UNIT

7

Equilibrium-I

(Equilibrium Processes & Phase Equilibria)

SYLLABUS

Dynamic nature of equilibrium, Equilibrium in physical processes, Equilibrium in chemical processes, law of chemical equilibrium, derivation of the relationship between K_p and K_c, Le-Chatelier's principle.

7.1. Introduction

In discussing problems based on chemical equations in Unit-1 and thermochemical equations in Unit 5, it was assumed that the reactants react completely if taken in the ratio of their number of moles as represented by the balanced chemical equation. However, in a number of cases, it is observed that the reaction does not proceed to completion. Instead, the reaction mixture contains reactants as well as products whose concentrations remain constant so long as the conditions of temperature, pressure etc. are kept constant. The reaction is then said to be in equilibrium. Equilibrium is a general term which applies not only to chemical reactions but applies to physical changes as well e.g. ice and water are in equilibrium at 0° C and atmospheric pressure. Hence equilibrium may be defined as follows :

Equilibrium ***represents the state of a process in which the properties like temperature, pressure, concentration of the system do not show any change with the passage of time.***

In all processes which attain equilibrium, two opposing processes are involved. Equilibrium is attained when the rates of the two opposing processes become equal.

If the opposing processes involve only physical changes, the equilibrium is called **physical equilibrium.** ***If the opposing processes involve chemical changes i.e. the opposing processes are chemical reactions, the equilibrium is called*** **chemical equilibrium.**

In general, a chemical equilibrium is represented as

$$aA + bB \rightleftharpoons xX + yY$$

where A and B are the reactants and X and Y are the products. The double arrow between the reactants and products shows that the reaction is taking place in both the directions simultaneously.

Based on the extent of reaction before equilibrium is attained, chemical reactions may be classified into following three categories :

(*i*) Those reactions which proceed almost to completion *i.e.* concentrations of the reactants left is negligible.

(*ii*) Those reactions in which only a small amount of the reactants reacts and equilibrium is attained *i.e.* the amount of product formed is very small and the amounts of the reactants left at equilibrium are quite large.

(*iii*) Those reactions which proceed to such an extent that the concentrations of the reactants and products at equilibrium are comparable.

The extent to which the reaction proceeds before equilibrium is attained depends upon the experimental conditions. The aim of the industrial as well as laboratory reactions is to determine the conditions which help in getting larger amount of the desired product.

In this unit, we shall discuss some important aspects related to equilibrium in physical and chemical processes.

7.2. Equilibria in Physical Processes

The different types of equilibria involving physical changes alongwith suitable examples are briefly described below :

(1) Solid – Liquid equilibrium (*Melting of ice*). If some ice cubes alongwith some water at 0°C and normal atmospheric pressure are placed in a thermos flask so that no heat can enter or leave the system, the mass of ice and water is found to remain constant. However, the two opposing processes going on at equilibrium are melting of ice and freezing of water.

Rate of melting of ice = Rate of freezing of water

The equilibrium is represented as

$$H_2O\,(s) \rightleftharpoons H_2O\,(l)$$

At equilibrium,

The temperature at which the solid and liquid form of a pure substance are in equilibrium at the atmospheric pressure is called the normal freezing point or melting point of that substance.

(2) Liquid – Gas equilibrium (*Evaporation of water in a closed vessel*). Consider a closed vessel connected to a manometer and having arrangement for evacuation and addition of liquid into it, as shown in Fig. 7.1. Suppose the vessel is first evacuated. The level of mercury in both the limbs of the manometer will be same. Now suppose water is added into the vessel and the whole apparatus is allowed to stay at room temperature (or at the desired temperature by placing it in a thermostat). It is observed that the level of mercury in the left limb of the manometer begins to fall and that in the right limb begins to rise. However, after some time, the levels become constant. The system is then said to have attained equilibrium. This observation indicates that in the beginning, more and more of the water is changing into vapours (a process called *evaporation*). Ultimately, the amount of water vapours becomes constant *i.e.* now as much water changes into vapours, the same amount of water vapours change back into the liquid water (a process called *condensation*). Thus at equilibrium

Rate of evaporation = Rate of condensation

The equilibrium is represented as

$$H_2O\,(l) \rightleftharpoons H_2O\,(g)$$

The difference in the levels of mercury in the two limbs gives the *equilibrium vapour pressure* of water at the room temperature (or temperature of the thermostat), as already discussed in unit 2.

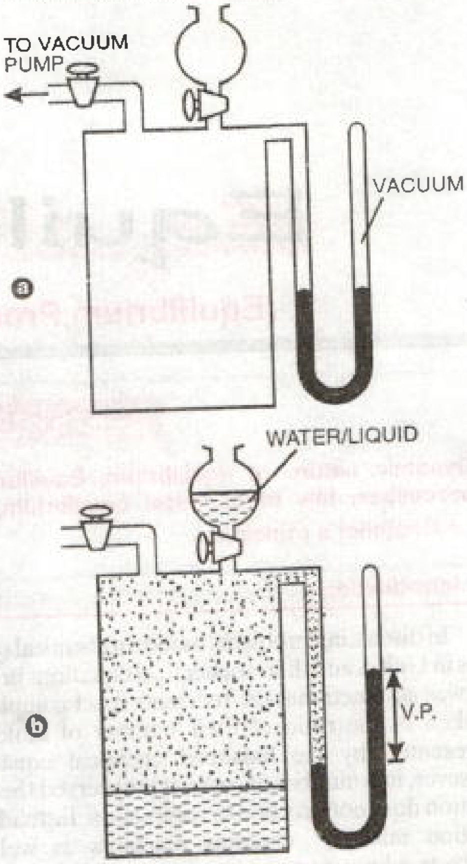

FIGURE 7.1. Method of studying the vapour pressure of a liquid (a) After evacuation but before adding the liquid (b) After adding the liquid into the evacuated vessel.

(3) Solid – Solution equilibrium (*Dissolution of sugar in water*). Suppose more and more of sugar is added into a fixed volume of water at room temperature and stirred thoroughly with a glass rod. First, the sugar will keep on dissolving but then a stage will come when no more sugar dissolves. Instead, it settles down at the bottom. The solution is now said to be saturated and in a state of equilibrium (Fig. 7.2). At this stage, as many molecules of sugar from the surface of the undissolved sugar go into the solution (a process called *dissolution*), the same number of molecules of sugar from the solution are deposited back on the surface of the undissolved sugar (a process called *precipitation*). As a result, the amount of the undissolved sugar

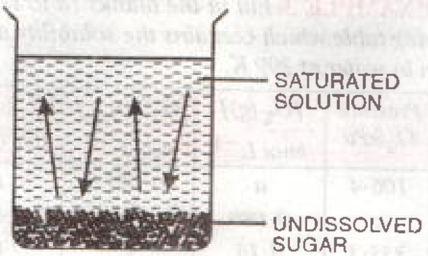

FIGURE 7.2. Equilibrium between undissolved sugar and saturated solution.

and the concentration of sugar in the solution remain constant.

Thus in this case, at equilibrium,

$$\boxed{\text{Rate of dissolution} = \text{Rate of precipitation}}$$

The equilibrium is written as

$$\text{Sugar (Solid)} \rightleftharpoons \text{Sugar (in solution)}$$

The amount of the solid in grams that dissolves in 100 g of the solvent to form a saturated solution at a particular temperature is called the solubility of that solid in the given solvent at that temperature.

(4) Gas – solution equilibrium (*Dissolution of a gas in a liquid under pressure in a closed vessel*). The best example of this type of equilibrium is that of a soda water bottle. The equilibrium that exists within the bottle is

$$CO_2\,(g) \rightleftharpoons CO_2\,(\text{in solution})$$

The amount of the gas dissolved is governed by **Henry's law** which states as follows : –

The mass of a gas dissolved in a given mass of a solvent at any temperature is directly proportional to the pressure of the gas above the solvent.

i.e. $\quad m \propto p \quad$ ***or*** $\quad m = kp$

where k is a constant of proportionality and is called Henry's constant. Its value depends upon the nature of the gas, nature of the liquid and temperature.

Alternatively, as the mass of the gas dissolved corresponds to the concentration of the gas in the solution and the pressure corresponds to the concentration of the gas above the solution (in the gaseous phase), we can write

$$\left[\begin{array}{l}\text{Concentration of the gas}\\ \text{in the aqueous solution}\end{array}\right] \propto \left[\begin{array}{l}\text{Concentration of the gas in the}\\ \text{gaseous phase}\end{array}\right]$$

or
$$\frac{\text{Concentration of gas in the aqueous solution}}{\text{Concentration of gas in the gaseous phase}}$$
$$(\textit{i.e.}\ \text{equilibrium pressure})$$
$$= \text{Constant at constant temperature}$$

e.g. for the equilibrium

$$CO_2\,(g) \rightleftharpoons CO_2\,(aq)$$

$$\frac{[CO_2\,(aq)]}{[CO_2\,(g)]} = \text{Constant at constant temperature.}$$

The reason why the gas fizzes out (bubbles out) when a soda water bottle is opened is as follows :

In the sealed soda water bottle, the pressure of the gas is very high above the liquid, so the mass of the CO_2 gas dissolved is also high. As soon as the bottle is opened, the pressure tends to decrease to atmospheric pressure, so the solubility decreases *i.e.* the dissolved gas escapes out.

To sum up, the results discussed above about physical equilibria are reproduced below :

(*i*) Solid $\rightleftharpoons$ liquid equilibrium exists only at one particular temperature *i.e.*, the melting point or freezing point. Thus for such an equilibrium, *temperature is constant*.

