
UNIT 14 CHEMICAL EQUILIBRIA

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14.1 INTRODUCTION

Three important aspects of a chemical reaction must be studied for a complete understanding of the subject. These are : (i) whether a chemical reaction is feasible at all (the feasibility of the reactions has already been dealt with in Unit 9 of this course) (ii) if the reaction is feasible, at what stage does it stop, and (iii) how fast or slow does the reaction occur. This last aspect we shall be studying under the heading of chemical kinetics in Unit 18. The present unit describes the second aspect of a chemical reaction i.e. upto what stage does a reaction proceed.

We have already defined, in general, the reversible and irreversible processes in Unit 9. However, for chemical reactions, the two processes can be defined as follows. Irreversible reactions are said to go to completion, implying thereby that the reaction proceeds until at least one of the reactants is completely used up. On the other hand, all those reactions which appear not to proceed beyond a certain stage after sometime even when the reactants are still available, are reversible reactions. They have only reached an equilibrium state. The present unit discusses the meaning of this state of equilibrium and how the equilibrium composition of the reactants and products are correlated with change in Gibb's free energy. It also explains the effects of different factors on chemical equilibrium.

Objectives

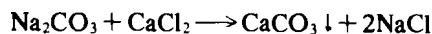
After studying this unit, you should be able to :

- describe chemical equilibrium,
- differentiate between reversible and irreversible reactions,
- derive an expression for equilibrium constant in terms of Gibb's free energy,
- express the equilibrium constant in different ways and apply it to different systems, and
- predict the shift in equilibrium position with the changes in the concentration, temperature or pressure of the system.

14.2 REVERSIBLE AND IRREVERSIBLE REACTIONS

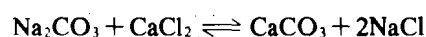
In general, chemical reactions can be divided into two types — reversible and irreversible. The reversible reactions are those in which the products can combine back to form the

reactants. However, in the irreversible reactions, the same reactants cannot be formed back from the products under normal set of experimental conditions. For the study of equilibrium, we are mainly concerned with reversible reactions. The idea of reversibility of chemical reactions was first realised by Berthollet in 1799. He was trying to explain the cause for substantial amount of deposits of sodium carbonate around some salt lakes of Egypt. He proposed that these deposits are formed due to high concentration of sodium chloride in lake water which reacted with the carbonates present on the shores. Normally, in a laboratory experiment, we find that calcium carbonate is precipitated by the reaction of sodium carbonate with calcium chloride as represented by the equation :

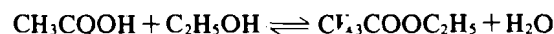


What Berthollet proposed was indeed a reverse reaction of the above and the cause for reversibility was in some way connected to the high concentration of dissolved sodium chloride.

Thus, we realise that a chemical reaction such as given above can proceed in both the directions—from left to right or vice-versa—depending on the experimental conditions. Each such reaction is usually written containing two half-arrows pointing in opposite directions (or a sign of equality between reactants and products) emphasising the fact that it is a reversible reaction :

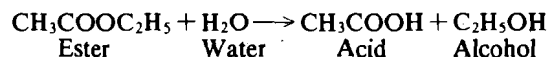


Further, experimental studies by Gilles and coworkers on the reaction between acetic acid and ethyl alcohol giving ester and water, showed that the amount of ester formed varied with the initial concentrations of the reactants at a fixed temperature and pressure.



In 1864, Guldberg and Wagge showed experimentally that there exists an equilibrium between the reactants and products in a chemical reaction and that this equilibrium can be reached from either direction (starting either from reactants or the products). Furthermore, the relation between the concentrations of the reactants and the products can be expressed by a simple mathematical expression. Let us consider two reactions to clarify these points.

van't Hoff, in 1877, studied the hydrolysis of ethyl acetate.



He observed that the ratio of the product of concentrations of the products to the product of concentrations of the reactants is always constant at equilibrium and is independent of the initial concentrations of the ester. Expressed mathematically,

$$K = \frac{c_{\text{C}_2\text{H}_5\text{OH}} \times c_{\text{CH}_3\text{COOH}}}{c_{\text{CH}_3\text{COOC}_2\text{H}_5} \times c_{\text{H}_2\text{O}}}$$

where 'c' represents concentration of a species which is written as subscript.

The constant, *K*, in the above expression has a fixed value for a particular reaction at a constant temperature and pressure and is a measure of the extent of reaction. A large value of *K* means numerator is greater than the denominator. This indicates the presence of a larger concentration of products as compared to the concentration of reactants at equilibrium.

Consider another example of the reaction involving hydrogen, iodine and hydrogen iodide, all in the gaseous state. If hydrogen and iodine are kept together in a closed vessel at 723 K, they react chemically to give hydrogen iodide. However, if pure hydrogen iodide is taken in a closed vessel and heated to the same temperature of 723 K, it decomposes to give hydrogen and iodine.

The true state of affairs is that, in both cases, after a sufficiently long time, you would find all the three species, hydrogen, iodine and hydrogen iodide—present in the container. At this stage, we say that an equilibrium has been reached between the reactants and the products as shown by the equation, $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$. Furthermore, at equilibrium, there exists a definite relationship between the concentrations of hydrogen iodide, hydrogen and iodine.

This state of chemical equilibrium can be viewed from a different point of view. The reaction between the two reactants, A and B, to give products, C and D, can be represented as follows :



Equilibrium is said to be reached if there is no further change in the concentration of reactants and products with respect to time.

Initially, there are only A and B present but as the reaction proceeds, some amount of C and D are formed. Once the products C and D are formed, they can also react to give A and B, if the reaction is reversible. Since, the concentration of C and D are small in the beginning, it seems logical that the rate of the reverse reaction, $C + D \rightarrow A + B$, should also be less than the rate of the forward reaction, $A + B \rightarrow C + D$. However, as the reaction proceeds, more and more of C and D are produced. Consequently, the rate of the reverse reaction would also increase. Ultimately, a situation would be reached when the rate of the reverse reaction would be exactly equal to that of the forward reaction. Since, these are reactions in opposite directions, there is no change in composition with time and it seems as if the reaction has stopped. We then say that the reacting system is in the equilibrium state. Actually the reactions in both directions do take place but rates of forward and reverse reactions are equal. It is said that a state of dynamic equilibrium has been reached. At this stage, no further change in the concentrations of the products and reactants will take place.

Based on such observations, Guldberg and Wagge gave a quantitative formulation known as the law of mass action. This law gives the relationship between equilibrium concentrations of all the substances taking part in a chemical reaction at equilibrium. Instead of just stating this law, we shall derive this relationship with the help of basic principles of thermodynamics.

14.3 DERIVATION OF GENERAL EXPRESSION FOR CHEMICAL EQUILIBRIUM

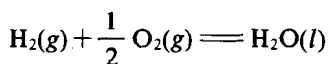
Even before derivation of equilibrium expression is attempted, we must recapitulate the following conventions in thermodynamics.

- 1) Any system, to which substances are added or from which they are taken away or in which a chemical reaction takes place, is called an open system.
- 2) A chemical reaction involving a number of substances is represented by

$$\sum_i \nu_i A_i = 0$$

Where A_i represents a chemical substance at the temperature and pressure of the reaction, and ν_i is called the stoichiometric coefficient of A_i .

ν values are positive for the products and negative for the reactants. This relationship can be explained using the following example :



can be written as

$$(1) \text{H}_2\text{O} - (1) \text{H}_2 - \left(\frac{1}{2}\right) \text{O}_2 = 0$$

and the values of ν_i 's are :

$$\nu_{\text{H}_2\text{O}} = 1, \nu_{\text{H}_2} = -1, \text{ and } \nu_{\text{O}_2} = -\frac{1}{2}$$

Again, note that ν is positive for the products, and negative for the reactants.

Let us now consider an open system represented by a general reaction :



The change in Gibb's free energy, dG , for the reaction is given by Eqs. 9.21, 9.23, 9.68 and 9.69.

$$dG = Vdp - SdT + \sum_i \mu_i dn_i \quad \dots (14.2)$$

where dn_i = change in the amount of any particular substance, 'i' and μ_i = chemical potential of that substance; all other symbols carry their usual meaning. At constant temperature and pressure, Eq. 14.2 reduces to :

$$dG_{T,P} = \sum_i \mu_i dn_i \quad \dots (14.3)$$

The symbol \sum_i stands for summation of terms; the terms are obtained by giving different values to i .

As per Eq. 9.68 given in Sec. 9.10 of Unit 9 of this course,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,N} dT + \left(\frac{\partial G}{\partial p}\right)_{T,N} dp + \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1} dn_2$$

Using Eqs. 9.21, 9.23 and 9.69, this expression can be written as,
 $dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2$
 Eq. 14.2 is a generalised form of the above equation.

