pressure processes the relations of free energy change to spontaneity and equilibrium may be summarized as follows:

$\Delta G < 0$ *(negative); the process is spontaneous*

$\Delta G > 0$ *(positive); the process is non-spontaneous*

$\Delta G = 0$; *the system is at equilibrium.*

It has to be pointed out that in these statements no mention is made of the surroundings and the free energy change is that for the system only. Thus the inconvenience of the entropy criterion of equilibrium has been eliminated.

7.12.3 Direction of chemical change

It is possible to calculate free energy change of a reaction and decide whether the reaction will take place spontaneously under the given conditions or not. The free energy change (ΔG) in a reaction may be obtained from calorimetric or other means of finding ΔH and ΔS. The relation $\Delta G = \Delta H - T\Delta S$ is used to determine the sign and magnitude of ΔG. It is clear that to make ΔG negative, ΔH should be negative (exothermic) and ΔS positive. For endothermic reactions (positive ΔH), ΔG can be negative only if ΔS is positive and $T\Delta S$ is larger in magnitude than ΔH. A reaction with a negative ΔS value may also take place spontaneously if the reaction is highly exothermic (ΔH negative) and ΔH is larger in magnitude than $T\Delta S$. Thus, the sign of ΔG can predict the direction and the feasibility of a process.

A negative value of ΔG for a given process does not necessarily mean that the process will take place. These calculations do not say how long it would take for the process to reach equilibrium. In fact, thermodynamics has nothing to say about the speeds of reactions. It can only predict the direction and the possibility of the process taking place.

7.12.4 Standard free energy change and equilibrium constant

Similar to standard enthalpy of formation of compounds, the standard free energy of formation, ΔG_f^o, of compounds have been defined as the change in free energy when one mole of the compound is formed from its elements in their states. The standard free energy of formation of elements in their stable state are assigned the value zero as in the case of standard enthalpies of formation. ΔG_f^o values of different compounds have been determined experimentally as indicated in *Section 7.12.3* above or using other methods. Table 7.1 gives some values of ΔG_f^o of compounds.

Table 7.1 Standard free energy of formation of some substances

Formula	ΔG_f^o kJ mol^{-1}	Formula	ΔG_f^o kJ mol^{-1}	Formula	ΔG_f^o kJ mol^{-1}
$H^+(aq)$	0	$C_6H_6(l)$	124.5	$HF(g)$	–275
$H_2(g)$	0	$CH_3OH(l)$	–166.2	$Cl^{-1}(aq)$	–131.2
$O_2(g)$	0	$C_2H_5OH(l)$	–174.8	$HCl(g)$	–95.3
$H_2O(g)$	–228.6	$CH_3CHO(l)$	–133.7	$Br^{-1}(aq)$	–102.2
$H_2O(l)$	–237.2	$CCl_4(l)$	–68.6	$Br_2(l)$	0
$OH^-(aq)$	–157.3	$CS_2(l)$	63.6	$I_2(s)$	0
$Na^+(aq)$	–261.9	$SiO_2(s)$	–856.5	$I^{-1}(aq)$	–51.7
$Na(s)$	0	$PCl_5(s)$	–305.0	$HI(g)$	1.7
$NaCl(s)$	–384	$PCl_3(s)$	–267.8	$Ag^+(aq)$	77.1
$NaHCO_3(s)$	–851.9	$PbO(s)$	–189.2	$AgF(s)$	–185
$Na_2CO_3(s)$	–1048.1	$PbS(s)$	–96.7	$AgCl(s)$	–109.7
$Ca^{2+}(aq)$	–553.0	$NH_3(g)$	–16.5	$AgBr(s)$	–95.9
$CaO(s)$	–603.5	$NO(g)$	86.6	$AgI(s)$	–66.3
$CaCO_3(s)$	–1128.8	$NO_2(g)$	51.3	$I_2(g)$	19.3
$C(graphite)$	0	$HNO_3(aq)$	–110.5	$Br_2(g)$	3.14
$C(diamond)$	2.9	$S(rhombic)$	0	$CH_3COOH(aq)$	–390.0
$CO(g)$	–137.2	$S(monoclinic)$	0.10	$PbSO_4(s)$	–813.2
$CO_2(g)$	–394.4	$SO_2(g)$	–300.2	$HBr(g)$	–53.4
$CH_4(g)$	–50.8	$SO_3(g)$	–371.1	$Al_2O_3(s)$	–1582.4
$C_2H_4(g)$	68.1	$H_2S(g)$	–33.6	$Fe_3O_4(s)$	–1015.5
$C_2H_6(g)$	–32.9	$F^{-1}(aq)$	–276.5		

By using the values of ΔG_f^o for substances in Table 7.1 the value of ΔG_f^o of any reaction involving the reactants and products may be calculated. For this purpose use is made of the following relationship: (7.61)

$$\Delta G^o = \sum \Delta G_f^o\,(products) - \sum \Delta G_f^o\,(reactants) \tag{7.61}$$

The following example illustrates this procedure.

Example 7.12: Calculate ΔG^0 for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ with all components at standard conditions at 298K.UseΔG_f^0 *from the Table above.*

Solution : $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$\begin{aligned}\Delta G^0 &= \Sigma\ \Delta G_f^0(products) - \Sigma\ \Delta G_f^0(reactants)\\ \Delta G^0 &= -603.5\ -(-394.4)\ -\ 1128.8\\ &= -209.1\ -\ 1128.8\\ \Delta G^0 &= -1337.9\ \text{kJ}\end{aligned}$$

It will be shown in Chapter 10 (*Section 10.35*) that

$$\Delta G^0 = -RT\ln K = -2.303\,RT\log K \tag{7.62}$$

This gives a direct relationship between standard free energy change of a reaction and the equilibrium constant. For a reaction ΔG^0can be calculated from ΔG_f^0 values of reactants and products in Table 7.1 and substitution of this value in equation (7.62) allows calculation of K.

7.12.5 Dependence of free energy on pressure and temperature

The relationships between free energy, temperature and pressure may be derived from the definition of free energy (7.51) and enthalpy (5.25):

$$\begin{aligned}G &= H - TS\\ &= U + PV - TS\end{aligned}$$

For small changes in U, P, V, T and S the change in free energy is given by,

$$dG = dU + PdV + VdP - SdT - TdS \tag{7.63}$$

Since $dU = dq + w$ and if the process is reversible, $TdS = dq$ and no work other than that of expansion is done, $-PdV = w$. The equation (7.63) reduces to

$$dG = VdP - SdT \tag{7.64}$$

Further, if the pressure is held constant, the variation of free energy with temperature is given by

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{7.65}$$

and if the temperature is kept constant the variation of free energy with pressure is given by

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{7.66}$$

$$\text{Or} \quad dG = VdP \tag{7.67}$$

For an ideal gas $V = nRT/P$ and the free energy change of an ideal gas when the pressure changes from P_1 to P_2 may be obtained by integration of equation (7.67) after substitution of V by $\frac{nRT}{P}$. Thus

$$G_2 - G_1 = \Delta G = \int VdP = nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$= nRT \ln \frac{P_2}{P_1} \tag{7.68}$$

Liquids and solids are quite incompressible and their volumes may be taken as independent of pressure. For such systems

$$\Delta G = \int_{G_1}^{G_2} dG = V \int_{P_1}^{P_2} dP = V(P_2 - P_1) \tag{7.69}$$

Example 7.13: Calculate the free energy change when one mole of an ideal gas has its pressure reduced isothermally and reversibly from 1.0 atm to 0.10 atm at 27°C.

Solution: $\Delta G = RT \ln \frac{P_2}{P_1}$

$$= RT \ln \frac{0.10}{1.0}$$

$$= (8.314)(300)(2.303) \log \frac{1}{10}$$

$$= -5.774 \text{ kJ mol}^{-1}$$

7.12.6 Helmholtz free energy (work function) and its significance

(a) Helmholtz free energy and maximum work

Like Gibbs free energy the Helmholtz free energy A is a state function. For change in A,

$$\Delta A = \Delta U - T\Delta S \tag{7.70}$$

If we consider an isothermal change at T, it can be shown, as in the case of Gibbs energy, by combining the first and second law of thermodynamics that,

$$-\Delta A = w_{\max} \tag{7.71}$$

Thus the decrease in Helmholtz free energy is equal to the maximum work done by the system in an isothermal process at constant volume. The Helmholtz free energy function is called a '*work function*', because of the relationship between A and w.

(b) Helmholtz free energy, spontaneity and equilibrium

For constant volume processes the relations of ΔA to spontaneity and equilibrium may be summarized as follows:

$\Delta A < 0$ *(negative); the process is spontaneous*
$\Delta A > 0$ *(positive); the process is non-spontaneous*
$\Delta A = 0$; *the system is at equilibrium.*

7.12.7 Dependence of Helmholtz free energy on volume and temperature

The dependence of work function A on volume and temperature may be obtained following similar procedure (7.12.3) as in the case of Gibbs energy function. Thus,

At constant volume : $$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad (7.72)$$

At constant temperature : $$\left(\frac{\partial A}{\partial V}\right)_T = -P \qquad (7.73)$$

7.13 Gibbs-Helmholtz Equation

A useful relation between the free energy change and enthalpy change in an isothermal process between two states may be deduced from equation (7.65). We can write:

For initial state: $\left(\frac{\partial G_1}{\partial T}\right)_P = -S_1$; and *for final state:* $\left(\frac{\partial G_2}{\partial T}\right)_P = -S_2$

Upon subtraction of initial condition from the final condition we get,

$$-S_2 - (-S_1) = \left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P \qquad (7.74)$$

$$-\Delta S = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P \qquad (7.75)$$

Substitution of (7.75) in the relation $\Delta G = \Delta H - T\Delta S$ gives:

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \qquad (7.76)$$

This was independently derived by Gibbs and Helmholtz and is known as the *Gibbs-Helmholtz equation.* An alternative form of the equation in terms of A and U is:

$$\Delta A = \Delta U + T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V \qquad (7.77)$$

which can be similarly deduced from equations (7.70) and (7.72).

The importance of these equations lie in the fact that ΔH or ΔU of a process may be calculated if ΔG or ΔA and their rate of change with temperature under proper conditions are known. Since most chemical reactions are carried out at constant temperature and under atmospheric pressure, the form in the equation (7.76) is of particular value for chemical problems.

7.14 Equilibrium between Phases : The Clapeyron Equation

If two phases of a given substance are in equilibrium, it follows from equation (7.60) that in transferring a given amount of the substance from one phase to the other at constant temperature and pressure,

$$\Delta G = 0$$

At any given temperature and pressure let the equilibrium be represented by,

$$\text{State } A \rightleftharpoons \text{State } B$$

Hence,
$$\Delta G_{P,T} = G_B - G_A = 0 \tag{7.78}$$

Or,
$$G_B = G_A \tag{7.79}$$

Now, if the temperature is raised by an amount dT, the pressure must also be increased by an amount dP in order to maintain equilibrium between the two phases. Under these conditions the free energy of the phases A and B will be $G_A + dG_A$ and $G_B + dG_B$ respectively. Since equilibrium is maintained,

$$G_A + dG_A = G_B + dG_B \tag{7.80}$$

From equations (7.79) and (7.80) we obtain:

$$dG_A = dG_B \tag{7.81}$$

Using the relation giving the influence of temperature and pressure on free energy, (7.63) we can write for the two phases

$$dG_A = V_A\,dP - S_A\,dT \tag{7.82}$$

$$dG_B = V_B\,dP - S_B\,dT \tag{7.83}$$

since dP and dT are the same for both the phases. Combining equations (7.81), 7.82) and (7.83) one obtains:

$$V_B dP - S_B dT = V_A dP - S_A dT \tag{7.84}$$

Equation (7.84) may be rearranged to give:

$$V_B dP - V_A dP = S_B dT - S_A dT$$

or
$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} \tag{7.85}$$

We know for an isothermal reversible process, $S_B - S_A = \Delta S = \frac{q_{rev}}{T} = \frac{\Delta H}{T}$

where ΔH represents the enthalpy change at the given temperature and pressure. Therefore, equation (7.85) may be converted to

$$\frac{dP}{dT}=\frac{\Delta H}{T(V_B-V_A)}=\frac{\Delta H}{T\Delta V} \tag{7.86}$$

This is known as the *Clapeyron equation.* This equation gives the rate of change of the equilibrium pressure with temperature during any phase change such as vaporization, fusion, sublimation or conversion of one solid form into another, in terms of ΔH and volumes of a given amount of the substance. The volumes must be measured at the temperature and pressure of equilibrium.

Equation (7.86) can also be used to calculate the effect of pressure on the temperature of phase transition, *viz.*, fusion, vaporization etc by writing it in the form

$$\frac{dT}{dP}=\frac{T(V_B-V_A)}{\Delta H} \tag{7.87}$$

In using this equation for solving numerical problems the units must be consistent. If the pressure is expressed in atmospheres and volume in L, the heat term should be expressed in L-atmospheres; if the pressure is given in atm, the heat should be expressed in J.

Example 7.14: Calculate the change in the freezing point of water when the pressure is increased by 1 atm. At 0°C, which is the freezing point under 1 atm pressure, the heat of fusion is 333.8 J g^{-1}, the densities of liquid water and ice are 0.9998 and 0.9168 g (mL)$^{-1}$ respectively.

Solution: Volume of 1.0 gram of ice$=\frac{1}{0.9168}$ mL = 1.0908 mL

Volume of 1.0 gram of water $=\frac{1}{0.9998}$ mL = 1.0002 mL

Change in volume ΔV of 1.0 mole on melting

$$\begin{aligned}&=(1.0002-1.0908)\times 18\ \text{mL}\\&=-0.0906\times 18\ \text{mL}\\&=-9.06\times 10^{-5}\times 18\ \text{L}\\&=-1.631\times 10^{-3}\ \text{L}\end{aligned}$$

Heat of fusion, ΔH, per mole = 333.8 × 18 = 6008 J

We know that the gas constant R = 8.314 J = 0.08205 L-atm

$1\ \text{J} = 9.869\times 10^{-3}$ L-atm

Heat of fusion, ΔH, per mole in L-atmosphere units

$$= 6008 \times 9.869\times 10^{-3} = 59.29\ \text{L-atm}$$

Therefore, using equation(7.87), $\frac{dT}{dP}=\frac{-(273)(1.631\times 10^{-3})}{59.29}$

$$=-7.50\times 10^{-3}\ \text{deg atm}^{-1}$$

So, an increase in pressure of 1 atm lowers the freezing point of ice by 7.50×10^{-3} °C. The negative sign indicates that an increase of pressure decreases the melting point. It should be noted that the negative sign arises from the fact that the volume of the final phase (*B*), water in this example, is less than that of the initial phase (*A*), ice. In evaporation, $V_B - V_A$ is positive as the vapour has higher volume than the liquid and hence dT/dP would, be positive, i.e., the boiling point would rise with increase of pressure. Note that in both the cases ΔH is positive. If ΔH is negative, proper attention has to be given to obtain the sign of dT/dP.

7.15 The Clausius-Clapeyron Equation

The Clapeyron equation is usually applied only to solid-liquid or solid-solid equilibria. When one phase is gas, a very useful extension was developed by Clausius, and the equation is known as Clausius-Clapeyron Equation.

(A) Differential form of Clausius-Clapeyron equation

Clausius made two assumptions -

(i) $V_g >> V_l$; therefore, $\Delta V \approx V_g$

(ii) Gas phase shows ideal behaviour; therefore, $V = \frac{RT}{P}$

Equation (7.86) then reduces to,

$$\frac{dP}{dT} = \frac{\Delta H}{T} \times \frac{1}{V} = \frac{\Delta H}{T} \times \frac{P}{RT} = \frac{P\,\Delta H}{RT^2} \tag{7.88}$$

which on rearrangement becomes

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta H}{RT^2} \tag{7.89}$$

or

$$\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2} \tag{7.90}$$

Equation (7.90) is the differential form of Clausius-Clapeyron equation. Here, ΔH is either enthalpy of vaporization or the enthalpy of sublimation, and T is the corresponding temperature. The results obtained from this equation are valid as long as the two assumptions are valid. Near the critical state $V_l \sim V_g$, so the equation is less reliable.

(B) Integrated form of Clausius-Clapeyron equation

Exact integration of equation (7.90) is not possible, because ΔH is a function of T. However, if it is assumed that ΔH does not depend on T, then we obtain the equation,

$$\int d\ln P = \frac{\Delta H}{R}\int \frac{1}{T^2}\,dT \tag{7.91}$$

Integration of (7.91) without limits yields,

$$ln\,P = \left(-\frac{\Delta H}{R}\right)\left(\frac{1}{T}\right) + C \tag{7.92}$$

Integration of (7.91) with limits P_2, T_2 and P_1, T_1 yields,

$$ln\frac{P_2}{P_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \frac{\Delta H}{R}\left(\frac{T_2-T_1}{T_2T_1}\right)$$

$$ln\frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{T_2-T_1}{T_2T_1}\right) \tag{7.93}$$

Equation (7.92) is the equation of a straight line; a plot of *ln P* versus *1/T* would have a slope $-\Delta H/R$ and intercept C. If for a system P_1, T_1 and P_2, T_2 are known ΔH can be calculated by using equation (7.93).

The Clapeyron-Clausius equation is a special case of a general formula for any equilibrium involving temperature. In the general equation the equilibrium vapour pressure is replaced by equilibrium constant of the chemical reactions or physical change and heat of vaporization is replaced by the corresponding heat of reaction of the physical change.

Example 7.15 : The boiling point of water at atmospheric pressure is 373 K. What will be the boiling point of water at a higher altitude where the pressure is 528 *mm Hg*? Given ΔH_{vap} is 41040 J $K^{-1}mol^{-1}$.

Solution : Here, $P_1 = 760$ *mm Hg*; $T_1 = 373$ K; $P_2 = 528$ *mm Hg*.

We have to find T_2.

Substituting these values in equation (7.92) we get,

$$ln\frac{528}{760} = \frac{\Delta H_{vap}}{8.314}\left(\frac{T_2-373}{373T_2}\right)$$

By solving for T_2 it can be shown that $T_2 = 383.5$ K

At lower pressure boiling point is higher.

QUESTIONS AND PROBLEMS

1. State the second law of thermodynamics and explain the conditions under which heat can be converted into work.
2. Derive an expression for the efficiency of a reversible Carnot cycle. Show that the efficiency of such a cycle is maximum.
3. What is your concept of entropy? Derive expressions for entropy changes of an ideal gas at constant pressure and at constant temperature.
4. Calculate the entropy change involved in (a) evaporation of 1 mole of water at 100°C to water vapour at 100°C and (b) converting 2 moles of hydrogen gas from 30 L at 2 atmospheres pressure to 100 L at 1 atm pressure, given that C_p of hydrogen is 30.9 J deg^{-1} mole^{-1}.

   [Ans. (a) 109.1 J deg^{-1}, (b) 43.0 J deg^{-1})]
5. How is the entropy change of an irreversible process determined? Show that in all irreversible processes the increase of entropy is more than that in a reversible process.
6. Deduce an expression for the efficiency of an engine operating thermodynamically reversibly.
7. One mole of an ideal gas at 27°C expands isothermally and reversibly from 1.0 L to 5.0 L. Calculate w and each of the thermodynamic quantities ΔU, ΔH, ΔG, ΔA and ΔS.

   [Ans. $w = q = 4004$ J; $\Delta H = \Delta U = O$; $\Delta G = \Delta A = 4004$ J; $\Delta S = 13.3$ J K^{-1}]
8. Calculate the change in entropy of 2 moles of an ideal gas when it is heated from 300°K to 600°K at (i) constant pressure and at (ii) constant volume. The molar heat capacity at constant pressure, C_p = (20.9/R) J mol^{-1} deg^{-1}.

   [Ans. (i) 26.5 J K^{-1}; (ii) 17.2 J K^{-1}]
9. The heat of fusion of water at 0°C is 6.02 kJ mole^{-1}; its heat of vaporization is 40.7 kJ mole^{-1}at 100°C. What are ΔS for the melting and boiling of 1.0 mole of water? Can you explain why ΔS_{vapour} is greater than $\Delta S_{\text{melting}}$?
10. Calculate ΔG^o for

$$H_2O\,(\text{g}, 25°\text{C}) \;=\; H_2O\,(\text{l}, 25°\text{C})$$

   The vapour pressure of water at 25°C is 23.76 mm Hg. [Ans. 8.59 kJ mol^{-1}]

11. One mole of toluene is vaporized at its boiling point, 111°C. Calculate (a) the work done against the atmosphere, (b) q, (c) ΔU, (d)ΔH, (e) ΔG and (f) ΔS.

   [Ans.(a) 3193, (b) 33.342 kJ, (c) 33,342, (d) 30,149, (e) 0 J mole^{-1} (f) 86.8 J $K^{-1}\text{mol}^{-1}$]

8 SOLUTIONS

A solution is a system one comes across every day; it is so well known that it needs no explanation. If a little sugar is added to water, the sugar slowly disappears and sugar particles cannot be seen even under the most powerful microscope. It is said that sugar has dissolved in water to form a solution. *A solution is usually defined as a homogeneous mixture of two or more substances whose compositions can be varied over certain ranges.* This definition normally serves the purpose, but a careful scrutiny reveals some complications.

Is a solution really homogeneous? If the molecules in a solution are picked up mentally one by one what could be seen? Once or twice a molecule of water would be picked up and once or twice a molecule of sugar could be picked up. Thus in a solution the molecules of water and sugar are lying side by side and since a molecule of water is different from a molecule of sugar there cannot be any homogeneity. Thus, judged on the molecular level, a solution is heterogeneous. But if a solution is considered on a macroscopic scale, then it is homogeneous since even in a fraction of a drop, millions of water and sugar molecules are present in a fixed proportion, thus giving an homogeneity to the solution. The scale of our observation is thus important. Again, if a careful measurement of the number of solute molecules are made in a solution it will be found that the concentrations of the solute molecules are not the same in the solution bulk and on the solution surface. For practical purposes we still stick to the definition given above but we must bear in mind the incompleteness of the definition.

In a solution containing two constituents which has been described as above the constituent which is present in a larger amount is called the *solvent* and the one which is present in lesser amount is called the *solute***.** The physical properties of solutions depend on the relative proportions of the components of which the solution is composed. If the components interact with each other then it is not a solution. It becomes a reaction. For example ammonia and hydrogen chloride gases dissolve in water but they react with the solvent. The discussion in this chapter will be concerned with systems where the components do not react with each other.

Experience has taught us that substances differ widely in their solubility in various solvents. For example we know that gases mix with each other completely. The solubility of some gases in water is high, while others dissolve only slightly in water. Solubility of gases in solids is a different process. Some liquid pairs are completely miscible with each other. Examples are hexane and heptane, water and ethanol. We find pairs of liquids which are almost completely insoluble in each other and when mixed together they form separate layers. Again there are pairs of liquids which are miscible with each other partly in some concentrations and are completely miscible in some regions of concentration. In solutions of solids in liquids we find a similar range of solubility, from complete solubility to insolubility. Answers to the reason for such diverse behaviour in solubility of substances in each other are not known in all cases. Some insight has been arrived at from consideration of the interaction of the particles of these substances in the molecular level in the case of covalent substances and ionic level in the case of ionic substances. Attempts will be made to present the current ideas about the solution process in different cases.

8.1 Types of Solutions

Solutions may be divided into the following types : (i) Gas in gas, (ii) Gas in liquid, (iii) Gas in solid, (iv) Liquid in liquid, (v) Liquid in solid, (vi) Solid in solid, (vii) Solid in liquid.

Most of the discussions in this chapter will be confined to solutions of gas in liquid, gas in solid, liquid in liquid and solid in liquid only. Other types of solutions have been discussed in different chapters. Thus gas in gas has been included in *Section 2.10*. The remaining types are excluded because of their complex nature.

8.2 Units of Concentration

Whenever the concentration of a solution is reported, the appropriate unit in which it is given is also mentioned. In chemical literature the following units are used:

(i) *Molarity (mol L^{-1}):* The molarity of a solution *is the number of moles of the solute dissolved in 1000 mL of the solution.* Thus if 60 *g* (one mol) of urea is dissolved in water to form a solution occupying a volume of 1000 *mL* at a specified temperature, the solution is said to be 1.0 *molar.* 6.0 g of urea per 1000 *mL* of solution will give a 0.1 molar solution whereas 0.6 g of urea in 1000 *mL* solution will give a 0.01 molar solution. Since the volume of the solution will depend on the temperature, molarity will vary with temperature.

(ii) Molality (m): Molality of a solution *is the number of moles of the solute dissolved in 1000 g of the solvent*. In other words, if one mol of a substance is dissolved in 1000 *g* of the solvent, the solution is said to be 1.0 *molal*. 60 *g* of urea dissolved in 1000 *g* of water gives a 1.0 molal solution. Molality is independent of temperature.

(iii) *Mole fraction:* Mole fraction of the solute is defined as the ratio of the number of moles of the solute to the total number of moles of the solute and solvent taken together (*Section 2.11*). If n be the number of moles of solute and N the number of moles of the solvent then the mole fraction of the solute is $\frac{n}{(n+N)}$. Taking the previous example, if 60 *g* of urea is dissolved in 1000 *g* of water, then $n = \frac{60}{60}$ and $N = \frac{1000}{18} = 55.56$. Therefore, mole fraction of urea in the solution is $\frac{1}{1+55.56} = 0.0176$. The mole fraction of water can be easily calculated. Thus it is equal to $\frac{55.56}{1+55.56} = 0.9823$. It is to be noted that in any solution the sum of the mole fractions of solute and solvent is always equal to unity. Mole fraction is a dimensionless quantity and represents a pure number. When mole fraction is multiplied by 100 it is called *mole percent*. Mole fraction is independent of temperature. If w is the mass of a substance of molecular mass m and if it is dissolved in W g of a solvent of molecular mass M then

$$\text{Mole fraction of the solute } X_2 = \left(\frac{w/m}{w/m+W/M}\right)$$

$$\text{Mole fraction of the solvent } X_1 = \left(\frac{W/M}{w/m+W/M}\right)$$

(iv) ***Normality (N) :*** It is another concentration unit used to be in use in the past. It was defined as, "*The number of equivalent mass of a substance present in 1 L of a solution.*" Normality is also temperature dependent. However, normality is no longer used in chemical calculations and can be found only in older text.

Other ways of expressing concentrations are also in use. These are, however, seldom used in scientific literature but they find application in technical fields. Weight percent is one such method which represents the weight in *g* of the substance per 100 *g* of the solvent. It is represented as *w/w*. In another method the weight in *g* of the substance per 100 *mL* solution or solvent is used and is represented as *w/v*.

Example 8.1: 5.30 *g* of Na_2CO_3 was dissolved in water to prepare 100 *mL* of solution. Calculate the molarity of the solution.