(*ii*) In liquid $\rightleftharpoons$ gas equilibrium, *the pressure of the vapours above the liquid (i.e. vapour pressure) is constant* at constant temperature.

(*iii*) In solid $\rightleftharpoons$ solution equilibrium, *the solubility of the solid in the solution is constant* at constant temperature.

(*iv*) In gas $\rightleftharpoons$ solution equilibrium, *the mass of the gas dissolved is constant* for constant equilibrium pressure at constant temperature.

PROBLEMS ON PHYSICAL EQUILIBRIA

EXAMPLE 1. *If 0.200 g of iodine is stirred in 100 cm*^{3} *of water at 298 K till equilibrium is reached, what will be the mass of iodine found in solution and the mass that is left undissolved. After equilibrium is reached with 0.200 g of iodine and 100 cm*^{3} *of water, we add 150 cm*^{3} *of water to the system. How much iodine will be dissolved and how much will be left undissolved and what will be the concentration of iodine in solution ?*

$[I_2\,(aq)]$ *at equilibrium* $= 0.0011\ mol\ L^{-1}$ *at 298 K*

Solution. As the solubility of iodine (concentration at equilibrium) is 0.0011 mol L^{-1} (Given), this means that at equilibrium,

1000 cm^3 of water dissolve I_2 = 0.0011 mole

= 0.0011 × 254 g

($\because$ Molar mass of I_2 = 254 g mol^{-1})

= 0.2794 g ≈ 0.28 g

$\therefore$ 100 cm^3 of water dissolve I_2 = **0.028 g**

$\therefore$ I_2 left undissolved = 0.200 − 0.028

= **0.172 g**

On adding 150 cm^3 of water to the above solution, total volume of water = 250 cm^3. As total solubility of iodine is 0.28 g L^{-1}, therefore iodine that will dissolve in 250 cm^3 of water

$$= \frac{0.28}{1000} \times 250 \text{ g} = \mathbf{0.070 \text{ g}}$$

$\therefore$ I_2 left undissolved = 0.200 − 0.070 g

= **0.130 g**

Molar concentration of the solution

$$= \frac{0 \cdot 130}{254} \times \frac{1}{250} \times 1000$$

$$= \mathbf{0 \cdot 0011 \text{ mol } L^{-1}}$$

EXAMPLE 2. *During bottling, a carbonated beverage was made by saturating flavoured water at 0° C with CO_2 at a pressure of 4.0 atm. Later, the bottle was opened and the soft drink allowed to come to equilibrium at 25° C with air containing CO_2 at a pressure of $4 \cdot 0 \times 10^{-4}$ atm. Find the concentration of CO_2 in the freshly bottled soda and in the soda after it had stood open and come to equilibrium. The Henry's constants for aqueous solution of CO_2 are*

At 0° C, $k = 7.7 \times 10^{-2}$ mol L^{-1} atm^{-1}

At 25° C, $k = 3.2 \times 10^{-2}$ mol L^{-1} atm^{-1}

Solution. By Henry's law, C = *kp* where C is gas concentration in solution, *p* is the partial pressure of that gas and *k* is Henry's constant.

(*a*) For the freshly bottled soft drink

C = *kp*

= (7.7×10^{-2} mol L^{-1} atm^{-1}) × (4.0 atm)

= **0 · 308 mol L^{-1}**

(*b*) For opened soft drink at equilibrium with atmospheric CO_2,

C = (3.2×10^{-2} mol L^{-1} atm^{-1}) × (4.0×10^{-4} atm)

= **$1 \cdot 28 \times 10^{-5}$ mol L^{-1}**

• EXAMPLE 3. *Fill in the blanks (a to i) in the following table which contains the solubility data of oxygen in water at 299 K.*

Expt.	*Pressure O_2/kPa*	*$[O_2(g)]$ /mol L^{-1}*	*$[O_2(aq)_{eq.}]$/ mol L^{-1}*	*$\frac{[O_2(aq)]_{eq.}}{[O_2(g)]_{eq.}}$*
I	*106·4*	*a*	*0·0012*	*b*
II	*c*	*0·080*	*d*	*0·029*
III	*333·3*	*0·13*	*e*	*0·029*
IV	*466·1*	*f*	*0·0053*	*g*
V	*598·8*	*h*	*i*	*0·028*

(N.C.E.R.T.)

Solution. Expt. I.

$$\mathbf{PV = nRT \text{ or } P = \frac{n}{V}RT = CRT}$$

$$\text{or} \quad \mathrm{C} = \frac{\mathrm{P}}{\mathrm{RT}}$$

$$= \frac{106 \cdot 4 \text{ kPa}}{(8 \cdot 314 \text{ kPa L K}^{-1} \text{ mol}^{-1})(299 \text{ K})}$$

$$= 0 \cdot 043 \text{ mol } L^{-1}$$

i.e. **$a = 0 \cdot 043$ mol L^{-1}**

$$\therefore \quad b = \frac{0 \cdot 0012}{a} = \frac{0 \cdot 0012}{0 \cdot 043} = \mathbf{0 \cdot 028}$$

Expt. II. $\frac{d}{0 \cdot 080} = 0 \cdot 029$

or **$d = 0 \cdot 0023$ mol L^{-1}**

$$\mathrm{P} = \mathrm{CRT} = 0 \cdot 080 \times 8 \cdot 314 \times 299$$

$$= 198 \cdot 9 \text{ kPa}$$

i.e. **$c = 198 \cdot 9$ kPa**

Expt. III. $\frac{e}{0 \cdot 13} = 0 \cdot 029$

or **$e = 00377$ mol L^{-1}**

Expt. IV. $f = \mathrm{C} = \frac{\mathrm{P}}{\mathrm{RT}}$

$$= \frac{466 \cdot 1}{8 \cdot 314 \times 299} = \mathbf{0 \cdot 187 \text{ mol } L^{-1}}$$

$$g = \frac{0 \cdot 0053}{f} = \frac{0 \cdot 0053}{0 \cdot 187} = \mathbf{0 \cdot 028}$$

Expt. V. $h = \mathrm{C} = \frac{\mathrm{P}}{\mathrm{RT}} = \frac{598 \cdot 8}{8 \cdot 314 \times 299}$

$$= \mathbf{0 \cdot 241 \text{ mol } L^{-1}}$$

$$\frac{i}{h} = 0 \cdot 028$$

$$\therefore \quad i = 0 \cdot 028 \times 0 \cdot 241 = \mathbf{0 \cdot 0067 \text{ mol } L^{-1}}.$$

7.3. General Characteristics of Equilibria Involving Physical Processes

Some of the important characteristics of physical equilibria are as follows :

1. *At equilibrium, some observable property of the system becomes constant (as explained in section 7.2).*

2. *Equilibria involving gases can be attained only in closed vessels.* This is because if the vessel is open, the gas will escape and there will be no equilibrium.

3. *Equilibrium is dynamic in nature i.e.* there are two opposing processes taking place at equal rates.

4. *At equilibrium, the concentrations of the different substances become constant at constant temperature* (as explained in equilibria (*ii*), (*iii*) and (*iv*) above)

5. *At equilibrium, there exists an expression involving the concentrations of the substances which is constant at constant temperature.*

e.g. for $CO_2(g) \rightleftharpoons CO_2(aq)$,

$$\frac{[CO_2(aq)]}{[CO_2(g)]} = \text{constant at constant temperature.}$$

This constant is called *equilibrium constant.*

6. *The magnitude of the equilibrium constant represents the extent to which the process proceeds before equilibruim is attained.* For example, greater value of the constant in the above case shows greater dissolution of CO_2 in water.

7.4. Equilibria in Chemical Processes

7.4.1. Reversible Reactions. In the various processes described above involving physical changes, we have seen that two opposing processes take place, the rates of which become equal when equilibrium is attained. When opposing processes take place in a chemical reaction, the reaction is said to be a reversible reaction. A reversible reaction may be defined more precisely as follows :

A reaction in which not only the reactants react to form the products under certain conditions but also the products react to form reactants under the same conditions is called a reversible reaction. In other words, a reaction which takes place not only in the forward direction but also in the backward direction under the same conditions is called a reversible reaction.

It is represented by putting a double arrow ($\rightleftharpoons$) between the reactants and the products, one arrow pointing towards the products and the other pointing towards the reactants. For example, a reversible reaction between A and B to form C and D is represented as

$$A + B \rightleftharpoons C + D$$

The concept of reversibility in a chemical reaction may be explained with the help of the following example :

If pieces of iron are placed in an *open glass tube* heated from below and steam is passed from the other end (Fig. 7.3 *a*), the following reaction takes place :

$$\underset{\text{Iron}}{3\,Fe\,(s)} + \underset{\text{Steam}}{4\,H_2O\,(g)} \longrightarrow \underset{\text{Iron oxide}}{Fe_3O_4\,(s)} + \underset{\text{Hydrogen}}{4H_2\,(g)}$$

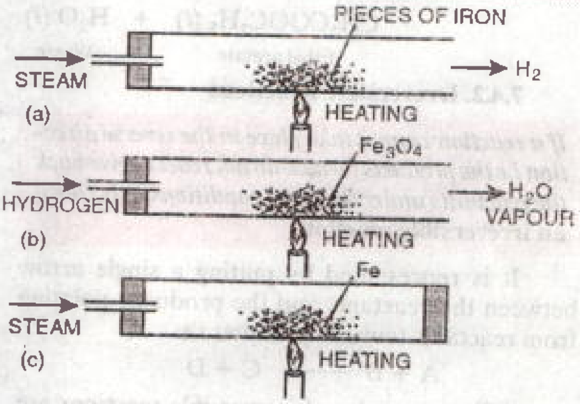

FIGURE 7.3. Reversible reaction occuring in a closed tube (c).