The change in the amount of any substance ' n_i ' can be more conveniently expressed in terms of another quantity ξ_i (pronounced as "xi") which is a measure of the extent of the reaction. For example, $\xi = 0$ for a substance 'i' means that it has not reacted at all; $\xi = 1$ means whole amount of 'i' has reacted and so on. For any reversible reaction the value of ξ should be between zero and unity.

Let us now derive an expression to specify the variation of free energy with respect to the extent of reaction. The number of moles (n_i) of a particular substance i present at different times, as a reaction proceeds, can be expressed by the relation :

$$n_i = n_i^{\circ} + \nu_i \xi \quad \dots (14.4)$$

where n_i is the number of moles of the substance i present before the reaction starts, ν_i is the stoichiometric coefficient of the same substance in the balanced chemical equation (with a proper sign) and ξ is the extent of the reaction. Note that n_i° and ν_i are constants for a substance while n_i varies as ξ changes. The change in n_i can be obtained by differentiating Eq. 14.4 as,

$$dn_i = \nu_i d\xi \quad \dots (14.5)$$

(since n_i° and ν_i are constants)

Combining Eqs. 14.3 and 14.5, we get,

$$dG_{T,p} = \sum_i \mu_i \nu_i d\xi$$

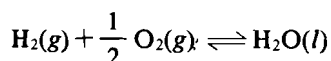
$$\text{Hence, } \left(\frac{\partial G}{\partial \xi} \right)_{T,p} = \sum_i \mu_i \nu_i \quad \dots (14.6)$$

From your study of Unit 9, you can understand that Eq. 14.6 represents Gibb's free energy change of the reaction ($\Delta_r G_{T,p}$) at constant temperature and pressure.

In Unit 9, you have studied that $\Delta_r G_{T,p}$ is equal to the sum of the Gibb's free energy of the products minus the sum of the Gibb's free energy of the reactants.

$$\text{i.e., } \left(\frac{\partial G}{\partial \xi} \right)_{T,p} = \sum_i \mu_i \nu_i = \Delta_r G_{T,p} \quad \dots (14.7)$$

Let us apply Eq. 14.7 to two reactions. First, let us consider the formation of water discussed in this section.

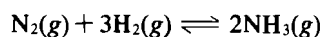


$\Delta_r G_{T,p}$ for the formation of water is given by

$$\Delta_r G_{T,p} = \mu_{\text{H}_2\text{O}} - \mu_{\text{H}_2} - \frac{1}{2} \mu_{\text{O}_2}$$

The ν_i values of H_2O , H_2 and O_2 are 1, -1 and $-\frac{1}{2}$, respectively.

As a second example, let us consider the formation of ammonia.



For this reaction,

$$\Delta_r G_{T,p} = 2\mu_{\text{NH}_3} - \mu_{\text{N}_2} - 3\mu_{\text{H}_2}$$

Again, note that the ν_i values of NH_3 , N_2 and H_2 are 2, -1 and -3, respectively.

From sec. 9.8 of Unit 9, we know that the Gibb's free energy of the system will be minimum at equilibrium at constant temperature and pressure (see Fig. 14.1). Hence, the derivative of the Gibb's free energy function with respect to the extent of the reaction, which is the slope of the curve in Fig. 14.1, is equal to zero at equilibrium at constant temperature and pressure. In other words,

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,p,\text{eq}} = \sum_i \mu_i \nu_i = \Delta_r G_{T,p} = 0 \quad \dots (14.8)$$

where 'eq' stands for equilibrium condition.

A chemical reaction will tend to proceed in a direction of decreasing free energy. At equilibrium, the reaction does not proceed in either direction, implying thereby that there would be an increase in Gibb's free energy of the system if the reaction proceeds in either direction. Hence, the Gibb's free energy of the system will be minimum at equilibrium.

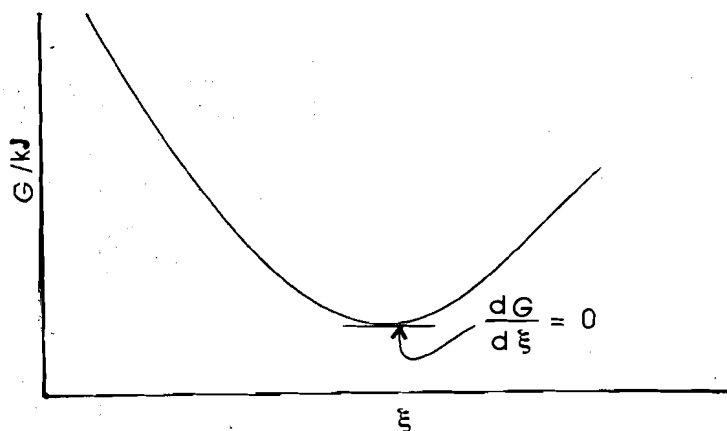


Fig. 14.1 : Change of Gibb's Free Energy and the extent of chemical reaction.

Equation 14.8 is a general expression which is applicable to any reversible chemical reaction under equilibrium conditions at constant temperature and pressure. The equation simply means that the sum of the chemical potentials of the products and reactants is equal to zero at equilibrium.

Equation 14.8 would be most useful if we could express the chemical potential in terms of some experimentally determinable or known quantities. There are a number of ways to express chemical potentials. The next section discusses the substitution for chemical potential in terms of partial pressure, mole fraction and concentration for ideal gas mixtures at equilibrium.

Try the following SAQ which is based on the above discussion.

SAQ 1

For the formation reaction of nitric oxide from nitrogen and oxygen gases, find the value of ν for each of the reactants and products.

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.....

.....

14.4 CHEMICAL EQUILIBRIUM IN IDEAL GAS MIXTURES

Let us derive an expression for the equilibrium constant in terms of partial pressures for a reaction between ideal gases.

14.4.1 Equilibrium Constant Expression in Terms of Partial Pressure

Consider a general reaction



At constant temperature ($dT=0$) and pressure ($dp=0$), the free energy change for the above reaction ($\Delta_r G_{T,p}$) is obtained by using Eq. 14.7.

$$\Delta_r G_{T,p} = (l\mu_L + m\mu_M + \dots) - (a\mu_A + b\mu_B + \dots) \quad \dots (14.10)$$

where $\mu_L, \mu_M, \mu_A, \mu_B, \dots$, etc., are the chemical potentials of the products and reactants; and $l, m, (-a), (-b), \dots$, etc., are ν_i values. Remember that the products (such as L and M) have positive ν_i values and the reactants (such as A and B) have negative ν_i values; because of this, there is a negative sign between the two terms on the right hand side of Eq. 14.10.

The Chemical potential, μ_i , of an ideal gas 'i' in a gaseous mixture is given by Eq. 9.83 of Unit 9.

$$\mu_i(p_i) = \mu_i^\circ(p) + RT \ln p_i \quad \dots (14.11)$$

where $\mu_i^\circ(p)$ is the chemical potential of i in the standard state and p_i is its partial pressure.

Using Eq. 14.11 in Eq. 14.10,

$$\Delta_r G_{T,p} = [l(\mu_L^\circ(p) + RT \ln p_L) + m(\mu_M^\circ(p) + RT \ln p_M) + \dots] - [a(\mu_A^\circ(p) + RT \ln p_A) + b(\mu_B^\circ(p) + RT \ln p_B) + \dots] \quad \dots (14.12)$$

$$\Delta_r G_{T,p} = [(l\mu_L^\circ(p) + m\mu_M^\circ(p) + \dots) - (a\mu_A^\circ(p) + b\mu_B^\circ(p) + \dots)] + RT \ln \frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \quad \dots (14.13)$$

Note that in the transformation of Eq. 14.12 to Eq. 14.13, we have used the relation :

$lRT \ln p_L = RT \ln p_L^l$; i.e., a coefficient (l) of a logarithmic term ($RT \ln p_L$) is taken inside the logarithmic term as a power.

$$\text{But } (l\mu_L^\circ(p) + m\mu_M^\circ(p) + \dots) - (a\mu_A^\circ(p) + b\mu_B^\circ(p) + \dots) = \Delta_r G_{T,p}^\circ \quad \dots (14.14)$$

where $\Delta_r G_{T,p}^\circ$ is the standard free energy change of the reaction at constant temperature and pressure.