Solution: Relative formula mass (RFM) of $Na_2CO_3 = 106$

$$\text{Moles of } Na_2CO_3 \text{ in 5.30 g} = \frac{5.30}{106} = 0.05$$

100 mL of the solution contains 0.05 moles
1000 mL of the solution contains $0.05 \times 10 = 0.50$ moles
Hence molarity = 0.50 mol L^{-1}

Example 8.2: 25 *mL* of 0.01 mol L^{-1} solution of *NaOH* was diluted to 75 *mL*. Calculate the molarity of the diluted solution.

Solution : 1000 *mL* of solution contain 0.01 moles.

No of moles of *NaOH* present in 25 *mL* of solution

$$= 0.01 \times 25 \times 10^{-3}$$
$$= 0.25 \times 10^{-3}$$

75 *mL* of the diluted solution contain 0.25×10^{-3} mole of *NaOH*

$$1000\ mL \text{ of the solution contains } \frac{(0.25\times10^{-3})(1000)}{75} \text{ moles}$$

$$= 0.0033 \text{ moles}$$

Thus the molarity of the diluted solution= 0.0033 mol L^{-1}

8.3 Solution of Gas in Liquids*

All gases are more or less soluble in liquids. The quantity of the gas dissolved under identical conditions of temperature, pressure and volume of the solvent, however, depends on the chemical nature of the gas and liquid. No general prediction of solubility is possible, only rough ideas can sometimes be made. Gases like He, Ne, H_2, O_2, N_2 is only slightly soluble in water, the solubility of CO_2, SO_2, H_2S is somewhat more, but the solubility of NH_3, HCl is very high.

The solubility of a gas is generally defined as *the volume of the gas, at the temperature and pressure of the experiment, dissolved in 1 mL of the liquid.* If the volume of the gas dissolved in 1 *mL* of the liquid at any temperature and pressure is reduced to *STP*, then the volume dissolved is called *absorption co-efficient*. In Table 8.1, the absorption co-efficients of some common gases are given. The values refer to water as solvent and the temperatures of 0 °C and 20 °C.

Table 8.1 Absorption co-efficient of some gases

Gas	Absorption co-efficient	
	0°C	20°C
Ammonia	1300	710
Hydrogen chloride	506	442
Sulphur dioxide	80	—
Hydrogen sulphide	4.7	2.7
Carbon dioxide	1.7	0.9
Oxygen	0.05	0.03
Nitrogen	0.024	0.015
Helium	0.01	0.009
Carbon monoxide	0.036	0.025

Example 8.3: The solubility of argon in water is 0.00515 *g* in 100 *g* of water at 25°C and 1 atm pressure. Calculate the absorption co-efficient.

Solution: By definition absorption co-efficient $\alpha = \frac{v_o}{V.P}$, where v_o is the volume of the gas dissolved at *STP* and *V* is the volume of the liquid and *P*, the pressure of the gas.
Let 0.00515 g of argon occupy a volume *v* litres at 25°C and 1.0 atm pressure

$$v = \frac{wRT}{MP} = \frac{(0.00515)(0.08206)(298)}{(39.94)(1.0)} = 3.15 \times 10^{-3}\ L = 3.15\ \text{mL}$$

at 25°C and 1.0 atm pressure

$$(R = 0.08206\ L\text{-}atm;\ T = 273 + 25 = 298;\ RAM \text{ of } Ar = 39.94)$$

---

* In this and the subsequent section it is assumed that there is no chemical interaction between the solute and solvent unless otherwise stated.

But $v_o\,(273) = (3.15)\,(298)$

$$v_o = \frac{(3.15)(298)}{273} = 3.49 \text{ mL}$$

$$\therefore \quad \alpha = \frac{3.49}{(100)(1.0)} = 0.0349$$

(Density of water is assumed to be equal to 1 $g\,(mL)^{-1}$.

8.4 Effect of Temperature

The solubility of a gas in a liquid is markedly affected by temperature. Usually, the solubility decreases with the increase of temperature. This can be seen from the data in Table 8.1. It can be readily shown that the variation of solubility with temperature follows a general pattern (*Section 10.14*). Considering solubility expressed as concentration as an equilibrium constant, for gas-liquid systems the relation between concentration and temperature assumes the form

$$\frac{d \ln C}{dT} = \frac{\Delta H}{RT^2} \tag{8.1}$$

or

$$\ln \frac{C_2}{C_1} = -\frac{\Delta H}{RT^2}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{8.2}$$

where C_1 and C_2 are the concentrations in mol L^{-1} at temperature T_1 and T_2 and ΔH is the *enthalpy of solution* of 1 mole of the gas in the saturated solution.

Theoretically all gases should be completely expelled from a solution at the boiling point of the liquid since at the boiling point the vapour pressure of the liquid is equal to the superincumbent pressure. This is obeyed by many solutions, but the removal of the last trace of the gas is sometimes difficult and takes a long time. In removing gases from solution this fact should be borne in mind. Thus in the Kjeldhal* method for estimation of nitrogen the ammonia solution formed in an intermediate step is boiled for a sufficiently long time to expel all ammonia.

8.5 Influence of Pressure

The solubility of gases in liquids is greatly influenced by pressure and in all cases the solubility increases with increase in pressure. This qualitative statement is expressed quantitatively by *Henry's Law* which states that *'the amount of a gas in g dissolved in a definite volume of solvent is directly proportional to the pressure of the gas at constant temperature'*. Mathematically,

$$w \propto P$$

or

$$\frac{w}{P} = \text{constant} \tag{8.3}$$

---

* This will be found in text books of Organic Chemistry or text books on Quantitative Chemical Analysis.

where w is the mass of the gas in g and P is the pressure. The solubility of oxygen and carbon dioxide in water at different pressures are given in Table 8.2. It can be seen that the values of w/P are approximately constant for both the gases.

Henry's law may also be stated in two other forms:

(a) Let w g of a gas of volume V mL at a pressure P is dissolved in a given volume of a liquid. If the pressure is increased to $2P$, the mass of gas dissolved in the same volume of the liquid will be $2w$ g according to Henry's law.

Table 8.2 Solubility of oxygen and carbon dioxide in water

Oxygen (25°C)			Carbon dioxide (20°C)		
Pressure, P cm of Hg	Mass of gas dissolved in 1 L water, $w\,(g) \times 10^2$	$\frac{w}{P} \times 10^4$	Pressure,P cm of Hg	Mass of gas dissolved in 1 L water, $w\,(g)$	$\frac{w}{P}$
76·0	4.08	5.37	72.55	38.60	0.515
61.0	3.25	5.32	52.45	27.24	0.519
41.4	2.20	5.31	52.37	27.08	0.517
30.0	1.60	5.33	52.31	27.28	0.521
17.5	0.95	5.43	–	–	–

In the case of an ideal gas obeying Boyle's law the volume of $2w$ g of gas at pressure P is $2V$ mL but at pressure $2P$ it is V mL. Hence it can be stated that

'*The volume of a gas, measured at the pressure of the experiment, dissolved in a given volume of liquid at a constant temperature is independent of pressure*'. This may be taken as one form of the law.

The equation of state for gases may also be used to obtain the same result. Equation (2.12) may be written in the form

$$V = \frac{g}{P} \times \frac{RT}{M} \tag{8.4}$$

where V is the volume of g gram of gas measured at pressure P and dissolved in a given volume of liquid. At a constant temperature for the same gas, RT/M is constant and g/P is constant according to Henry's law. Hence V, the volume of gas dissolved, is independent of pressure.

(b) When a gas dissolves in a liquid *the ratio of the concentrations of the gas in the liquid phase and in the gas phase is constant at a constant temperature*. This is the third form of statement of Henry's law and this is in the form of an important generalization known as the *Distribution law* (*Section 8.12*). From the kinetic theory it follows that the pressure P is proportional to the number of molecules in the gas phase, and hence is also proportional to the concentration in $mol\ L^{-1}$ of the gas phase. The mass w g of the gas dissolved in the liquid is proportional to the concentration of the gas in *mol* L^{-1} of the liquid phase. Hence from Henrys' law

$$\frac{\text{Concentration of gas in liquid phase}}{\text{Concentration of gas in gas phase}} = \text{Constant}$$

or

$$\frac{C_l}{C_g} = K \tag{8.5}$$

8.6 Validity and Limitations of Henry's Law

Henry's law is obeyed fairly satisfactorily by many gases of low solubility, provided the pressure is not too high or the temperature is not too low. This is because Henry's law is intimately connected with ideal gas law. Large deviations from Henry's law are observed in the case of gases of high solubility and particularly those which interact with the solvent liquid, e.g., ammonia and hydrogen chloride gas in water. Ammonia forms ammonium hydroxide which partly dissociates into ammonium and hydroxyl ions while hydrogen chloride gas forms hydrogen and chloride ions in water. Deviations from Henry's law in these cases are attributed to change in the molecular species as result of dissolution. The law is strictly applicable to those gases where the molecular species are the same in the liquid phase. If suitable corrections are applied to account for such interactions, and concentrations of the same molecular species in the two phases are determined, Henry's law might be applicable. This indeed was found to be true in the case of ammonia (see Table 8.6).

8.7 Solution of Gas in Solid

Gases are always taken up by solids but the extent of uptake varies widely. If the uptake is by adsorption only (*Section 18.3*) the uptake is quite small and this phenomenon in general cannot be taken as solution. There are three other ways in which the gases can be taken up by solids:

(i) A gas may be distributed uniformly giving rise to a homogeneous solution in such a way that there is no change in the molecular structure or composition of the gas. Such cases constitute true solutions and they resemble the solution of gas in liquid closely. Solutions of ammonia and sulphur dioxide on charcoal are examples of such cases. There is a decrease in the translational kinetic energy of the molecules while they dissolve in the solid and such solutions are exothermic in nature. These systems obey Henry's law like the solutions of gas in liquid. If *P* be the pressure at which the gas is dissolved at a constant temperature then the concentration of the gas in the solution is directly proportional to the pressure. If the concentration of the gas in the solid is *C*, then

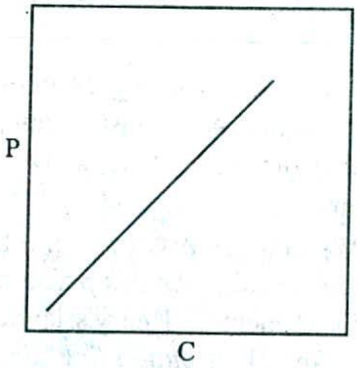


Figure 8.1 *P vs C* for solution of gas in solid

P/C = constant and a plot of P *vs* C will be a straight line, as shown in Figure 8.1. If the gas undergoes as sociation in the solution and if n is the degree of association, then $\frac{P}{\sqrt[n]{C}}$ = constant, whereas in case of dissociation the relation becomes $\frac{P}{C^n}$ = constant, where n now denotes the number of parts into which the molecule is dissociated (compare Distribution law, *Section 8.12*).

(ii) If the gas forms a solid solution a different behaviour is observed as shown in Figure 8.2.The part *ab* represents the usual true solution and the relation $P/C=K$ holds until the point *b* is reached. At *b* and up to *c* a new solid solution is formed. Since the curve is an isothermal the system is invariant (*Section 11.1*). Therefore, *bc* runs parallel to the pressure axis. On increasing the pressure still further this solid solution disappears at *c* and the usual relation $P/C=K$ is followed along *cd* except that the straight line does not pass through the origin.

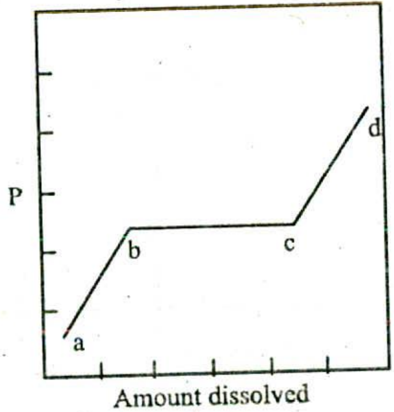


Figure 8.2 P *vs* amount of gas dissolved in solid

(iii) The third type of uptake of a gas by a solid is due to compound formation and no general conclusions are possible unless the dissociation pressure of the solid compound so formed is considered. Thus uptake of carbon dioxide by calcium oxide is an example of compound formation giving calcium carbonate.

8.8 Liquid - Liquid Solution: The Solution Process

When one substance dissolves in another, particles of the solute – either molecules or ions, depending on the nature of the solute – must be distributed throughout the solvent and, in a sense, solute particles in solution occupy positions that are normally taken by the solvent molecules. In a liquid the molecules are packed together very closely and interact strongly with each other. The ease with which a solute particle may replace a solvent molecule depends on the relative strength of the forces of attraction of solvent molecules for each other, solute particles for each other and the strength of the solute-solvent interaction. For example, in a solution formed between hexane (C_6H_{14}) and octane (C_8H_{18}) both species are non-polar and have weak London forces among the molecules of each compound. As it happens the strength of the forces of attraction between the pairs of hexane molecules and pairs of octane molecules are of nearly the same magnitude as those between the molecules of hexane and octane. For this reason the molecules of hexane can replace molecules of octane with ease. As a result these two substances are completely soluble in all proportions. They are said to be completely *miscible* with each other.

Water (H_2O) and ethanol (C_2H_5OH) are miscible in all proportions. The C_2H_5OH molecules can form hydrogen bonds with water molecules as well as with its own molecules. Because of this hydrogen bonding ability the solute – solute, solvent – solvent and solute – solvent interactions are not appreciably different from each other in a solution of the two substances. There is no significant difference between the environments of the molecules as they are mixed. So they are completely miscible. However, the number of carbon atoms in the alcohol molecule affects its solubility in water. This is shown in Table 8.3.

Table 8.3 Solubility of different alcohols in water

Substance	Formula	Solubility mol solute/100 g water
Methanol	$CH_3\,OH$	Completely miscible
Ethanol	C_2H_5OH	Completely miscible
Propanol	C_3H_7OH	Completely miscible
n - Butanol	C_4H_9OH	0.12
n– Pentanol	$C_5H_{11}OH$	0.031
n – Hexanol	$C_6H_{13}OH$	0.0059
n - Heptanol	$C_7H_{15}OH$	0.0015

As the length of the carbon chain increases, the *OH* group becomes an ever smaller part of the molecule and the molecule becomes more like a hydrocarbon. So the solubility decreases with increase of carbon atom in the chain. If the number of *OH* groups in the molecule increases, as in glucose ($C_6H_{12}O_6$) which contains five *OH* groups per molecule or sucrose ($C_{12}H_{22}O_{11}$) which contains ten *OH* groups per molecule, more hydrogen bonding with water molecules are possible. So the solubility of the compounds in water is high.

Now let us consider what happens when we try to dissolve water in C_8H_{18}. Because octane molecules are non-polar, the forces of attraction that exist between them are relatively weak London forces. In contrast, water is a polar substance and strong hydrogen bond exists between their molecules. Attractive forces between polar water molecules and non-polar octane molecules are much weaker than hydrogen bonds. The H_2O – C_8H_{18} interactions are insufficient to overcome the H_2O – H_2O interactions; consequently the C_8H_{18} molecules can not penetrate between the water molecules. When the water molecules meet one another they tend to stick together simply because they attract each other more strongly than they do molecules of C_8H_{18}. This 'clumping together' continues until the two liquids form two distinct layers: one layer consisting of water with a very small amount of octane and the other layer consisting of octane with a very small amount of water. The liquid pairs are said to be *immiscible* with each other.

Apart from the miscible and immiscible liquid pairs there is a host of other liquid pairs which are partly miscible with each other.

8.9 Ideal and Non - ideal Solutions

One property of completely miscible liquid pairs is the energy change involved when two liquids are mixed. It has been mentioned that when one liquid dissolves in another we can imagine that the molecules of the solvent are caused to move apart so as to make room for the molecules of the solute. Since there are attractive forces between the molecules of the solute and those of the solvent, energy has to be added in order to separate from one another the molecules of the solvent as well as of the solute. When the molecules of the solvent and solute come together to form the solution, energy is released because of the attractions between the molecules of the solvent and the solute.

Let us consider three different scenarios:

(a) The attractive forces between the molecules of the solute, between the molecules of the solvent and between the molecules of solvent and of the solute are similar, as in the solution of hexane and octane. The energy absorbed in the separation of the molecules of the solvent and the molecules of the solute becomes equal to the energy released when the solvent and solute molecules mix together to form the solution. No heat is absorbed or released on mixing the two liquids. Such a solution is called an *ideal* solution. Such solutions obey Raoult's law. *A solution is said to be* ***ideal*** *when it obeys Raoult's law (Section 9.2) over all compositions and at all temperatures.*

(b) If the molecules of the solvent and the solute attract each other more strongly than molecules of their own kind, more energy can be released when the solute and solvent molecules are brought together than was required to separate them. Under these circumstances the overall solution process can result in the evolution of heat and the mixing will be exothermic. When acetone and water are mixed heat is evolved and the container in which the mixing is done becomes warm.

(c) When the solute – solvent molecular interaction is weaker than those between pure solvent molecules and pure solute molecules the formation of a solution requires addition of energy. This is because more energy is required to separate the molecules in the solute and solvent than is evolved when these molecules are mixed. In such cases the solution becomes cool as it is formed, indicating that the process is endothermic. Solution of ethanol and hexane is an example. The non- polar hexane molecules come between ethanol molecules effectively destroying the hydrogen bond between ethanol molecules. This absorbs energy and the solution is cool.

Liquid – liquid solution of the types described in (b) and (c) are *non-ideal* as these do not obey Raoult's law.

The properties of liquid – liquid solutions, particularly Liquid – Vapour equilibria of these three types of mixture will be dealt with in Chapter 9.

8.10 Solid - Liquid Solution: The Solution Process

An understanding of the solution process will help us in the study of solutions. In all cases in this discussion water will be taken as the solvent.

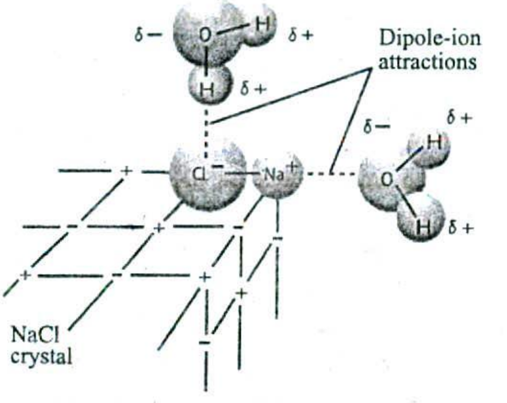


Figure 8.3 Interactions between water molecules and the Na^+ and Cl^- ions in $NaCl$ crystal surfaces.

Let us look at what happens when we dissolve $NaCl$, an ionic compound, in water, a polar liquid. When $NaCl$ is added to water the water molecules, being polar, orient themselves on the surface of the crystal as shown in Figure 8.3.

The negative end of the polar water molecule orients towards the positive Na^+ ions , while the positive end is oriented towards the negative Cl^- ions. The dipole – ion attraction is strong enough to pull these ions from their positions in the crystal. Once removed from the crystal, the Na^+ and Cl^- ions are surrounded by the water molecules as shown in Figure 8.4. Such interaction between the water molecules and the ions is called *hydration*. If the solvent is other than water this interaction is termed *solvation*. To form a solution the water molecules must also separate to make room for the ions.

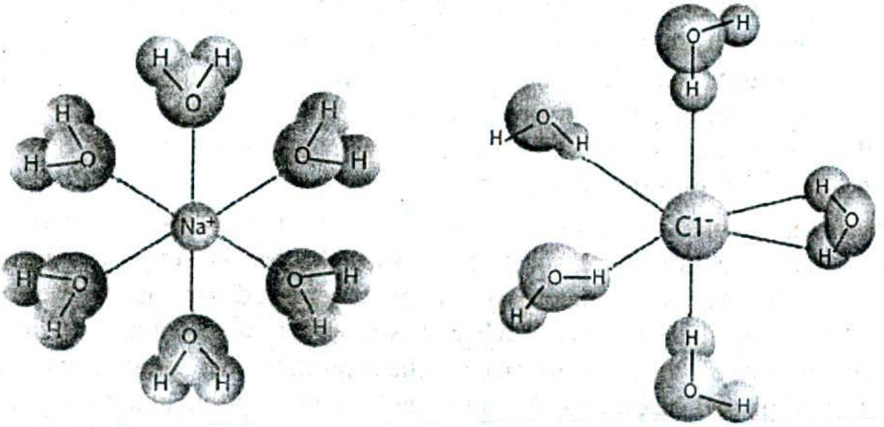


Figure 8.4 Hydrated Na^+ and Cl^- ions. Ions are surrounded by water molecules.

The layer of oriented water molecules that surrounds ions help to neutralize the ion's charge and keep ions of opposite charge from attracting each other strongly over long distances within the solution. In a sense, the solvent insulates the ions from each other. We can imagine that three types of interaction taking place in the solution process: (i) interaction between solute particles of the solid, i.e. ions or molecules; (ii) interaction between solvent particles; (iii) interaction between solute and solvent particles. Energy is required to overcome the attraction between the solute particles in the solid, and the attraction between solvent particles, while energy is released when solute and solvent particles interact with each other. The net solution process can be either exothermic or endothermic depending on the relative magnitude of the three energy changes. The solution of NH_4NO_3 in water is endothermic as the energy change in steps (i) and (ii) is greater than the energy change in step (iii). Conversely, solution of $LiCl$ is exothermic because more heat is released in step (iii) than is absorbed in steps (i) and (ii).

8.11 Solubility

When a solid is added to a liquid and the solution process takes place the concentration of the solute in the solution increases. The particles – ions or molecules – move about at random in the solution and may by chance collide with a crystal of the solute and get attached to it. This process which is opposite to the solution process is called *crystallization.* As the solute continues to dissolve, more particles enter the solution and the rate at which the particles return to the crystalline state increases. Eventually a *dynamic equilibrium* is set up between the solute particles in solution and those in the undissolved state, as the rate at which the solid particles dissolve becomes equal to the rate at which the particles return to the solid crystalline state.

$$\text{Solute (in solution) + water} \quad \rightleftharpoons \quad \text{Solute (solid undissolved state)}$$

At equilibrium no more solid appears to dissolve. For example, if we add 45.0 g of KCl to 100 g of water at 30 °C only 37.0 g of the solute will be found to dissolve and the remaining 8.0 g will remain at the bottom of the solution in the solid undissolved state. A solution that contains as much of the dissolved solid as it can hold at a particular temperature is said to be *saturated*. In other words a solution that is in equilibrium with solid solute is a *saturated* solution. If it contains less than that required for saturation the solution is said to be *unsaturated.* The solubility of a solid in a liquid is usually defined *'as the amount of the solid in grams which is dissolved by 100 g of the liquid to make a saturated solution at a definite temperature'*. Thus the solubility of KCl in water at 30°C is 37.0 g means that at 30°C temperature 100 g of water can dissolve a maximum of 37.0 g of the salt. Since in a saturated solution dynamic equilibrium exists, the solubility of the solute in 1000 g of the solution can be considered as an equilibrium constant, K_c.

The terms saturated and unsaturated are in no way directly related to the terms *concentrated* and *dilute*. A saturated solution of silver chloride at room temperature contains only 0.000089 g of $AgCl$ per 100 g of water. This is a very dilute solution as it contains very small amount of the solute in 100 g of water. On the other hand a saturated solution of $LiClO_3$ in 100 g of water at the same temperature contains 500 g of the solute. A solution of $LiClO_3$ in 100 g water containing 300 g of the solute is unsaturated but definitely concentrated. Thus a saturated solution can be dilute and an unsaturated solution can be concentrated.

There are some substances which can form solutions that are termed *supersaturated* as these can contain more of the solute than is required to make a saturated solution. A saturated solution of sodium acetate at 0°C contains 119 *g* of the solute in 100 *g* of water. It is more soluble at higher temperature. If an unsaturated hot solution of sodium acetate containing more than 119 *g* of solute, say 125 *g*, in 100 *g* of water is cooled slowly to 0°C the excess solute remains dissolved: the solution is now *supersaturated*. The supersaturated solution is in unstable equilibrium as the introduction of a small crystal or a little jerk will start crystallization until the excess solid is separated.

8.12 Effect of Temperature on Solubility

When solids dissolve in a liquid heat is generally absorbed, i.e., dissolution of a solid in a liquid is an endothermic process. The solubility of such solids increases with the increase of temperature in accord with Le Chatelier principle (*Section 10.12*). When dissolution is accompanied by evolution of heat the solubility is found to decrease with rise of temperature, again in agreement with the Le Chatelier principle.

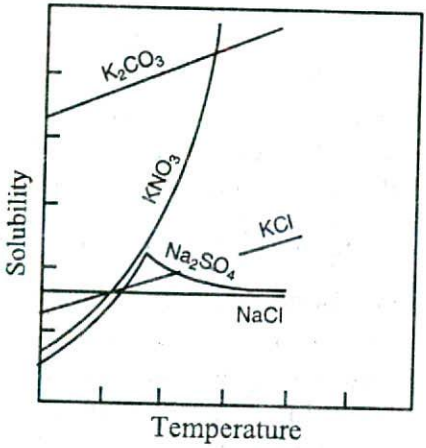


Figure 8.5 Solubility as a function of temperature

The solubilities of a few solids in water at different temperatures are given in Figure 8.5 and Table 8.4.

Table 8.4 Solubility of salts at different temperatures (*g* solute/100 *g* H_2O)

Substances	Temperature						
	10°C	20°C	30°C	40°C	50°C	60°C	70°C
NH_4Cl	33.3	37.2	41.4	45.8	50.4	55.2	60.2
$(NH_4)_2SO_4$	73.3	75.4	78.0	81.0	—	88.0	—
$BaCl_2,2H_2O$	33.3	35.7	38.2	40.7	43.6	46.4	49.4
$Ba(NO_3)_2$	7.0	9.2	11.6	14.2	17.1	20.3	—
KCl	31.0	34.0	37.0	40.0	42.6	45.5	48.3
KNO_3	20.9	31.6	45.8	63.9	85.5	11.0	138.0
$NaCl$	35.8	36.0	36.3	36.6	37.0	37.3	37.8
$CuSO_4,5H_2O$	17.4	20.7	25.0	28.5	33.3	40.0	—

By treating solubility as an equilibrium constant (*Section 10.14*), one can deduce the relation between solubility and temperature, e.g.,

$$\frac{d\,ln\,S}{dT} = \frac{\Delta H_{soln}}{RT^2} \tag{8.6}$$

or

$$ln\,S = -\frac{\Delta H_{soln}}{RT} + constant \tag{8.7}$$

where S is the solubility at temperature T and ΔH_{soln} is the enthalpy of solution. Equation (8.7) may be integrated within limits to the following form:

$$ln\frac{S_2}{S_1} = -\frac{\Delta H_{so\ln}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \tag{8.8}$$

According to equation (8.7) a plot of *ln* S against *1/T* should give a straight line (Figure 8.6) with a slope of ($-\Delta H_{soln}/R$). If the solubility values at different temperatures are known, the heat of solution can be calculated from the slope of the straight lines as in Figure 8.6.