Again if in place of iron, iron oxide (Fe_3O_4) is placed in the tube, heated from below and hydrogen is passed over it (Fig. 7.3*b*), the following reaction takes place :

$$Fe_3O_4\,(s) + 4H_2\,(g) \longrightarrow \underset{\text{Iron}}{3Fe\,(s)} + \underset{\text{Water vapour}}{4H_2O\,(g)}$$

Since in both the above cases, the tube was open, hydrogen in the first case and water vapour in the second case escape out. However, if the *tube is closed* (Fig. 7.3 *c*), both the reactions take place simultaneously and hence the reaction becomes reversible. It may be represented as

$$3Fe\,(s) + 4H_2O\,(g) \rightleftharpoons Fe_3\,O_4\,(s) + 4H_2\,(g)$$

Obviously, whereas the first two reactions can go to completion (*i.e.* whole of iron can be converted into iron oxide in the first case and iron oxide into iron in the second case), the last reaction viz. the reversible reaction does not go to completion. In fact, ultimately, an *equilibrium mixture* of the various reactants and products is obtained in a reversible reaction (as will be discussed later).

A few more common examples of reversible reactions carried out in closed vessels are given below:

(*i*) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

(*ii*) $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

(*iii*) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

(*iv*) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

(*v*) $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

(*vi*) $\underset{\text{Acetic acid}}{CH_3COOH\,(l)} + \underset{\text{Ethyl alcohol}}{C_2H_5OH\,(l)} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5\,(l)} + \underset{\text{Water}}{H_2O\,(l)}$

7.4.2. Irreversible Reactions

If a reaction cannot take place in the reverse direction i.e the products formed do not react to give back the reactants under the same conditions, it is called **an irreversible reaction.**

It is represented by putting a single arrow between the reactants and the products, pointing from reactants towards products *i.e.*

$$A + B \longrightarrow C + D$$

A few examples of irreversible reactions are as follows :

(*i*) $AgNO_3\,(aq) + NaCl\,(aq) \longrightarrow AgCl\,(s) + NaNO_3\,(aq)$

(*ii*) $BaCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + NaCl\,(aq)$

(*iii*) $2Mg\,(g) + O_2\,(g) \longrightarrow 2MgO\,(s)$

It is interesting to note that a reversible reaction becomes irreversible if one of the products (which is gaseous) is allowed to escape out. It is for this reason that the reaction between iron and steam is irreversible if carried out in the open tube because hydrogen gas formed escapes out.

7.4.3. Concept of Chemical Equilibrium.

Consider the general reversible reaction

$$A + B \rightleftharpoons C + D$$

In the beginning (*i.e.* at time $t = 0$), the concentrations of A and B are maximum and the concentrations of C and D are minimum (equal to zero, because no C and D are yet formed). As the reaction proceeds, the concentrations of A and B are decreasing with the passage of time whereas the concentrations of C and D are increasing. Therefore, the rate of forward reaction is decreasing while the rate of backward reaction goes on increasing.

Ultimately a stage comes, when the rate of forward reaction becomes equal to the rate of backward reaction. The reaction is then said to be in a *state of chemical equilibrium*.

The variation of the reaction rates with time and ultimately the attainment of chemical equilibrium may be represented diagrammatically as shown in Fig. 7.4.*

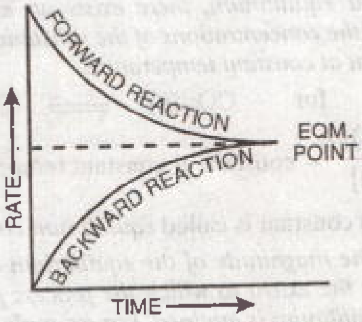

FIGURE 7.4. Variation in reaction rates for the forward and backward reaction with time.

Examples. The following examples illustrate how the equilibrium is attained :

(1) Decomposition of Calcium carbonate in a closed vessel. If calcium carbonate is heated in a closed vessel, the reaction is reversible as shown below :

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

If the temperature of the furnace is kept constant (say at 1073 K) and the vessel is connected to a manometer (Fig. 7.5), the pressure (due to CO_2 gas) first keeps on increasing and ultimately becomes constant. This is obviously due to the fact that now as much of CO_2 is formed from $CaCO_3$, the same amount of CO_2 reacts with CaO to give

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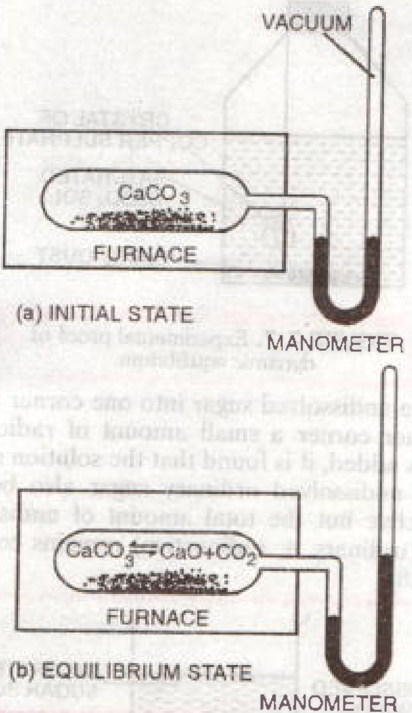
*This is the general diagram. For the evaporation of a liquid in a closed vessel, the diagram is different as discussed in unit 2, under Vapour Pressure.



(a) INITIAL STATE

(b) EQUILIBRIUM STATE

FIGURE 7.5. Equilibrium in the decomposition of $CaCO_3$

back $CaCO_3$. In other words, the rate of forward reaction and backward reaction have become equal. Hence the reaction has attained chemical equilibrium.

(2) Decomposition of N_2O_4 in a closed vessel. The decomposition of N_2O_4 in a closed vessel is a reversible reaction as represented below :

$$\underset{\text{(Colourless)}}{N_2O_4\,(g)} \rightleftharpoons \underset{\text{(Reddish brown)}}{2NO_2\,(g)}$$

N_2O_4 is almost stable at 0°C and is almost colourless. Thus if N_2O_4 is taken in a glass bulb which is then sealed and placed in ice, it is almost colourless. Now if the sealed glass bulb is shifted into a vessel containing water at 25°C, the bulb starts acquiring brown colour which first deepens and then becomes constant. This indicates a state of equilibrium in which the concentrations of N_2O_4 and NO_2 have become constant. That both are present in the reaction mixture can be tested by increasing the temperature of the bulb further when brown colour deepens (indicating more dissociation of N_2O_4) and by cooling the bulb down from 25°C when the brown colour fades (indicating combination of NO_2 molecules to form N_2O_4).

(3) Combination of H_2 and I_2 to form HI. It is a reversible reaction as represented below :

$$\underset{\text{(Colourless)}}{H_2\,(g)} + \underset{\text{(Purple)}}{I_2\,(g)} \rightleftharpoons \underset{\text{(Colourless)}}{2\,HI\,(g)}$$

If H_2 and I_2 (say in equimolar ratio) are enclosed in a glass bulb at 500°C, the colour is deep purple in the beginning but as the time passes, the intensity of the colour decreases and then no further change in colour is observed. This again indicates that the reaction has attained a state of equilibrium.

(4) Reaction between ferric nitrate and potassium thiocyanate solutions. It is again a reversible reaction and may be represented in the ionic form as follows :

$$\underset{\text{(Yellow)}}{Fe^{3+}\,(aq)} + \underset{\text{(Colourless)}}{(SCN)^-\,(aq)} \rightleftharpoons \underset{\text{(Deep red)}}{[Fe(SCN)]^{2+}\,(aq)}$$

The details of this reaction have been discussed later in Section 7.14.

7.4.4. Dynamic Nature of Chemical Equilibrium. When the equilibrium is reached, the most important observable property is that the concentration of each of the reactants and products becomes constant. For example, in the reaction between H_2 and I_2 to form HI, the colour becomes constant because the concentrations of H_2, I_2 and HI become constant. Similarly, in the decomposition of $CaCO_3$ in a closed vessel at a particular temperature, the amount of CO_2 becomes constant and in the dissociation of N_2O_4 at a particular temperature, the percentages of N_2O_4 and NO_2 become constant. Thus when the equilibrium is reached, it appears that the reaction has stopped. However, this is not the case. The reaction is still going on in the forward as well as backward direction but the rate of forward reaction becomes equal to the rate of backward reaction. In other words, as much of the reactants react to form the products, the same amount of products react to give back the reactants in the same time. Hence *the equilibrium is dynamic in nature and not static.*

Experiment to illustrate dynamic nature of chemical equilibrium. In the Haber's process, starting with definite amounts of N_2 and H_2 and carrying out the reaction at a particular temperature, when equilibrium is attained, the concentrations of N_2, H_2 and NH_3 become constant as shown in Fig. 7.6. If the experiment is repeated by taking deuterium (D_2) in place of H_2 but with the same amounts and exactly similar conditions as before, equlibrium is attained containing D_2 and ND_3 in place of H_2 and NH_3 but in the same amounts. Now if the two reaction mixtures are mixed, then after some time, it is found that the concentrations of ammonia and hydrogen are same except that now all forms of ammonia (*i.e.* NH_3, NH_2D, NHD_2, ND_3) and all forms of hydrogen (*i.e.* H_2, HD, D_2) are present. This shows that at equilibrium, the reaction is still going on *i.e.* equilibrium is dynamic in nature.