Using Eqs. 14.13 and 14.14, we can write

$$\Delta_r G_{T,p} = \Delta_r G_{T,p}^\circ + RT \ln \frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \quad \dots (14.15)$$

Let us now assume that the above system is under equilibrium. Using Eqs. 14.8 and 14.15, we can write that at equilibrium,

$$\Delta_r G_{T,p} = \Delta_r G_{T,p}^\circ + RT \ln \left[\frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \right]_{\text{eq}} = 0$$

The subscript 'eq' stands for equilibrium values of partial pressures.

$$\text{i.e., } \Delta_r G_{T,p}^\circ = -RT \ln \left[\frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \right]_{\text{eq}} \quad \dots (14.16)$$

$$\text{or } \Delta_r G_{T,p}^\circ = -RT \ln K_p = -2.303 RT \log K_p \quad \dots (14.17)$$

where K_p is called the equilibrium constant in terms of partial pressures. The relationship is known as van't Hoff isotherm. K_p is given by the relationship,

$$K_p = \frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \text{ at equilibrium} \quad \dots (14.18)$$

$$= \frac{\text{Multiplication of } (p_i)^{\nu_i} \text{ terms of the products}}{\text{Multiplication of } (p_i)^{-\nu_i} \text{ terms of the reactants}} \text{ at equilibrium}$$

where $p_L, p_M, p_A, p_B, \dots$, etc., are the partial pressures of L, M, A, B, ..., etc., at equilibrium. In subsequent sections, we leave out the subscript 'eq' while referring to equilibrium partial pressures. Eq. 14.18 can also be written as,

$$K_p = p_L^l \cdot p_M^m \dots p_A^{-a} \cdot p_B^{-b} \dots \quad \dots (14.19)$$

where $p_L, p_M, p_A, p_B, \dots$, etc., are the equilibrium partial pressures and $l, m, (-a), (-b) \dots$, etc., are the respective ν_i values of L, M, A, B, ..., etc. Eq. 14.19 can also be represented as,

$$K_p = \prod_i p_i^{\nu_i} \quad \dots (14.20)$$

where the symbol \prod represents the multiplication of different $p_i^{\nu_i}$ terms given in Eq. 14.19.

Again, from Eqs. 14.18 to 14.20, we can see that the dimensions of K_p will depend upon the ν_i values of the reactants and products. This particular aspect will be clear when you study the examples worked out in this unit.

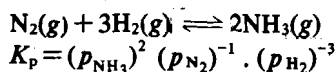
Some authors prefer to give K_p as a dimensionless quantity by dividing p_i by p° where $p^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$. To represent K_p as a dimensionless quantity, Eq. 14.20 is modified as,

$$K_p = \prod_i \left(\frac{p_i}{p^\circ} \right)^{\nu_i} \quad \dots (14.21)$$

Let us apply Eq. 14.19 to ammonia synthesis reaction.

It is quite interesting to note that Eq. 14.17 relates equilibrium constant of a reaction to the change in standard free energy that takes place during a reaction. In Unit 9, you have studied the method of calculation of $\Delta_r G^\circ$ from the free energies of formation of the reactants and products; once $\Delta_r G^\circ$ is known at a particular temperature, K_p can be calculated using Eq. 14.17. In Unit 17 on Electrochemical cells, you will study the electrochemical method of calculating the equilibrium constant.

Note that ν_i written as power is positive for the product, NH_3 , whereas it is negative for N_2 and H_2 , these two being reactants.



$$\text{or } K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3}$$

Since the partial pressures are expressed in Pa unit, K_p for ammonia synthesis has the unit Pa^{-2} . If K_p for ammonia synthesis is to be dimensionless, then K_p expression is to be written following 14.21 as,

$$K_p = \frac{p_{\text{NH}_3}^2 (p^\circ)^2}{p_{\text{N}_2} \cdot p_{\text{H}_2}^3}$$

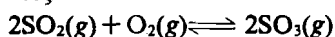
Let us illustrate the use of Eq. 14.19 with an example.

Example 1

Suppose that, in an experiment at 1000 K, it is found that

$$p_{\text{SO}_2} = 3.42 \times 10^4 \text{ Pa}, p_{\text{O}_2} = 3.13 \times 10^4 \text{ Pa} \text{ and}$$

$$p_{\text{SO}_3} = 3.58 \times 10^4 \text{ Pa} \text{ for the reaction,}$$



Calculate the value for the equilibrium constant, K_p .

Solution

At the given temperature, K_p is given by the expression

$$K_p = p_{\text{SO}_3}^2 \cdot p_{\text{SO}_2}^{-2} \cdot p_{\text{O}_2}^{-1}$$

$$\text{or } K_p = \frac{p_{\text{SO}_3}^2}{p_{\text{SO}_2}^2 \cdot p_{\text{O}_2}} = \frac{(3.58 \times 10^4 \text{ Pa})^2}{(3.42 \times 10^4 \text{ Pa})^2 \times (3.13 \times 10^4 \text{ Pa})}$$

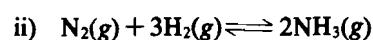
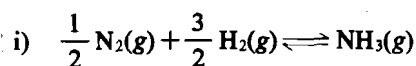
$$= 3.50 \times 10^{-4} \text{ Pa}^{-1}$$

Note that the unit of K_p as per Eq. 14.19 is given by $(\text{Pa})^{\sum \nu_i}$. In the reaction discussed in Example 1,
 $\sum \nu_i = 2 - 2 - 1 = -1$
 Hence, the unit of K_p is Pa^{-1} .

Try the following SAQ now.

SAQ 2

Suppose that we write the ammonia synthesis reaction in two different ways :



Would you expect any difference in the expression for K_p in the two cases? (Usually, K_p values are calculated using equations of the type (ii) which have integral stoichiometric coefficients).

14.4.2 Equilibrium Constant Expression in Terms of Mole Fraction

Since Dalton's law tells us that partial pressure of a gas is equal to the mole fraction times the total pressure, Eq. 14.19 can be written as,

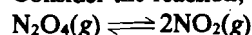
$$K_p = (x_L p_t)^l (x_M p_t)^m \dots (x_A p_t)^{-a} (x_B p_t)^{-b}$$

$$K_p = \prod (x_i p_t)^{\nu_i} \quad \dots (14.22)$$

where, x_i = mole fraction of the species i , and p_t = total pressure.

Example 2

Consider the reaction,



If a mixture of NO_2 , and N_2O_4 at equilibrium has a total pressure of $1.5 \times 10^5 \text{ Pa}$, calculate the fraction of N_2O_4 that has dissociated at 303 K. K_p for the reaction is $1.4 \times 10^4 \text{ Pa}$ at 303 K.

Solution

Suppose that ξ is the fraction of the amount of N_2O_4 which has dissociated at equilibrium or it represents the extent of the reaction. Then, $1 - \xi$ is the fraction of the amount of N_2O_4

According to Dalton's law of partial pressures, partial pressure (p_i) of an ideal gas, i , is given by,

$$p_i = p_t \cdot x_i$$

where p_t is the total pressure, and x_i is the mole fraction of the gas in a gaseous mixture.

remaining at equilibrium and is proportional to the actual number of moles of N_2O_4 present at equilibrium.

From the balanced reaction, it is seen that for each mole of N_2O_4 decomposed, there are two moles of NO_2 produced. Therefore, at equilibrium, 2ξ will be proportional to the actual number of moles of NO_2 produced.

The total number of moles at equilibrium would then be proportional to $1 - \xi + 2\xi$ or $1 + \xi$.

The mole fractions of the two gases at equilibrium can be written as,

$$x_{N_2O_4} = \frac{1-\xi}{1+\xi} \text{ and } x_{NO_2} = \frac{2\xi}{1+\xi} \text{ where } x \text{ denotes mole fraction.}$$

$$\text{Using Eq. 14.22, } K_p = (x_{NO_2} \cdot p_i)^2 \cdot (x_{N_2O_4} \cdot p_i)^{-1}$$

$$\text{i.e., } K_p = \frac{(x_{NO_2} \cdot p_i)^2}{(x_{N_2O_4} \cdot p_i)}$$

Substituting for x_{NO_2} and $x_{N_2O_4}$ we get,

$$K_p = \frac{\left(\frac{2\xi}{1+\xi} \cdot p_i\right)^2}{\frac{1-\xi}{1+\xi} \cdot p_i}$$

$$\text{or } K_p = \frac{4\xi^2}{(1-\xi)(1+\xi)} p_i = \frac{4\xi^2}{1-\xi^2} \cdot p_i$$

Substituting the given values, we get,

$$1.4 \times 10^4 \text{ Pa} = \frac{4\xi^2}{1-\xi^2} \times 1.5 \times 10^5 \text{ Pa}$$

$$\text{or } \frac{1-\xi^2}{\xi^2} = \frac{1.5}{0.14} \times 4$$

$$\text{or } \frac{1}{\xi^2} = 1 + \frac{1.5 \times 4}{0.14}$$

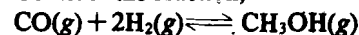
$$\text{or } \xi^2 = 0.023$$

$$\xi = 0.15$$

The fraction of N_2O_4 dissociated is thus calculated to be 0.15.

Example 3

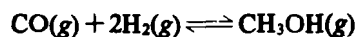
Consider the reaction,



where initially 1 mol of CO and 2 mol of H_2 were mixed together. Derive an expression for the equilibrium constant, K_p , in terms of the extent of the reaction, ξ and the total pressure, p_i .