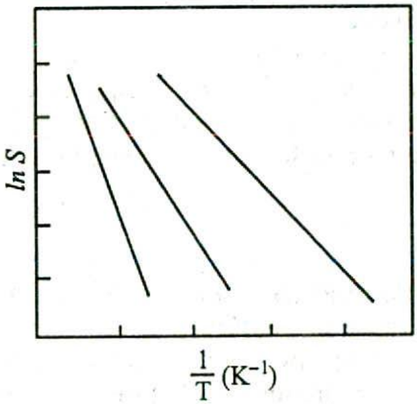


Figure 8.6 *ln S vs 1/T*

Equation (8.8) may be used to calculate the value of ΔH_{soln} from solubility values at any two temperatures. From equation (8.8) it can be seen that the temperature effect on solubility depends on the heat of solution. Breaks in the solubility curves are noticed in the case of salts which exist in different hydrated forms as, for example, sodium sulphate (Figure 8.5). The first part is the solubility curve for sodium sulphate decahydrate ($Na_2SO_4.10H_2O$) while the higher temperature part is that for the unhydrated salt. This difference in solubility behaviour may be traced to difference in the heats of solution of the two forms. Transition temperatures of hydrated salts may thus be obtained from solubility data.

Example 8.4: The solubility of KNO_3 in water is 31.6 g at 20°C and 63.9 g at 40°C. Calculate the enthalpy of solution of KNO_3 in water.

Solution : Substituting the values of the solubility, R and temperature in equation (8.8) and using log to the base 10 we get

$$2.303\log\frac{63.9}{31.6} = -\frac{\Delta H_{soln}}{8.314}\left(\frac{1}{313}-\frac{1}{293}\right)$$

$$\Delta H_{soln} = 26.3\ kJ\ mol^{-1}$$

8.13 Distribution of a Solid between Two Immiscible Liquids : The Distribution Law

Iodine dissolves in water only slightly to form a pale yellow solution. If some solid potassium iodide, KI, is added to the solution it turns deep brown and the iodine dissolves. The colour is due to the formation of I_3^- ion which is deep brown in solution. Now some carbon tetrachloride is added to the solution. Water and carbon tetrachloride being immiscible with each other the two liquids form separate layers. If the mixture of the two liquids is now shaken and then allowed to settle down it will be found that the carbon tetrachloride layer has become violet. This is because iodine dissolves in carbon tetrachloride. Thus iodine has been extracted by the organic layer from the aqueous layer.

In general it has been found that *when a solute is shaken up with two liquids which are immiscible with each other, but in both of which the solute is soluble, then the solute distributes itself between the two liquids in such a way that the ratio of the concentrations of the solute in the two liquids is a constant at a constant temperature, provided the solute is in the same molecular condition in the two liquids.* This is the statement of what is known as *Nernst Distribution Law.* If C_1 and C_2 are the concentrations of this solute in solvent *1* and solvent *2* respectively, then according to this law

$$\frac{C_1}{C_2} = K_D = \text{constant} \tag{8.10}$$

The ratio K_D is known as the *Distribution Co-efficient, or Partition Co-efficient.* As mentioned in *Section* 8.5, the third form of Henry's law is another way of stating the distribution law. The statement of Nernst distribution law came long after Henry's law was stated, indicating that the full significance of Henry's law was not understood earlier.

Example 8.5: Iodine was shaken with an immiscible mixture of water and carbon tetrachloride. After equilibrium was established the concentrations of I_2 in two layers were determined. It was found that the concentration of I_2 in CCl_4 was 560×10^{-4} mol L^{-1} while in H_2O it was 6.55×10^{-4} mol L^{-1}. Calculate the distribution co-efficient of I_2.

Solution: Since an equilibrium has been established between I_2 in H_2O and I_2 in CCl_4, we can write,

$$I_2 \text{ in } H_2O \rightleftharpoons I_2 \text{ in } CCl_4$$

Then according to equation (8.10),

$$K_D = \frac{[I_2]_{CCl_4}}{[I_2]_{H_2O}} = \frac{560 \times 10^{-4}}{6.55 \times 10^{-4}} = 85.5$$

8.13.1 Kinetic theory of the distribution law

The distribution law can be derived from the kinetic theory and the rate law. Since the solute is at equilibrium in both the liquids, the rate at which it leaves one phase must be equal to the rate at which it leaves the other phase, i.e., dynamic equilibrium is established. Consequently

$$\text{Solute } (\textit{in solvent I}) \rightleftharpoons \textit{Solute (in solvent II)}$$

At equilibrium
$$k_1C_1 = k_2C_2 \tag{8.11}$$

Or
$$\frac{C_1}{C_2} = \frac{k_2}{k_1} = K_D \tag{8.12}$$

where k_1 and k_2 are rate constants and C_1 and C_2 are concentrations of the solute in the two phases.

As mentioned the distribution law is valid only when the molecular species of the solute in the two solvents remain the same, i.e., there is no association or dissociation of the solute in any of the solvents. If, however, suitable corrections for such processes are made and only the two solvents are considered the law is found to be fairly obeyed (*Section 8.14*). Deviations are also found to occur when the solute concentration is either very low or very high.

Distribution co-efficient for a particular system changes with temperature as the influence of temperature on the solubility of the solute is different for the two solvents.

In Table 8.5, the distribution co-efficients of two solutes in immiscible liquid pairs are given. It can be seen that the values of the distribution co-efficients are reasonably constant showing the validity of the law.

Table 8.5 Distribution co-efficients

Iodine in $H_2O - CCl_4$ at 18°C			Oxalic acid in water – ether at 10°C		
$g\,L^{-1}$ in $CCl_4 (C_1)$	$g\,L^{-1}$ in $H_2O\,(C_2)$	C_1/C_2	$g\,L^{-1}$ in $H_2O\,(C_1)$	$g\,L^{-1}$ in ether (C_2)	C_1/C_2
5.1	0.060	85	47.3	5.3	9.2
10.2	0.119	86	43.6	4.6	9.5
15.2	0.178	85	30.4	3.1	9.8
20.3	0.236	86	20.3	2.1	9.9
25.4	0.290	88	---	---	----

8.14 Deviations from Distribution Law

(a) *Association:* In several cases it has been found that the deviation from the law is marked and there is a systematic increase or decrease in the value of the distribution co-efficient with change in the concentration of the solute. Such deviations have been explained on the basis of molecular association of the solute in the solution.

If the solute undergoes association in one of the solvents but remains unchanged in the other, as shown in Figure 8.7, the law cannot be applied as such since the molecular species have undergone a change.

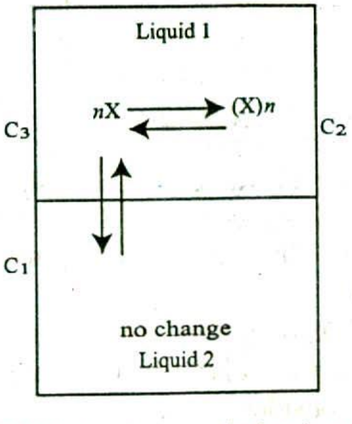


Figure 8.7 Molecular association in one liquid

Modification for this can be done by use of the equilibrium quotient (*Section 10.2*). Considering the equilibrium between the different molecular species of X which undergoes association in liquid 1 as shown in Figure 8.7 (equation 8.17) can be easily obtained:

$$\begin{array}{ccc} nX & \rightleftharpoons & (X)_n \\ C_3 & & C_2 \end{array} \qquad (8.13)$$

Here $(X)_n$ is the species formed by association and C_2 and C_3 are the concentrations of species $(X)_n$ and X in liquid 1.

$$\frac{C_2}{(C_3)^n} = K \qquad \text{(Equilibrium quotient)} \qquad (8.14)$$

or $$\frac{\sqrt[n]{C_2}}{C_3} = \text{constant} \qquad (8.15)$$

Let C_1 be the concentration of X in liquid 2. Then

$$C_1/C_3 = \text{constant} \qquad \text{(distribution co-efficient)} \qquad (8.16)$$

Or we can write $$\frac{C_1/C_3}{\sqrt[n]{C_2}/C_3} = \frac{C_1}{\sqrt[n]{C_2}} = \text{constant} \qquad (8.17)$$

Thus C_1/C_2 will not be constant but $\frac{C_1}{\sqrt[n]{C_2}}$ will be constant. Some values of distribution of benzoic acid between benzene and water are given in Table 8.6. The dissociation of benzoic acid in the aqueous phase being small is neglected.

Table 8.6 Distribution of benzoic acid between water and benzene

g of acid per 10 mL water	g of acid per 10 mL benzene	$\frac{C_1}{C_2}$	$\frac{C_1}{\sqrt{C_2}}$
0.0150	0.242	0.062	0.030
0.0190	0.422	0.045	0.029
0.0289	0.970	0.030	0.029

While the values of C_1/C_2 show a systematic drift, the values of $C_1/\sqrt{C_2}$ are found to be reasonably constant. This suggests that benzoic acid exists as *dimers* in benzene solution. Thus distribution law can be used to determine molecular association in solution.

(b) *Dissociation:* The solute may undergo appreciable dissociation in one of the solvents, particularly if it is water. In this case the distribution law assumes a different form. Consider a weak electrolyte MA which remains unchanged in liquid *1*, but undergoes dissociation in liquid *2*. Let one mole of MA pass into *1.0 L* of the liquid 2 of which x moles undergo dissociation giving rise to x moles each of the cation M^+ and the anion A^-. Therefore, $(1-x)$ moles remain undissociated. The equilibrium in the system is

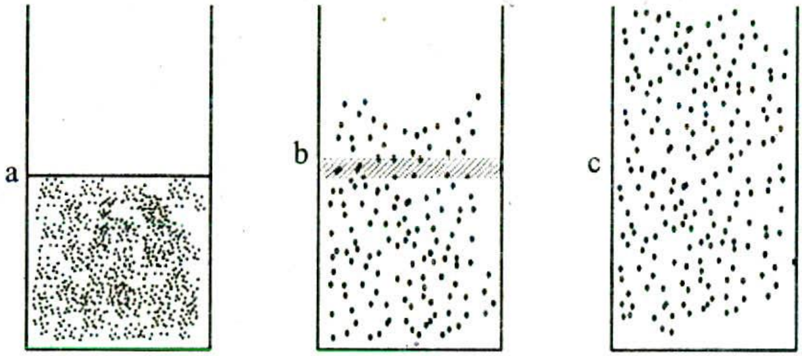


Figure 8.8 : Dissociation of electrolyte in two layers

shown in Figure 8.8. If C_1 is the concentration in liquid *1* and C_2 in liquid *2*, then concentration of undissociated molecule in liquid *2* is $C_2\,(1-x)$. Thus the distribution law assumes the form

$$\frac{C_1}{C_2(1-x)} = K_D \tag{8.18}$$

This form of the law can be used for calculating the degree of dissociation. The above treatment is quite general and can be used in gas/liquid phase also. Thus if NH_3 is dissolved in water it forms NH_4OH which dissociates partly to $NH_4{}^+$ and OH^-. In the gas phase NH_3 remains as it is. The constancy of K_D when dissociation is taken into account is shown in Table 8.7.

Table 8.7 Ammonia–water at 10 °C

$C_1 (mol\ L^{-1})$	$C_2\ (mol\ L^{-1})$	$\frac{C_1}{C_2}$	$(1-x)$	$C_2(1-x)$	$K_D = \frac{C_1}{C_2(1-x)}$
16.20	1.256	12.9	0.987	1.24	13.0
7.98	0.633	12.6	0.981	0.62	12.9
1.835	0.148	12.4	0.963	0.142	12.9
0.467	0.0386	12.1	0.926	0.0357	13.0
0.123	0.0107	11.5	0.864	0.0092	13.3

(c) *Compound formation:* If the solute forms compound with one of the solvents (or with the liquid in gas/liquid systems) the distribution law remains valid except that the numerical value of the distribution co-efficient changes. Thus chemical reaction of solute does not have any effect on the simple form of the law.

The distribution law may also be modified to explain the system when the solute undergoes association in one phase and dissociation in another phase. All the four cases can be summarized as follows for the different changes in the solute molecule.

Phase I C_1	Phase II C_2	Distribution Law
Normal	Normal	$\frac{C_1}{C_2} = K_D$
Normal	Association	$\frac{C_1}{\sqrt[n]{C_2}} = K_D$
Normal	Dissociation	$\frac{C_1}{C_2(1-x)} = K_D$
Dissociation	Association	$\frac{C_1(1-x)}{\sqrt[n]{[C_2(1-x)]}} = K_D$

8.15 Applications of Distribution Law

The distribution law can be applied to a number of physical and chemical processes some of which have already been mentioned. Thus association of the solute in one phase can be ascertained, and degree of association and, therefore, the molecular mass of the solute in a given liquid can be found out. The law may also be used to determine the degree of dissociation of acids, bases or salts in a solvent. Other examples are given below.

(a) The degree of hydrolysis of substances can be conveniently studied. The hydrolysis of aniline hydrochloride in water can be followed from the distribution of aniline hydrochloride between water and benzene. Thus for this reaction,

$$\underset{\text{Salt}}{\text{Aniline hydrochloride}} + \underset{H_2O}{\text{Water}} \rightleftharpoons \underset{\text{Base}}{\text{Aniline}} + \underset{\text{Acid}}{\text{Hydrochloric acid}}$$

Thus, $$K_h = \frac{[base] \times [acid]}{[salt] \times [H_2O]} \tag{8.19}$$

By applying the principle cf equilibrium it can be shown that,

$$K_h = \frac{C_1^2(1 + vK)}{C_2 - C_1(1 + vK)} \tag{8.20}$$

where C_1 is the concentration of the base in aqueous layer (C_1 and C_2 are expressed in mol L^{-1}), C_2 the original concentration of the salt, K the distribution co-efficient and v is the volume of benzene in litres added to 1 litre of water.

(b) The formula of the complex $CuSO_4.4NH_3$ was confirmed from the studies of distribution of ammonia between chloroform and aqueous copper sulphate solution.

Example 8.6: 25 mL of a 0.20 mol L^{-1} solution of copper(II) sulphate was mixed with 25 mL of 1.0 mol L^{-1} ammonia solution. A deep blue solution results because of the formation of a complex ion $Cu(NH_3)_x{}^{2+}$. The total 50 mL of the mixture were shaken well with 50 mL of chloroform, and then allowed to settle. The layers were then separated with the help of a separating funnel, the ammonia extracted from the organic layer. The amount of ammonia in the organic layer was determined by titration with a standard acid solution and was found to be 0.20×10^{-3} mol L^{-1}. Given that the distribution coefficient of ammonia between the water and chloroform is 25.0 at the temperature of the experiment, determine the formula of the species which gives the blue colour of the solution in water, i.e. find the value of x.

Solution: (Moles of uncombined ammonia in 50 mL of aqueous layer)/(Moles of uncombined ammonia in 50 mL of chloroform layer) = 25.0

(as volumes of the two layers are equal)

Hence, (Moles of uncombined ammonia in 50 mL of aqueous layer)/0.20×10^{-3}) = 25.0

Moles of uncombined ammonia in 50 mL of aqueous layer $= 25.0 \times 0.20 \times 10^{-3}$

$= 5.0 \times 10^{-3}$

Total moles of uncombined ammonia = Moles of ammonia in water layer + moles of ammonia in the organic layer $= 5.0 \times 10^{-3} + 0.2 \times 10^{-3} = 5.2 \times 10^{-3}$

Original number of moles of ammonia $= (25 \times 1)/1000 = 25 \times 10^{-3}$

Moles of ammonia combined with copper (II) ion $= (25 - 5.2) \times 10^{-3}$

$= 19.8 \times 10^{-3}$

Moles of copper (II) ions in 25 mL $= (0.2 \times 25)/1000$

$= 5.0 \times 10^{-3}$

Hence the ratio of moles of copper(II) ions to combined ammonia

$= 5.0 \times 10^{-3}$ to 19.8×10^{-3}, i.e. 1 to 4 (the ratio must be a whole number)

The formula of the complex ion of copper is $Cu(NH_3)_4{}^{2+}$.

(c) Another example of the application of the distribution law can be demonstrated by finding the equilibrium constant for the equilibrium

$$I_2\,(aq) + I^-\ (aq) \rightleftharpoons I_3^-(aq)$$

The expression for the equilibrium constant is given by,

$$K = \frac{[I_3^-]}{[I_2][I^-]} \tag{8.21}$$

An aqueous solution of KI of concentration C_o, is shaken up with a solution of iodine in carbon tetrachloride. Iodine will distribute itself between the organic layer and aqueous layer. In the aqueous layer the equilibrium between I_2 and I^{-1} is established. Titration of an aliquot portion from the aqueous phase gives C_l the total concentration of I_2 in the aqueous phase.

$$C_1 = C_2 + C_3 \tag{8.22}$$

where C_2 and C_3 are concentration of free I_2 and I_3^- respectively. Titration of an aliquot from the organic layer gives C_4 the concentration of I_2 in this layer. If K_D is the partition coefficient of I_2 between the organic layer and water, then

$$C_2 = \frac{C_4}{K_D} \tag{8.23}$$

Putting this value of C_2 in equation (8.22), the value of C_3 can be obtained.

If the initial concentration of the of I^- is C_o, then the equilibrium concentration C_5 of I^- is given by

$$C_5 = C_0 - C_3 \tag{8.24}$$

Equation (8.21) can be written as

$$K = \frac{C_3}{C_2 \times C_5} \tag{8.25}$$

It may be noted that without the help of the organic layer it would not have been possible to determine the concentration of free iodine in the aqueous layer in presence of the I_3^- ion. By a similar method the equilibrium constants of a number of other reactions have been determined.

8.16 Solvent Extraction

An important application of the distribution law is in the extraction of a solute from a solvent by another solvent. If the solubility of a solid in two mutually ***immiscible*** liquids are different then on shaking the solution of the solid in solvent I with the second solvent II, a considerable amount of the solid passes into the solvent II, depending on the relative solubility of the solute in the two liquids. If now solvent I is separated from solvent II a part of the solid, which has been extracted away from solvent may be recovered. A second part of the solute may be extracted from solvent I by shaking with a fresh portion of solvent II and separating. Continuation of this extraction process will eventually lead to almost complete removal of the solute from solvent I. This process of separation is known as *solvent extraction*. The method is particularly suitable for separation or purification of heat sensitive or high boiling organic compounds from aqueous solutions by an organic liquid. If separation from aqueous solution is desired the process of extraction is facilitated by the addition of soluble inorganic salts as the solubility of the organic compound in water is lowered by salts.

The efficiency of the extraction process will depend on the value of $K_D = C_{Organic}/C_{Water}$. If K_D is large, one extraction will result in the separation of a relatively large quantity of the solute. It may be easily shown that with a given volume of the extracting solvent several extractions with small portions of the solvent lead to better recovery than when the whole of the solvent is used for a single extraction. The following calculation will justify this statement.

Let w g of solute be in solution in v mL of solvent I and this is extracted with l mL of solvent II, which is immiscible with solvent I. If w_1 g of solute remains in solvent I after first extraction $(w - w_1)$ g of the solute would be extracted by solvent II. The concentrations (g/mL) of the solute in solvent I and solvent II are respectively w_1/v and $(w - w_1)/l$. The distribution co-efficient, K_D, is then given by

$$K_D = \frac{w_1/v}{(w - w_1)/l} \tag{8.26}$$

Solving for w_1 one obtains

$$w_1 = w\left(\frac{K_D v}{K_D v + l}\right) \tag{8.27}$$

After the second extraction with fresh l mL of solvent II, let w_2 g of the solute remain in solvent I; then

$$K_D = \frac{w_2/v}{(w_1 - w_2)/l} \tag{8.28}$$

Or,

$$w_2 = w_1\left(\frac{K_D v}{K_D v + l}\right) \tag{8.29}$$

$$= w\left(\frac{K_D v}{K_D v + l}\right)^2 \tag{8.30}$$

If the extraction is repeated n number of times with l mL of solvent II at each step the mass of solute w_n, remaining in solvent I after n extraction is given by,

$$w_n = w\left(\frac{K_D v}{K_D v + l}\right)^n \tag{8.31}$$

For a given system the value of n will depend on v and l. It can be easily seen from equation (8.31) that when the total volume of the extracting liquid is constant, w_n will be smaller when n is large and l is small, i.e., the efficiency of the extraction process is higher.

The principle of Parke's process of desilverization of lead is based on the distribution law. Molten lead and zinc are immiscible with each other. Silver is soluble in both molten lead and molten zinc, the distribution co-efficient, C_{Zn}/C_{Pb}, being 300 at 800°C. The argentiferrous lead is heated to 800°C and treated with zinc. Silver goes mostly into the zinc layer and can be removed. By repeating the process most of the silver present in lead may be removed and recovered.

Example 8.7: The solubility of methylamine at 18°C in water is 8.49 times greater than that in chloroform. What percentage of the substance remains in 1000 *mL* of chloroform solution of methylamine if it is extracted (a) four times with 200 *mL* of water each time and (b) twice with 400 *mL* of water each time?

Solution: From equation (8.31),

$$w_n = w\left[\frac{K_D v}{K_D v + l}\right]^n$$

So for (a)

$$w_4 = 100\left[\frac{(1/8.49)\times 1}{(1/8.49)\times 1 + 0.2}\right]^4$$

$$= 100 \times 0.0189$$

$$= 1.89\%$$

where the volumes have been expressed in litres and *w* shown as 100 for expressing in per cent.

For (b),

$$w_2 = 100\left[\frac{(1/8.49)\times 1}{(1/8.49)\times 1 + 0.4}\right]^2$$

$$= 100 \times 0.0517$$

$$= 5.17\%$$

QUESTIONS AND PROBLEMS

1. Explain what is meant by 'molarity and 'molality' of solutions. Which of these two is temperature dependent?
2. What are the different ways of expressing concentrations of solutions? Illustrate your answer with suitable examples.
3. State and explain Henry's law. What are the different forms in which this law can be expressed? Discuss why all gases should be completely driven off from a solution at the boiling point?
4. What is absorption co-efficient of a gas? The solubility of oxygen at a constant temperature is given at different values of pressure;

Pressure (mm Hg)	Amount of gas dissolved ($g\ L^{-1}$) $\times 10^2$
760	4·08
610	3·25
414	2·22
300	1·60

Show that the above data support Henry's law.

5. What are the causes for the deviation from Henry's law? How have these deviations been explained? Illustrate your answer.

6. State and clearly explain the 'Distribution law'. Discuss one of its important applications. How can you ascertain molecular association from values of the partition co-efficient? Give examples.

7. What is the principle of solvent extraction? Derive an expression relating the amount of unextracted solute in a solvent extraction process with the number of extractions.

8. The distribution co-efficient for aniline between benzene and water is 10 at 25°C. Compare the ratio of the masses of aniline extracted from a solution in one litre of water by 500 *mL* of benzene (i) using all the benzene in one extraction and (ii) using the benzene in 10 successive extractions with 50 *mL* each time. Ans. $\frac{w_1}{w_2} = \frac{(1.5)^{10}}{6}$

9. State Henry's law and discuss its limitations.
   (b) How does the solubility of a gas in a liquid depend on temperature?
   (c) 100 *mL* of carbon tetrachloride containing 1.136 *g* of iodine are shaken at 25°C with a litre of water. The aqueous layer is found to contain 0.118 *g* of iodine. Calculate the partition co-efficient of iodine.

10. In determining the partition co-efficient of phenol between water and amyl alcohol at 25°C it was found that the amyl alcohol layer contained 0.60 *g* phenol per litre and the aqueous layer contained 0.66 $g\ L^{-1}$. What is the partition co-efficient C_{al}/C_w? Calculate the mass of phenol extracted from 500 *mL* of an aqueous solution containing 0.5 $g\ mole\ L^{-1}$ by shaking it twice with amyl alcohol using 100 *mL* each time? [Ans. Partition co-efficient. = 16.1 ; 17.95 *g*]

11. The partition co-efficient of iodine between CS_2 and water, $K_p = C_{org}/C_{water}$ is 410, at 25°C. A solution containing 8 *g* of $KI\ L^{-1}$ was shaken with iodine and CS_2 till equilibrium was established. The concentration of iodine in the aqueous and organic layers were found to be $8.46 \times 10^{-3}\ mol\ L^{-1}$ and $13.9 \times 10^{-2}\ mol\ L^{-1}$ respectively. Calculate the equilibrium constant of the reaction, $KI + I_2 \rightleftharpoons KI_3$.
    [Ans. *K*=606]

12. The distribution co-efficient of H_2S between benzene and water, $K_D = C_b/C_w$ is 6.0 at 25°C. Calculate the minimum volume of benzene necessary at this temperature to extract in a single step 80% of the H_2S from 0.5 *L* of a 0.1 $mol\ L^{-1}$ aqueous solution of H_2S. [Ans. 333 *L*]

9 DILUTE SOLUTIONS : COLLIGATIVE PROPERTIES

In the previous chapter we discussed the properties of solutions in general. If the concentration of the solute in a solution is very low, the solution is called a dilute solution. Four properties of dilute solutions are so intimately connected with each other that they are grouped together and are commonly known as the *'colligative properties'* (*colligative* means "tied together"). These four properties are:

(i) Lowering of vapour pressure,
(ii) Elevation of boiling point,
(iii) Depression of freezing point and
(iv) Osmotic pressure.

All the four properties depend *only on the number of particles* (*molecules or ions*) in a solution, but they are independent of molecular structure. A litre of solution containing one mole of sodium chloride contains twice the number of particles if one mole of sugar molecules dissolved in the same volume of solution. This is because each sodium chloride unit gives two particles, one Na^+ ion and one Cl^- ion, and the above solution will contain two moles of particles. The property of the sodium chloride solution will, therefore, be twice the value of the same property of a solution of sugar of the same concentration. A solution of urea (RMM = 60) has the same value of the properties as that of a solution of sucrose (RMM = 342) of the same concentration in mol L^{-1}. Pressure exerted by a gas is also independent of molecular structure and so the gas pressure or volume should be termed as colligative properties. However, colligative properties have almost universally been associated with dilute solutions.

The properties are quantitatively expressed in the form of certain laws, the validity of which is restricted to dilute solutions. One use of the study of these properties is that the molecular mass of solutes may be determined from measurements of any one of them with the help of these laws.