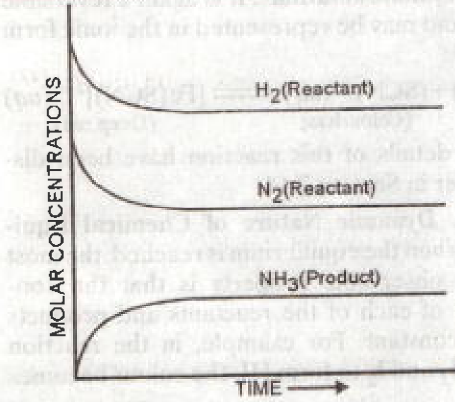


FIGURE 7.6. Representing the attainment of equilibrium for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons NH_3(g)$

Experiments to illustrate dynamic nature of physical equilibrium.

Expt. 1. Suspend a crystal of copper sulphate in a saturated solution of copper sulphate contained in a glass bottle (Fig. 7.7). After a few hours, the shape of the crystal is found to be deformed and $CuSO_4$ dust is found to accumulate at the bottom of the bottle. This shows that although the solution continues to remain saturated, the process of breaking away of the particles from the $CuSO_4$ crystal and the deposition of the particles from the solution on the crystal continue at the same rate. This is a special case of chemical equilibrium (called solubility equilibrium) in which rate of dissolution = rate of precipitation.

Expt. 2. In the system containing undissolved sugar in equilibrium with the dissolved sugar in the saturated solution, if the beaker is tilted so as to shift the undissolved sugar into one corner and at the other corner a small amount of radioactive sugar is added, it is found that the solution as well as the undissolved ordinary sugar also become radioactive but the total amount of undissolved sugar (ordinary + radioactive) remains constant (Fig. 7.8).

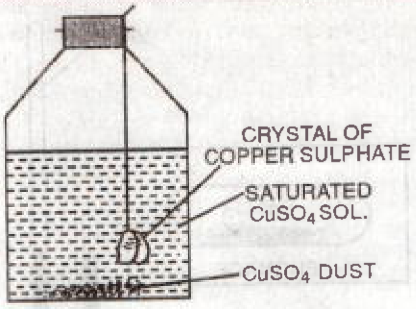


FIGURE 7.7. Experimental proof of dynamic equilibrium.

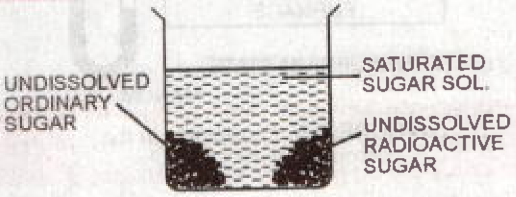


FIGURE 7.8. Experimental proof of dynamic equilibrium.

This experiment clearly proves that after the attainment of equilibrium, the sugar molecules are breaking off from the surface of the solid sugar and passing into the solution but the same number of sugar molecules from the solution are being deposited back on the surface of the solid sugar.

Analogies to illustrate dynamic nature of equilibrium. The following analogies will help to understand the dynamic nature of equilibrium more clearly :

(*i*) Suppose in a chicken-house, there are two compartments separated by a door. Suppose one compartment has white chickens and the other has brown chicknes. If the door is now opened, some chickens from each compartment rush to the other compartment. After some time, however, a stage comes when as many chickens of each type leave each compartment as enter it and the percentage of white and brown chickens in each compartment becomes constant. Though the equilibrium is said to have been reached, the movement of chickens does not stop.

(*ii*) If in a vessel fitted with a tap and containing some water, the water is coming in and going out at the same speed, the level of water in the vessel remains constant (Fig. 7.9). Thus it appears as if nothing is happening to the water of the vessel.

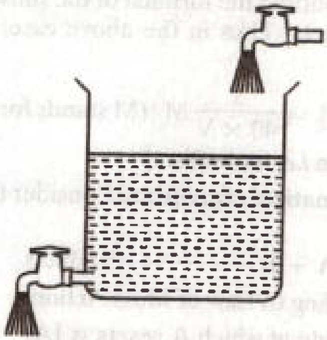


FIGURE 7.9. Rate of inflow = Rate of outflow (level remains constant)

7.4.5. Characteristics of Chemical Equilibrium. Some of the important characteristics of chemical equilibrium are follows :

(i) At equilibrium, the concentration of each of the reactants and the products becomes constant.

The experiments showing the constancy of pressure in the evaporation of water and decomposition of calcium carbonate and constancy of colour at equilibrium in the decomposition of N_2O_4 (already discussed in section 7.4.3) prove the above characteristic.

(ii) At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and hence the equilibrium is dynamic in nature.

The experimental proofs for this property have already been discussed in section 7.4.4.

(iii) A chemical equilibrium can be established only if none of the products is allowed to escape out or separate out as a solid.

This is obvious because if any product is allowed to escape out *e.g.* CO_2 gas in case of decomposition of $CaCO_3$, the reaction will no longer remain reversible. A chemical equilibrium has a meaning only for a reversible reaction.

Similarly, the reaction is irreversible if one of the products separates out as solid *e.g.,*

$$AgNO_3 + KCl \longrightarrow AgCl \downarrow + KNO_3$$

(iv) Chemical equilibrium can be attained from either direction i.e. from the direction of the reactants as well as from the direction of the products.

To understand this characteristic, let us reconsider the reaction

$$\underset{\text{(Colourless)}}{N_2O_4\,(g)} \rightleftharpoons \underset{\text{(Reddish brown)}}{2NO_2\,(g)}$$

Suppose two identical glass bulbs A and B are filled with NO_2 gas at the same pressure. The bulb A is placed in ice and the bulb B is placed in boiling water (Fig. 7.10). The gas in bulb A is found to be almost colourless whereas in bulb B it is found to be reddish brown. Experiments show that most of the molecules in bulb A have the formula N_2O_4 whereas most of the molecules in bulb B have the formula NO_2. Now suppose both the bulbs are placed in a vessel containing water at 298 K. It is observed that the colour in the bulb A deepens whereas the colour in the bulb B fades. Obviously, the reaction taking place in bulb A is

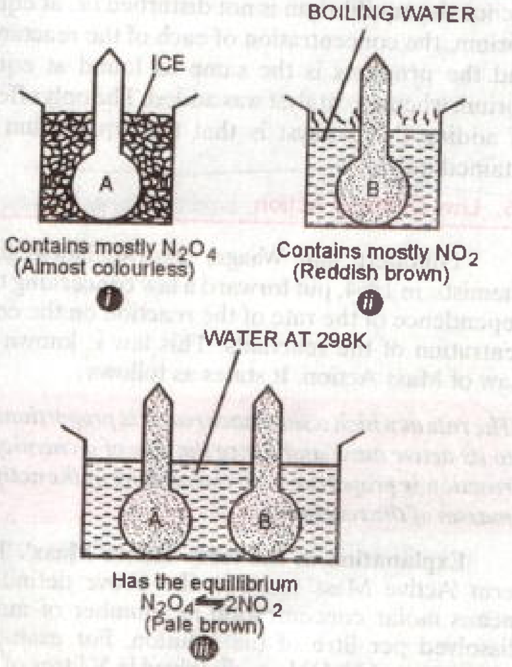


FIGURE 7.10. Equilibrium reaction $N_2O_4 \rightleftharpoons 2NO_2$ at (i) 273 (ii) 373K and (iii) 298K.

$$\underset{\text{(Colourless)}}{N_2O_4} \longrightarrow \underset{\text{(Reddish brown)}}{2NO_2}$$

whereas the reaction taking place in bulb B is

$$\underset{\text{(Reddish brown)}}{2\,NO_2} \longrightarrow \underset{\text{(Colourless)}}{N_2O_4}$$

Ultimately, the colour in the two bulbs becomes identical and no further colour change occurs. This shows a state of equilibrium in both the bulbs. Thus the equilibrium can be reached from either side.

Similarly, reconsider the reaction

$$\underset{\text{(Colourless)}}{H_2\,(g)} + \underset{\text{(Purple)}}{I_2\,(g)} \rightleftharpoons \underset{\text{(Colourless)}}{2\,HI\,(g)}$$

If 1 mole of H_2 and 1 mole of I_2 are taken in bulb A at 500°C and 2 moles of HI are taken in an identical bulb B at 500° C, the intensity of colour in bulb A decreases while that of the bulb B increases and ultimately both have the same intensity of colour. This again proves that the equilibrium can be attained from either direction.

(v) A catalyst does not alter the state of equilibrium

This is obviously due to the fact that a catalyst increases the speed of the forward reaction as well as that of the backward reaction to the same extent. Hence the equilibrium is not disturbed *i.e.* at equilibrium, the concentration of each of the reactants and the products is the same as found at equilibrium when no catalyst was added. The only effect of adding the catalyst is that the equilibrium is attained quickly.

7.5. Law Of Mass Action

Guldberg and Waage, the two Norwegian chemists, in 1864, put forward a law concerning the dependence of the rate of the reaction on the concentration of the reactants. This law is known as Law of Mass Action. It states as follows :

The rate at which a substance reacts is proportional to its active mass and hence the rate of a chemical reaction is proportional to the product of the active masses of the reactants.