Solution

If the extent of the reaction at equilibrium is represented by ξ then we have,



Moles at equilibrium $1 - \xi$ $2 - 2\xi$ ξ

Mole fraction at equilibrium $\frac{1-\xi}{3-2\xi}$ $\frac{2-2\xi}{3-2\xi}$ $\frac{\xi}{3-2\xi}$

$$\text{Using Eq. 14.22, } K_p = (x_{CH_3OH} \cdot p_i)^1 \cdot (x_{CO} \cdot p_i)^{-1} \cdot (x_{H_2} \cdot p_i)^{-2}$$

$$\text{i.e., } K_p = \frac{(x_{CH_3OH} \cdot p_i)}{(x_{CO} \cdot p_i) (x_{H_2} \cdot p_i)^2}$$

Hence,

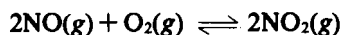
$$K_p = \frac{\left(\frac{\xi}{3-2\xi} \cdot p_t\right)}{\left(\frac{1-\xi}{3-2\xi} \cdot p_t\right) \left(\frac{2-2\xi}{3-2\xi} \cdot p_t\right)^2}$$

$$= \frac{(3-2\xi)^2 \xi}{(1-\xi)(2-2\xi)^2 \cdot p_t^2}$$

You should be able to do the following SAQ, if you have understood the above examples.

SAQ 3

Express the equilibrium constant K_p for the reaction,



in terms of (i) partial pressures and (ii) mole fractions of the gaseous species.

.....

14.4.3 Equilibrium Constant Expression in Terms of Concentration

We know that for an ideal gas,

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

where c_i represents molar concentration of a gaseous substance 'i'; other symbols have their usual meaning. Hence we can express Eq. 14.19 in terms of concentrations.

$$K_p = (c_L RT)^l (c_M RT)^m \dots (c_A RT)^{-a} (c_B RT)^{-b}$$

$$= \frac{(c_L RT)^l (c_M RT)^m \dots}{(c_A RT)^a (c_B RT)^b \dots} \quad \dots (14.23)$$

i.e., $K_p = \prod (c_i RT)^{\nu_i}$... (14.24)

Eqs. 14.18 and 14.26 are the mathematical expressions of the law of mass action.

Where ν_i represents the stoichiometric coefficient (along with proper sign) in the chemical equation.

Eq. 14.23 can be written as,

$$K_p = \frac{c_L^l c_M^m \dots (RT)^{(l+m+\dots)-(a+b+\dots)}}{c_A^a c_B^b \dots}$$

$$= \frac{c_L^l c_M^m \dots}{c_A^a c_B^b \dots} (RT)^{\sum \nu_i}$$

i.e., $K_p = K_c (RT)^{\sum \nu_i}$... (14.25)

where K_c is defined by,

$$= \frac{c_L^l c_M^m \dots}{c_A^a c_B^b \dots} = \frac{\text{Multiplication of } (c_i)^{\nu_i} \text{ terms of the products}}{\text{Multiplication of } (c_i)^{-\nu_i} \text{ terms of the reactants}} \quad \dots (14.26)$$

i.e., $K_c = \prod (c_i)^{\nu_i}$... (14.27)

Eq. 14.25 holds good for reactions between ideal gases.

The dimensions of K_c depend of the ν_i values of the reactants and the products. In case K_c is to be expressed as a dimensionless quantity, c_i in Eq. 14.27 is to be replaced by c_i/c_o where c_o is the standard concentration and is equal to 1 mol dm⁻³.

i.e., $K_c = \prod \left(\frac{c_i}{c_o}\right)^{\nu_i}$... (14.28)

It is important to note that K_p and K_c are functions of temperature; we shall discuss this aspect in Sec. 14.7.

Let us study an application of Eq. 14.26.

Chemical Equilibria and Electrochemistry

The unit, mol dm^{-3} , is for denoting molarity and is represented by the letter, M.

Note that concentration in molarity = $\frac{\text{Number of moles}}{\text{Volume in dm}^3}$

The unit of K_c as per Eq. 14.26 is given by $(\text{M})^{\sum \nu}$. In Example 4, $\sum \nu_i = 1 + 1 - 1 = 1$.

Hence, the unit of K_c in this example is M.

The solution of a quadratic equation of the form

$$ax^2 + bx + c = 0$$

is given by

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Square brackets are used to denote the concentration of a species. For example, $[\text{PCl}_5]$ is to be read as : concentration of PCl_5

Example 4

Calculate the equilibrium concentrations of all the species at 613 K for the reaction,



if the initial concentrations of the three gases is 0.15 M each and $K_c = 0.800$ M at 613 K. The volume of the vessel is 1 dm^3 .

Solution

Suppose that x mol of PCl_5 has decomposed at equilibrium. Since volume is 1 dm^3 , the concentration expressed in molarity is equal to the number of moles of a particular substance.

	PCl_5	PCl_3	Cl_2
Equilibrium concentration/M	$0.15 - x$	$0.15 + x$	$0.15 + x$

Using Eq. 14.26, we get

$$K_c = \frac{c_{\text{PCl}_3} \cdot c_{\text{Cl}_2}}{c_{\text{PCl}_5}}$$

Substituting the given values, we get,

$$0.800 \text{ M} = \frac{(0.15 + x) \cdot (0.15 + x)}{(0.15 - x)} \text{ M}$$

$$\text{or } 0.800(0.15 - x) = (0.15 + x)^2$$
$$\text{or } x^2 + 1.1x - 0.0975 = 0$$

Using the principle of solution of standard quadratic equation, we get,

$$x = 0.082 \text{ M} \text{ or}$$
$$\text{or } -1.183 \text{ M}$$

We take $x = 0.082 \text{ M}$, since the second root of the quadratic equation gives the concentrations of PCl_3 and Cl_2 as $(0.15 \text{ M} - 1.183 \text{ M}) = -1.033 \text{ M}$ which is impossible. Hence, the equilibrium concentrations are :

$$[\text{PCl}_5] = (0.15 - 0.082) \text{ M} = 0.068 \text{ M}$$
$$\text{and } [\text{PCl}_3] = [\text{Cl}_2] = 0.15 + 0.082 = 0.232 \text{ M}$$

We can verify the answer by substituting the values for concentrations in evaluating K_c .

Based on the above discussion, answer the following SAQ.

SAQ 4

How are K_p and K_c related to each other for a reaction between ideal gases?

.....

.....

.....

14.5 DETERMINATION OF EQUILIBRIUM CONSTANTS

It is now clear from the above examples that if the initial concentrations and the extent of the reaction are known, equilibrium constants can be calculated. In fact, if we want to make use of any of the equations derived in the previous two sections, we must be sure that the equilibrium has indeed been reached. The following two criteria confirm the presence of equilibrium condition :

- 1) The value of equilibrium constant should be same when the equilibrium is approached from either side.
- 2) The value of equilibrium constant should be same when the concentrations of the reacting substances are varied greatly.

Once it is established that an equilibrium has been reached, the next step is to find out the equilibrium concentration of at least one of the reactants or products in order to calculate the extent of the reaction. This can be achieved either by chemical analysis or by

measurement of some physical property. The difficulty with the chemical analysis is that the concentration will change during the course of the analysis. Hence, only when the reaction can be stopped at equilibrium by some means (like sudden cooling), can this method be used. Physical methods are more convenient since they do not require stopping of the reaction. The physical properties commonly used for this purpose are density, refractive index, electrical conductivity, light absorption etc.

14.6 APPLICATIONS OF EQUILIBRIUM STUDIES

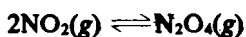
The law of mass action, as represented by Eqs. 14.18 to 14.28, finds many useful applications in chemical calculations like finding out the amounts of products formed at equilibrium or change in free energy of the system etc. We have already seen a few examples of the application of these equations; however, to simplify, we shall categorise the problems into three subsections, namely, homogeneous systems, heterogeneous systems and liquid solutions.

14.6.1 Homogeneous Systems

When all the reactants and products are present in the same phase (i.e., gaseous or liquid) we call it a homogeneous system. Let us consider a few examples :

Example 5

At 298 K, it was found that $K_p = 7.13$, for the reaction :



What is $\Delta_r G^\circ$ for the reaction?

Solution

It is worth noting that K_p is given as a dimensionless quantity as per Eq. 14.21.

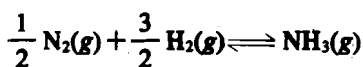
$$\begin{aligned} \text{Using Eq. 14.17, } \Delta_r G^\circ &= -RT \ln K_p \\ &= -2.303 RT \log K_p \end{aligned}$$

Substituting the values of R , T and K_p in the above equation, we get,

$$\Delta_r G^\circ = (-2.303 \times 8.314 \times 298 \log 7.13) \text{ J mol}^{-1} = -4.868 \text{ kJ mol}^{-1}$$

Example 6

What is the value of K_p for the ammonia synthesis reaction at 500 K as represented by,



if $\Delta_r G^\circ = 4.833 \text{ kJ mol}^{-1}$?