9.1 Lowering of Vapour Pressure

If a non-volatile and non-electrolyte solute like sucrose, glucose or urea is dissolved in a solvent like water the vapour pressure of the solution is found to be lower than that of pure water. The magnitude of the lowering of vapour pressure is dependent on the concentration of the solute in solution. Although attempts had been made to relate vapour pressure lowering quantitatively to concentration since the days of Berthollet and

Faraday, the credit for stating the correct relationship goes to F.M. Raoult (1837-1888). He stated that *the relative lowering of vapour pressure of a solvent due to the addition of a non-volatile and non-electrolyte solute is equal to the mole fraction of the solute in the solution.* This statement, which is known as *Raoult's law*, is an important generalization in Physical Chemistry and is fundamental to the study of solutions.

Relative lowering is defined as the ratio of the difference of vapour pressures of the pure solvent and the solution to the vapour pressure of the pure solvent. The mole fraction of the solute on the other hand is the ratio of the number of moles of the solute to the total number of moles in solution. If p^0 and p are vapour pressures of the solvent and the solution respectively, the lowering of vapour pressure is $(p^0 - p)$, and relative lowering of vapour pressure is $(p^0 - p) / p^0$. In a solution containing, n moles of solute in N moles of solvent the mole fraction of the solute is $n/(N + n)$. Then according to Raoult's law,

$$\frac{p^0 - p}{p^0} = \frac{n}{N + n} = x_2 \tag{9.1}$$

where x_2 is the mole fraction of the solute. Experimental supports in favour of the law have been obtained by various investigators. The law is, however, valid only for dilute solutions of solutes which do not undergo association or dissociation in the dissolved state.

Equation (9.1) may be written in the form

$$1 - \frac{p^0 - p}{p^0} = 1 - x_2 \tag{9.2}$$

which reduces to $$\frac{p}{p^0} = x_1, \quad \text{or} \quad p = p^0 . x_1 \tag{9.3}$$

where x_1 is the mole fraction of the solvent. Thus the vapour pressure of the solution is directly proportional to the mole fraction of the solvent. This is considered as an alternative way of stating Raoult's law. When both the components of a binary ideal solution are volatile, Raoult's law is applicable to both the components. If p_A and p_B are the partial vapour pressures of the components A and B in a solution, then according to Raoult's law

$$p_A = x_A p_A^0 \qquad \text{and} \quad p_B = x_B p_B^0$$

where x_A and x_B are the mole fractions of A and B respectively in the solution and p_A^0 *and* p_B^0 are the vapour pressures of pure liquids A and B. The total vapour pressure p of the ideal solution containing components A and B is equal to

$$p = p_A + p_B = x_A p_A^0 + x_B p_B^0 \tag{9.4}$$

9.2 Ideal Solution

As mentioned in *Section 8.2 a solution is said to be ideal when it obeys Raoult's law over all compositions and at all temperatures.* Such a solution is formed from its components without heat being given out or absorbed ($\Delta H=0$) and the solution process is not accompanied by any volume change ($\Delta V=0$). It follows from Raoult's law that if the solution is ideal the escaping tendency of each component will be proportional to the mole fraction of that component in the solution. From the molecular point of view one can say that in an ideal solution of *A* and *B* the intermolecular forces between *A* and *A* molecules, *A* and *B* molecules, and *B* and *B* molecules are the same and the escaping tendency of the *A* molecules will be the same whether these are surrounded by other *A* molecules, or *B* molecules or partly by *A* and partly by *B* molecules. If there is interaction the solution will deviate from ideal behaviour. In reality there are very few solutions which obey Raoult's law strictly, i.e., behave ideally; but the more dilute a solution is, the more nearly does it approach ideality. When the solution is infinitely dilute it is expected to be ideal.

9.3 Molecular Mass from Lowering of Vapour Pressure

For a dilute solution $n/(N + n)$ in equation (9.1) may be replaced by n/N as n is negligible in comparison to N. Equation (9.1) may, therefore, be written as

$$\frac{p^0 - p}{p^0} = \frac{n}{N} \tag{9.5}$$

If w_2 *g* of a solute of molecular mass M_2 be present in w_1 *g* of solvent of molecular mass M_1, then

$$\frac{n}{N} = \frac{w_2/M_2}{w_1/M_1} \tag{9.6}$$

and equation (9.5) becomes

$$\frac{p^0 - p}{p^0} = \frac{w_2/\mathrm{M}_2}{w_1/\mathrm{M}_1} \tag{9.7}$$

By measuring p° and p for a solution of known concentration M_2 may be obtained.

Example 9.1: What will be the vapour pressure exerted by an aqueous solution containing 0.5 mole of a substance in 1000 *g* of water at 20.0°C if the vapour pressure of water at the working temperature is 17.574 mm Hg ?

Solution: From equation (9.1) $\dfrac{p^0 - p}{p^0} = x_2$

Or $p^0 - p = (17.574)\dfrac{0.5}{0.5 + 1000/18}$

and $p = 17.574 - 0.157 = 17.417$ mm Hg

(RMM of $H_2O = 18$)

9.4 Derivation of Raoult's Law

The vapour pressure of a liquid is governed by the '*escaping tendency*' of the molecules in the liquid and the number of molecules per unit volume. If a solute is dissolved, the number of solvent molecules per unit volume decreases, since in the solution solute molecules will also be present. If we assume that the intermolecular forces between the solvent molecules remain unchanged, which is true for dilute solutions, then the number of solvent molecules leaving unit area of the solution surface per unit time will be less than the number leaving the surface of the pure solvent under the same conditions. Hence the vapour pressure of the solution will be lower than that of the solvent because the number of molecules per unit volume of the solvent in the vapour phase over liquid solvent will be more than the number of solvent molecules over the solution. The vapour pressure p of the solution will be proportional to the ratio of the number of solvent molecules, N, in solution to the total number of molecules in the solution, $(n + N)$. Thus

$$p = K\,\frac{N}{n+N} = K\,x_N \tag{9.8}$$

where K is the proportionality constant and x_N is the mole fraction of the solvent. For the pure solvent $x_N = 1$ and p becomes equal to p^0. Therefore, K is equal to p^0. Thus

$$p = p^0\,x_N \tag{9.9}$$

which is one form of Raoult's law as shown in equation (9.3). It has, however, been assumed that the vapour of the solvent above the solution and the pure liquid behave like an ideal gas. Further assumptions have been made regarding the constancy of the intermolecular forces of the liquid in presence of the solute.

9.5 Measurement of Lowering of Vapour pressure

A number of methods for the determination of vapour pressure of liquids have been discussed in *Section3.6*. These methods are not suitable for accurate measurement of the lowering of vapour due to addition of solute, because the change in vapour pressure is rather small. In order to avoid this difficulty vapour pressures may be measured at elevated temperatures where both p^0 and p are high. But even then sufficient precision is not assured. However, a new type of manometer, known as *differential manometer*, has been designed to directly measure ($p^0 - p$). A high precision *differential manometer* has been designed by Rayleigh and used by Frazer and Lovelace for measuring small differences in vapour pressure of the solvent and solution.

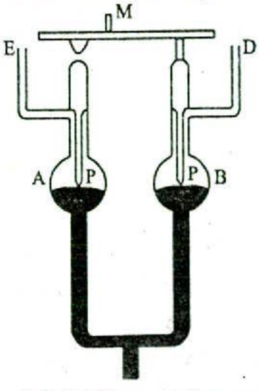


Figure 9.1 Differential manometer designed by Rayleigh

The manometer (Figure 9.1) essentially consists of small glass bulbs, A and B, which are connected by a moveable mercury reservoir. Two glass points, PP, are sealed to the bulbs which are securely fixed to the horizontal beam carrying a mirror, M. The bulbs are connected to side tubes, D and E. Pressure in the two bulbs are made equal by means of fine screws (not shown) by adjusting the height of the mercury. This is achieved when the two glass pins exactly touch the mercury surface. This can be ascertained by observing the image of the glass pins on the clean mirror-like mercury surface. This corresponds to zero reading of the manometer. One of the two bulbs is then connected to the vapour of the solution and the other to that of the solvent through the side tubes *D* and *E*. Due to difference in the vapour pressure, the mercury levels in two bulbs are displaced. The level of mercury is brought back to the initial positions by carefully tilting the apparatus and adjusting the reservoir till *PP* again coincides with their images. When the instrument has been tilted the mirror *M* has also been tilted. The magnitude of this tilt is measured by the displacement of the reflected light from the mirror, a method known commonly as *'lamp and scale arrangement'*. The extent of the tilt is a measure of the vapour pressure difference between the solution and the solvent. By careful work it is claimed to give vapour pressure difference with an accuracy of about 0.0006 mm of mercury.

A number of other devices have been developed for measurement of difference of vapour pressure. All these are known as *static methods* to differentiate them from the dynamic method due to Ostwald and Walker which is described below.

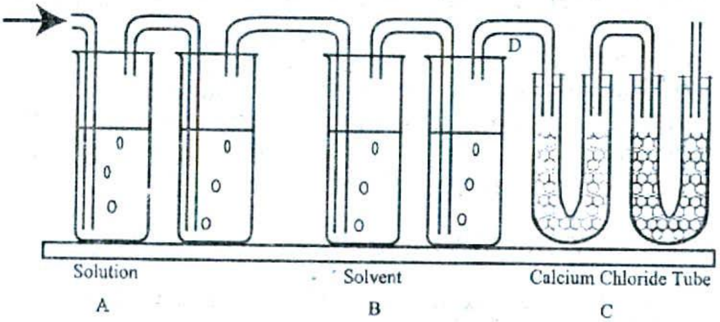


Figure 9.2 Transpiration method of Ostwald and Walker

In this method the solution and the solvent are taken in a series of gas washing bottles (Figure 9.2) and a slow stream of dry air or nitrogen is bubbled through the solution and the solvent. The stream of gas coming out through *D* is saturated with the solvent vapour which is absorbed in a series of absorption tubes containing a suitable absorbing agent. The dry gas after passage through the solution becomes saturated with the solvent vapour from the solution but is still unsaturated with respect to the solvent vapour from the pure solvent because the vapour pressure of the solvent is higher than that of the solution. The gas on passage through the solvent carries with it more vapour from it. After a sufficient flow of the gas the absorption tubes and the two series of washing bottles are separately weighed. The increase in the mass of the absorption tube is proportional to the vapour pressure of the solvent and the loss in mass of the bottles containing solution is proportional to the vapour pressure of the solution, while loss in mass of the bottles, *B*, is proportional to the lowering of vapour pressure. Thus

$$\frac{p^0 - p}{p^0} = \frac{loss\ in\ mass\ of\ B}{loss\ in\ mass\ of\ C} \tag{9.10}$$

Since the concentration of the solution is known the molecular mass of the solute is easily calculated. If temperature control is good and this experiment is carried out carefully, the method is capable of giving results of high accuracy. The method is simple and inexpensive. If water is used as the solvent, the absorption tube may be filled with fused anhydrous calcium chloride. The last tube should be guarded against moisture absorption from the atmosphere. If organic solvents are used, as often is the case, the absorption tubes are dispensed with and the results can be obtained by weighing the tubes, *A* and *B*. The current of gas should be passed slowly otherwise fine stream of liquid drops may escape with the gas. The total volume of the gas passed should be large so that appreciable loss in mass in the two bulbs may occur.

Example 9: Dry air was passed first through a set of bulbs containing a solution of 3.458 *g* of a substance in 100 *g* of ethanol and then through a series of bulbs containing pure ethanol. The first set of the bulbs underwent a loss of 0.9675 *g* and the latter series a loss of 0.0255 *g*. Calculate the molecular mass of the solute.

Solution: Total loss of solvent = 0.9675 + 0.0255 = 0.9930 *g*. From equation (9.10) we get,

$$\frac{p^0 - p}{p^0} = \frac{0.0255}{0.9930}$$

Now

$$\frac{p^0 - p}{p^0} = \frac{w_2/M_2}{w_1/M_1} \qquad \text{[from equation (9.7)]}$$

Or

$$\frac{0.0255}{0.9930} = \frac{3.458 \times 46}{M_2 \times 100}$$

And

$$M_2 = \frac{3.458 \times 46 \times 0.9930}{100 \times 0.0255} = 62$$

(RMM of ethanol = 46)

9.6 Elevation of Boiling Point

The boiling point of a liquid is defined as *the temperature at which the vapour pressure is equal to the atmospheric pressure*. As the vapour pressure of a solution is less than that of the solvent, the vapour pressure of the solution will become equal to the atmospheric pressure at a higher temperature. In other words, the boiling point of the solution will be higher than that of the solvent. The vapour pressure-temperature diagrams of pure solvent and solution (Figure 9.3) clearly explain the elevation of boiling point of the solution as compared with that of the pure solvent.

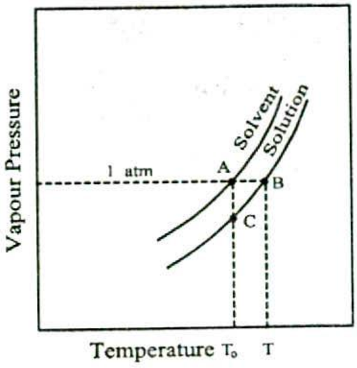


Figure 9.3 Vapour pressure vs temperature curves

The dotted horizontal line corresponds to 1.0 atm pressure. It intersects the vapour pressure curves at points corresponding to temperatures, T_o and T. It is seen that the boiling point, T, of the solution is higher (elevated) than the boiling point, T_o, of the solvent. Thus the elevation of boiling point of a solution is a direct consequence of the lowering of vapour pressure on addition of solute.

Experimental results on the elevation of boiling point by solutes were summarized in the form of the following laws which are generally called Raoult's laws of elevation of boiling point:

(*i*) *The elevation of the boiling point of solution is proportional to its molal concentration, i.e., to its molality, m.*

Or $\Delta T_b = K_b \,.\, m$ [where $\Delta T_b = (T - T_o)$] (9.11)

(ii) *Equimolecular quantities of different substances dissolved in the same quantity of a particular solvent raise its boiling point to the same extent.*

The relation between ΔT_b and m may be easily deduced with the help of Figure 9.3. The distance AB corresponds to ΔT_b. Since the solution is assumed to be dilute the decrease in vapour pressure and boiling point elevation will be very small. The vapour pressure curves for the solution and solvent may be considered to be parallel near the boiling temperature. The ratio AB/AC may, therefore, be taken to be constant for such solutions. Now AC is equivalent to the lowering of vapour pressure, $p^o - p$, at temperature, T_o. Hence one may write,

$$\frac{AB}{AC} = \frac{\Delta T_b}{p^0 - p} = constant,\ k \tag{9.12}$$

Using equation (9.3) and remembering that p^0 is constant and $1 - x_1 = x_2$ one obtains,

$$\begin{aligned}\Delta T_b = (p^o - p)k &= (p^o - p^o . x_1)k \\ &= p^o\,(1 - x_1)k \\ &= k'.x_2 \end{aligned} \tag{9.13}$$

The constant of proportionality $k'(= p^0 . k)$ does not depend in any way on the nature of the solute. For a dilute solution the approximate form of x_2, as in equation (9.5), may be used and one obtains,

$$\Delta T_b = k' \frac{w_2/M_2}{w_1/M_1} \tag{9.14}$$

where w_2 and w_1 are the masses and M_2 and M_1 are the molecular masses of the solute and solvent respectively. When m moles are present in 1000 g of the solvent equation (9.14) reduces to the form

$$\Delta T_b = k' \frac{M_1}{1000} \times \frac{\frac{w_2}{M_2}}{w_1} \times 1000 \tag{9.15}$$

$$= K_b . \frac{w_2/M_2}{w_1} \times 1000 \tag{9.16}$$

$$= K_b . m$$

where $K_b = k'\dfrac{M_1}{1000}$ is a constant for a given solvent and is known as the *molal boiling point elevation constant* or the *molal ebullioscopic constant.* For a solution of unit molality $K_b = \Delta T_b$. The molal boiling point elevation of a liquid may then be defined *'as the elevation of boiling point when the concentration of the solution is 1 molal.*

9.7 Thermodynamic Derivation of Boiling Point Elevation

Equation (9.16) may be derived thermodynamically which will allow independent calculation of K_b from the known properties of the solvent. The Clapeyron-Clausius equation in the integrated form is written as,

$$ln\ \frac{p}{p^0} = -\frac{\Delta H}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \tag{9.17}$$

Equation (9.17) may be used for the calculation of K_b. In applying this relation to the vapour pressures of solution between the boiling point T_o of solvent and T of solution it should be noted (Figure 9.3) that the vapour pressure of the solution is p at T_o and p^o at T, where p and p^o are the vapour pressures of the solvent and solution respectively at T_o. Hence from equation (9.17)

$$ln\frac{p}{p^0} = -\frac{\Delta H_{ev}}{R}\left[\frac{1}{T_0}-\frac{1}{T}\right] \tag{9.18}$$

$$= -\frac{\Delta H_{ev}}{R}\left[\frac{T-T_0}{TT_0}\right] = -\frac{\Delta H_{ev}}{R}\times\frac{\Delta T_b}{T_0^2} \tag{9.19}$$

since T and T_o are not very different and ΔH may be taken as constant over this temperature range. Again, $p/p_o = x_1$ according to Raoult's law where x_1 is the mole fraction of the solvent; but $x_1 = (1 - x_2)$, where x_2 is the mole fraction of the solute. Hence equation (9.19) takes the form

$$ln\ (1 - x_2) = -\frac{\Delta H_{ev}}{R}\times\frac{\Delta T_b}{T_0^2} \tag{9.20}$$

For a dilute solution x_2 is small compared to unity and

$$ln\ (1 - x_2) \approx -x_2$$

so that

$$\frac{\Delta H_{ev}}{R}\times\frac{\Delta T_b}{T_0^2} = x_2 \tag{9.21}$$

or

$$\Delta T_b = \frac{RT_o^{\ 2}}{\Delta H_{ev}}\ .\ x_2 \tag{9.22}$$

On further simplification equation (9.22) reduces to

$$\Delta T_b = \left(\frac{RT_0^2}{\frac{\Delta H_{ev}}{M_1} \times 1000}\right) \times \frac{w_2 / M_2}{w_1} \times 1000 \tag{9.23}$$

$$= K_b . \frac{w_2/M_2}{w_1} \times 1000 \tag{9.24}$$

$$= K_b . m \tag{9.25}$$

where $$K_b = \frac{RT_0^2}{\frac{\Delta H_{ev}}{M_1} \times 1000}$$

Since all the quantities within the bracket on the right hand side of equation (9.23) are constants for a particular solvent, K_b is independent of the nature of the solute. This is the Raoult's law of boiling point elevation.

In the case of water as solvent,

$T_o = 373.16$ K, $\Delta H_{ev} = 2255.18$ J g^{-1},
R = 8.314 J K^{-1}mol^{-1} and hence

$$K_b = \frac{8.314 \times (373.16)^2}{2255.18 \times 1000} = 0.513 \text{ K kg mol}^{-1}$$

Thus K_b may be calculated for a given solvent from its latent heat of vaporization and boiling point.

The observed and calculated values of K_b of some solvents are given in Table 9.1. The agreement between the values is satisfactory in most cases.

Table 9.1 Ebullioscopic and cryoscopic constants

Solvent	K_b (K kg mol^{-1})	K_f (K kg mol^{-1})
Acetic acid	3.09	3.90
Benzene	2.53	5.12
CCl_4	5.02	30.00
Cyclohexane	----	20.20
CS_2	2.37	3.80
Naphthalene	5.80	6.94
Phenol	3.04	7.27
Water	0.513	1.86

Since the boiling point of a liquid changes with atmospheric pressure and ΔH_{ev} may also change, the value of K_b is likely to be different at different atmospheric pressures. For concentrated solutions the derivations are not valid as the assumptions made are not justified.

9.8 Determination of Molecular Mass from Boiling Point Elevation

It may be seen from equation (9.25) that if K_b for a solvent is known the molecular mass of a solute in the solution may be determined by experimental measurement of the *elevation of boiling point.* A number of methods are available for the measurement of elevation of boiling point. In this text only two methods will be discussed.

9.8.1 Measurement of elevation of boiling point

In dilute solution the elevation of boiling point is very small which necessitates the use of very sensitive thermometers. The Beckmann thermometer, which is most widely used for the purpose, will be described below.

Beckmann thermometer : Beckmann thermometer is a *differential thermometer.* It was designed to record a very small change in temperature, and never measures the actual temperature of the solvent or of solution. Several designs of this apparatus are now commercially available. One of the common forms is shown in Figure 9.4.

The thermometer essentially consists of a large bulb *B* at the bottom, and a reservoir of mercury *R* at the top. The thermometer is calibrated from 0 to 6 K and the scale *S is* subdivided into 0.01 K. The amount of mercury in the two reservoirs can be adjusted by careful manipulation depending on whether *ebullioscopic* or *cryoscopic* measurements are carried out.

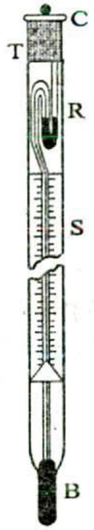


Figure 9.4 Beckmann thermometer

(a) Beckmann's method : The Beckmann apparatus generally used for measuring the elevation of temperature is given in Figure 9.5. A known volume of a given mass of the solvent is first taken into the boiling tube to fill about two-third of its capacity.

The boiling tube is connected to a condenser on one side, and there is a small side tube, E, for introducing the solute. The boiling tube is generally surrounded by an insulated jacket. The Beckmann thermometer is introduced into the boiling tube through a rubber stopper in such a way that the lower bulb

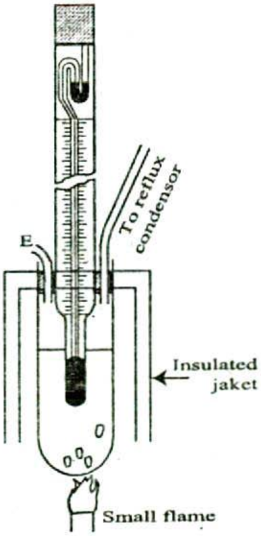


Figure 9.5 Complete Beckmann apparatus

completely immerses into the solvent. The heating of the boiling tube is carried out by a Bunsen burner or by electric means. At first the thermometer reading corresponding to the boiling of the pure solvent is recorded, and then the experiment is repeated after addition of a known mass of a solute. The difference of Beckmann reading in these two experiments gives a measure of elevation of boiling point. Since the mass of the solute, solvent and K_b for the solvent are known, the relative molar mass of the solute can easily be determined.

(b) Cottrell's method: Cottrell (1910) devised an ingenious method for measurement of boiling point in which superheating was completely eliminated. The assembly is shown in Figure 9.6. A funnel with two or three pronged tubes fits into the boiling tube in such a way that the ends of the 'U'-shaped pronged tubes lie a little above the thermometer bulb, as shown in the figure.

The solvent-layer remains well below the thermometer bulb. On boiling, the liquid is forced through the pronged tubes and is pumped on the thermometer bulb and form a continuous layer of the boiling liquid on the bulb. This pumping device followed by ejection of the liquid on the tube eliminates superheating. The thermometer, therefore, records the true boiling point. Other experimental procedures are identical with the Beckmann method. This method gives a more reliable measurement of the boiling point. In all boiling point measurements correction due to change in the barometric reading, if any, should be incorporated.

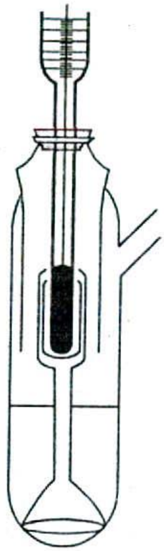


Figure 9.6 Cottrell's apparatus

Example 9.3: 0.562 *g* of naphthalene was dissolved in 30 *g* of carbon tetrachloride. If the normal boiling point of carbon tetrachloride is taken as 76.91°C, at what temperature will the solution boil at atmospheric pressure if $K_b = 5.02$?

Solution: Molar mass of naphthalene = 128.

From equation (9.24) $$\Delta T_b = \frac{0.562 \times 5.02 \times 1000}{30 \times 128} = 0.74°\text{C}$$

Boiling point of the solution will, therefore, be $(76.91 + 0.74) = 77.65°\text{C}$.

Example 9.4: A solution containing 0.35 *g* of an unknown non-volatile solute *X* in 40 *g* of CCl_4 boils at 350.40 K. Calculate the RMM of the solute *X*. The boiling point of CCl_4 is 350.00 K, and K_b is 5.03 K kg mol^{-1}.

Solution: Mass of solvent $w_1 = 40$ *g*; mass of solute $w_2 = 0.4$ *g* and $K_b = 5.02$ K kg mol^{-1}. Also, $\Delta T_b = 350.40 - 350.00 = 0.40$ K.

Substituting these data in equation (9.16) we get,

$$0.40 = 5.02 \times \frac{0.35}{40 \times M_2} \times 1000$$

$$M_2 = \frac{5.02 \times 0.35 \times 1000}{0.40 \times 40}$$

Or $$M_2 = 111.0$$

9.9 Depression of Freezing Point

The freezing point of a liquid is *defined as the temperature at which the liquid and solid forms are in equilibrium* and the *freezing point of a* ***solution*** *is the temperature at which the solution is in equilibrium with the pure crystalline solvent.* The depression of freezing point of a liquid by the addition of a non-volatile and non-electrolytic solute may be discussed more conveniently with the help of vapour pressure-temperature curves as in Figure 9.7. The vapour pressure curves of liquid solvent and solid solvent meet at *A*. Hence this corresponds to the freezing point T_o of the solvent. *D* corresponds to the freezing point *T* of the solution as this is the temperature at which the solution and solid solvent have the same vapour pressure. It is clear that *T* is lower than T_o and the freezing points of solutions will always be lower than those of pure solvent as the vapour pressure curves for the former lie below that for the latter.

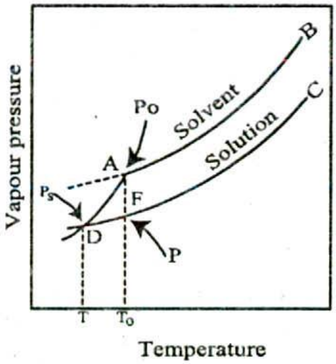


Figure 9.7 Depression of freezing point

A quantitative relationship between the concentration of solute in solution and the depression of freezing point was given by F.M. Raoult (1878–86) in the form of two laws which are generally known as Raoult's laws of depression of freezing point.

(i) *The depression of freezing point of a solvent due to the addition of a solute is proportional to the molality, m, of the solution.* Expressed mathematically

$$\Delta T_f = K_f . m \tag{9.25}$$

where K_f is a constant known as the *molal depression of freezing point constant* or *cryoscopic constant.*

(ii) *Equimolecular quantities of different substances dissolved in the same quantity of the same solvent lower the freezing point to the same extent.*

It may be noted that these laws are similar to the laws of boiling point elevation and have the same limitations as those, *i.e.,* these are applicable to dilute solutions of non-volatile non-electrolytes, which do not undergo association or dissociation in solution. An additional condition is that during freezing only pure solvent should separate as the solid phase.