Explanation of the term 'Active Mass'. The term 'Active Mass' used in the above definition means molar concentration *i.e.* number of moles dissolved per litre of the solution. For example, suppose x g of NaOH are dissolved in V litres of the solution. Then we can say :

Concentration of NaOH solution

$$= x \text{ g in V litres}$$

$$= \frac{x}{40} \text{ moles in V litres}$$

$$(\because \text{Molar mass of NaOH} = 40 \text{ g mol}^{-1})$$

$$= \frac{x}{40 \times V} \text{ moles/litre}$$

This is the active mass of the given NaOH solution.

The active mass of a substance is usually represented by putting the formula of the substance in square brackets. Thus in the above case, we can write

$$[NaOH] = \frac{x}{40 \times V} \text{ M} \quad \text{(M stands for 'Molar'}$$

concentration *i.e.* moles/litre)

Mathematical expression. Consider the reaction

$$A + B \longrightarrow \text{Products}$$

According to Law of Mass Action,

$$\text{Rate at which A reacts} \propto [A]$$

$$\text{Rate at which B reacts} \propto [B]$$

$$\therefore \text{ Rate at which A and B react together}$$

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

where k is a constant of proportionality and is called *'velocity constant'*.

Again, consider the reaction

$$2A + 3B \longrightarrow \text{Products}$$

It can be written as

$$A + A + B + B + B \longrightarrow \text{Products}$$

$$\text{Rate at which first A reacts} \propto [A]$$

$$\text{Rate at which second A reacts} \propto [A]$$

$$\therefore \text{ Rate at which A reacts} \propto [A]\,[A] = [A]^2$$

Similarly rate at which B reacts

$$\propto [B]\,[B]\,[B] = [B]^3$$

$$\therefore \text{ Rate of reaction between A and B}$$

$$\propto [A]^2\,[B]^3$$

Hence, for the most general reaction

$$aA + bB + cC + \ldots \longrightarrow \text{Products}$$

$$\text{Rate of reaction} \propto [A]^a\;[B]^b\;[C]^c \ldots\ldots$$

Thus the Law of Mass Action may be defined in a more general way as follows :

The rate of a reaction is proportional to the product of the active masses of the reactants, each raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation.

7.6. Law of Chemical Equilibrium

Law of Chemical Equilibrium is a result obtained by applying the Law of Mass Action to a reversible reaction in equilibrium. For example, consider the general reversible reaction

$$A + B \rightleftharpoons C + D$$

At equilibrium, suppose the active masses of A, B, C and D are represented as [A], [B], [C] and [D] respectively. Applying the Law of Mass Action,

Rate at which A and B react together *i.e.* Rate of the forward reaction $\propto [A]\,[B]$

$$= k_f [A]\,[B]$$

where k_f is a constant of proportionality and is called velocity constant for the forward reaction.

Similarly, Rate at which C and D react together *i.e.* Rate of the backward reaction

$$\propto [C]\,[D]$$

$$= k_b [C]\,[D]$$

where k_b represents the velocity constant for the backward reaction.

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$$k_f [A]\,[B] = k_b [C]\,[D]$$

$$\text{or} \quad \frac{[C]\,[D]}{[A]\,[B]} = \frac{k_f}{k_b} = K$$

At constant temperature, as k_f and k_b are constant, therefore, $k_f/k_b = K$ is also constant at constant temperature and is called **'Equilibrium constant'**.

[**Note :** By convention, the active masses of the products are written in the numerator and those of the reactants in the denominator].

Again, consider the more general reversible reaction

$$aA + bB + \ldots\ldots \rightleftharpoons xX + yY + \ldots\ldots$$

Applying the Law of Mass Action, as before, we get

$$\frac{[X]^x\,[Y]^y \ldots\ldots}{[A]^a\,[B]^b \ldots\ldots} = K \text{ or } K_c \quad \ldots(i)$$

where K is equilibrium constant. It is constant at constant temperature.

The above mathematical equation is called the Law of Chemical Equilibrium. Expressed in words, it may be defined as follows :

***The product of the molar concentrations of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar concentrations of the reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temperature and is called* Equilibrium constant.**

It is customary to use K_c for equilibrium constant expressed in terms of concentrations. Where there is no doubt that K is in terms of concentration, *c* is omitted.

Concentration Quotient or Reaction Quotient and Predicting the direction of reaction. *For the reaction*

$$aA + bB \rightleftharpoons xX + yY,$$

at any stage of the reaction, other than the stage of chemical equilibrium, concentration ratio given on the L.H.S. of eqn. (i) is called concentration quotient or reaction quotient. It is usually represented by Q_c or Q. Thus

$$\textit{Concentration quotient, } Q_c = \frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b}$$

(i) If Q = K, the reaction is in equilibrium

(ii) If Q > K, Q will tend to decrease so as to become equal to K. As a result, the reaction will proceed in the backward direction.

(iii) If Q < K, Q will tend to increase. As a result, the reaction will proceed in the forward direction.

The three cases may be represented diagrammatically as follows :

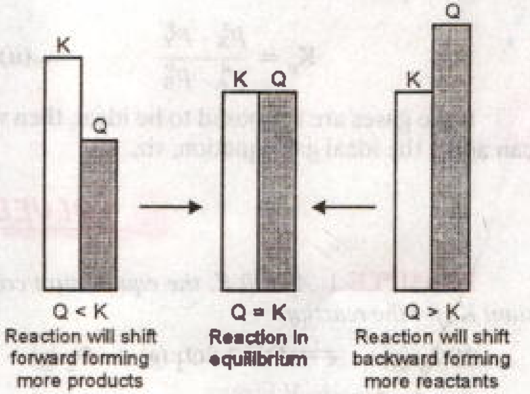


FIGURE 7.11. Direction of shift of reaction depending upon the value of Q as compared with K.

For Gas-phase Reactions, (*i.e.* when the reactants and the products are gaseous), the equilibrium constant can be expressed either in terms of concentrations in moles per litre or in terms of the partial pressures of the reactants and the products. If expressed in terms of partial pressures, it is denoted by K_p. Thus if A, B, X and Y are gaseous in the above general reaction, we can write

$$\boxed{K_p = \frac{p_X^x \cdot p_Y^y}{p_A^a \cdot p_B^b}}$$

where p_A, p_B, p_X and p_Y are the partial pressures of A, B, X and Y respectively in the reaction mixture at equilibrium. It may be noted that the pressures in the above equation are taken in *atmospheres or bars or pascals* (in SI units).

7.7. Relationship between Kp and Kc

Consider the general reversible reaction

$$aA + bB \rightleftharpoons xX + yY$$

If the equilibrium constant for this reaction is expressed in terms of concentrations, we may write

$$K_C = \frac{[X]^x\ [Y]^y}{[A]^a\ [B]^b}$$

or simply as $K_C = \dfrac{C_X^x \cdot C_Y^y}{C_A^a \cdot C_B^b}$ ...(*i*)

where C_A, C_B, C_X and C_Y represent the molar concentrations of A, B, X and Y respectively.

If A, B, X and Y are gaseous, the equilibrium constant for the above reaction may be expressed in terms of pressures as

$$K_p = \frac{p_X^x \cdot p_Y^y}{p_A^a \cdot p_B^b} \quad \text{...}(ii)$$

If the gases are supposed to be ideal, then we can apply the ideal gas equation, viz.

$$pV = n\,RT \quad \text{or} \quad p = \frac{n}{V}RT = CRT$$

$$\left[\because \frac{n}{V} = \text{no. of moles/litre} = C \text{ (molar concentration)}\right]$$

$\therefore$ For the gases A, B, X and Y, we may write

$$p_A = C_A\,RT, \qquad p_B = C_B\,RT,$$

$$p_X = C_X\,RT \quad \text{and} \quad p_Y = C_Y\,RT$$

Putting these values in equation (*ii*), we get

$$K_p = \frac{(C_X\,RT)^x \cdot (C_Y\,RT)^y}{(C_A\,RT)^a \cdot (C_B\,RT)^b}$$

$$= \frac{C_X^x \cdot C_Y^y\ (RT)^{x+y}}{C_A^a \cdot C_B^b\,(RT)^{a+b}}$$

$$= \frac{C_X^x \cdot C_Y^y}{C_A^a \cdot C_B^b}(RT)^{(x+y)-(a+b)}$$

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

where $K_c = \dfrac{C_X^x \cdot C_Y^y}{C_A^a \cdot C_B^b}$ according to equation (*i*)

and $\Delta n = (x + y) - (a + b)$

= No. of moles of products – No. of moles of reactants

= Change in the number of moles

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

As the partial pressures are taken in atmospheres, the value of R to be used in the above equation will be 0.0821 litre atmospheres/degree/mole. Temperature T will, of course, be in degree Kelvin (°K).

Further, as already mentioned in unit 1 and unit 2,

1 pascal, Pa = 1 Nm^{-2} and 1 bar = 10^5 Pa.

If pressure is expressed in bars,

R = 0·0831 litre bar K^{-1} mol^{-1}.

SOLVED EXAMPLE

EXAMPLE 1. *At 700 K, the equilibrium constant K_p for the reaction*

$$2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$$

is 1.80×10^{-3} k Pa. What is the numerical value of K_c in moles per litre for this reaction at the same temperature ?