Solution

$$\Delta_r G^\circ = 4833 \text{ J mol}^{-1} = -(2.303 \times 8.314 \times 500 \log K_p) \text{ J mol}^{-1}$$

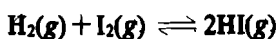
$$\text{Substituting the given values, we get, } \log K_p = \frac{-4833}{2.303 \times 8.314 \times 500} = -0.5048$$

$$\begin{aligned} \therefore \log \frac{1}{K_p} &= 0.5048; \frac{1}{K_p} = 10^{0.5048} \\ &= \text{Antilog of } 0.5048 = 3.197 \end{aligned}$$

$$\text{hence, } K_p = \frac{1}{3.197} = 0.3128$$

Example 7

Hydrogen and iodine react at 699 K according to the equation,



If 1.00 mol of H_2 and 1.00 mol of I_2 are placed in a 1.00 dm³ flask and allowed to react, what mass of hydrogen iodide will be present at equilibrium? At 699 K, $K = 55.3$.

Solution

First thing you should notice in this case is that the equilibrium constant is written with a

In Example 5, the term inside the log factor is greater than 1; hence the calculation is done as in the case of Example 3 of Unit 6 of this course.

Calculation of K_p from $\Delta_r G^\circ$

If $\Delta_r G^\circ$ is a negative quantity, then $\log K_p$ is a positive quantity. If we assume $\log K_p$ to be equal to x , then K_p can be calculated as follows :

$$\begin{aligned} \log K_p &= x; \text{ hence} \\ K_p &= 10^x = \text{Antilog of } x. \end{aligned}$$

If $\Delta_r G^\circ$ is a positive quantity, then $\log K_p$ is a negative quantity. If we assume $\log K_p$ to be equal to $-x$, then K_p can be calculated as follows :

$$\begin{aligned} \log K_p &= -x; \text{ hence } \log \frac{1}{K_p} = x \\ \frac{1}{K_p} &= 10^x = \text{Antilog of } x \\ \text{or } K_p &= \frac{1}{\text{Antilog of } x} \end{aligned}$$

Example 6 is worked out using this principle.

symbol K and not as K_p or K_c since the total number of moles of the products are equal to those of the reactants (i.e., $\sum \nu_i = 0$); so, K_p must be equal to K_c (see Eq. 14.25). Hence, we can write, $K = K_c = 55.3$.

$$\text{Using Eq. 14.26, } 55.3 = \frac{c_{\text{HI}}^2}{c_{\text{H}_2} \cdot c_{\text{I}_2}}$$

If ξ represents the extent of the reaction, the equilibrium concentrations can be written as, $c_{\text{HI}} = 2\xi$, $c_{\text{H}_2} = 1 - \xi$ and $c_{\text{I}_2} = 1 - \xi$; note that the amount of each material is equal to its concentration since volume is 1 dm^3 . Substituting these values in the above equation, we get,

$$55.3 = \frac{(2\xi)^2}{(1 - \xi)(1 - \xi)}$$

or $\xi = 0.731$ or 1.269 ; the value, 1.269 , is rejected since the value of ξ cannot be greater than one.

Hence, the amount of HI at equilibrium = 2ξ or $2 \times 0.731 = 1.46 \text{ mol}$; the mass of HI at equilibrium = $1.46 \times 0.128 \text{ kg} = 0.188 \text{ kg}$.

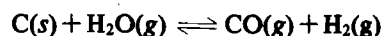
14.6.2 Heterogeneous Systems

Chemical reactions may also involve reactants or products in different phases. The most common examples are found where solids and gases are present together at equilibrium. Recall that at standard pressure of 1 bar, the activity of pure solid is unity. Hence, in writing the expression for equilibrium constant the activity or partial pressure terms for solids can be eliminated. Thus, for the reaction,



as per Eq. (14.19), $K_p = p_{\text{CaO}}^1 p_{\text{CO}_2}^1 p_{\text{CaCO}_3}^{-1} = p_{\text{CO}_2}$ [since $p_{\text{CaO}} = p_{\text{CaCO}_3} = 1$]

Again for the reaction,



as per Eq. 14.19, $K_p = \frac{p_{\text{CO}} \cdot p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}$ since $p_{\text{C}} = 1$, carbon being in the solid form.

Let us illustrate the heterogeneous systems with another example.

Example 8

$\text{NH}_4\text{HS}(s)$ evaporates in an evacuated container at 298 K according to the equation.



Find the pressure of each gas at equilibrium if $K_p = 1.10 \times 10^9 \text{ Pa}^2$ at 298 K.

Solution

We can write for the above reaction,

using Eq. 14.19, $K_p = p_{\text{NH}_3} \cdot p_{\text{H}_2\text{S}}$ (since $p_{\text{NH}_4\text{HS}} = 1$)

Since the two gases produced in the reaction are in equimolar quantities,

$$p_{\text{NH}_3} = p_{\text{H}_2\text{S}}$$

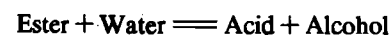
$$\text{or } K_p = p_{\text{NH}_3}^2 = 1.10 \times 10^9 \text{ Pa}^2$$

$$p_{\text{NH}_3} = p_{\text{H}_2\text{S}} = 3.32 \times 10^4 \text{ Pa.}$$

14.6.3 Liquid Solutions

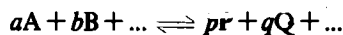
So far we have discussed the reactions which take place in gaseous state or those involving gaseous and solid phases. But the majority of reactions are carried out in liquid solutions.

For example, you have already seen hydrolysis of an ester which can be written as :



Let us arrive at an expression useful in calculating the equilibrium constants of such reactions.

In an ideal solution, the concentration of each component can be conveniently expressed in terms of molarity. We can use Eq. 14.26 to express K_c of a general reaction (given below) which takes place in a liquid solution; of course, the solution has to exhibit ideal behaviour.



In this reaction, A, B, ... etc., and P, Q, ... etc., are the reactants and products; a, b, \dots etc., and p, q, \dots etc., are the stoichiometric coefficients.

Similar to Eq. 14.26, we can write K_c for the above reaction as,

$$K_c = \frac{c_P^p \cdot c_Q^q \dots}{c_A^a \cdot c_B^b \dots} \quad \dots (14.29)$$

$$K_c = \frac{m_P^p \cdot m_Q^q \dots}{m_A^a \cdot m_B^b \dots} = \frac{[P]^p [Q]^q}{[A]^a [B]^b} \quad \dots (14.30)$$

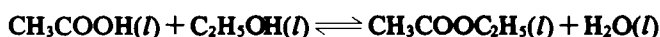
where m_p, m_q, \dots etc., are the molarities of substances. In Eq. 14.30, the square brackets denote the concentrations of the species within the brackets.

Eqs. 14.29 and 14.30 can be applied to the solutions showing ideal behaviour. Similarly even in the case of gas phase reactions, equations such as 14.19 or 14.26 can be used only if the reactants and products are ideal gases. In case of deviation from ideal behaviour, whether it is a gas phase or a liquid phase reaction, activities of the substances must be used in the place of partial pressures or concentrations. But the equilibrium constant expressions become more complicated in such cases and we do not discuss them in this course.

Let us work out an example showing the use of Eq. 14.30.

Example 9

Calculate the equilibrium constant for the reaction,



at 298 K if 1.00 mol of acetic acid and 1.00 mol of ethyl alcohol are mixed together. At the equilibrium point, the amount of water is 0.333 mol.

Solution

The concentrations of substances are given below assuming the total volume to be $V \text{ dm}^3$:

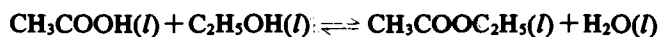
	$[\text{CH}_3\text{COOC}_2\text{H}_5]$	$[\text{H}_2\text{O}]$	$[\text{CH}_3\text{COOH}]$	$[\text{C}_2\text{H}_5\text{OH}]$
Concentration at equilibrium (mol dm^{-3})	$0.333/V$	$0.333/V$	$(1 - 0.333)/V$	$(1 - 0.333)/V$

$$K_c = \frac{(0.667/V)(0.667/V)}{(0.333/V)(0.333/V)} = 4.01$$

Note that K_c is a dimensionless quantity since $\sum \nu_i$ for this reaction is equal to zero. In cases such as this, volume need not be known as it cancels out in the final expression. If in any reaction $\sum \nu_i$ is not equal to zero, the final expression would contain volume term and K_c will have suitable dimensions.