The relation between freezing point depression and concentration may be derived easily with the help of Figure 9.7. Let p° be the vapour pressure of the solvent at its freezing point T_o, and p and p_s are the vapour pressures of the solution at T_o and T, its freezing point, respectively. For very dilute solutions the freezing point depressions ($\Delta T_f = T_o - T$) will be small, and to a good approximation the line segments AF and DF may be considered as straight lines. Again, the vapour pressure curves for a number of solutions near the freezing point will be parallel and then $\frac{DF}{AF}$ for these curves will be constant, i.e., $\frac{DF}{AF} = k$. But the length of DF equals ΔT_f and AF is proportional to $(p^\circ - p)$. If k is replaced by a new constant k' ($= k.p^\circ$), then equation (9.25) becomes,

$$\frac{\Delta T_f}{p^0 - p} = \frac{k'}{p^0} \tag{9.26}$$

or

$$\Delta T_f = k' \, \frac{p^0 - p}{p^0} \tag{9.27}$$

since p°, the vapour pressure of the solvent, is constant at its freezing point.
Using Raoult's law

$$\Delta T_f = k'. x_2 \tag{9.28}$$

where x_2 is the mole fraction of the solute. This equation is very similar to equation (9.13) derived for the boiling point elevation.

By following similar arguments as in the case of boiling point elevation it can be shown that

$$\Delta T_f = K_f . \frac{w_2/M_2}{w_2} \times 1000 \tag{9.29}$$

$$= K_f . m$$

When $m = 1, \Delta T = K_f.$

9.10 Thermodynamic Derivation of the Freezing Point Depression

The derivation is based on the use of the Clapeyron-Clausius equation and may be explained with the help of Figure 9.7. Let p_s and p^0 be the vapour pressures of solid solvent at temperatures T and T_o respectively. Use of the Clapeyron-Clausius equation leads to

$$ln \; \frac{p^0}{p_s} = -\frac{\Delta H_s}{R}\left[\frac{1}{T_0} - \frac{1}{T}\right] \tag{9.30}$$

where ΔH_s is the molar latent heat of sublimation of the solvent. The vapour pressures of the solution at temperatures T and T_o are p_s and p and we have in the same way as for the solid solvent

$$ln\frac{p}{p_s} = -\frac{\Delta H_{ev}}{R}\left[\frac{1}{T_0}-\frac{1}{T}\right] \tag{9.31}$$

where ΔH_{ev} is the molar latent heat of vaporisation of the solvent. Subtracting equation (9.31) from equation (9.30) one obtains :

$$ln\frac{p^0}{p_s} - ln\frac{p}{p_s} = -\frac{(\Delta H_s - \Delta H_{ev})}{R}\left[\frac{1}{T_0}-\frac{1}{T}\right] \tag{9.32}$$

This equation may be simplified by using the relation:

$$\Delta H_s = \Delta H_f + \Delta H_{ev},$$

where ΔH_f is the molar latent heat of fusion.

$$ln\ \frac{p^0}{p} = -\frac{\Delta H_f}{R}\left[\frac{1}{T_0}-\frac{1}{T}\right] \tag{9.33}$$

or

$$ln\ \frac{p}{p^0} = -\frac{\Delta H_f}{R}\left[\frac{1}{T}-\frac{1}{T_0}\right] \tag{9.34}$$

$$= -\frac{\Delta H_f}{R}\times\frac{T_0 - T}{TT_0} \tag{9.34}$$

$$= -\frac{\Delta H_f}{R}\cdot\frac{\Delta T_f}{T_0^2} \tag{9.35}$$

where ΔT_f is the depression of freezing point. As in the case of elevation of boiling point equation (9.35) can be transformed into

$$\Delta T_f = \frac{RT_0^2}{\Delta H_f}\times x_2 \tag{9.36}$$

For dilute solutions equation (9.36) reduces to

$$\Delta T_f = \frac{RT_0^2}{\frac{\Delta H_f}{M_1}\times 1000}\cdot\frac{w_2/M_2}{w_1}\times 1000 \tag{9.37}$$

$$= \frac{RT_0^2}{1000\ l_f}\cdot m = \mathrm{K}_f.m \tag{9.38}$$

where l_f is the latent heat of fusion per gram, and K_f is the cryoscopic constant where

$$K_f = \frac{RT_0^2}{1000 l_f}\cdot$$

The freezing points and the cryoscopic constants of a number of common solvents are given in Table 9.2.

9.11 Measurement of Depression of Freezing Point

The arrangement for cryoscopic determination of molar mass of a solute is shown in Figure 9.8.

The apparatus essentially consists of a freezing tube *F* fitted with a stirrer *S* and a side tube *A*. The freezing tube is surrounded by an air jacket *J* to reduce the rate of cooling. The Beckmann thermometer is introduced into the freezing tube through an opening at the rubber or velvet cork fitted at the open end of the freezing tube. The entire assembly is then placed in an ice bath, B, kept at a temperature of 3 – 5°C below the freezing point of the solvent.

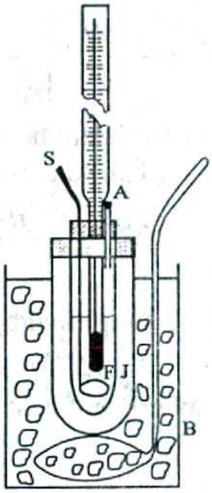


Figure 9.8 Apparatus for cryoscopic measurements

The depression of freezing point is determined first by recording the Beckmann reading corresponding to the freezing point of the pure solvent, and then that of the solution. The molar mass of the solute is determined by using the equation (9.38) since all the quantities are now known.

In cryoscopic method uniform stirring of the solvent (or solution) is an important step. The solvent is stirred uniformly and slowly by the stirrer *S*, otherwise incorrect result may be obtained due to supercooling. The temperature gradually falls as the solvent cools down. At one point the thermometer will show a rapid rise of about 0.2 – 0.3°C, after which the mercury meniscus will remain steady for a considerable time. The sudden rise is due to initial supercooling, but as soon as a small amount of solid phase is formed the system quickly goes back to the true freezing point indicated by the constant reading of the thermometer. This is the true freezing point of the solvent shown as *cd* in Figure 9.9.

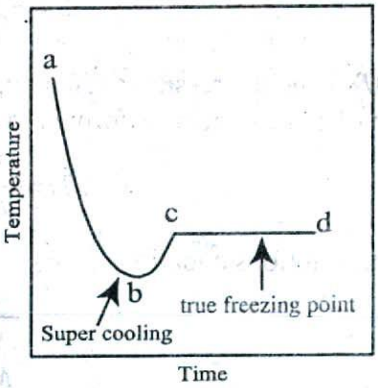


Figure 9.9 Time *vs* temperature during cooling (*Further details may be found in books on Practical Physical Chemistry.*)

Example 9.5: 0.565 *g* of a solute dissolved in 20 mL of benzene (density = 0.877 $g\ mL^{-1}$) depressed the freezing point by 0.355°C. Given K_f for benzene is 5.12, calculate the molecular mass of the solute.

Solution: 20 *mL* of benzene has mass = (20 × 0.877) *g* = 17.57 *g*

Then from equation (9.29) we get,

Or $$M = \frac{5.12 \times 0.565 \times 1000}{17.57 \times 0.355} = 46.3$$

Example 9.6: Calculate the freezing point of a 0.050 molal solution of a non-volatile compound that does not associate or dissociate in cyclohexane. T_f^0 (cyclohexane) = 6.5°C and K_f= 20.0 K kg mol^{-1}.

Solution: We know from equation (9.38) that,

$$\Delta T_f = K_f.m = 20.0 \times 0.050 = 1.0\ ^\circ\text{C}$$

Or, $$T_f = T_f^0 - \Delta T_f = 5.5\ ^\circ\text{C}.$$

9.12 Osmosis and Osmotic Pressure

We know that a gas or vapour spreads out from a region of high pressure to a region of low pressure. Similarly, if a concentrated solution and a dilute solution of the same solute are placed together in the same container the solute particles move from the concentrated solution into the dilute solution. These spreading out of gases or solutes in solution is spontaneous, and continue till the mixtures are homogeneous. The process is known as *diffusion (Section 2.10)*. This migration of the gas molecules or solute particles is caused by translational motion of the molecules/particles. If, however, a solution is separated from the solvent (or a dilute solution is separated from a concentrated solution) by a *semi-permeable membrane* a reverse process will take place in which only the solvent molecules migrate through the membrane but not the solute molecules. This is shown in Figure 9.10.

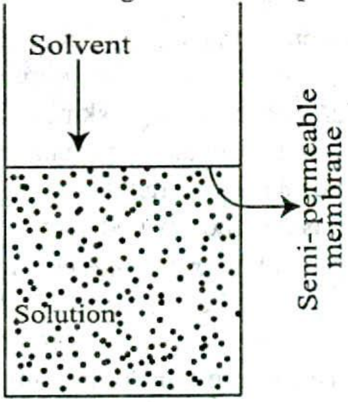


Figure 9.10 Osmosis

Due to difference in concentration the solvent molecules will go on migrating through the semi-permeable membrane unless it is prevented by external forces to do so. *This phenomenon of selective migration of the solvent molecules through the separating semi-permeable membrane to the solution is called osmosis.* As a result of osmosis the solute concentration on either side of the membrane becomes equal at equilibrium. Due to spontaneous inflow of the solvent through the membrane to the solution side, a pressure is developed in the solution side. This continues to increase as long as the solvent flows. However, the inflow of the solvent can be stopped from the beginning by application of an appropriate external pressure to the solution side. For equilibrium the external pressure must be equal to the pressure developed by osmosis. This external pressure is denoted by *P*, as in Figure 9.11.

The osmotic pressure may, therefore, be defined as the external pressure that must be applied on the solution side to just prevent the inflow of the solvent through the semi-permeable membrane which separates the solvent and solution. In this case the pressure, *P*, shall be equal to the osmotic pressure. If the semi-permeable membrane separates two solutions of different concentrations then also the solvent from the lower concentration side will flow to the higher concentration side. Thus concentration difference is the cause of osmotic pressure. Osmotic pressure is a colligative property.

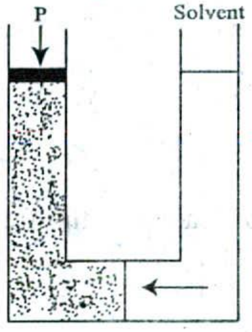


Figure 9.11 Osmotic pressure

It must be clearly understood that during diffusion migration of solvent molecules take place in both directions. But in osmosis the solvent molecules migrate in one direction only.

9.13 Semi-permeable Membrane

A membrane that allows only the solvent molecules to pass through it, but not the solute molecules is known as a *semi-permeable membrane*. Natural membranes are mostly semi-permeable. For examples, skin inside the egg shell, membranes around the red blood corpuscle, animal bladder, vegetable tissue are all semi-permeable. A variety of synthetic semi-permeable membranes are now available. The mechanism of the action of the membrane is only poorly understood. A brief discussion of the existing concept follows.

(i) *Molecular sieve theory:* According to this theory the semi-permeable membrane is supposed to contain a large number of extremely minute pores which allow the small solvent molecules to pass but not the solute molecules. The membrane, therefore, acts like a *sieve* by allowing preferential migration of the solvent. However, the *molecular sieve theory* is not satisfactory, because cases are known where the solute molecules are smaller than the solvent molecules and yet only the solvent molecules pass through the membrane.

(ii) Membrane solution theory: Membrane solution theory envisages that the membrane contains protein bearing functional groups such as, –COOH, –OH, $-NH_2$ etc., which 'dissolves' water molecules by hydrogen bonding or chemical interaction. As a result the solvent molecules pass on to the solution side. Since solute particles are not dissolved in the membrane these cannot pass through. This theory can explain a number of facts but again is found to be unsatisfactory in many cases.

(iii) Vapour pressure theory: The vapour pressure theory assumes that neither the solute nor the solvent molecules can pass through the tiny holes or capillaries present in the membrane. Thus the capillaries have pure solvent on one side and solution on the other side with a '*finite gap*' separating them. Since the vapour pressure of the solution is lower than that of the pure solvent, the diffusion of vapour from the solvent side to the solution side will occur across the finite gap. It is thus assumed that only the molecules in the vapour phase can pass through the membrane. The vapour pressure theory can explain the mechanism of osmosis in most cases.

(iv) Membrane bombardment theory: The fundamental idea behind this theory is the unequal bombardment of the *solvent molecules* on the two sides of the semi-permeable membrane. Since there are fewer solvent molecules on the solution side of the membrane compared to the solvent side, there are fewer bombardments per unit area of the surface on the solution side than on the solvent side. Thus, solvent molecules will diffuse slowly through the membrane from the solution side than on the solvent side. The net result is the flow of solvent from the pure solvent to the solution across the membrane.

9.14 Determination of Osmotic Pressure

Abbe Nollet (1748) was the first to observe the phenomenon of osmosis and made measurements of osmotic pressure. His measurements with pig's bladder as the semi-permeable membrane gave only semi-quantitative results as the pig's bladder is not a good semi-permeable membrane. It was the botanist Pfeffer who successfully developed the technique for preparing good semi-permeable membranes and made measurements of osmotic pressure.

(a) Pfeffer's method : Pfeffer developed a technique of depositing gelatinous copper ferrocyanide in the pores of an earthenware pot and used this pot to act as a semi-permeable membrane. His apparatus for the measurement of osmotic pressure is shown in Figure 9.12. The porous pot, P, having the deposit of copper ferrocyanide in its pores is connected to a manometer, M, as shown. The pot is filled with the experimental solution and then placed n a vessel containing the solvent. The entire assembly is then placed in a thermostat and allowed to stand until equilibrium is reached. At equilibrium the difference in the heights of mercury columns in the two tubes gave the osmotic pressure.

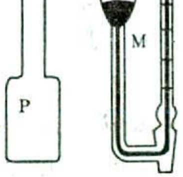


Figure 9.12 Pfeffer's apparatus for measurement of osmotic pressure

The method is slow because it might take couple of days to reach equilibrium. Also, if the pressure is high, the membrane may break and cannot be used. Pfeffer's method was improved by Berkeley and Hartley.

(b) Berkeley and Hartley's method: The principle of the method is illustrated in Figure 9.13.

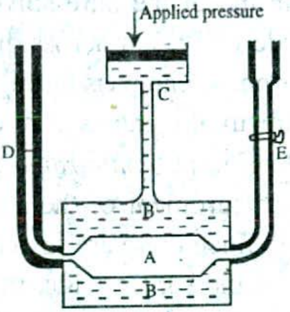


Figure 9.13 Berkeley and Hartley's apparatus

The apparatus consists of two concentric cylindrical tubes, *A* and *B*. The porous tube, *A*, carries in it the semi-permeable membrane of copper ferrocyanide. The inner tube is surrounded by the outer tube, *B*. The outer tube has an opening at *C* through which pressure could be applied from outside. The porous tube *A* has two side tubes, *D* and *E*. The solvent is added to *A* through *E*. The side tube *D* is a capillary tube so that any small change in pressure in *A* could be easily detected by the movement of the liquid meniscus in the tube. Due to osmosis the water from tube *A* flows to the solution in *B* and causes a movement in the liquid meniscus in *D*. Berkeley and Hartley prevented the inflow of water in tube *B* by applying an external pressure through *C* and maintained the liquid meniscus in *D* at the same position until equilibrium. The excess pressure thus applied to the solution side to prevent water inflow gave the osmotic pressure at the temperature of the experiment. The apparatus is capable of giving good results in a relatively short time compared to other methods where the solvent is allowed to flow into the solution. In this method there is no change in concentration of the solution because no solvent is allowed to enter the solution tube. Pressures up to 150 atmosphere can be measured by this method. Some results of Berkeley and Hartley are given in Table 9.2

Table 9.2 Osmotic pressure of sucrose solutions at 30°C

g of sucrose per 1000 *g* of water	Osmotic pressure (atmosphere)
202	15.5
370	29.7
569	48.8
820	74.9

(c) Modern methods: Different types of membrane osmometers have been developed for quick and accurate measurements of osmotic pressure. The membrane osmometers generally used for the determination of osmotic pressures may be divided into two classes:

(i) *Static osmometer:* This type of osmometer is based on the attainment of equilibrium osmotic pressure due to diffusion of solvent through a membrane.

(ii) *Dynamic osmometer:* In this case the flow of solvent through the membrane is prevented by the application of appropriate pressure to the solution side.

A simple form of *static osmometer* is illustrated in Figure 9.14. The solution under investigation is taken in the inner bulb which carries at one end the semi permeable membrane like cellophane. The other end of the bulb is attached to a graduated capillary tube. This bulb is placed inside a wider vessel which contains the solvent. The solvent passes into the solution and causes the liquid to rise until an equilibrium height, *h,* is attained. After incorporating necessary corrections the osmotic pressure is calculated.

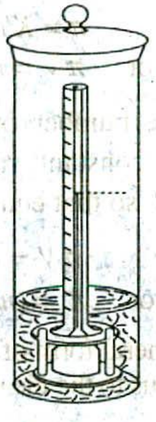


Figure 9.14 A modern osmometer

Dynamic osmometer, like vapour phase osmometer, is particularly used for the determination of molar mass of high molecular mass polymers or macromolecules.

9.15 Van't Hoff's Laws of Osmotic Pressure

Quantitative relations between the concentration of the solution and the osmotic pressure were first derived by van't Hoff in1886. These are known as *van't Hoff's laws of osmotic pressure.*

First law: *The osmotic pressure (π) of a solution is directly proportional to the molar concentration of the solute at constant temperature.* Mathematically,

$$\pi \propto c \qquad (T = \text{constant}) \tag{9.39}$$

$$\text{or} \quad \pi \propto \frac{1}{V} \quad \left(\text{since } c = \frac{1}{V}\right) \tag{9.39a}$$

$$\text{and} \quad \pi V = constant \tag{9.40}$$

where c is the concentration of the solution in mol L^{-1} and V is the volume containing one mole of the solute. Equation (9.40) is similar to Boyle's law for gas pressure.

Second law: *The osmotic pressure of a solution of given concentration varies directly as the temperature in Kelvin (K).* Expressed mathematically,

$$\pi \propto T \qquad (c = \text{constant}) \tag{9.41}$$

$$\text{or} \quad \pi = KT \tag{9.42}$$

Equation (9.42) is similar to Charles' law for gas pressure.

Third law: *Equimolecular quantities of different solutes dissolved in such volumes of the solvent as to give the same volume of the solution have the same osmotic pressure at the same temperature.*

Laws of variation are used to combine of equations (9.39) and (9.41) to give equation (9.43).

$$\pi = K'cT$$

$$\text{or} \quad \pi V = nK'T \tag{9.43}$$

where n is the number of moles of the solute in V L of the solution and K' is the proportionality constant. van't Hoff also found that K' has the same value as the universal gas constant, R, so that equation (9.43) may be written as

$$\pi V = nRT \tag{9.44}$$

$$\text{or} \quad \pi = (n/V)RT = cRT \tag{9.44a}$$

which is the general form of osmotic pressure equation. Thus, the osmotic pressure equation is exactly analogous to the ideal gas equation including the numerical value of the constant R.

Example 9.7: What will be the osmotic pressure exerted by 100 *mL* of an aqueous solution containing 1.00 *g* of glucose at 27°C?

Solution: 1.00 *g* glucose is present in 100 *mL* solution.

So, the molar concentration, $c = \dfrac{1.00 \times 1000}{180 \times 100}$, (molar mass of glucose is 180)

Substituting the values in the equation $\pi = cRT$ we get,

$$\pi = \frac{1000 \times 0.082 \times 300}{180 \times 100} = 1.36 \text{ atm (unit of } R \text{ is } L\text{-}atm\ K^{-1}mol^{-1})$$

9.16 Determination of Molecular Mass from Osmotic Pressure Measurements

Like the other colligative properties, osmotic pressure measurements are extensively used for the determination of molecular masses of substances. If the number of moles in a solution of volume V litres is n then equation (9.44) takes the form

$$\pi V = n\,RT = \frac{w}{M}RT \tag{9.45}$$

where w is the mass of the solute and M its molecular mass. This equation readily gives a method of calculating molecular masses of solutes in solution. Equation (9.45) may also be written as,

$$\pi = cRT \tag{9.46}$$

where c is the molar concentration. This is the same as equation (9.44a).

Example 9.8: The molecular mass of an enzyme is 25,000. How much of the substance is present in 100 *mL* of a solution which has an osmotic pressure of 157.0 *mm* of H_2O at 25°C?

Solution: From (9.45), $\pi V = \dfrac{w}{M}RT$, or $w = \dfrac{M\pi V}{RT}$

Now 157.0 *mm* of H_2O is equivalent to 157.0/13.6 = 11.55 *mm Hg* since the density of mercury is = 13·6 $g\ (mL)^{-1}$

$$\text{Or,}\quad w = \frac{25000 \times 11{\cdot}55 \times 0{\cdot}1}{760 \times 0{\cdot}082 \times 298}$$

$$= 1.55\ g$$

(volume is expressed in L and pressure in atm and R in L - $atm\ K^{-1} mol^{-1}$).

Example 9.9: 2.05 g of an unknown compound is dissolved in 200 mL of solution at 25 °C. If the osmotic pressure is 2.25 atmosphere, calculate the molecular mass of the solute.

Solution: From (9.45),

$$\pi V = \frac{w}{M} RT \quad \text{or} \quad M = \frac{wRT}{\pi V}$$

$$V = 200\ mL = 0.2\ L$$

Substituting the values we get

$$M = \frac{2.05 \times 0.082 \times 298}{2.25 \times 0.2} = 111.3.$$

The osmotic pressure method is widely used for determination of molecular mass of high polymers like cellulose, proteins, polystyrene etc. The other three colligative properties are not suitable, since the magnitude of lowering of vapour pressure, elevation of boiling point and depression of freezing point is so small that these methods become useless for any practical purpose when the molecular mass of the solute exceeds a few thousand.

9.17 Thermodynamic Derivation of Osmotic Pressure Laws

The laws of osmotic pressure can be deduced in a number of ways by thermodynamic principles. Only one is given which makes use of the Raoult's law of lowering of vapour pressure. Let us take the pure solvent and the solution in two chambers separated by a semi-permeable membrane and let the equilibrium be established at constant temperature T (Figure 9.15).

Let p^0 and p be the vapour pressures of the solvent and solution respectively. A cyclic process comprising the following isothermal reversible steps may be imagined to be carried out.

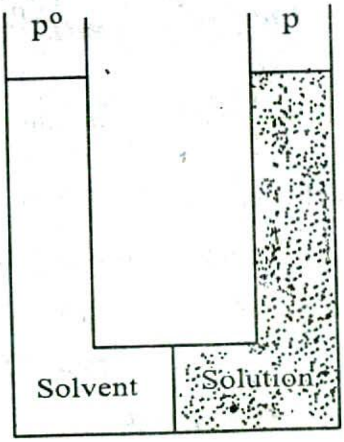


Figure 9.15 Semi-permeable membrane separating solvent from solution

(i) dx mole of the liquid solvent is converted to the vapour phase from the solvent chamber.

$$\text{Work done } w_1 = dx\ RT \tag{9.47}$$

(ii) dx mole of the vapour is transferred to the solution side and expanded from pressure p^0 to p.

$$\text{Work done } w_2 = dx\, RT\, ln \frac{p^0}{p} \tag{9.48}$$

(iii) dx mole of the vapour is condensed at pressure p on the solution side.

$$\text{Work done } w_3 = -\, dx\, RT \tag{9.49}$$

(iv) dx mole of the solvent is now transferred through the semi-permeable membrane from the solution side to the solvent side by applying a pressure infinitesimally greater than the osmotic pressure π.

$$\text{Work done } w_4 = -\, dx\, \pi V' \tag{9.50}$$

where V′ is the volume of 1.00 mole of the solvent.

The total work done by this isothermal and reversible process is obtained by adding all the work terms in the four steps. Since a cyclic process has been completed isothermally and reversiblv the net work is zero. Therefore,

$$dx\, RT + dx\, RT\, ln \frac{p^0}{p} - dx\, RT - dx\, \pi V' = 0 \tag{9.51}$$

$$\text{or} \quad \pi V' = RT\, ln \frac{p^0}{p} = RT\, ln \left(1 + \frac{p^0 - p}{p}\right)$$

$$\cong RT \left(\frac{p^0 - p}{p}\right) = RT \frac{n}{N} \tag{9.52}$$

$$\text{or,} \quad \pi V' \times \frac{N}{n} = RT \qquad \left(\text{for dilute solutions } \frac{p^0 - p}{p} \approx \frac{p^0 - p}{p^0}\right) \tag{9.53}$$

If n moles of solute are associated with N moles of solvent then one mole of the solvent will contain n/N moles of solute. Therefore, $V' \times \frac{N}{n} = V$, which represents the volume of the solution containing one mole of the solute.

Or

$$\pi V = RT$$

9.18 Relative Osmotic Pressure

In 1884 De Vries, a botanist, developed an approximate method for comparing the osmotic pressures of solutions by using plant cells. The primary plant cell generally has a relatively rigid cellulosic wall which is permeable to water only. The cellulosic wall is not normally permeable to the solutes in the cell sap (*liquid*). If such a cell is placed in a solution of osmotic pressure lower than the solution in the sap, there will be no change in the cell shape, because water from the more dilute solution outside the cell will not be able to cause any deformation due to the rigid cell wall. But if such a cell is immersed in a solution of higher osmotic pressure, water will pass out through the cell and consequently there will be partial collapse of the cell membrane causing a change in the shape of cytoplasm (Figure 9.16).

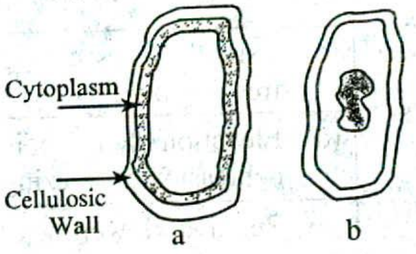


Figure 9.16 (a) Normal plant cell
(b) Plasmolyzed plant cell

The cell is then said to be *plasmolyzed* and the phenomenon is known as *plasmolysis*. The osmotic pressure of cell saps may be determined by immersing the cell in a series of solutions of varying concentrations and observing the cell under the microscope. The concentration of the solution which just causes a shrinkage of the membrane is noted. The osmotic pressure of this solution is approximately equal to the osmotic pressure of the sap solution. (Solutions having the same osmotic pressure are said to be *isotonic* or *iso-osmotic*). Consequently, *plasmolysis* may be used for comparing osmotic pressure of solutions.