Solution. Here n_p = 3 moles, n_r = 2 moles

$\therefore \quad \Delta n = n_p - n_r = 3 - 2 = 1$ mole

$$K_p = 1.80 \times 10^{-3}\ \text{kPa}$$

$$= 1{\cdot}80\ \text{Pa} = \frac{1{\cdot}80}{10^5}\ \text{bar}$$

$$= 1{\cdot}80 \times 10^{-5}\ \text{bar}$$

$$R = 0\cdot 0831 \text{ L bar K}^{-1}\text{ mol}^{-1}$$
$$T = 700 \text{ K}$$

Using the relation,

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

$$K_c = \frac{K_p}{RT} = \frac{1.80 \times 10^{-5}\text{ bar}}{0\cdot 0831 \text{ L bar K}^{-1}\text{ mol}^{-1} \times 700 \text{ K}}$$
$$= \mathbf{3\cdot 09 \times 10^{-7}\ mol\ L^{-1}}$$

Alternatively,

$$K_c = \frac{K_p}{RT} = \frac{1\cdot 8 \text{ Pa}}{(8\cdot 314 \text{ JK}^{-1}\text{ mol}^{-1})\,(700 \text{ K})}$$
$$= \frac{1\cdot 8 \text{ Nm}^{-2}}{(8\cdot 314 \text{ Nm K}^{-1}\text{mol}^{-1})\,(700 \text{ K})}$$
$$(\because \text{Pa} = \text{Nm}^{-2},\ \text{J} = \text{Nm})$$
$$= 3\cdot 09 \times 10^{-4}\text{ mol m}^{-3}$$
$$= \mathbf{3\cdot 09 \times 10^{-7}\ mol\ dm^{-3}\ or\ mol\ L^{-1}}$$

Note. With respect to standard state pressure of 1 bar, $K_p = 1\cdot 80$ *i.e.* dimensionless. Similarly with respect to standard state concentration of 1 mol L^{-1}, $K_c = 3\cdot 09 \times 10^{-7}$ *i.e.* dimensionless (as discussed later in section 7.12).

• **EXAMPLE 2.** *AT 773 K, the equilibrium constant K_c for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is $6\cdot 02 \times 10^{-2}\ L^2\ mol^{-2}$. Calculate the value of K_p at the same temperature.*

Solution. $\Delta n_g = 2 - 4 = -2$

$$K_p = K_c\,(RT)^{\Delta n}$$
$$= 6\cdot 02 \times 10^{-2}\text{ L}^2\text{ mol}^{-2}\,(0\cdot 0821 \text{ L atm K}^{-1}\text{ mol}^{-1} \times 773 \text{ K})^{-2}$$
$$= \mathbf{1\cdot 5 \times 10^{-5}\ atm^{-2}}$$

PROBLEMS FOR PRACTICE

1. K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is $0\cdot 157$ atm at 27°C and 1 atm pressure. Calculate K_c for the reaction. **[Ans. $6\cdot 37 \times 10^{-3}$ mol L^{-1}]**

2. For the reaction $A(g) + B(s) \rightleftharpoons C(g) + D(g)$, $K_c = 49$ mol dm^{-3} at 127°C. Calculate K_p. **[Ans. $1\cdot 61 \times 10^3$ atm]**

3. Find out the value of K_c for each of the following equilibria from the value of K_p

   (*a*) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, $K_p = 1\cdot 8 \times 10^{-2}$ at 500 K

   (*b*) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_p = 167$ at 1073 K.

   [Ans. (*a*) $4\cdot 33 \times 10^{-4}$ (*b*) $1\cdot 87$]

HINTS FOR DIFFICULT PROBLEMS

1. $\Delta n = n_p - n_r = 2 - 1 = 1,\ K_c = K_p / (RT)^{\Delta n}$

$$= (0\cdot 157 \text{ atm})/(0\cdot 0821 \text{L atm K}^{-1}\text{ mol}^{-1} \times 300\text{K})^1$$
$$= 6\cdot 37 \times 10^{-3}\text{ mol L}^{-1}.$$

2. $\Delta n = n_p - n_r = 2 - 1 = 1,\ K_p = K_c\,(RT)^{\Delta n}$

$$= (49 \text{ mol dm}^{-3})\,(0\cdot 0821 \text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1} \times 400 \text{ K})^1 = 1\cdot 61 \times 10^3\text{ atm}.$$

3. (*a*) $\Delta n_g = 3 - 2 = 1,\quad K_p = K_c\,(RT)$

$$\text{or}\quad K_c = \frac{K_p}{RT} = \frac{1\cdot 8 \times 10^{-2}}{0\cdot 0831 \times 500}$$
$$(R = 0\cdot 0831 \text{ bar litre mol}^{-1}\text{ K}^{-1})$$
$$= 4\cdot 33 \times 10^{-4}$$

(*b*) $\Delta n_g = 1 - 0 = 1,$

$$K_c = \frac{K_p}{RT} = \frac{167}{0\cdot 0831 \times 1073} = 1\cdot 87$$

ADD TO YOUR KNOWLEDGE

1. **Law of chemical equilibrium in term of a activities.** Stricitly speaking, activities are used in place of molar concentrations.

   Activity = Activity coefficient × Molality (or molarity) *i.e.* $a = \gamma \times m$

   For the reaction $aA + bB \rightleftharpoons cC + dD$, we write $K_a = \dfrac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$

2. **Equilibrium constant in terms of mole fractions (K_x).** Consider the general gaseous reaction

   $$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

   If at equilibrium, the mole fractions of A, B, C and D are x_A, x_B, x_C and x_D respectively then $K_x = \dfrac{x_C^c \cdot x_D^d}{x_A^a\, x_B^b}$.

3. **Relationship between K_p and K_x.** Considering the above general gaseous reaction again, if P is the total pressure of the reaction mixture at equilibrium, then partial pressures of A, B, C and D will be

   $$p_A = x_A\,P, \quad p_B = x_B\,P, \quad p_C = x_C\,P, \quad p_D = x_D\,P$$

   Applying Law of Chemical Equilibrium $K_p = \dfrac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} = \dfrac{(x_C\,P)^c \cdot (x_D\,P)^d}{(x_A\,P)^a\,(x_B\,P)^b} = \dfrac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b}\,\dfrac{P^{c+d}}{P^{a+b}} = K_x\,(P)^{\Delta n}$

   where $\Delta n = n_p - n_r = (c+d) - (a+b)$.

4. From the relation $K_p = K_c\,(RT)^{\Delta n}$, we may conclude that

   (*i*) If $\Delta n = 0$, $K_p = K_c$ (*ii*) If $\Delta n = +\text{ve}$ (*i.e.* $n_p > n_r$), $K_p > K_c$ (*iii*) If $\Delta n = -\text{ve}$ (*i.e.* $n_p < n_r$), $K_p < K_c$

7.8. Characteristics of Equilibrium Constant

Some of the important characteristics of equilibrium constant are as follows :

(i) The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start or the direction from which the equilibrium is approached.

For example, for the reaction between acetic acid and ethyl alcohol at 25°C, the value of the equilibrium constant is found to be 4.0., *i.e.* for the reaction

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetale}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O}$$

$$K_c \text{ at } 25°C = \frac{[CH_3COOC_2\,H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5\,OH]} = 4 \cdot 0$$

(ii) If the reaction is reversed, the value of the equilibrium constant is inversed.

For example, if the above reaction is written in the reverse manner i.e. as

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

the value of the equilibrium constant will be

$$K'_c = \frac{[CH_3COOH]\,[C_2H_5\,OH]}{[CH_3COOC_2\,H_5]\,[H_2O]} = \frac{1}{K_C} = \frac{1}{4} = 0 \cdot 25 \text{ at } 25°C$$

(iii) If the equation (having equilibrium constant K) is divided by 2, the equilibrium constant for the new equation is the square root of K (i.e. $\sqrt{K}$).

For example, if K is the equilibrium constant for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad ...(i)$$

then for the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3 \quad ...(ii)$$

the value of equilibrium constant, $K' = \sqrt{K}$

It is obvious because

$$K = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}, \qquad \text{[For reaction } (i)]$$

$$K' = \frac{[NH_3]}{[N_2]^{1/2}\,[H_2]^{3/2}} = \sqrt{K} \quad \text{[For reaction } (ii)]$$

(iv) If the equation (having equilibrium constant K) is multiplied by 2, the equilibrium constant for the new equation is the square of K (i.e., K²).

It can be seen in a manner similar to the above.

(v) If the equation (having equilibrium constant K) is written in two steps (having equilibrium constant K₁ and K₂) then K₁ × K₂ = K.

For example, consider the reaction

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

$$\text{For this reaction, } K = \frac{[NO_2]^2}{[N_2]\,[O_2]^2}$$

Suppose the above reaction takes place in two steps as

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$\text{For the 1st step, } K_1 = \frac{[NO]^2}{[N_2]\,[O_2]}$$

$$\text{For the 2nd step, } K_2 = \frac{[NO_2]^2}{[NO]^2\,[O_2]}$$

$$\therefore K_1 \times K_2 = \frac{[NO]^2}{[N_2]\,[O_2]} \times \frac{[NO_2]^2}{[NO]^2\,[O_2]}$$

$$= \frac{[NO_2]^2}{[N_2]\,[O_2]^2} = K$$

[according to equation (*i*)]

The characteristics (*ii*) to (*v*) are summarized in the Table below.