SAQ 5

For the reaction,



assuming that the reaction has attained equilibrium, calculate the concentration of water at 298 K for a mixture with

$$[\text{CH}_3\text{COOC}_2\text{H}_5] = 2.0 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 0.10 \text{ M and}$$

$$[\text{C}_2\text{H}_5\text{OH}] = 0.50 \text{ M}$$

K for this reaction is 4.01 at 298 K.

14.7 EFFECT OF TEMPERATURE ON CHEMICAL EQUILIBRIUM

The equilibrium constant, K , of a reversible chemical reaction is a constant at a given temperature; but it varies with temperature. Let us derive an expression useful in bringing out the relationship between the equilibrium constant and temperature.

From Eq. 14.17, we get,

$$\Delta_r G^\circ = -RT \ln K_p$$

$$\text{or } \ln K_p = \frac{-\Delta_r G^\circ}{RT}$$

Differentiating this expression with respect to temperature,

$$\text{or } \frac{d \ln K_p}{dT} = -\frac{1}{R} \frac{d}{dT} \left(\frac{\Delta_r G^\circ}{T} \right) \quad \dots (14.31)$$

Using Eq. 9.45 we can write

$$\frac{d}{dT} \left(\frac{\Delta_r G^\circ}{T} \right) = -\frac{\Delta_r H^\circ}{T^2} \quad \dots (14.32)$$

Combining Eqs. 14.31 and 14.32, we get,

$$\frac{d \ln K_p}{dT} = \frac{\Delta_r H^\circ}{RT^2} \quad \dots (14.33)$$

Eq. 14.33 tells us that equilibrium constant varies with temperature and depends on the standard enthalpy of the reaction.

Assuming that the standard enthalpy change ($\Delta_r H^\circ$) of the reaction remains constant over a small range of temperature; the above equation on integration between limits K_{p1} , K_{p2} , and T_1 , T_2 gives,

$$\int_{K_{p1}}^{K_{p2}} d \ln K_p = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ}{RT^2} dT$$

$$\text{or } \ln \frac{K_{p2}}{K_{p1}} = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

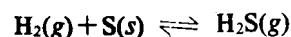
$$\text{or } \log \frac{K_{p2}}{K_{p1}} = \frac{\Delta_r H^\circ}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$= \frac{\Delta_r H^\circ (T_2 - T_1)}{2.303 RT_1 T_2} \quad \dots (14.34)$$

Eq. 14.34 correlates the equilibrium constant values K_{p1} and K_{p2} (expressed in terms of partial pressures) at two different temperatures T_1 and T_2 to the standard enthalpy of reaction.

Example 10

The equilibrium constant for the reaction



is 18.5 at 925 K and 9.25 at 1000 K, respectively. Calculate the standard enthalpy of the reaction. Also calculate $\Delta_r G^\circ$ and $\Delta_r S^\circ$ at 925 K.

Solution

Substituting the given values in Eq. 14.34, we get,

$$\log \frac{K_{1000}}{K_{925}} = \frac{\Delta_r H^\circ}{(2.303 \times 8.314)} \left(\frac{1}{925} - \frac{1}{1000} \right)$$

$$\text{or } \log \frac{9.25}{18.5} = \frac{\Delta_r H^\circ}{2.303 \times 8.314} \left(\frac{75}{925 \times 1000} \right)$$

$$\text{hence } \Delta_r H^\circ = -71.1 \text{ kJ mol}^{-1}$$

According to Eq. 14.25, which is applicable for ideal gases,

$$K_p = K_c (RT)^{\Delta n}$$

Using this equation and Eq. 14.33, it is possible to relate K_c values to the respective temperatures as,

$$\log \frac{K_{c2}}{K_{c1}} = \frac{\Delta_r U^\circ (T_2 - T_1)}{2.303 RT_1 T_2} \quad \dots (14.35)$$

where K_{c1} and K_{c2} are the equilibrium constants (in terms of concentrations) at temperatures T_1 and T_2 and $\Delta_r U^\circ$ is the standard internal energy change of the reaction. Since reactions are generally carried out at constant pressure, Eq. 14.34 is of greater importance for us. Eq. 14.35 is known as van't Hoff's isochore.

Using Eq. 14.17, $\Delta_r G^\circ = -2.303 \times 8.314 \times 925 \log 18.5 = -22.4 \text{ kJ mol}^{-1}$

$$\begin{aligned} \text{Rearranging Eq. 9.15 of Unit 9, } \Delta_r S^\circ &= \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(-71100 + 22400) \text{ J}}{925 \text{ K}} \\ &= -52.6 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

SAQ 6

For the dissociation of mercuric oxide, K_p values are 0.0196 and 0.1794 at 693 K and 723 K, respectively. Calculate the standard enthalpy of the reaction.

14.8 LE CHATELIER'S PRINCIPLE AND CHEMICAL EQUILIBRIA

The equilibrium expressions derived in Secs. 14.3 to 14.7 are very useful to perform numerical computations of various kinds as we have already seen with different examples given. However, often one is more interested in predicting qualitatively the results of a change brought about by external forces on the system under equilibrium. For instance, if pressure, temperature or volume is changed for a system under equilibrium, what would be its effect, if any, on the equilibrium itself? Of course, we can find out the effect of such factors on the system under equilibrium with the help of expressions such as, Eq. 14.17 or Eq. 14.34. However, it is much more easily predicted with the help of Le Chatelier's principle.

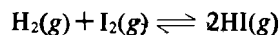
Le Chatelier's principle can be stated as follows :

If a stress is applied to any system under equilibrium, the system would tend to shift in such a way so as to neutralise the effect of that stress (if possible).

The stress for a chemical reaction could be in the form of a change in pressure, temperature or concentration at equilibrium. According to the above principle then, the equilibrium would shift in such a direction so that the effect of these changes is neutralised. We shall consider the effect of each one of these factors on equilibrium separately.

14.8.1 Effect of Change of Concentration

Let us consider the reaction,

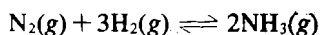


which has attained equilibrium. Now, if we add some H_2 to the equilibrium mixture, it will obviously upset the equilibrium. According to Le Chatelier's principle, the equilibrium would shift in such a way so as to oppose the effect of this excess H_2 . It can do so by using up this excess H_2 to react with more I_2 to give more of HI . We describe this process by saying that the final position of equilibrium has shifted to the right of the equation. In this final state of equilibrium, then, more amount of HI is formed as compared to earlier equilibrium state. Just the opposite would be the fate of the reaction if, instead of H_2 , some HI is added to the system under equilibrium. In short, by changing the concentration at equilibrium, the reaction will move forward or in the reverse direction so that the equilibrium constant has the same value.

14.8.2 Effect of Change of Pressure

If we consider the above reaction again and suppose that the pressure of the system is increased—perhaps by reducing the volume of the container—the system should react in such a way so as to reduce the effect of the increase in pressure. However, there is no way by which this can be achieved. The forward reaction or the reverse reaction will not be favoured by pressure change since the total number of moles of the reactants is the same as the total number of moles of the products.

However, the situation changes if we consider the synthesis of ammonia :



If the pressure of the system is increased at the equilibrium as was done in the previous example, the effect of this increase could be eliminated by the formation of more ammonia. This becomes obvious if you realise that the total number of moles of the reactants is four as compared to the moles of product which is two. Four moles will exert greater pressure than two moles; so, if the system wants to reduce the extra pressure, it can do so by moving in the forward direction. On the other hand, if we decrease the external pressure on the system, more of ammonia will decompose to give nitrogen and hydrogen. Thus, if we want to produce ammonia industrially, it is preferable to carry out the reaction at high pressures.

Comparing the two reactions given above, we can conclude that changes in pressure at equilibrium will affect the amounts of products formed for only those reactions where the total number of moles of reactants are different from the total number of moles of products.

14.8.3 Effect of Change of Temperature

Consider once again the synthesis of ammonia from nitrogen and hydrogen which is an exothermic reaction. If the temperature of the system is increased at equilibrium, Le Chatelier's principle tells us that the system should react in such a way so as to neutralise this effect. Let us see how this is possible. We know that the formation of ammonia is an exothermic reaction and, therefore, the reverse reaction of decomposition of ammonia will be endothermic. Thus, the excess heat supplied by raising the temperature of the system can be absorbed by the system if the reaction goes more towards left. This will increase the amounts of N_2 and H_2 and decrease the amount of NH_3 at equilibrium. We can generalise this observation by saying that by raising the temperature of a system undergoing exothermic reaction, we will decrease the amount of the products and increase the amount of the reactants. Just the opposite will be true for all endothermic reactions.

The effect of these factors gains special importance for the production of a substance on large scale. In any industrial production of a substance it is imperative to know the optimum conditions of temperature, pressure and concentrations in order to get the maximum yield at a minimum cost. For instance, in the production of ammonia we know from Le Chatelier's principle that high pressure and high concentration of N_2 and H_2 will favour the reaction. Similarly, the above principle also predicts that the reaction would be more favourable at low temperatures since it is exothermic. However, we cannot carry out the reaction at a very low temperature since another factor comes into the picture. That is, the rate of the reaction becomes too slow at lower temperatures. Hence, the reaction is performed at pressures of several megapascals and temperatures between 650 and 750 K.