Hamburger in 1890 suggested that red blood corpuscles (the cell wall is permeable to water) may be used conveniently for comparing osmotic pressures of solutions. If a red blood corpuscle is immersed in a solution of lower osmotic pressure, water will pass into the cell, make it swell and finally cause it to burst - a phenomenon known as *haemolysis.*

On the other hand, if the red blood corpuscle is put in a solution of higher osmotic pressure, water will flow out of the cell and it will shrink. Blood plasma contains 0.85% of *NaCl* in addition to trace quantities of other salts. If a stronger solution of *NaCl* is injected in large dose the red blood corpuscles will shrink, whereas if only distilled water is injected in massive dose the red blood corpuscles will first swell and finally burst causing fatal effects. Saline injection is a solution of 0.85 % *NaCl* in distilled water.This solution is isotonic with the contents of the red blood corpuscles. Balance of osmotic pressure in living beings is of extreme importance. The osmotic pressure is of vital importance to life.

9.19 Interrelation between the Colligative Properties

The colligative properties of solutions are related with each other, and mathematical relationships between these properties may be deduced. However, for the sake of brevity only the final results are given below:

Pair of properties	Nature of relationship
(*a*) Osmotic pressure and elevation of boiling point.	$\pi = l_{ev}.\ \rho \dfrac{\Delta T_b}{T_o}$
(b) Osmotic pressure and relative lowering of vapour pressure.	$\dfrac{p^0 - p}{p^0} = \dfrac{\pi}{RT} \cdot \dfrac{M}{\rho}$
(c) Osmotic pressure and depression of freezing point.	$\pi = l_f \rho \dfrac{\Delta T_f}{T_o}$
(d) Elevation of boiling point and depression of freezing point.	$\dfrac{\Delta T_b}{\Delta T_f} = \dfrac{l_f T^2}{l_{ev} T_o^2}$
(e) Relative lowering of vapour pressure and elevation of boiling point	$\dfrac{p^0 - p}{p^0} = \dfrac{l_{ev}}{R} \cdot \dfrac{\Delta T_b}{T_o^2}$
(f) Relative lowering of vapour pressure and depression of freezing point.	$\dfrac{p^0 - p}{p^0} = \dfrac{l_f}{R} \cdot \dfrac{\Delta T_f}{T_o^2}$

In the above relations M is the molecular mass of the solvent and ρ is its density; l_f and l_{ev} represent latent heat of fusion and latent heat of evaporation respectively.

It may be noted here that except osmotic pressure all other colligative properties are dependent on the solvent, e.g., extent of the elevation of boiling point or depression of freezing point depends on the solvent since K_b is related to the boiling point and latent heat of vaporisation and K_f to freezing point and latent heat of fusion. The relative lowering of vapour pressure depends on the solvent vapour pressure. But the osmotic pressure is independent of the solvent. As long as the molar concentration remains the same the osmotic pressure remains unchanged at constant temperature.

9.20 Abnormal Molecular Masses from Colligative Properties

The laws of the colligative properties are applicable only for very dilute solution, and when there are no association and dissociation of the solutes in solution. Sometimes abnormal molecular masses of the solutes were observed when calculated from the laws of colligative properties. Let us consider association and dissociation of solutes in solutions.

(a) *Association in solution:* Compounds like ethanoic acid, phenol, benzoic acid etc. in benzene solutions give values of osmotic pressure, freezing point depression, boiling point elevation much lower than those expected from the respective equations. Consequently, the molecular masses derived from these values were higher than those indicated by the molecular formula. This was explained by assuming association of solute molecules to form aggregates having large molecular mass. Acetic acid and benzoic acid are known to form dimers at higher concentrations and the existence of an equilibrium of the type $2A \rightleftharpoons (A)_2$ at appreciable concentration has been predicted.

(b) *Dissociation in solution:* Van't Hoff pointed out that dilute aqueous solutions of inorganic salts, acids and bases give abnormally large osmotic pressure. He could not account for the anomaly but found that the introduction of an empirical factor, i, in the osmotic pressure equation (9.46) gave agreement with experimental values. This equation then becomes

$$\pi_{obs} = = i\,cRT \tag{9.53}$$

where π_{obs} is the experimental osmotic pressure and i is known as the van't Hoff factor. From equations (9.46) and (9.53) one can see that

$$i = \frac{\pi_{obs}}{\pi_{theor}} \tag{9.54}$$

Such anomaly was also observed in the case of freezing point depression, boiling point elevation and lowering of vapour pressure and i could be expressed in the form

$$i = \frac{\pi}{\pi_o} = \frac{\Delta p}{(\Delta p^0)} = \frac{\Delta T_f}{(\Delta T_f)_o} = \frac{\Delta T_b}{(\Delta T_b)_o} \tag{9.55}$$

where the numerators are the experimental values and the quantities in the denominator are the values expected from the respective equations.

At first i was regarded as a constant, but subsequent investigation showed that the value increases with the decrease of concentration of the solute. The values of i for several salts in water are given in Table 6·10.

Table 9.3 van't Hoff factor for several salts in water obtained from measurements of freezing point depression

Concentration (molality)	$NaCl$	$MgSO_4$	$Pb(NO_3)_2$
1·0	1·81	1·09	1·13
1·1	1·87	1·21	2·13
0·01	1·94	1·53	2·63
0·001	1·91	1·82	2·89
infinite dilution	(2·00)	(2·00)	(3·00)

The abnormally high values of the colligative properties of salts, acids and bases in aqueous solution were explained by Arrhenius who proposed that in aqueous solutions a certain fraction of the molecules of acids, bases and salts dissociate to form positively and negatively charged ions. As a result the number of discrete units in solution increases giving abnormally large colligative properties of such solutions. He proposed that the degree of dissociation increases with the decrease of concentration. This explains why the value of the van't Hoff factor increases as the concentration is decreased. On the basis of a postulate that an equilibrium exists between the dissociated and undissociated molecules Arrhenius was able to calculate the degree of dissociation of the electrolytes from osmotic pressure, freezing point depression and boiling point elevation of solutions.

If α is the fraction of the molecules dissociated, each molecule being dissociated into *n* ions, the total number of discrete units in solution is $1 - \alpha + n\,\alpha$, or $1 + (n - 1)\alpha$. Hence

$$i = \frac{\Delta T_f}{(\Delta T_f)_o} = \frac{\Delta T_b}{(\Delta T_b)_o} = 1 + (n - 1)\alpha \tag{9.56}$$

This method of calculating α is not, however, applicable to strong electrolytes as these are now regarded as completely ionized in solution.

9.21 Importance of Osmosis Phenomenon

Osmosis is an important phenomenon in many biological and technological processes.

Animal and vegetable cells containing solutions of salts and sugars (cell *saps*) are surrounded by *semi-permeable* membranes. The osmotic pressure of the solution surrounding the cell must be equal to that within the cell. If such a cell is placed in water or solution having lower osmotic pressure than that of the cell sap, water enters into the cell causing *haemolysis* (*Section 9.18*). On the other hand if such a cell is immersed in a solution of higher osmotic pressure, water will pass out through the cell and consequently lead to *plasmolysis* (*Section9.18*). The flow of water from soil to plants is due to osmosis. The osmotic pressure inside the plant cell in the root in contact with soil is higher than that inside the plant cell. As a result water from soil flows into the cell by osmosis. Plant movement such as opening and closing of flowers and leaves are also regulated by osmosis.

As has already been discussed, in osmosis solvent molecules flow through a semi-permeable membrane from pure solvent to solution, or from a dilute solution to concentrated solution. We also know that the flow of solvent (i.e, osmosis) through the semi-permeable membrane can be stopped by applying equal pressure to the solution side. If, however, the applied pressure is higher than the osmotic pressure, osmosis is forced to take place in the opposite direction, i.e., from solution to solvent. This is called '*reverse osmosis*'. This concept has been applied in many countries to remove salinity of ocean water.

QUESTIONS AND PROBLEMS

1. What are the colligative properties and why are they so called? Deduce from Raoult's law an expression relating the molecular mass of a solute with the lowering of vapour pressure of a solvent on the addition of a solute.

   10.0 *g* of urea are dissolved in 100 *g* of water. If the vapour pressure of water at the working temperature is 27.32 *mm Hg*, what will be the vapour pressure of the solution? [Ans. 26.74 *mm Hg*]

2. From the kinetic theory explain why the vapour pressure of a solution of non-volatile solid is lower than that of the solvent.

3. State Raoult's law of vapour pressure lowering. A solution of a non-volatile non-electrolyte solid in water has a vapour pressure of 26.1 *mm Hg* at 25°C. The vapour pressure of water at this temperature is 27.3 *mm Hg*. Calculate the molecular mass of the solid.

4. State and explain the Raoult's law of relative lowering of vapour pressures. Show with a suitable graph how as a result of lowering of vapour pressure of a solution the boiling point and freezing point of the solution are affected.

5. A current of dry air was passed first through a series of bulbs containing a solution of 8.750 *g* of a solute in 100 *g* of ethyl alcohol and then through a series of bulbs containing pure alcohol at a temperature of 15°C. After the passage of the air the decrease in mass of the bulbs containing the solution was 2.0040 *g* and that of the bulbs containing the pure solvent was 0.0664 *g*. Calculate the molecular mass of the solute in solution. [Ans. 125.5]

6. The latent heat of evaporation of carbon disulphide is 359.1 $J\ g^{-1}$. Calculate the molar ebullioscopic constant of carbon disulphide. When 1.643 g of benzoic acid is dissolved in 50.1 *g* of CS_2, its boiling point is raised by 0.32°C. What is the molecular mass of benzoic acid in this solution? The boiling point of CS_2 is 46.2°C. [Ans. $K_b = 2.36$; $M_r = 242$]

7. Describe briefly Cottrell's method for the determination of elevation of boiling point. Why is this method thought to be superior to the Beckmann's method?

8. State Raoult's law of lowering of vapour pressure. Under what conditions is this law valid? What will be the vapour pressure of a solution of urea containing 4.00 *g* of urea per 100 *g* of water at 27°C? (vapour pressure of water at 27°C=26.7 *mm Hg*). [Ans. 26·4 *mm Hg*]

9. State Raoult's law of lowering of vapour pressure. What are its limitations? Explain with the help of a diagram why the boiling point of a solution is higher than that of the solvent.

10. Calculate the concentration in mole per 1000 *g* of water of an aqueous solution of a solid which at 100°C has a vapour pressure of 758.2 *mm* of *Hg*.
(Latent heat of evaporation of water is 40128 $J\ mol^{-1}$). [Ans. 0.936]

11. Describe briefly the experimental details of the cryoscopic method. Deduce a relation between the molecular mass of a solute and the depression of the freezing point of the solution.
0.523 *g* of naphthalene was dissolved in 20 *g* of benzene. Given K_f for benzene = 5.12, what will be the depression of the freezing point? [Ans. 1.04°C]

12. What is the significance of the cryoscopic constant K_f and ebullioscopic constant K_b? Show how these constants are related to the latent heat of fusion and latent heat of vaporisation respectively.

13. Name the colligative properties. State and explain the Raoult's law of relative lowering of vapour pressure.
0·555 *g* of a solute, when dissolved in 25 *mL* of benzene, depressed the freezing point of the solvent by 0.35°C. Calculate the molecular mass of the solute.
(K_f = 5.12 and density of benzene = 0·877 $g\ mL^{-1}$.). [Ans. 382.7]

14. A solution containing 2.38 *g* of sulphur in 100 *g* of naphthalene (melting point = 80.1°C) gave a lowering of freezing point of 0.62°C. Calculate the value of K_f of naphthalene, if its latent heat of fusion is 151.3 $J\ g^{-1}$, and the molecular mass of sulphur. [Ans. $K_f = 6.89$; $M_r = 264$]

15. An aqueous solution of ethyl alcohol containing 10.95 *g* of alcohol per 1000 *g* of water gave a freezing point of – 0.445°C. Calculate the molecular mass of alcohol in this solution. (K_f= 1.86) [Ans. 46]

16. What are colligative properties and why are they so called? A solution of a non-volatile non-electrolyte solute in a liquid volatile solvent has a lower vapour pressure than the pure solvent. Use this fact to show that the solution shall have a higher boiling point and a lower freezing point corresponding to the respective values of the pure solvent.
In a transpiration experiment dry nitrogen was drawn through a bulb containing a solution of 1.729 *g* of a solute in 50 *g* of ethyl alcohol and the nitrogen gas was subsequently passed through a bulb containing the pure solvent. The first bulb lost 0.484 *g* in mass and the second bulb lost 0.013 *g*. Calculate the molecular mass of the solute. [Ans. 61.71]

17. Explain clearly the principles underlying the determination of molecular mass of a non-volatile solute by the method of elevation of boiling point.
A solution containing 0.5042 *g* of a non-volatile solute dissolved in 42.02 *g* of benzene boils at 80.38 °C. Calculate the molecular mass of the solute given that boiling point of benzene is 80.20 °C and its latent heat of evaporation is 392.9 $J\ g^{-1}$. [Ans. 176]

18. Of the cryoscopic and the ebullioscopic methods which one, you think, gives a more reliable value of molecular mass? Justify your answer.

    Describe the method you have chosen above. Give suitable diagrams.

19. State and explain the van't Hoff's laws of osmotic pressure. Can you see any similarity between the ideal gas equation and the osmotic pressure equation? How can you account for such similarity?

20. State the laws of osmotic pressure. The osmotic pressure of a 2% solution of acetone in water is 590 cm of Hg at 10oC. What is the molecular mass of acetone? [Ans. 59.9]

21. How can measurement of the osmotic pressure be employed for molecular mass determination? What substances produce abnormal results and why?

22. The osmotic pressure of a solution of cane sugar is 2.85 atm at 29°C. What is the concentration of the solution in $mol\ L^{-1}$? [Ans. 15]

23. What is the osmotic pressure of a glucose (M_r =180) solution containing 2.5 *g* in 100 *g* of water at 27°C? [Ans. 0.342 atm]

24. State clearly and .explain mathematically the laws of osmotic pressure. Under what conditions are these laws valid?

    A solution contains 10.2 *g* of a solute per litre of solution. This solution is isotonic with a 2 % aqueous solution of glucose. Calculate the molecular mass of the solute (molecular mass of glucose is 180). [Ans. 91.9]

25. Describe one experimental method for the determination of osmotic pressure.

    A molar solution of *NaCl* will have an osmotic pressure different from that of a molar solution of glucose (solutions are aqueous) at the same temperature. How can you account for this?

26. If a large volume of a saturated solution of *NaCl* is injected quickly in a human body what will happen to the osmotic balance of the system? Explain your answer.

27. Deduce thermodynamically the osmotic pressure equation. Show how osmotic pressure is related to the lowering of vapour pressure.

28. What will be the freezing point of a solution containing 5.86 *g* of *NaCl* in 100 *g* water assuming complete dissociation of the salt (K_f= 1·86). (Ans. 269·44 *K*)

29. Discuss from the practical point of view the relative merits and demerits of the colligative methods for measurement of molecular mass. Which method do you consider to be the most reliable and why?

30. The boiling point of a solution containing 0.440 *g* of *NaCl* in 100 *g* of water is 100.075°C. Calculate the apparent molecular mass of *NaCl* and its degree of dissociation in this solution. (K_b= 0.52)

    [Ans. M_r = 30.5; α = 0.92]

31. The vapour pressure of a solution containing 6.69 g of $Ca(NO_3)_2$ in 100 *g* of water is 746.9 *mm Hg* at 100°C. Calculate the degree of dissociation of the salt .[Ans. 67.5%]

32. A solution containing 9.21 *g* of mercuric cyanide in 100 *g* of water has a vapour pressure of 755.2 *mm Hg* at 100°C. What is the molecular mass of mercuric cyanide? [Ans. 262.5]

33. A 0.1 molal aqueous solution of *KCl* freezes at – 0.340°C. Calculate *i* and the osmotic pressure at 0°C. Assume density of solution to be unity. [Ans. *i* = 1.83; O.P. = 4.1 atm]

34. At 27°C a 0.1 molal aqueous solution of CH_3COOH is 1.5% dissociated. Calculate the freezing point and osmotic pressure of the solution. Compare your results with those expected under condition of no dissociation. [Ans. *F.P.* = – 0.189°C ; *O.P.* = 2.5 atm]

35. Discuss briefly the theories associated with semi-permeable membrane.

10 CHEMICAL EQUILIBRIUM

Equilibrium is an important concept in chemistry. The study of chemical equilibria gives us an idea about the extent (*how far*) of a reaction and the conditions upon which an equilibrium is dependent. It does not, however, say anything about the rate of reactions. The concept of equilibrium is applicable only for reversible reactions.

10.1 Reversible Reactions

When a fuel is burnt for cooking in a kitchen or for driving a motor car the reaction goes to completion until the supply of the fuel or oxygen is stopped. In kitchens using gas to produce the heat for cooking methane, CH_4, is burnt. The reaction is :

$$CH_4(g) + 3\,O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Like all reactions in which a fuel is burnt this is a one way reaction because the products do not combine to form the reactants, and the reaction as written goes on until the gas or oxygen supply is stopped. For a given supply of one of the gases the reaction is complete.

Many reactions, however, are *reversible*. This means that the reaction goes in both directions, i.e., if we start with the products, reactants will also start forming. Such reactions do not go to completion. Reactants are not entirely converted into products, and at any time after start of the reaction, from the reactant side or the product side, one finds a mixture of the reactants and the products. Reaction from the reactant side is called the *forward reaction* and that from the product side is called the *reverse reaction*. The forward and reverse reactions together form a *reversible reaction*. The sign $\rightleftharpoons$ between the reactants and the products indicate this type of a reaction.

Consider the reaction

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

If some $N_2O_4(g)$, which is yellow at about 30°C, is heated in a closed vessel it turns brown because of the formation of $NO_2(g)$, which is brown. Again if some brown NO_2 (g) is taken in a closed vessel and it is cooled it starts turning yellow because of the formation of $N_2O_4(g)$. So the above reaction is reversible. However, if some $N_2O_4(g)$ or twice as much $NO_2(g)$ is kept in a vessel at a constant temperature the colour gradually changes, but after a while it will be observed that the colour remains the same and does not change. This is because the proportion of the reactants and products remains unchanged. At this point the reaction is said to have reached *equilibrium. A chemical equilibrium in a system is the state of the system when there is no observable change in the concentration of the reactants and products.*

The constancy of the concentrations of the reactants and the products does not mean that at equilibrium no change is taking place. It has been shown by use of radioactive isotopes and other means that at equilibrium reaction is still going on in both the forward and reverse directions. This is why chemical equilibria are said to be dynamic. *A dynamic chemical equilibrium is one in which there is no net change of concentrations of the reactants and the products, although the reaction is proceeding in both directions.* The concentrations of the reactants and products do not change because the rate of the forward and the rate of the reverse reaction are equal.

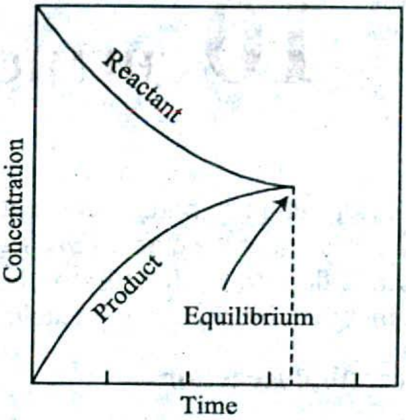


Figure 10.1 Concentration of the reactant and product as a function of time and attainment of equilibrium

Equilibrium systems could be divided into two groups: homogeneous and heterogeneous. *Homogeneous equilibria are those in which all the species (reactants and products) are in the same physical state.* $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is an example of homogeneous equilibrium. Some other examples of homogeneous equilibrium are:

(1) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

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

(3) $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

If one or more of the species in the equilibrium system is in a different physical state from the others then it is a heterogeneous equilibrium.

The equilibrium between liquid and vapour, as discussed in *Section 3.2*, is an example of heterogeneous equilibrium. Some other examples are:

(4) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(5) $3Fe(s) + H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

In all cases the equilibrium is dynamic in the sense that changes are continuously taking place in the forward and in the reverse directions although there is no net change in the state of the system.

Chemical equilibrium has the following important characteristics :

(a) At this state the concentrations of all species remain unchanged if other factors like temperature, pressure remain constant.

(b) The reaction can be started either from the reactant side or from the product side.

(c) For systems containing gaseous or volatile substances the reaction should be carried out in a closed vessel. The system should be isolated, which means that nothing is allowed to enter or leave the system.

(d) Catalysts do not affect equilibrium, because a catalyst affects the rate of the forward and reverse reactions equally.

[Note: This concept of dynamic equilibrium in chemical reactions arose from the idea of reversibility in chemical reactions introduced by Berthollet (1799) who was the scientific adviser to Napoleon. During Napoleon's Egyptian campaign Berthollet observed large deposits of sodium carbonate on the shores of some Egyptian lakes. His conclusion about the origin of these sodium carbonate deposits was that sodium chloride present in the lake water reacted with calcium carbonate (limestone) of the rocks to form sodium carbonate and calcium chloride. This is contrary to the ordinary experience in the laboratory where a precipitate of calcium carbonate is formed when sodium carbonate and calcium chloride solutions are mixed. The reversal of the ordinary course of reaction was attributed by Berthollet to the influence of the quantity of the substances reacting. The large quantity of sodium chloride present in the lake water drove the reaction in the reverse direction forming sodium carbonate. Subsequent investigations, chiefly by Wilhelmy, Berthollet, P. St. Gilles and others, confirmed the observation of Berthollet on the effect of mass on the reaction. These conclusions were summarized by M. Guldberg and P. Waage (1864) in the form of *The Law of Mass Action* which is stated as follows : *The rate of a chemical reaction at a given temperature is proportional to the 'active mass' of each of the reactants present in the system.* By active mass Guldberg and Waage meant the molar concentration, i.e., the number of moles per litre, or of any term proportional to this, such as partial pressure in case of gases. *We now know that the rate of a reaction is not always directly proportional to the concentration of a reactant.*]

10.2 The Equilibrium Law: the Equilibrium Constant

Let us consider a simple reversible reaction of the type

$$\mathrm{a}\,A + b\,B \rightleftharpoons lL + m\,M \tag{10.1}$$

Let *[A]*, *[B]*, *[C]* and *[D]* represent the molar concentration of *A*, *B*, *C* and *D* respectively at any instant. It is possible to show experimentally that at equilibrium,

$$K_c = \frac{[L]_e^l \times [M]_e^m}{[A]_e^a \times [B]_e^b} \tag{10.2}$$

where the subscript *e* indicates concentrations at the equilibrium position. This is the mathematical expression for the **law of chemical equilibrium** or simply **the equilibrium law**. The law states that *the equilibrium constant of a reaction at a given temperature equals the product of the equilibrium concentrations of the reaction products divided by the product of the equilibrium concentrations of the reactants, each concentration being raised to the power equal to the coefficient of the species (molecules or ions) in the balanced equation.*

The constant K_c is called the ***equilibrium constant**** and applies to reactions in solution.

The right hand side of the above equation is **the equilibrium quotient.** Note that it contains only concentration terms. It should not include terms for, (i) any pure solid, (ii) any pure liquid, unless it is a reactant or product of the reaction, or (iii) any solvent.

The equilibrium constant is a true constant for a given reaction. Its value does not depend on the initial concentrations of the reactants or products. *The value of the equilibrium constant does, however, vary with temperature.*

As the equilibrium constant expression contains concentration terms it will have a unit. The unit will depend on the units of all the concentration terms.

Example 10.1: Write the expressions for the equilibrium constants for the homogeneous and heterogeneous reactions shown below:

$$(a) 4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

$$(b)\ 2NO_2(g) + 7H_2(g) \rightleftharpoons 2NH_3(g) + 4H_2O(g)$$

$$(c)\ SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$(d) 3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Solution: (a) $K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$ (b) $K_c = \frac{[NH_3]^2[H_2O]^4}{[NO_2]^2[H_2]^7}$

(c) $K_c = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$ (d) $K_c = \frac{[H_2]^4}{[H_2O]^4}$

Example 10.2: A 5.00 L vessel contained 0.0185 mole of phosphorous trichlide, 0.0158 mole of phosphorous pentachloride, and 0.0870 mole of chlorine at 230°C in an equilibrium mixture. Calculate the value of K_c for the reaction:

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

Solution: Here, $[PCl_3] = \frac{0.0185}{5} = 0.0037 \text{ mol L}^{-1}$, $[Cl_2] = \frac{0.0870}{5} = 0.0174 \text{ mol L}^{-1}$

$$[PCl_5] = \frac{0.0158}{5} = 0.0032 \text{ mol L}^{-1}$$

The expression for K_c for this reaction is $\frac{[PCl_3][Cl_2]}{[PCl_5]}$

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* *The equilibrium constant could as well be expressed by writing the concentration of the reactants in the numerator. The convention is, however, to write the products in the numerator and the reactants in the denominator.*

Substituting these values in the above expression we get

$$K_c = \frac{0.0031 \times 0.0174}{0.0032}$$

$$= 20.77 \times 10^{-3} \text{ mol L}^{-1}$$

The unit of K_c for this equilibrium $= \frac{(mol\ L^{-1})(mol\ L^{-1})}{(mol\ L^{-1})}$

$$= mol\ L^{-1}$$

Example 10.3: In the reaction between N_2 and H_2 to form NH_3 according to the equation :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

K_c has a value of 6.0×10^{-2} $(\text{mol L}^{-1})^{-2}$ at 450°C. If, in a particular reaction vessel at this temperature, 0.250 mol $\text{L}^{-1}$of H_2 and 0.050 mol $\text{L}^{-1}$of NH_3 are present at equilibrium, what is the concentration of N_2?

Solution: The expression for the equilibrium constant K_c is

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 6.02 \times 10^{-2}$$

We have at equilibrium $[H_2] = 0.250 \text{ mol L}^{-1}$

$$[NH_3] = 0.050 \text{ mol L}^{-1}$$

Substitution in the expression for K_c gives : $\frac{(0.050)^2}{[N_2](0.250)^3} = 6.02 \times 10^{-2}$

from which we get $[N_2] = \frac{(0.050)^2}{(0.250)^3\,(6.02 \times 10^{-2})}$

$$= 2.66 \text{ mol L}^{-1}$$

The equilibrium concentration of N_2 is 2.66 mol L^{-1}

Example 10.4: The following hypothetical reaction was allowed to come to equilibrium :

$$2D(aq) + E(aq) \rightleftharpoons F(aq)$$

The initial amounts of reactants D and E in 1.00 L of the solution were 1.00 and 0.75 moles respectively. At equilibrium the amounts were 0.70 mole D and 0.60 mole E. Calculate the equilibrium constant of the reaction.