TABLE 7.1. Variation of equilibrium constant with variation of the reaction equation (K = equilibrium constant for original reaction)

When the equation is	the new equilibrium constant is
Reversed	$1/K$
Divided by 2	$\sqrt{K}$
Multiplied by 2	K^2
Divided into 2 steps	$K = K_1 \times K_2$

***(vi) Prediction of the extent of reaction.** The magnitude of the equilibrium constant gives an idea of the relative amounts of the reactants and the products.*

(*a*) Large value of the equilibrium constant ($> 10^3$) shows that forward reaction is favoured *i.e.* concentration of products is much larger than that of the reactants at equilibrium *e.g.* for the reactions

$$H_2\,(g) + Br_2\,(g) \rightleftharpoons 2\,HBr\,(g)$$

$$K_p = 5{\cdot}4 \times 10^{18}$$

$$H_2\,(g) + Cl_2\,(g) \rightleftharpoons 2\,HCl\,(g),$$

$$K_p = 4{\cdot}0 \times 10^{31}$$

This shows that at equilibrium, concentration of the products *i.e.* HBr and HCl is very high *i.e.* the reactions go almost to completion.

(*b*) Intermediate value of K (10^{-3} to 10^3) shows that the concentrations of the reactants and products are comparable *e.g.* for the reaction

$$Fe^{3+}\,(aq) + SCN^-\,(aq) \rightleftharpoons [Fe(SCN)]^{2+}\,(aq),$$

$$K_c = 138 \text{ at } 298\text{ K}$$

(*c*) Low value of K ($< 10^{-3}$) shows that backward reaction is favoured *i.e.* concentration of reactants is much larger than that of the products *i.e.* the reaction proceeds to a very small extent *e.g.* for the reaction

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g),$$

$$K_c = 4{\cdot}8 \times 10^{-31} \text{ at } 298\text{ K}$$

This shows that at equilibrium, the mixture contains mainly N_2 and O_2 and very little of NO.

(vii) The value of the equilibrium constant is not affected by the addition of a catalyst to the reaction.

This is because the catalyst increases the speed of the forward reaction and the backward reaction to the same extent.

7.9. Effect of Temperature on the Equilibrium Constant

The numerical value of the equilibrium constant for a particular reaction is constant as long as the temperature is kept constant. It is a well known fact that the rate of a chemical reaction increases with increase in temperature. However, the extent of this increase in rate depends upon the energy of activation of the reaction. Now, since the energy of activation for the forward and backward reactions are different, so a given increase in temperature will increase the rate of the forward and backward reactions to different extents. In other words, the values of the velocity constants for forward and backward reactions *i.e.* k_f and k_b will change differently with a given rise or fall in temperature. Further since $K = k_f/k_b$, therefore, the value of the equilibrium constant (K) will change *i.e.*, the state of equilibrium is altered. Thus we conclude that the equilibrium constant for a particular reaction changes with temperature. Further, it has been found that the value of the equilibrium constant of an endothermic reaction increases (k_f increases more than k_b) and that of an exothermic reaction decreases (k_b increases more than k_f) with rise in temperature. For reactions having zero heat of reaction, temperature has no effect on the value of K.

Quantitatively, the effect of temperature on the equilibrium constant is given by **van't Hoff equation,** viz.

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

where ΔH° is the standard enthalpy change of the reaction or in the **integrated form,** it may be written as (assuming ΔH° to be constant in the temperature range T_1 to T_2)

$$\log \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H^\circ}{2 \cdot 303\, R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

where $(K_p)_1$ = equilibrium constant at temperature T_1

$(K_p)_2$ = equilibrium constant at temperature T_2

R = gas constant

7.10. Types of Chemical Equilibria

There are two types of chemical equilibria. These are

(i) Homogeneous Equilibria :

When in an equilibrium reaction, all the reactants and the products are present in the same phase (i.e. gaseous or liquid), it is called a homogeneous equilibrium.

Examples of the reactions in the **gaseous phase** are :

Type I : *in which the number of moles of products is equal to the number of moles of reactants*

$$H_2 + I_2 \rightleftharpoons 2\,HI$$

$$N_2 + O_2 \rightleftharpoons 2\,NO$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Type II : *in which the number of moles of products is not equal to the number of moles of reactants*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$N_2O_4 \rightleftharpoons 2NO_2$$

Two common examples of the reactions in the liquid phase are

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

$$Fe^{3+}(aq) + (SCN)^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$$

(ii) Heterogeneous Equilibria :

When in an equilibrium reaction, the reactants and the products are present in two or more than two phases, it is called a heterogeneous equilibrium.

A few common examples are as follows :

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

$$3Fe\,(s) + 4H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s) + 4H_2\,(g)$$

$$C\,(s) + H_2O\,(g) \rightleftharpoons \underbrace{CO\,(g) + H_2\,(g)}_{\text{Water gas}}$$

7.11. Writing Expression for Equilibrium Constant (K) or Reaction Quotient (Q)

In writing expressions for the equilibrium constant, the most important convention to be kept in mind is that *the active mass of a pure solid is constant irrespective of its amount and if a pure liquid is present in excess (e.g. as a solvent), its active mass is also constant. In either case, we put their active mass equal to 1* (because their constant values are included into the equilibrium constant) *i.e.* we put

$$[\text{Pure solid}] = 1, [\text{Pure liquid}] = 1.$$

The reason why molar concentration of a pure solid or a pure liquid is taken as constant is explained below :

Molar concentration of a substance means moles L^{-1} of the substance which is obtained by dividing the amount of the substance in moles by the volume of the substance in litres

$$i.e. \text{ Molar conc.} = \frac{\text{Moles of the substance}}{\text{Volume of the substance}}$$

Converting moles into mass, we can write

Molar conc.

$$= \frac{\text{Mass of the substance/Molecular mass}}{\text{Volume of the substance}}$$

$$= \frac{\text{Mass of the substance}}{\text{Volume of the substance}} \times \frac{1}{\text{Molecular mass of the substance}}$$

$$= \frac{\text{Density of the substance}}{\text{Molecular mass of the substance}}$$

As density of a particular pure substance at a particular temperature is constant (being an *intensive property* depending only on the nature of the substance and not on the amount) and molecular mass of the substance is also constant, therefore, molar concentration is constant.

A few examples are given below :

(A) For Homogeneous Equilibrium

(*i*) For the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_c = \frac{[HI(g)]^2}{[H_2(g)]\,[I_2(g)]}, \quad K_p = \frac{p^2_{HI}}{p_{H_2} \times p_{I_2}}$$

(*ii*) For the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)]\,[H_2(g)]^3}, \quad K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}}$$

(*iii*) For the reaction

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

$$K_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}, \quad K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}$$

(*iv*) For the reaction

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

$$K_c = \frac{[PCl_3(g)]\,[Cl_2(g)]}{[PCl_5(g)]},$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

(*v*) For the reaction

$$Fe^{3+}(aq) + (SCN)^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$$

$$K_c = \frac{[Fe(SCN)^{2+}(aq)]}{[Fe^{3+}(aq)]\,[(SCN)^-(aq)]}$$

(*vi*) For the reaction

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Here no liquid is present in excess, hence

$$K = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

(*vii*) For the reaction

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K = \frac{[NH_4^+(aq)]\,[OH^-(aq)]}{[NH_3(aq)]\,[H_2O(l)]}$$

As H_2O is present in excess (being the solvent) therefore by convention, $[H_2O]$ is constant and put equal to 1. Hence we write

$$K = \frac{[NH_4^+(aq)]\,[OH^-(aq)]}{[NH_3(aq)]}$$

(B) For Heterogeneous Equilibria

(*i*) For the reaction

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

Applying the law of chemical equilibrium, we have

$$K = \frac{[CaO(s)]\,[CO_2(g)]}{[CaCO_3(s)]}$$

But by convention, we put $[CaO(s)] = 1$ and $[CaCO_3(s)] = 1$

Hence $K = [CO_2 (g)]$

Since the concentration of a gas is usually expressed in terms of partial pressures, hence we better write $K_p = p_{CO_2}$

This explains why pressure of CO_2 becomes constant when equilibrium is attained in the decomposition of $CaCO_3$ in a closed vessel.

(*ii*) For the reaction

$$3Fe\,(s) + 4H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s) + 4H_2\,(g)$$

Applying the law of chemical equilibrium, we have

$$K_c = \frac{[Fe_3O_4\,(s)]\,[H_2\,(g)]^4}{[Fe\,(s)]^3\,[H_2O\,(g)]^4}$$

But by convention, we put $[Fe_3O_4\,(s)] = 1$ and $[Fe\,(s)] = 1$

Hence $K_c = \dfrac{[H_2\,(g)]^4}{[H_2O\,(g)]^4}$

or in terms of pressures, $K_p = \dfrac{p^4_{H_2}}{p^4_{H_2O}}$

Taking the 4th root of both the sides

$$K'_p = \frac{p_{H_2}}{p_{H_2O}}$$

(*iii*) For the equilibrium

$$H_2O\,(l) \rightleftharpoons H_2O\,(g)$$

$$K_c = \frac{[H_2O\,(g)]}{[H_2O\,(l)]}$$

But by convention, we put $[H_2O\,(l)] = 1$

Hence $K_c = [H_2O\,(g)]$

or in terms of pressures, $K_p = p_{H_2O\,(g)}$

This explains why vapour pressure of water is constant at constant temperature.