You should be able to do the following SAQs which are based on the above discussion.

SAQ 7

Consider the reaction, $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. How would the equilibrium be affected by,

- i) the addition of Cl_2 and
- ii) decrease in the volume of the container?

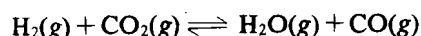
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SAQ 8

If $\Delta H^\circ = 41 \text{ kJ mol}^{-1}$ for the reaction,



what will be the effect of increase of temperature on the equilibrium?

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14.9 SUMMARY

In this unit we have discussed the meaning of chemical equilibrium. A general expression for the equilibrium constant was derived from the basic principles of thermodynamics. Different forms of the general expression were then utilised in understanding the equilibria of homogeneous and heterogeneous systems. We then learnt Le Chatelier's principle and its use in predicting the shift in the position of equilibrium by the changes brought about in concentration, temperature and pressure of the system.

14.10 TERMINAL QUESTIONS

- In a reaction $A + 2B \rightleftharpoons 2C + D$, A and B are taken in a closed vessel at 300 K. The initial concentration of B is 1.5 times that of A. At equilibrium, the concentration of A and D are equal. Calculate the equilibrium constant at 300 K.
- At 1000 K for the equilibria,
 - $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ $K_p = 4.0 \times 10^3 \text{ Pa}$
 - $\text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g)$ $K_p = 2.0 \times 10^5 \text{ Pa}$
 Solid C, CaO and CaCO_3 are mixed and allowed to attain equilibrium at 1000 K. What is the pressure of CO?
- Show that for the reaction,

$$2\text{H}_2\text{S}(g) \rightleftharpoons 2\text{H}_2(g) + \text{S}_2(g)$$
 the equilibrium constant, K_p , is given by

$$K_p = \frac{\xi^3 p_t}{(2 + \xi)(1 - \xi)^2}$$
 where the symbols have their usual meaning.
- In a 10.0 dm^3 mixture of H_2 , I_2 and HI at equilibrium at 698 K, there are 0.100 mol of H_2 , 0.100 mol of I_2 and 0.740 mol of HI. If 0.500 mol of HI are now added to this system, what will be the concentrations of H_2 , I_2 and HI, once equilibrium has been reestablished?
- At a certain temperature, $K_c = 7.5 \text{ m}^3 \text{ mol}^{-1}$ for the reaction,

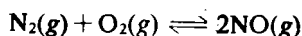
$$2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$$
 - If 2.0 mol of NO_2 are placed in a 2.0 dm^3 container and allowed to react, what will be the concentrations of NO_2 and N_2O_4 at equilibrium?
 - What will be the equilibrium concentration, if the volume of the container is doubled?
- Find the ν value of the reactants and the products in the following cases :
 - $\text{C}_2\text{H}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{C}_2\text{H}_5\text{OH}(g)$
 - $2\text{CH}_4(g) \rightleftharpoons \text{C}_2\text{H}_6(g) + \text{H}_2(g)$
- If $K_p > 1$ for a reaction, comment on the sign of standard free energy change of the reaction.
- At 298.15 K, the standard free energies of formation of $\text{CH}_3\text{COOH}(aq)$, $\text{CH}_3\text{COO}^- (aq)$ and $\text{H}^+ (aq)$ are -396.6 , -369.4 and 0 kJ mol^{-1} , respectively. Using this data, calculate the equilibrium constant for the dissociation of acetic acid at 298.15 K.
- For the reaction,

$$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$$
 K_p is $1.4 \times 10^4 \text{ Pa}$ at 303 K. Find K_c at this temperature.

14.11 ANSWERS

Self Assessment Questions

- The formation of nitric oxide can be represented by the equation,



ν values are as follows : $\nu_{\text{NO}} = 2$; $\nu_{\text{N}_2} = -1$ and $\nu_{\text{O}_2} = -1$.

- 2) Let us denote the equilibrium constant for the two equations as K'_p and K_p .

$$K'_p = \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^{1/2} \cdot P_{\text{H}_2}^{3/2}}$$

and

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \cdot P_{\text{H}_2}^3}$$

hence,

$$K_p = (K'_p)^2$$

Remember that generally the equilibrium constant value is obtained from the balanced chemical equation representing the reactants in their normal state of existence.

3) i)
$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \cdot P_{\text{O}_2}}$$

- ii) Let us assume that 2 mol of NO and 1 mol of O₂ are mixed together initially. Let the total pressure be p_t .

Let ξ be the fraction of number of moles of O₂ which has reacted at equilibrium.

Total Number of moles
 $= (2 - 2\xi) + (1 - \xi) + (2\xi)$
 $= (3 - \xi)$

	NO	O ₂	NO ₂
Hence, number of moles at equilibrium	$2 - 2\xi$	$1 - \xi$	2ξ
Mole fraction at equilibrium	$\frac{2 - 2\xi}{3 - \xi}$	$\frac{1 - \xi}{3 - \xi}$	$\frac{2\xi}{3 - \xi}$

$$K_p = 4\xi^2(3 - \xi) / (2 - 2\xi)^2(1 - \xi) p_t$$

- 4) $K_p = (RT)^{\Delta\nu} K_c$ [see Eq. 14.25]
 where $\Sigma \nu_i = \{\text{Sum of the stoichiometric coefficients of the products}\} - \{\text{sum of the stoichiometric coefficients of the reactants}\}$

- 5) Substituting the given values in Eq. 14.29, we get,

$$4.01 = \frac{(2.0)(x)}{(0.10)(0.50)}$$

$$x = \frac{4.01 \times 0.050}{2.0} = 0.10 \text{ M}$$

Hence, the concentration of water at equilibrium is 0.10 M.

- 6) Using Eq. 14.34, we get,

$$\Delta_r H^\circ = \frac{2.303 \times 8.314 \times 693 \times 723}{30} \log \frac{0.1794}{0.0196} \text{ J mol}^{-1}$$

$$= 308 \text{ kJ mol}^{-1}$$

- 7) The equilibrium expression for the reaction,



can be written as,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

When,

- i) Cl₂ is added, [PCl₅] must increase in order to keep the K_c value constant; i.e., some Cl₂ will combine with PCl₃ to give more of PCl₅. Hence, the equilibrium will shift towards left.
- ii) volume of the container is decreased, the pressure will increase. According to Le Chatelier's principle, the equilibrium would shift in such a direction so as to neutralise or reduce this increase. Since the total number of moles on the L.H.S. is less than in R.H.S., the equilibrium has to shift towards left in order to bring about pressure decrease.
- 8) For endothermic reactions, the increase in temperature will move the equilibrium in the forward direction according to Le Chatelier's principle explained in Sec. 14.8.

Terminal Questions

- 1) Let the initial concentration of A be $a \text{ mol dm}^{-3}$,
then, the initial concentration of B = $1.5a \text{ mol dm}^{-3}$.
In the beginning, C and D were not present. Suppose that at equilibrium, $x \text{ mol dm}^{-3}$
of A has reacted. The equilibrium concentration will be then,

$$[A] = (a - x) \text{ mol dm}^{-3}$$

$$[B] = (1.5a - 2x) \text{ mol dm}^{-3}$$

$$[C] = 2x \text{ mol dm}^{-3}$$

$$[D] = x \text{ mol dm}^{-3}$$

But it is given that at equilibrium, the concentrations of A and D are equal; hence,

$$(a - x) = x$$

$$\text{or } x = \frac{a}{2}$$

$$\therefore [A] = \left(a - \frac{a}{2}\right) \text{ mol dm}^{-3} = \frac{a}{2} \text{ mol dm}^{-3}; [C] = a \text{ mol dm}^{-3}$$

$$[B] = \left(1.5a - 2 \cdot \frac{a}{2}\right) \text{ mol dm}^{-3} = 0.5a \text{ mol dm}^{-3}; [D] = \frac{a}{2} \text{ mol dm}^{-3}$$

The equilibrium constant is given by the expression;

$$K_c = \frac{[C]^2[D]}{[A][B]^2} = \frac{[C]^2}{[B]^2} \text{ since } [A] = [D]$$

Substituting the values for [C] and [B], we get,

$$K_c = \frac{(a)^2}{(0.5a)^2} = 4; K_c \text{ is dimensionless, since } \sum \nu_i = 0$$

- 2) For the two reactions (i) and (ii), the equilibrium constants can be expressed as,

$$K_p = p_{\text{CO}_2}$$

$$K'_p = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}}$$

For the overall reaction; $\text{CaCO}_3(s) + \text{C}(s) \rightleftharpoons \text{CaO}(s) + 2\text{CO}(g)$, let the equilibrium constant be K_p^* .