Solution: At equilibrium 0.70 mole of D remains. Hence 0.30 moles have reacted. As 2 moles of D produce one mole of F then moles of F at equilibrium will be 0.30/2 = 0.15. This also agrees with the amount of E reacting, which is 0.15 moles. Hence moles of E remaining would be 0.75 – 0.15 = 0.60.

Let us write the reaction and the initial and equilibrium concentrations of reactants and products as follows:

	$2D(aq)$	+ $E(aq)$	$\rightleftharpoons$ $F(aq)$
Initially 1 mol L^{-1}	1.00	0.75	0.00
At equilibrium 1 mol L^{-1}	0.70	0.6	0.15

Substituting these data in equation (10.2) we get,

$$K_c = \frac{[F]}{[D]^2[E]} = \frac{0.15}{(0.70)^2 \times 0.60} = 0.51 \text{ mol}^{-2} \text{ L}^2$$

10.3 Gaseous Equilibria

The concentrations of gases in a mixture usually are expressed in terms of the partial pressure of the gases. Since the partial pressure of an ideal gas is proportional to its concentration, c, the expression for the equilibrium constant for the reaction

$$a\,A(g) + b\,B(g) \rightleftharpoons l\,L(g) + m\,M(g)$$

may be written in the form

$$K_p = \frac{p_L^l \times p_M^m}{p_A^a \times p_B^b} \qquad (10.3)$$

when K_p is the equilibrium constant in terms of partial pressure and the partial pressures are the equilibrium values. K_p and K_c are not always identical. This is because the partial pressures are proportional to, but *not equal to,* gas concentration expressed in mol L^{-1}.

Example 10.5: The gases SO_2, O_2 and SO_3 were allowed to come to equilibrium in a closed vessel under certain conditions of temperature and pressure. The partial pressures of the gases were $p_{SO_2} = 0.050\,atm$, $p_{O_2} = 0.025\,atm$ and $p_{SO_3} = 1.00\,atm$. Find the values of K_p for the following equilibria:

(a) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Solution: For (a), $K_p = \dfrac{p_{SO_3}}{p_{SO_2} \times p_{O_2}^{1/2}} = \dfrac{1.00}{0.050 \times (0.025)^{\frac{1}{2}}} = 126.58$

For (b),
$$K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} \times p_{O_2}}$$
$$= \frac{(1.00)^2}{(0.050)^2 \times 0.025} = 16 \times 10^3$$

Note: It can be seen that the value of the equilibrium constant for the same reaction may be different when the mole ratios of the reactants and products are shown differently in a balanced equation.

10.4 Relation between K_p and K_c

A relation between K_p and K_c can be easily deduced for ideal gases so that if K_p is known K_c may be evaluated and *vice versa.* For n moles of a gas in a mixture of volume V L and temperature T, the partial pressure (in atmosphere) is $p = \frac{n}{V}RT$; but $\frac{n}{V}$ is equal to c mol L^{-1}, so that $p = cRT$. Substituting this value of p for each species at equilibrium in equation (10.3) one obtains

$$K_p = \frac{([L]RT)^l \times ([M]RT)^m}{([A]RT)^a \times ([B]RT)^b}$$
$$K_p = \frac{[L]^l [M]^m \times (RT)^{l+m}}{[A]^a [B]^b \times (RT)^{a+b}}$$
$$= K_c (RT)^{(l+m)-(a+b)}$$
$$= K_c (RT)^{\Delta n} \tag{10.4}$$

where Δn = difference in the number of moles of the product gases and the number of moles of the reactant gases in the equilibrium mixture. When there is no difference in the number of moles of the gas during the reaction, i.e., $\Delta n = 0$, $K_p = K_c$.

Example 10.6: For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ *at 25°C* $K_p = 0.14$. Calculate K_c.

Solution: Here $\Delta n = 2 - 1 = 1$. From equation (10.4) we get,

$$K_p = K_c (RT)^{\Delta n} = K_c (8.314 \times 298.16) = 0.14$$

Or $$K_c = \frac{0.14}{8.314 \times 298.16} = 5.64 \times 10^{-5}$$

Example 10.7: Methanol, CH_3OH, is manufactured commercially by the following reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

At equilibrium at 500 K a 1.50 L vessel contained 0.112 mole CO, 0.222 mole H_2 and 0.120 mole CH_3OH. Calculate K_c and K_p of the reaction.

Solution: $[CO] = \frac{0.112}{1.50} = 0.075 \text{ mol L}^{-1}$, $[H_2] = \frac{0.222}{1.50} = 0.148 \text{ mol L}^{-1}$

$$[CH_3OH] = \frac{0.120}{1.50} = 0.080 \text{ mol L}^{-1}$$

From equation (10.2) we get, $K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.080}{0.075\times(0.148)^2} = 48.70$

From equation (10.4), $K_p = (K_c)(RT)^{\Delta n}$, here $\Delta n = 1 - 3 = -2$

Or, $K_p = 48.70(8.314 \times 500)^{-2} = 2.82 \times 10^{-6}$

10.5 Determination of Equilibrium Constants

In determining the equilibrium constants the concentrations of the various species at equilibrium are to be known. This has to be done in a manner so that the equilibrium is not disturbed by the method of analysis used for the purpose. Analytical procedure should be so chosen that the concentrations of all the species may be obtained from the initial concentrations and from the experimental determination of a minimum number of chemical entities at equilibrium. Often this calls for a considerable amount of ingenuity on the part of the chemist.

Many chemical and physical methods have been used for the determination of the equilibrium constants of reactions. Physical methods based on measurement of absorption of light, refractive index, pressure or volume change, electrical conductance etc. are more suitable for the purpose. In chemical methods often the equilibrium is frozen (quenched) and then the equilibrium mixture is analysed. The freezing of the equilibrium is achieved by sudden cooling or addition of an excess of a chemical reagent or simply by large dilution. In any case, the analysis has to be performed very rapidly. In some cases a suitable precipitating agent may be added to remove the reactants or the products and then the precipitate is quickly filtered out under a suction pump.

10.6 Criteria of Chemical Equilibrium

Whether in a system true equilibrium has been established or not need careful consideration. Several changes, both physical and chemical, appear at the first sight to be in a state of equilibrium but analysis reveals that true equilibrium had not been attained. For example, pure water, carefully freed from any suspended impurity and kept in an unstirred condition, can be easily cooled well below zero degree centigrade without the formation of ice. A temperature of about – 5°C can easily be reached without freezing taking place. The liquid water at temperatures below 0°C is not *in true* equilibrium since suitable stirring, addition of a small quantity of ice or even sometime introduction of fine glass particle, scratching of the walls of the vessel etc. will cause rapid crystallization of ice and the temperature of the system quickly attains the true equilibrium value of 0°C. Thus water below 0°C was in a state of *false* or *unstable* equilibrium; such unstable equilibrium is also called *metastable* equilibrium. A mixture of H_2 and O_2 at not too elevated temperatures is not in true equilibrium because introduction of platinum black causes the reaction. A true equilibrium cannot be disturbed by a catalyst (see *Chapter 13*). Several reactions in which a precipitate should form instantaneously attain the equilibrium state only slowly. Such cases do not comprise true equilibrium. A true equilibrium, when established, will remain in that state for infinite time if the conditions governing the equilibrium, e.g., temperature, composition, pressure etc. are not altered. However, time required for attainment of equilibrium may vary widely from fraction of seconds to months or years. The time depends on the relative values of the velocity constants of the forward and backward reactions. Once the true equilibrium is established, it will continue to remain so as long as it is not disturbed. Thus the equilibrium is permanent.

The statement and the physical concept of equilibrium, chemical or physical, clearly show that the equilibrium is dynamic. Thus equilibrium can be approached from either direction. The reaction discussed in *Section 10.2* clarifies the point. Whether the equilibrium is attained *via* the forward reaction or the reverse reaction, the equilibrium constant remains the same as long as the conditions are not altered. The approachability of the equilibrium from both sides can be easily understood from Figure 10.1. When equilibrium has been established there will be no change in the concentrations of either the reactants or the products. This state can be ascertained from the analysis of the products or the reactants as shown in Figure 10.1. At this state the forward and the reverse reactions proceed with the same velocity.

The very nature of the equilibrium constant suggests that a reversible reaction is not complete. If the reaction proceeds to completion, the equilibrium constant will assume a value of infinity or zero. Under both these conditions the concept of chemical or physical equilibrium loses meaning and the equilibrium law cannot be used. Chemists, therefore, believe in dynamic nature of equilibrium and consequently in the incompleteness of chemical reactions. However, in many reactions the equilibrium constants may be very large or very low. A range of 10^{-10} to 10^{10} is often met. Nevertheless, values of infinity or zero are not acceptable to the physical chemists. Many reactions which appear to be unidirectional can be made to occur reversibly if suitable conditions are created. This concept has significant philosophical aspects ingrained in it.

10.7 Activity and Activity Co-efficient

It must be emphasized that the expressions for equilibrium constant [equations (10.2) and (10.3)] are strictly valid for ideal systems, e.g., for ideal gases or gases at low pressures and ideal solutions. All real systems deviate from the ideal behaviour, and for such systems activities (*Section 15.13*), instead of concentrations, are to be used in the expression for the equilibrium constant. The correct expression for the equilibrium constant then becomes

$$K = \frac{a_L^l \times a_M^m}{a_A^a \times a_B^b} \tag{10.5}$$

Here a is the activity.

Activity of a constituent of a process may be looked upon as the effective concentration or idealized concentration which when replaced for the actual concentration in the expression for a physicochemical law will make the law apply exactly. When the pressure is high or the concentration is large the deviation from ideality increases and the activity differs considerably from concentration.

The ratio of the activity to the actual concentration is known as activity *co-efficient, f.* That is,

$$\frac{a}{c} = f \qquad (10.6)$$

When $f = 1$, activity is equal to the concentration when a solution is very dilute and in the case of gases when the pressure is low.

10.8 Calculations Involving Chemical Equilibrium

For solving most problems relating to finding equilibrium moles and equilibrium constant the following steps can be followed:

1. Set up a table of moles of each species in equilibrium stating initial (starting) moles, change of moles in terms of α, and equilibrium moles involving α.
2. If partial pressures are to be found, calculate the total moles (involving α) at equilibrium, and hence the mol fraction of each species.
3. For calculating K_c the values of the equilibrium concentrations in mol L^{-1} calculated from step 1 are to be substituted in the appropriate expression for K_c.
4. For calculating K_p the mol fraction of each species obtained in step 2 is multiplied by the equilibrium pressure to obtain values of partial pressures of the components in the mixture. Substitution of the partial pressure values in the appropriate expression for K_p gives the result.

10.9 Homogeneous Equilibria

Examples of few homogeneous equilibrium systems are given below:

(1) Dissociation of nitrogen tetroxide: The dissociation of nitrogen tetroxide is represented by the equation

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

for which the equilibrium constant is

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} \qquad (10.7)$$

p_{NO_2} and $p_{N_2O_4}$ being the partial pressures of NO_2 and N_2O_4 respectively:

The experimental method applied in determining the equilibrium constant consists in measuring the total pressure at equilibrium in a flask of known volume in which a known mass of N_2O_4 was placed. Using the ideal gas equation (2.8) the apparent molecular mass of the partially dissociated gas is calculated and equation (2.66) is used to determine the degree of dissociation at equilibrium. If α represents the degree of dissociation, $(1-\alpha)$ is proportional to the number of moles of undissociated N_2O_4 and 2α is proportional to the number of moles of NO_2 so that $(1-\alpha+2\alpha)$ or $(1+\alpha)$ is proportional to the total number of moles.

If P is the total pressure, the partial pressures are given by *(Section 2.10)*

$$p_{NO_2} = \frac{2\alpha}{1+\alpha}P \text{ and } p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}P$$

Hence,
$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha}P\right)^2}{\frac{1-\alpha}{1+\alpha}P} = \frac{4\alpha^2}{1-\alpha^2}P \tag{10.8}$$

Example 10.8: The partial pressures of N_2O_4 and NO_2 in an equilibrium mixture of two gases at 25°C are 0.69 and 0.31 atmosphere respectively. Calculate (a) the equilibrium constant K_p, (b) the degree of dissociation of N_2O_4 at this temperature and (c) the pressure at which the degree of dissociation would be 0.30.

Solution: (a) $K_p = \frac{(0.31)^2}{(0.69)} = 0.139$ atm (Equation 10.7)

(b) Total pressure, $P = p_{N_2O_4} + p_{NO_2} = 0.69 + 0.31 = 1.00$ atm

Substituting the value of p_{NO_2} in the expression for the partial pressure of NO_2 as shown above one obtains

$$0.31 = \frac{2\alpha}{1+\alpha} \times 1$$

Rearranging we get, $0.31(1+\alpha) = 2\alpha$ or $(2-0.31)\,\alpha = 0.31$

or $\alpha = \frac{0.31}{1.69} = 0.184$ or 18.4%

(c) $0.30 = \frac{2(0.30)}{1+0.30}P$ or, $P = 0.67$ atm

Example 10.9: For the reaction, $2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$, $K_p = 7.04 \times 10^{-4}$ atm^{-1} at 25°C. At equilibrium the partial pressure of NO_2 in a container is 0.15 atmosphere. What is the partial pressure of N_2O_4 in the equilibrium mixture?

Solution: For K_p we have

$$K_p = \frac{p_{N_2O_4}}{\left(p_{NO_2}\right)^2} = 7.04 \times 10^{-4}$$

Substituting the value of p_{NO_2} in this expression

$$\frac{p_{N_2O_4}}{(0.15)^2} = 7.04 \times 10^{-4};$$

$$p_{N_2O_4} = 7.04 \times 10^{-4} \times (0.15)^2 = 1.58 \times 10^{-6}$$

Example 10.10: Starting with 1.00 mole each of CO and H_2O in a vessel of capacity 50.0 L the following reaction:

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

was allowed to reach equilibrium at 1000°C. The equilibrium constant K_c for the reaction at this temperature was found to be 0.58. Calculate (a) the concentration of each gas at equilibrium and (b) the moles of CO reacted at equilibrium,

Solution: The initial concentrations of CO and H_2 are

$$[CO] = \frac{1.00}{50.0} = 0.020 \text{ mol L}^{-1} \qquad [H_2] = \frac{1.00}{50.0} = 0.020 \text{ mol L}^{-1}$$

Using the procedure suggested in *Section 10.8* a table is prepared as follows:

Concentrations / mol L^{-1}	$CO\,(g)$	+	$H_2O\,(g)$	⇌	$CO_2\,(g)$	+	$H_2\,(g)$
Initial	0.020		0.020		0		0
Change	$-x$		$-x$		$+x$		$+x$
Equilibrium	$0.020-x$		$0.020-x$		x		x

Substitution of the equilibrium concentrations in the expression for K_c gives

$$K_c = \frac{[CO_2][H_2O]}{[CO][H_2]};$$

or $$0.58 = \frac{(x)(x)}{(0.020-x)(0.020-x)} = \frac{x^2}{(0.020-x)^2}$$

To get the value of x it may be noted that the right hand side is a perfect square. Taking the square root of both sides one obtains

$$\pm 0.76 = \frac{(x)}{(0.020-x)}$$

Therefore, $x = 0.0086$ or -0.063

Taking the positive value the answer is $x = 0.0086$, since negative value does not have any significance.

Hence $[CO] = [H_2O] = 0.020 - 0.0086 = 0.011 \text{ mol L}^{-1}$

$[CO_2] = [H_2] = 0.0086 \text{ mol L}^{-1}$

(2) Dissociation of phosphorus pentachloride: When heated, phosphorus pentachloride dissociates and the reaction is represented by the following equation:

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

The equilibrium constant for this reaction is

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} \tag{10.9}$$

which can be determined by measuring the degree of dissociation at the given temperature as in the case of the dissociation of nitrogen tetroxide.

Let α be the degree of dissociation at equilibrium under the given conditions. If one starts with 1 mole of PCl_5 then at equilibrium there will be $1-\alpha$ moles of undissociated PCl_5 and α moles each of PCl_3 and Cl_2. If the reaction is carried out in a vessel of capacity V L, then the concentrations of the gases are

$$[PCl_5] = \frac{1-\alpha}{V};\quad [PCl_3] = \frac{\alpha}{V} \quad \text{and} \quad [Cl_2] = \frac{\alpha}{V}$$

The equilibrium constant (K_c) in terms of mol L^{-1} is obtained by substituting these concentrations in the equation

$$K_c = \frac{\frac{\alpha}{V}\cdot\frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V} \tag{10.10}$$

The expression for K_p may be derived by determining the partial pressures of the gases and substituting in the relation

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

$$= \frac{\alpha^2}{1-\alpha^2}.P \tag{10.11}$$

(3) Formation and decomposition of *hydrogen iodide gas:*

A classical example of gaseous homogeneous equilibrium is the following reaction above 400 °C,

$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

This reaction was extensively studied by Bodenstein and others. Known quantities of hydrogen iodide were sealed in quartz vessels of known volume and heated at the desired temperature for sufficient time until equilibrium was reached. The vessels were then suddenly cooled and the contents analysed for iodine by titration with standard sodium thiosulphate solution. As the equation above shows, the concentration of hydrogen is the same as that of iodine while the concentration of hydrogen iodide at equilibrium is the initial concentration of hydrogen iodide minus twice the concentration of iodine.

The equilibrium has also been approached from the opposite direction, i.e., the formation of hydrogen iodide from gaseous iodine and hydrogen. For this purpose known quantities of hydrogen and excess of iodine in different proportions were treated as before and equilibrium mixture after sudden cooling was analysed for hydrogen iodide and iodine. Some of the experimental data are given in Table 10.1 where the combination reactions are designated by *c*, and the decomposition reaction by *d*. Corrections for diffusion of hydrogen through the walls of the vessel were made in arriving at the value of *K*.

The expression for the equilibrium constant for the decomposition reaction may be arrived at by considering the volume of the vessel to be V L and the amounts in moles are as follows:

Concentration / mol L^{-1}	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	$+$	$I_2(g)$
Initial	a		0		0
Change	$-2x$		$+x$		$+x$
Equilibrium	$(a-2x)$		x		x

$$\text{Then, } K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\dfrac{x}{V}\times\dfrac{x}{V}}{\left(\dfrac{a-2x}{V}\right)^2} = \frac{x^2}{(a-2x)^2} \tag{10.12}$$

Table 10.1 The equilibrium $2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$

Temperature (K)	Type of reaction	Equilibrium concentration× 10^2(mol L^{-1})			$K_c \times 10^2$
		$[H_2]$	$[I_2]$	$[HI]$	
666.8	d	0.1395	0.1395	1.079	1.644
666.8	c	0.3258	0.1295	1.587	1.642
698.6	d	0.0479	0.0479	0.353	1.812
698.6	c	0.4565	0.0738	1.354	1.812
763.8	d	0.2424	0.2424	1.641	2.172
763.8	c	0.4262	0.1185	1.494	2.196

For the combination reaction let the concentration in mole L^{-1} of hydrogen, iodine and hydrogen iodide be as follows:

Concentration/ mol L^{-1}	$H_2(g)$	$+$	$I_2(g)$	$\rightleftharpoons$	$2HI\,(g)$
Initial	a		b		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$(a-x)$		$(b-x)$		$2x$

If these values are substituted in the expression in equation (10.12) we obtain

$$K'_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(a-x)(b-x)}{4x^2} \qquad (10.13)$$

When K'_c is calculated from experimental data the values are found to be the same as those calculated for K_c with data for the decomposition of $HI(g)$. That is the value of the equilibrium constant for a particular reaction when the equilibrium is approached from the forward and reverse directions are the same. This proves the reversibility of reactions.

10.10 Equilibria in Solution

Applications of the equilibrium constants in solutions are numerous in connection with ionic equilibria. These will be discussed in *Chapter 17.* Such equilibria are also of great importance in dealing with biological phenomena. Here some non-ionic equilibria will be discussed. Of historical interest is the reaction between ethanoic acid and ethyl alcohol producing ethyl acetate and water according to the equation

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

all components being in the liquid phase. Mixtures of known quantities of the acid and alcohol or ester and water are placed in sealed tubes and kept in a constant temperature bath for sufficiently long time to ensure attainment of equilibrium. This can be tested by occasional withdrawal of a fixed volume of the mixture and analysis for acid content. This is generally done by titrating with standard NaOH solution after diluting the reaction mixture to a large volume to stop the reaction. When equilibrium has been established no change in the acid concentration can be detected. A complete analysis is then made and the quantities of acid and alcohol reacted are evaluated. The equilibrium constant, K_c, is then given by

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} \qquad (10.14)$$

K_c then calculated from the following concentration data in mol L^{-1}:

Conc. / mol L^{-1}	$CH_3COOH(l)$ +	$C_2H_5OH(l)$ ⇌	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
Initial	a	b	0	0
Change	$-x$	$-x$	$+x$	$+x$
Equilibrium	$(a-x)$	$(b-x)$	$+x$	$+x$

Then $$K_c = \frac{(x)(x)}{(a-x)(b-x)} = \frac{x^2}{(a-x)\,(b-x)} \qquad (10.15)$$

Example 10.11: Calculate the amount of ester formed when 0.5 moles of *n*-butyric acid and 2 moles of ethanol are mixed in a container of volume 1.0 L and allowed to come to equilibrium at 25 ^{0}C. K_c for this reaction is 0.48.

Solution: Let x be the number of moles of ester formed at equilibrium. Then, at equilibrium the number of moles of various species are shown as follows :

Concentration / mol L^{-1}	$C_3H_7COOH(l)$ +	$C_2H_5OH(l)$ ⇌	$C_3H_7COOC_2H_5(l)$ +	$H_2O(l)$
Initial	0.5	2.0	0	0
Change	$(0.5-x)$	$(2-x)$	x	x

Evidently,
$$K_c = \frac{x^2}{(0.5-x)(2-x)} = 0.48.$$

On solving this equation for x, we get a positive value of $x = 0.35$. Thus the number of moles of ester formed is 0.35 moles.

Example 10.12: A mixture of 0.500 mol of ethanoic acid and 2.50 mol of ethanol were allowed to come to equilibrium in a reaction vessel of volume 1.0 L. The reaction mixture was quenched by cooling in an ice bath and then titrated with sodium hydroxide solution of concentration 0.200 mol L^{-1} in presence of a suitable indicator. It was found that 145 mL of alkali was required for complete neutralization of the unreacted acid present at the equilibrium. Calculate the equilibrium constant, K_c, of the reaction.

Solution: Moles of unreacted acid = $0.200 \times 145 \times 10^{-3} = 0.029$. So the number of moles of acid reacted = $0.500 - 0.029 = 0.471$. From stoichiometry we find that 0.471 moles of alcohol reacted to produce 0.471 moles each of ester and water. We can write,

Concentration / mol L^{-1}	$CH_3COOH(l)$ +	$C_2H_5OH(l)$ ⇌	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
Initially	0.500	2.50	0.0	0.0
Change	-0.471	-0.471	$+0.471$	$+0.471$
Equilibrium	0.029	2.029	0.471	0.471

$$K_c = \frac{0.471 \times 0.471}{0.029 \times 2.029} = 3.77$$

10.11 Heterogeneous Equilibria

These types of equitibria will be discussed in more details in *Chapter 11.* A few systems will be discussed here. Consider the decomposition of calcium carbonate when heated to a high temperature:

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

There are three phases at equilibrium. The equilibrium constant in terms of partial pressures may be written as

$$K_p = p_{CO_2} \qquad (10.16)$$

since at any temperature p_{CaO} and p_{CaCO_3} are considered to be constant. The value of the equilibrium constant at any temperature is determined solely by the equilibrium pressure of carbon dioxide evolved. This has been proved by experiments.

If, however, two or more gaseous substances are involved in the reaction the situation becomes complicated. For example, for the dissociation of solid ammonium hydrogen sulphide according to the equation

$$NH_4HS\,(s) \rightleftharpoons NH_3\,(g) + H_2S\,(g)$$

the equilibrium constant, K_p, is

$$K_p = p_{NH_3} \times p_{H_2S} \tag{10.17}$$

Here the equilibrium constant is the product of the partial pressure of ammonia and hydrogen sulphide gas. If the partial pressure of one of the two is increased, the partial pressure of the other must decrease so that K_p remains the same.

Evaporation of a liquid and sublimation of a solid may also be regarded as examples of heterogeneous equilibria in so far as more than one phase are existing together at equilibrium. Hence the vapour pressure of a liquid or a solid is one type of equilibrium constant. But these are physical equilibria.

Another type of physical equilibrium is a saturated solution in contact with the solute

$$Solid\ solute + aq \rightleftharpoons Saturated\ solution \tag{10.18}$$

The equilibrium constant in its most correct form is

$$K' = \frac{a_{solution}}{a_{solute}} \tag{10.19}$$

where a stands for activity. The solute being solid its activity is taken as unity so that $K' = a_{solution}$. As the solution is saturated $a_{solution}$ at the temperature may be replaced by solubility, S, and we obtain

$$K = Solubility(S) \tag{10.20}$$

As will be seen in *Chapter 17,* important information may be derived with the help of these deductions.

10.12 Factors Influencing Equilibrium: The Principle of Le Chatelier

A chemical reaction at equilibrium will maintain this condition indefinitely unless disturbed by changes from outside. Factors which may cause such disturbances are

(a) a change in concentration of any of the species present at equilibrium,

(b) a change in pressure in the case of equilibria where gases are present,

(c) change in temperature of the reaction, or

(d) addition of an inert substance.

The effect of these changes on the position of chemical equilibrium was qualitatively summarized by what is known *as the principle of Le Chatelier.* The principle states that

'When a system is at equilibrium, a change in any one of the factors upon which the equilibrium depends will cause the equilibrium to shift in a direction such that the effect of the change is diminished'. Alternatively,

'If a stress is applied to a system at equilibrium, the position of equilibrium shifts in such a way that the effect of the stress is minimized.'

The resulting system will, however, be still in equilibrium unless the change is very large. ***Equilibrium constant depends only on temperature but remains unchanged if any of the other factors is changed.*** The principle is of general utility and may also be applied to physical equilibria. This principle is also known as *the principle of mobile equilibrium,* clearly indicating that the equilibrium position can be easily shifted by changing conditions of the reaction. The equilibrium may be shifted to the right (product side) or to the left (reactant side), the direction of the change depending on the nature of the change brought into the system by altering the conditions that govern the equilibrium.

10.12.1 Effect of change in concentration

Let us consider the equilibrium position for the dissociation of phosphorous pentachloride to phosphorous trichloride and chlorine:

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

If to the system at equilibrium some chlorine is added the concentration of chlorine increases. According to Le Chatelier principle the system tries to diminish the effect of added chlorine. This is possible if the added chlorine is used up by combining with phosphorous trichloride until a new equilibrium is reached. This means that the equilibrium shifts to the left forming some phosphorous pentachloride. Same thing happens if some phosphorous trichloride is added to the above equilibrium system. If, on the other hand, some phosphorous pentachloride is added to the equilibrium system the equilibrium will shift to the right.

The same conclusion can be arrived at by using the value of the equilibrium constant. At a given temperature the equilibrium constant for a particular reaction has a definite value even though one may start with different initial concentrations of either the reactants or products. Data in Table 10.1 confirm this statement. The value of the equilibrium constant will not change if to the system at equilibrium some additional quantity of either the reactant or product is added. Considering the above equilibrium the equilibrium constant, K_c, is

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

If to the system at equilibrium some chlorine is added the concentration of chlorine increases. As the value of K_c remains constant the denominator must increase. This is achieved

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if some chlorine combines with phosphorus trichloride to form phosphorus pentachloride, i.e., if the equilibrium shifts to the left. This is in accordance with Le Chatelier principle

Similarly, if some phosphorus pentachloride is added to this system at equilibrium, part of it dissociates so that by adjustment of concentrations the value of K_c is maintained constant.

10.12.2 Effect of pressure change on chemical equilibrium

Homogeneous reactions in solution or in solid state are not accompanied by appreciable change in volume but this is not always the case with reactions involving gases. According to the principle of Le Chatelier, an increase of pressure on a reaction involving a gas or gases should cause the equilibrium to shift in the direction which will result in a decrease in volume, because by doing so the effect of the pressure is diminished. The decrease in volume takes place if, as a result of the reaction, the number of gaseous moles is decreased. However, in reactions where there is no volume change, i.e., there is no change in the number of mole, pressure has no effect on the equilibrium. These general remarks may be illustrated with the following examples.

(a) For the dissociation of phosphorus pentachloride into phosphorus trichloride and chlorine, the equilibrium constant in terms of the degree of dissociation (*Section 10.9*) is given by

$$K_p = \frac{\alpha^2}{1-\alpha^2} \times P \qquad (10.21)$$

If pressure P is increased, the denominator in equation (10.21) must increase in order to keep K_p constant. This is possible if the degree of dissociation, decreases, i.e., if some phosphorus trichloride and chlorine combine to form back phosphorus pentachloride. Conversely, if P is decreased, the degree of dissociation must increase so as to keep K_p constant. For this reaction the expression for K_p contains P as there is a change in the number of moles in the gaseous phase.

(b) The expression for equilibrium constant in terms of partial pressures for the decomposition of hydrogen iodide into iodine and hydrogen is

$$K_p = \frac{p_{H_2} \times p_{I_2}}{(p_{HI})^2} = \frac{x^2}{(1-2x)^2}$$

It will be noticed that there is no residual P term in the expression for K_p and, therefore, a change in the value of P will have no effect on the point of equilibrium. This occurs because $\Delta n = 0$ as a result of the decomposition of a given amount of hydrogen iodide. For all such reactions where there is no change in volume during the reaction, the equilibrium constant is independent of pressure, or volume.

10.12.3 Effect of temperature on equilibrium

The effect of temperature on equilibrium depends on whether the reaction is exothermic or endothermic.

According to the principle of Le Chatelier, an increase of temperature will cause the equilibrium to move in the direction in which the effect of the temperature rise may be minimized. For this to happen the equilibrium moves in a direction in which heat is absorbed. In the case of an exothermic reaction equilibrium moves to the reactant side as in this direction the reaction is endothermic. In the case of endothermic reaction equilibrium moves to the product side as the added heat can be used up if more products are formed. Conversely, a decrease of temperature will shift an exothermic equilibrium to the right and an endothermic equilibrium to the left. These conclusions are illustrated below:

The synthesis of ammonia by the Haber-Bosch process is exothermic

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ}$$

As heat is evolved in this reaction an increase of temperature will cause the equilibrium to shift to the left, i.e., the yield of ammonia will be decreased on increasing the temperature. Conversely, if the temperature is decreased more of the product will be formed and the equilibrium shifts to the right.

If a reaction is endothermic, as in the production of nitric oxide by the Birklende and Eide process

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = +180.0 \text{ kJ}$$

an increase in temperature (addition of heat) increases the amount of the product while cooling (removal of heat) decreases the amount of product, i.e., shifts the equilibrium towards the left.

The change of equilibrium constant with temperature may be expressed quantitatively (*Section 7.17*) in the form of the equation

$$\log K_p = -\frac{\Delta H}{2.303RT} + \text{constant} \tag{10.22}$$

where ΔH is the enthalpy change of the reaction. If ΔH is constant, a plot of $\log K_p$ vs $1/T$ gives a straight line whose slope is $\Delta H/(2.303\ R)$. A schematic representative plot is given in Figure 10.2. If ΔH is positive the slope is negative, while if ΔH is negative the slope is positive.

Hence for an exothermic reaction K_p decreases with increase of temperature, while for an endothermic reaction it increases with a rise in temperature. This is in agreement with Le Chatelier principle.

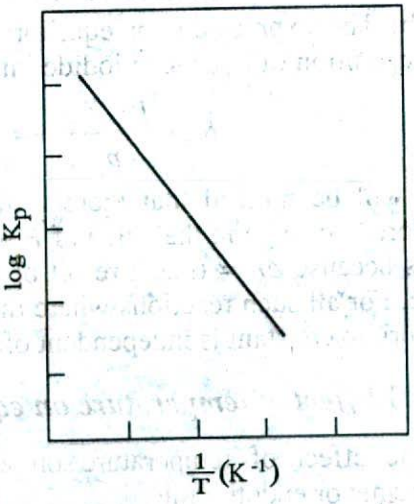

Figure 10.2 Plot of $\log K_p$ vs $\frac{1}{T}$ (endothermic reaction).

As pointed out earlier the vapour pressure of a liquid or solid and solubility of a substance in a solvent may be regarded as equilibrium constants. The effect of temperature on vapour pressure (p) and solubility (S) may be represented by similar equations, e.g.,

$$\log p = -\frac{\Delta H_{vap}}{2.303RT} + \text{constant} \tag{10.23}$$

$$\log S = -\frac{\Delta H_{solution}}{2.303\ RT} + \text{constant} \tag{10.24}$$

Equation (10.23) is one of the forms of Clausius-Clapeyron equation. If the enthalpy of reaction is known it is possible to calculate an equilibrium constant K_2 at temperature T_2 from the known value of K_1 at temperature T_1 from the following relationship:

$$\log \frac{K_2}{K_1} = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \tag{10.25}$$

$$= -\frac{\Delta H}{2.303R}\left(\frac{T_1-T_2}{T_1T_2}\right) \tag{10.26}$$

Example 10.13: The equilibrium constant for the synthesis of NH_3 by Haber-Bosch process is 1.65×10^{-4} at 673 K. What will be the equilibrium constant at 773 K if the enthalpy of reaction is – 105.20 kJ?

Solution: According to equation (10.26),

$$\log \frac{K_{773}}{K_{673}} = -\frac{\Delta H}{2.303R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\log K_{773} - \log (1.65 \times 10^{-4}) = -\frac{-105.20\times10^3}{2.303\times8.314}\left(\frac{1}{773}-\frac{1}{673}\right)$$

$$= -1.056$$

or, $\log K_{773} = -1.056 + \log (1.65 \times 10^{-4})$

$= -4.839$

Hence $K_{773} = 1.45 \times 10^{-5}$

10.12.4 Effect of adding an inert gas

If an inert (non-reacting) gas is added to a system of gaseous equilibrium at constant volume (the total pressure will increase), the equilibrium is not affected. This follows from Dalton's law of partial pressures, because according to this law the presence of a foreign inert gas in a closed space does not influence the partial pressure exerted by the reacting substances. This is true whether the reaction involves a change in the number of molecules or not. If, however, the pressure is kept constant while the inert gas is added to the system at equilibrium, (there is a consequent increase in volume), the equilibrium *is* displaced, according to the Le Chatelier principle, in cases of reactions where K_p is dependent on pressure. If K_p is independent of pressure, as in the decomposition of hydrogen iodide, there is no effect.

10.12.5 Effect of catalyst on equilibrium

A catalyst does not affect the position of equilibrium and hence it does not have any effect on the value of equilibrium constant of a reaction. This is because a catalyst affects the forward and reverse reaction equally.

10.13 Applications of the Principles of Chemical Equilibrium to Reactions of Industrial Importance

In industrial processes the primary objective is to maximize the yield of products at a minimum cost in a shorter period of time. To attain this objective in the case of gaseous reactions of industrial importance advantage is taken of the influence of pressure and temperature on the equilibrium yield of the desired product. These points will be illustrated with the help of a few industrially important reactions.

10.13.1 Synthesis of ammonia

The synthesis of ammonia on a commercial scale by the Haber-Bosch process is based on following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \qquad \Delta H_{291} = -92.0 \text{ kJ}$$

$$\Delta H_{924} = -111.2 \text{ kJ}$$

For the calculation of the equilibrium constant, let the concentration (mol L^{-1}) of the various species at equilibrium be as follows:

	$N_2(g)$ +	$3H_2(g) \rightleftharpoons$	$2NH_3(g)$
Initial (mol L^{-1})	1	3	0
Change	$-x$	$-3x$	$+2x$
Equilibrium	$1-x$	$3(1-x)$	$2x$

Hence
$$K_c = \frac{(2x)^2}{(1-x)(3-3x)^3}$$

Total number of moles at equilibrium $= 1 - x + 3(1-x) + 2x = 4 - 2x$

where x is the number of moles of N_2 reacted. Let the equilibrium pressure be P atmosphere. The mole fractions of the components are :

$$x_{N_2} = \frac{1-x}{4-2x}; \quad x_{H_2} = \frac{3-3x}{4-2x} \text{ and } x_{NH_3} = \frac{2x}{4-2x}$$

Partial pressures $$p_{N_2} = \frac{1-x}{4-2x} \times P;\; p_{H_2} = \frac{3-3x}{4-2x} \times P \text{ and } p_{NH_3} = \frac{2x}{4-2x} \times P$$

or $$p_{N_2} = \frac{1-x}{2(2-x)} \times P;\; p_{H_2} = \frac{3(1-x)}{2(2-x)} \times P \text{ and } p_{NH_3} = \frac{2x}{2(2-x)} \times P$$

So, $$K_p = \frac{p^2_{NH_3}}{p^3_{H_2} \times p_{N_2}} = \frac{\left(\frac{2x}{2(2-x)}\right)^2 \times P^2}{\left(\frac{1-x}{2(2-x)}\right) \times P \left(\frac{3(1-x)}{2(2-x)}\right)^3 \times P^3}$$

$$= \frac{16}{27} \cdot \frac{x^2(2-x)^2}{(1-x)^4 P^2} \qquad (10.27)$$

If x is small in comparison to unity, this reduces to

$$K_p = \frac{64x^2}{27P^2}$$

Or $$x^2 = \frac{27}{64} K_p \times P^2 \qquad (10.28)$$

The reaction is a highly exothermic one and as equation (10.28) shows the equilibrium yield of ammonia depends on the pressure to a large extent. The suitable reaction conditions are low temperatures and high pressures. Some of the experimental results for this reaction are shown in Figure 10.3.

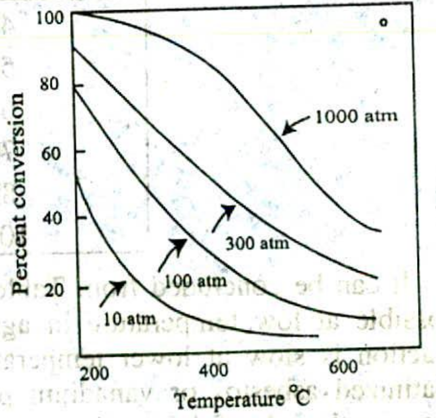

Figure 10.3 Yield of ammonia at different temperatures and pressures

At low temperature, however, the reaction is slow and the time to attain the desired yield is long. For the process to be economical the reaction should be conducted at the lowest temperature at which the reaction would proceed at the desired speed. In such industrial processes advantage is taken of the catalytic effect (see *Chapter 13*) of certain substances in increasing the speed of reaction. Iron with the addition of small amounts of the oxides of aluminum and potassium acts as good catalyst. For all catalytic reactions there is an optimum temperature at which the rate is such that the yield of the product is best for the cost involved.

As the reaction involves a decrease of volume, the yield of ammonia increases with increase of pressure. In the actual manufacturing process by the Haber-Bosch process a pressure of about 200 atm and temperature of about 450° to 550°C are used. In other modifications of the process, pressure as high as 1000 atmosphere is used.

10.13.2 Formation of sulphur trioxide for the manufacture of sulphuric acid by the contact process

An essential step in the manufacture of sulphuric acid is the oxidation of sulphur dioxide to sulphur trioxide according to the following exothermic reaction:

$$SO_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g) \qquad \Delta H = -96.0\ kJ$$

The equilibrium constant for this reaction in terms of partial pressures may be expressed as

$$K_p = \frac{p_{SO_3}}{p_{SO_2} \times p_{O_2}^{1/2}} \tag{10.29}$$

Some experimental values of K_p based on partial pressures in atmospheres are given in Table 10.2.

Table 10.2 Equilibrium constants for the reaction

$SO_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g)$ at different temperatures

Temperature (°C)	K_p
400	397.0
500	48.1
600	9.53
700	2.63
800	0.915
1000	0.185

It can be concluded from Table 10.2 that high conversion of $SO_2(g)$ into $SO_3(g)$ is possible at low temperature in agreement with Le Chatelier principle. However, the reaction is slow at lower temperatures. So for economic reasons a catalyst, such as platinized asbestos or vanadium pentoxide admixed with other materials, is used to increase the rate of the reaction. In the above reaction the number of moles of products is less than that of the reactants. Therefore, an increase of pressure would shift the equilibrium to the right, i.e. should lead to an increase in the yield of sulphur trioxide. However, as the yield at 1 atmosphere pressure and at temperatures between 400 – 450°C in the presence of the catalyst is about 97%, the reaction is carried out at a pressure of 1 to 2 atmosphere at a temperature of 400 – 450°C when the conversion is optimum.

10.14 Free Energy Change and Equilibrium Constant

We already know (*Section 7.12.2*) that the thermodynamic criterion for a chemical reaction at equilibrium is $(\Delta G)_{T,P} = 0$. This conclusion enables us to derive thermodynamically the relation between the equilibrium concentrations of reactants and products. Physical equilibria may also be described with the help of this criterion.

Let us consider a reaction involving four gases *A*, *B*, *K* and *L*

$$aA(g) \;+\; bB(g) \rightleftharpoons \;kK(g) \;+\; lL(g)$$

where a, *b*, *k* and *l* are the number of moles of the reactants and products as shown in the stoichiometric equation. For one mole of an ideal gas if the pressure is changed from P_1 to P_2 the difference in free energy is given by (*Section* 5.40)

$$G_2 - G_1 = RT \ln \frac{P_2}{P_1} \tag{10.30}$$

If P_1 = 1 atmosphere, i.e., the gas is in its standard state, then $G_1 = G° =$ free energy of the gas at its standard state. Hence it follows from equation (10.30) that

Free energy of *a* moles of $A = \; aG_A = aG°_A + aRT \ln p_A$ (10.31a)

Free energy of *b* moles of $B = \; bG_B = bG°_B + bRT \ln p_B$ (10.31b)

Free energy of *k* moles of $K = \; kG_K = kG°_K + kRT \ln p_K$ (10.31c)

Free energy of *l* moles of $L = \; lG_L = lG°_L + lRT \ln p_L$ (10.31d)

In these equations p_A, p_B, p_K and p_L are the pressures of the species. The free energy change for the reaction is then given by

$$\begin{aligned}\Delta G &= G_{products} - G_{reactants} \\ &= kG_K + lG_L - aG_A - bG_B \\ &= (kG°_K + lG°_L) - (aG°_A - bG°_B) + RT \ln \frac{(p_K)^k (p_L)^l}{(p_A)^a (p_B)^b}\end{aligned} \tag{10.32}$$

$$\Delta G = \Delta G° + RT \;\ln \frac{(p_K)^k (p_L)^l}{(p_A)^a (p_B)^b} \tag{10.33}$$

This relation gives free energy change of the reaction when the reactants at some arbitrary pressures, p_A and p_B, are converted into products at pressures, p_K and p_L, relative to the free energy change occurring when both reactants and products are in their standard states. In the special case when the reactants and products are in their standard states of 1 atmosphere, the term containing *P*'s vanish and ΔG is equal to $\Delta G°$ according to equation (10.33). When the system has reached equilibrium and the pressures are the equilibrium values $\Delta G_{\text{(reaction)}} = 0$ and equation (10.33) becomes

$$\Delta G° = -RT \ln \frac{(p_K)_e^k (p_L)_e^l}{(p_A)_e^a (p_B)_e^b} \tag{10.34}$$

But $$K_p = \frac{(p_K)_e^k (p_L)_e^l}{(p_A)_e^a (p_B)_e^b}$$

for the reaction at equilibrium. The subscript is added to indicate that the system is at equilibrium. Hence

$$\Delta G^\circ = -RT \ln K_p \tag{10.35}$$

Since ΔG° is constant, K_p must be a constant at a given temperature. This equation represents one of the most useful and important relation in thermodynamics. This relation enables one to calculate K_p for a reaction from the value of ΔG°. Conversely, if K_p can be determined the value of ΔG° may be calculated and hence the direction of chemical reaction may be predicted.

Expressions similar to equation (10.35) may be derived for other standard states. When the concentrations are expressed in mol L^{-1}, the equilibrium constant is related to standard free energy change by the relation

$$\Delta G^\circ = -RT \ln K_c \tag{10.36}$$

It must be noted that the value of ΔG^0 in equation (10.35) is not always the same as that of equation (10.36). The difference in the values of ΔG^o is due to choice of standard states.

Example 10.14: K_p for the reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ at 25°C is 0.14 atmosphere. Calculate the standard free energy change for this reaction. Will the reaction be spontaneous at this temperature?

Solution: $\Delta G^\circ = -RT \ln K_p = -(8.314)(298{\cdot}1)(2.303) \log 0.14$

$$= +4.85 \text{ kJ}$$

As ΔG^o is positive, the reaction will not be spontaneous and will not proceed without outside aid.

10.15 Influence of Temperature on Equilibrium Constant : Thermodynamic Derivation

Since K_p depends on temperature, differentiation of equation (10.35) with respect to temperature yields

$$-\frac{\partial(\Delta G^0)}{\partial T} = R \ln K_p + \frac{RT\partial \ln K_p}{\partial T} \tag{10.37}$$

When the reactants and products are in their standard states, the Gibbs–Helmholtz equation (*equation 7.74*) is written as

$$\Delta G^\circ = \Delta H^\circ + T\,\frac{\partial(\Delta G^0)}{\partial T} \tag{10.38}$$

Multiplying both sides of equation (10.37) by T we get

$$-T\frac{\partial(\Delta G^0)}{\partial T} = RT\ln K_p + \frac{RT^2\partial\ln K_p}{\partial T} \tag{10.37a}$$

Substituting for $T\dfrac{\partial(\Delta G^0)}{\partial T}$ from equation (10.38) into equation (10.37a) yields

$$-(\Delta G^\circ - \Delta H^\circ) = RT\ln K_p + \frac{RT^2\partial\ln K_p}{\partial T} \tag{10.38a}$$

Combining equations (10.35) and (10.38a) it follows that

$$\Delta H^\circ = \frac{RT^2\partial\ln K_p}{\partial T}$$

Rearrangement and use of ordinary differential gives

$$\frac{d\ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{10.39}$$

This expression gives the relation between the equilibrium constant and temperature in the differential form and is known as the *van't Hoff reaction isochore*. This is a very important equation and may be used to determine heats of reaction from measurements of equilibrium constant of reactions. For this purpose more convenient forms are the integrated forms:

$$\ln K_p = -\frac{\Delta H^0}{RT} + constant$$

and

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \tag{10.40}$$

to which references were made in *Section 10.12.3*.

Example 10.15: The equilibrium constant, K_c, of the reaction

Cyclohexane $\rightleftharpoons$ *Methylcyclopentane*

at 25°C and 45°C are respectively 0.143 and 0.193. Calculate ΔH° for this reaction over this temperature range.

Solution: 25°C = 298 K and 45°C = 318 K

Using equation(10.40)

$$\ln\frac{K_{318K}}{K_{298K}} = -\frac{\Delta H^\circ}{R}\left[\frac{1}{318}-\frac{1}{298}\right]$$

$$\text{or} \quad (2.303)\log\frac{0.193}{0.143} = -\frac{\Delta H^0}{(8.314)} \times \frac{298-318}{318\times298}$$

$$= +\frac{\Delta H^0}{(8.314)} \times \frac{20}{318\times298}$$

$$\therefore \quad \Delta H^\circ = \frac{(8.314)(318)(298)(2.303)}{20}\log\frac{0.193}{0.143}$$

$$= 11.8 \text{ kJ mol}^{-1}$$

QUESTIONS AND PROBLEMS

1. What is a reversible reaction? Write expressions for the equilibrium constant K_c and K_p for the following reactions:
   (a) $2\,NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$
   (b) $2H_2S\,(g) + 3\,O_2\,(g) \rightleftharpoons 2H_2O(g) + 2SO_2(g)$
   (c) $4NH_3\,(g) + 5O_2\,(g) \rightleftharpoons 4NO\,(g) + 6H_2O\,(g)$
   (d) $NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$
   (e) $C\,(s) + 2N_2O\,(g) \rightleftharpoons CO_2\,(g) + 2N_2\,(g)$
   (f) $2NaHCO_3\,(s) \rightleftharpoons Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(g)$
2. In the case of the reaction: $3H_2\,(g) + N_2\,(g) \rightleftharpoons 2NH_3\,(g)$ write the expression for the equilibrium constant in terms of partial pressures.
3. Establish the relation between K_p and K_c. Explain, with the help of Le Chatelier's principle, the effect of pressure on the reaction :
   $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
4. Clearly explain your concept of dynamic equilibrium. What are the criteria of chemical equilibrium? At 49 °C and under a pressure of 4 atm., N_2O_4 is 63% dissociated into NO_2. Calculate the equilibrium constant.
5. What are the factors that influence chemical equilibrium? Explain with suitable examples the principle of Le Chatelier
6. For the reaction, $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ at equilibrium at 1000°K and 1.00 atm. total pressure the following mole fraction data were obtained :
   $SO_2 = 0{\cdot}309$, $SO_3 = 0{\cdot}338$, $O_2 = 0.353$
   Calculate the values of K_p and K_c stating the units in which they are expressed. Use the atmosphere and the litre as units of pressure and volume respectively.
   [Ans. $K_p = 0.295$ atm ; $K_c = 3{\cdot}60 \times 10^{-3}$ mol L^{-1}]
7. The dissociation constant for N_2O_4 at 8°C in chloroform solution is $1{\cdot}10 \times 10^{-5}$. If 0.40 mole of N_2O_4 is dissolved in 600 mL of chloroform solution, calculate (a) the concentration of NO_2 in the solution at equilibrium, and (b) the per cent dissociation of N_2O_4. [Ans. (a) 2.7×10^{-3} mol L^{-1} ; (b) 0.20 %]
8. Water expands when it freezes. Use the principle of Le Chatelier to predict the effect of pressure change on the freezing point of water.
9. The value of K_c for the reaction :
   $$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
   is 3.3×10^{-2} at 300 °C. Calculate the number of grams of HI formed when 1 mole each of hydrogen and iodine vapour and 0.001 mole of HI are allowed to come to equilibrium at this temperature in a 2 L flask. [Ans. 187 g]

10. At 400°C in an equilibrium mixture of nitrogen, hydrogen and ammonia the partial pressures are : $p_{N_2} = 6.74$ atm., $p_{H_2} = 20.23$ atm, $p_{NH_3} = 3.03$ atm. Calculate K_p for each of the following reactions at this temperature

    (a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

    (b) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ [Ans. (a) 1.65×10^{-4} ; (b) 1.28×10^{-2}]

11. One mole of ethyl alcohol is mixed with 1 mole of ethanoic acid. At equilibrium at 25 °C it is found that 0.667 mole of ethyl acetate has been formed.

    (a) Calculate the equilibrium constant for the reaction :

    $$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

    (b) When 0.50 mole of ethanol is added to 1 mole of acetic acid how much ester will be formed at equilibrium? [Ans. (a) 4; (b) 0.422 g]

12. How may the equilibrium constant-temperature data be used to calculate the heat of reaction?

13. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the values of K_P at 25°C and 65°C are 0.141 and 2.80 respectively. Calculate the average heat of reaction. [Ans. 62.5 kJ]

14. A saturated solution of silver nitrite contains 3.40 g and 13.63 g of solute per 1000 g of water at 20 °C and 60 °C respectively. Calculate the mean heat of solution of the salt over this temperature range. [Ans. 28.2 kJ mol $^{-1}$]

15. The dissociation pressure of the system: $Ca(OH)_2(s) \rightleftharpoons CaO(s) + H_2O(g)$ is 10.5 mm Hg at 340 °C and 101.2 mm at 421°C. Calculate the mean heat of dehydration over this temperature range. [Ans. –1001.9 J mol $^{-1}$]

16. Establish a relation between standard free energy change and the equilibrium constant of a reaction.

17. The ΔG^0 of the reaction is – 28.0 kJ :

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

    Calculate the value of K_p. [Ans. 1.02×10^5]

18. In the reaction :

    $$3\,Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_{2(g)}$$

    there is equilibrium at 200 °C when the partial pressure of steam is 46 mm Hg and that of H_2 is 960 mm Hg. Calculate the pressure of hydrogen when that of steam is 6.4 mm Hg. [Ans. 1338 mm Hg]

19. Phosphorus pentachloride when heated dissociates as follows: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ Calculate the equilibrium constant K_p of the reaction at 250 °C if 80% is dissociated when the total pressure is 1.00 atmosphere.

20. At 30°C the equilibrium constant K_P of the reaction: $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is 2.9×10^{-2} atm. Calculate the degree of dissociation when the total equilibrium pressure is 1.00 atmosphere. [Ans. 0.17]

21. For the dissociation :

    $$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

    at 247 °C the equilibrium constant K_p is 1.06. Calculate (a) the standard free energy change of the reaction and (b) the degree of dissociation at this temperature. [Ans. (a) – 290.5 J; (b) $\alpha = 0.718$]

22. At 900 K the equilibrium constant K_p of the reaction :

    $$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

    is 6.55. (a) Calculate $\Delta G°$ value for the reaction at this temperature. (b) If $K_p = 1.86$ at 1000 K, what is the heat of the reaction, assuming that the value is constant over the temperature range.

    [Ans. (a) –14.1 kJ; (b) –94.5 kJ]