$$K_p^* = p_{\text{CO}}^2$$

$$\text{or } K_p^* = K'_p \times p_{\text{CO}_2}$$

$$K_p^* = K'_p \times K_p$$

Substituting the given values, we get,

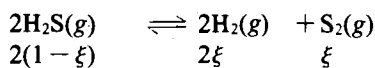
$$K_p^* = 4.0 \times 10^3 \text{ Pa} \times 2.0 \times 10^5 \text{ Pa}$$

$$= 8.0 \times 10^8 \text{ Pa}^2$$

$$\therefore p_{\text{CO}} = \sqrt{K_p^*} = \sqrt{8.0 \times 10^8 \text{ Pa}^2}$$

$$= 2.8 \times 10^4 \text{ Pa}$$

- 3) At equilibrium, the concentration will be given by,



$$\text{Total moles} =$$

$$2 - 2\xi + 2\xi + \xi = 2 + \xi$$

The corresponding mole fractions will be,

$$\frac{2(1 - \xi)}{2 + \xi} \qquad \frac{2\xi}{2 + \xi} \qquad \frac{\xi}{2 + \xi}$$

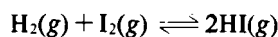
The partial pressures of each substance can be obtained by multiplying the mole fraction by total pressure, p_t . Substituting the proper values in the equilibrium equation,

$$K_p = \frac{p_{\text{S}_2} \times p_{\text{H}_2}^2}{p_{\text{H}_2\text{S}}^2}$$

$$= \frac{\left\{ \left(\frac{\xi}{2 + \xi} \right) p_t \right\} \left\{ \left(\frac{2\xi}{2 + \xi} \right) p_t \right\}^2}{\left\{ \left(\frac{2(1 - \xi)}{2 + \xi} \right) p_t \right\}^2}$$

$$\text{or } K_p = \frac{\xi^2 p_t}{(2 + \xi)(1 - \xi)^2}$$

4) For the reaction,



equilibrium concentrations can be written as,

$$[\text{HI}] = \frac{0.740}{10.0} \text{ mol dm}^{-3} \quad (\text{since the volume of the container is } 10.0 \text{ dm}^3)$$

$$[\text{I}_2] = \frac{0.100}{10.0} \text{ mol dm}^{-3}$$

$$[\text{H}_2] = \frac{0.100}{10.0} \text{ mol dm}^{-3}$$

Substituting the values in the equilibrium constant expression,

$$\begin{aligned} K &= \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.0740)^2}{(0.0100) \cdot (0.0100)} \\ &= \frac{5.48 \times 10^{-3}}{1.00 \times 10^{-4}} = 54.8 \end{aligned}$$

Due to the addition of 0.500 mol of HI at equilibrium, the concentration of HI would become $(0.074 \text{ mol dm}^{-3} + 0.05 \text{ mol dm}^{-3}) = 0.124 \text{ mol dm}^{-3}$. The equilibrium will shift in such a direction so as to reduce the excess of added HI; that is, some more H_2 and I_2 will be formed. Suppose this amount is $x \text{ mol dm}^{-3}$ for each of these (H_2 and I_2) gases, then the new equilibrium concentrations would be,

$$[\text{H}_2] = (0.0100 + x) \text{ mol dm}^{-3}$$

$$[\text{I}_2] = (0.0100 + x) \text{ mol dm}^{-3}$$

$$[\text{HI}] = (0.124 - 2x) \text{ mol dm}^{-3}$$

Substituting the values in equilibrium expression, we get,

$$54.8 = \frac{(0.124 - 2x)^2}{(0.0100 + x)(0.0100 + x)}$$

$$\text{or } 7.40 = \frac{(0.124 - 2x)}{(0.0100 + x)}$$

$$0.0740 + 7.40x = (0.124 - 2x)$$

$$\text{or } 9.40x = 0.050$$

$$x = 5.3 \times 10^{-3}$$

Hence, $[\text{H}_2] = (0.01 + 0.0053) \text{ M} = 0.0153 \text{ M} = [\text{I}_2]$

and $[\text{HI}] = 0.113 \text{ M}$.

5) i) Initial concentration of $\text{NO}_2 = \frac{2.0 \text{ mol}}{2.0 \text{ dm}^3} = 1.0 \text{ mol dm}^{-3} = 1.0 \text{ M}$

Suppose that at equilibrium, $x \text{ mol dm}^{-3}$ of N_2O_4 is formed. Then,

$$[\text{NO}_2] = (1 - 2x) \text{ M}; [\text{N}_2\text{O}_4] = x \text{ M}$$

Substituting in the equilibrium constant expression, we get,

$$7.5 \text{ m}^3 \text{ mol}^{-1} = \frac{x \text{ mol m}^{-3}}{(1 - 2x)^2 (\text{mol m}^{-3})^2}$$

$$\text{or } 7.5 + 30x^2 - 31x = 0$$

$$\text{or } x = \frac{31 \pm \sqrt{(31)^2 - 120 \times 7.5}}{60}$$

$$x = \frac{31 \pm 7.8}{60} = 0.39 \text{ or } 0.65$$

If $x = 0.65$ value is considered, then

$$\begin{aligned} [\text{NO}_2] \text{ at equilibrium} &= (1 - 2x) \text{ M} \\ &= (1 - 1.30) \text{ M} \\ &= -0.30 \text{ M} \end{aligned}$$

This is meaningless and hence is discarded.

M stands for mol dm

We consider only the value, $x = 0.39$, since the second root of the equation has no physical significance.

$$[\text{NO}_2] = (1 - 2 \times 0.39) \text{ M} = (1 - 0.78) \text{ M} = 0.22 \text{ M}$$

$$[\text{N}_2\text{O}_4] = 0.39 \text{ M}$$

ii) When the volume of the container is doubled, initial concentration

$$\text{of NO}_2 = \frac{2.0 \text{ mol}}{4.0 \text{ dm}^3} = 0.5 \text{ mol dm}^{-3} = 0.5 \text{ M}$$

Following the same procedure as before, we get,

$$7.5 \text{ M}^{-1} = \frac{x \text{ M}}{(0.5 - 2x)^2 \text{ M}^2}$$

$$7.5(0.25 + 4x^2 - 2x) = x$$

$$1.875 + 30x^2 - 15x = x$$

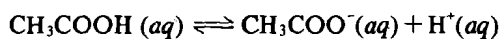
$$30x^2 - 16x + 1.875 = 0$$

$x = 0.17$ or 0.36 ; only the value $x = 0.17$ is considered since the other value has no physical significance.

Hence at equilibrium, $[\text{NO}_2] = (0.5 - 2x) \text{ M} = (0.5 - 0.34) \text{ M} = 0.16 \text{ M}$

$$[\text{N}_2\text{O}_4] = x \text{ M} = 0.17 \text{ M}.$$

- 6) i) $\nu_{\text{C}_2\text{H}_5\text{OH}} = +1$, $\nu_{\text{C}_2\text{H}_4} = -1$, and $\nu_{\text{H}_2\text{O}} = -1$,
 ii) $\nu_{\text{C}_2\text{H}_6} = +1$, $\nu_{\text{H}_2} = +1$ and $\nu_{\text{CH}_4} = -2$
- 7) If $K_p > 1$, $\Delta_r G^\circ$ is a negative quantity and the reaction is feasible.
- 8) The dissociation of acetic acid can be represented by the equation,



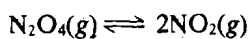
$$\begin{aligned} \Delta_r G^\circ &= (\text{sum of standard free energies of formation of } \text{CH}_3\text{COO}^- \text{ and } \text{H}^+ \text{ ions}) - \\ &\quad (\text{standard free energy of formation of acetic acid}) \\ &= [(-369.4 + 0) - (-396.6)] \text{ kJ mol}^{-1} \\ &= 27.2 \text{ kJ mol}^{-1} \end{aligned}$$

Let us represent the equilibrium constant for the dissociation of acetic acid as K_a .

$$\begin{aligned} \log K_a &= \frac{-\Delta_r G^\circ}{2.303 RT} \\ &= \frac{-27.2 \times 1000 \text{ J mol}^{-1}}{2.303 \times 8.314 \times 298.15 \text{ J mol}^{-1}} \end{aligned}$$

$$K_a = 1.72 \times 10^{-5}$$

- 9) For the reaction



$$\sum \nu_i = +2 - 1 = +1$$

According to Eq. 14.25,

$$\begin{aligned} K_c &= K_p (RT)^{-\sum \nu_i} \\ &= K_p (RT)^{-1} \\ &= \frac{1.4 \times 10^4 \text{ Pa}}{8.314 \times 303 \text{ J mol}^{-1}} \\ &= 5.56 \text{ mol m}^{-3} \end{aligned}$$