(*iv*) For the reaction

$$Cu(s) + 2Ag^+\,(aq) \rightleftharpoons Cu^{2+}\,(aq) + 2Ag\,(s)$$

$$K_c = \frac{[Cu^{2+}\,(aq)]\,[Ag\,(s)]^2}{[Cu\,(s)]\,[Ag^+\,(aq)]^2}$$

By convention, putting $[Ag\,(s)] = 1$, and $[Cu\,(s)] = 1$, we have

$$K_c = \frac{[Cu^{2+}\,(aq)]}{[Ag^+\,(aq)]^2}$$

7.12. Units of Equilibrium Constant

For the general reaction

$$a\,A + b\,B \rightleftharpoons x\,X + y\,Y$$

$$K_c = \frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b} = \frac{(\text{mol L}^{-1})^{x+y}}{(\text{mol L}^{-1})^{a+b}}$$

$$= (\text{mol L}^{-1})^{(x+y)-(a+b)} = (\text{mol L}^{-1})^{\Delta n}$$

$$K_p = \frac{p^x_X\,p^y_Y}{p^a_A\,p^b_B} = \frac{(\text{atm})^{x+y}}{(\text{atm})^{a+b}} \text{ or } \frac{(\text{bar})^{x+y}}{(\text{bar})^{a+b}}$$

$$= (\text{atm or bar})^{(x+y)-(a+b)} = (\text{atm})^{\Delta n} \text{ or } (\text{bar})^{\Delta n}$$

Evidently if $\Delta n = 0$ *i.e.* number of moles of products = number of moles of reactants, K_c or K_p will have no units.

For example, in case of reactions

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$$

$$\text{or} \quad N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$$

K_c or K_p will have no units (as $n_p = n_r$ *i.e.* $\Delta n = 0$)

For the reaction

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g),$$

as $\Delta n = 2 - (1 + 3) = -2$

K_c has the units $(\text{mol L}^{-1})^{-2}$ and K_p has the units atm^{-2} or bar^{-2}

Similarly, for the reaction

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

as $\Delta n = 2 - 1 = 1$

K_c has the units mol L^{-1} and K_p has the units atm or bar.

Why K_c or K_p are taken as dimensionless ? Now a days, activities are used in place of molar concentrations or pressures. These represent concentrations or pressures with respect a standard state concentration (c_0) of 1 mol L^{-1} or standard state pressure (p_0) of 1 bar. Thus a pressure of 5 bar with respect to a standard state pressure of 1 bar means 5 bar/1 bar = 5, a dimensionless quantity. Similarly, a concentration of $0 \cdot 5$ mol L^{-1} with respect to standard state of 1 mol L^{-1} means $0 \cdot 5$ mol L^{-1}/1 mol L^{-1} = $0 \cdot 5$, again a dimensionless quantity. Hence K_c or K_p are dimensionless.

However, the magnitude of the equilibrium constant will depend upon the standard state chosen.

PROBLEMS ON LAW OF CHEMICAL EQUILIBRIUM

EXAMPLE 1. *For the reaction,*

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

the concentration of an equilibrium mixture at 298 K are $N_2O_4 = 4{\cdot}50 \times 10^{-2}$ *mole/litre and* $NO_2 = 1{\cdot}61 \times 10^{-2}$ *mole/litre. What is the value of equilibrium constant ?*

Solution. $K = \dfrac{[NO_2]^2}{[N_2O_4]}$

Taking concentrations with respect to standard state concentration of 1 mol L^{-1}, we have

$$K = \frac{(1.61 \times 10^{-2})^2}{4.50 \times 10^{-2}} = \mathbf{5.76 \times 10^{-3}}$$

EXAMPLE 2. *For an equilibrium reaction, the rate constants for the forward and the backward reaction are* 2.38×10^{-4} *and* 8.15×10^{-5} *respectively. Calculate the equilibrium constant for the reaction.*

Solution. Equilibrium constant $K = \dfrac{k_f}{k_b}$

$$= \frac{2.38 \times 10^{-4}}{8.15 \times 10^{-5}} = \mathbf{2.92}$$

EXAMPLE 3. *In a reaction between* H_2 *and* I_2 *at a certain temperature, the amounts of* H_2, I_2 *and HI at equilibrium were found to be 0.45 mole, 0.39 mole and 3.0 moles respectively. Calculate the equilibrium constant for the reaction at the given temperature.*

Solution. The reaction between H_2 and I_2 may be represented as

$$H_2 + I_2 \rightleftharpoons 2HI$$

Amounts of H_2, I_2 and HI at equilibrium are given to be

$$H_2 = 0.45 \text{ mole}, \; I_2 = 0.39 \text{ mole}$$

and $\quad HI = 3.0$ mole

Suppose the volume of the vessel (*i.e.* reaction mixture) = V litres.

Then the molar concentrations at equilibrium will be

$$[H_2] = \frac{0.45}{V}, \; [I_2] = \frac{0.39}{V}$$

and $\quad [HI] = \dfrac{3.0}{V}$ moles/litre

Applying the law of chemical equilibrium to the above reaction, we get

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(3.0/V)^2}{(0.45/V)\,(0.39/V)}$$

$$= \frac{(3.0)^2}{0.45 \times 0.39} = \mathbf{51.28}$$

EXAMPLE 4. *Two moles of* PCl_5 *were heated to 327°C in a closed two litre vessel and when equilibrium was achieved,* PCl_5 *was found to be 40% dissociated into* PCl_3 *and* Cl_2*. Calculate the equilibrium constants* K_p *and* K_c *for this reaction.*

Solution. PCl_5 dissociates as

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial anount of PCl_5 = 2 moles (*Given*)

% age dissociation at equilibrium = 40%

$\therefore$ PCl_5 dissociated at equilibrium

$$= 40/100 \times 2 = 0.8 \text{ mole}$$

$\therefore$ Amounts of PCl_5, PCl_3 and Cl_2 at equilibrium will be

$$PCl_5 = 2 - 0.8 = 1.2 \text{ mole}$$

$$PCl_3 = 0.8 \text{ mole}$$

$$Cl_2 = 0.8 \text{ mole}$$

[$\because$ 1 mole of PCl_5 on dissociation gives 1 mole of PCl_3 and 1 mole of Cl_2]

Since the volume of the vessel is 2 litres, therefore, the molar concentrations at equilibrium will be

$$[PCl_5] = \frac{1.2}{2} = 0{\cdot}6 \text{ mol } L^{-1}$$

$$[PCl_3] = \frac{0{\cdot}8}{2} = 0{\cdot}4 \text{ mol } L^{-1}$$

and $\quad [Cl_2] = \dfrac{0{\cdot}8}{2} = 0{\cdot}4 \text{ mol } L^{-1}$

Applying the law of chemical equilibrium to the dissociation equilibrium, we get

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{0{\cdot}4 \times 0.4}{0{\cdot}6} = \mathbf{0{\cdot}267}$$

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

Here $\quad \Delta n = n_p - n_r = 2 - 1 = 1$

$$\therefore \quad K_p = K_c\,(RT)$$

But T = 327 + 273 = 600 K (Given)

R = 0.0821 litre atmosphere/degree/mole

$$\therefore \quad K_p = 0.267 \times 0.0821 \times 600 = \mathbf{13 \cdot 15}$$

• **EXAMPLE 5.** *For the reaction,*

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g),$$

the partial pressures of N_2 and H_2 are 0.80 and 0.40 atmosphere respectively at equilibrium. The total pressure of the system is 2.80 atmospheres. What is K_p for the above reaction ?

Solution. The reaction is

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

We are given that at equilibrium

$$p_{N_2} = 0.80 \text{ atmosphere}$$

$$p_{H_2} = 0.40 \text{ atmosphere}$$

$$p_{N_2} + p_{H_2} + p_{NH_3} = 2.80 \text{ atmosphere}$$

$$\therefore \quad p_{NH_3} = 2.80 - (0.80 + 0.40) = 1.60 \text{ atmospheres.}$$

Applying the law of chemical equilibrium, we get (taking pressures with respect to standard state pressure of 1 atm)

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}} = \frac{(1 \cdot 60)^2}{0 \cdot 80 \times (0 \cdot 40)^3} = \mathbf{50 \cdot 0}$$

• **EXAMPLE 6.** *0.1 mole of PCl_5 is vaporised in a litre vessel at 260°C. Calculate the concentration of Cl_2 at equilibrium, if the equilibrium constant for the dissociation of PCl_5 is 0.0414.*

Solution. Suppose the concentration of Cl_2 at equilibrium is x moles/litre. Then we will have

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
Initial conc.	0.1 mole	0	0
Conc. at eqm. (moles/litre)	$(0.1 - x)$	x	x

Applying the law of chemical equilibrium, we get

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

Here $K_c = 0 \cdot 0414$ (*Given*)

$$\therefore \quad 0 \cdot 0414 = \frac{x \times x}{(0 \cdot 1 - x)}$$

or $$\frac{x^2}{0 \cdot 1 - x} = 0 \cdot 0414$$

or $$x^2 + 0 \cdot 0414\,x - 0 \cdot 00414 = 0$$

$$x = \frac{-0 \cdot 0414 \pm \sqrt{(0 \cdot 0414)^2 - 4 \times 1 \times (-0 \cdot 00414)}}{2}$$

$$\left[\text{Using the formula } x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$= \frac{-0 \cdot 0414 \pm \sqrt{0 \cdot 0017 + 0 \cdot 1656}}{2}$$

$$= \frac{-0 \cdot 0414 + 0 \cdot 01826}{2}$$

$$= \frac{-0 \cdot 0414 \pm 0 \cdot 135}{2}$$

$$= 0 \cdot 0468 \text{ mol L}^{-1}$$

(The negative value of x is meaningless and hence is rejected)

Thus the concentration of Cl_2 at equlibrium will be **0·0468 mol L^{-1}**.

• **EXAMPLE 7.** *Ethyl acetate (an ester) is formed by reaction between ethanol and acetic acid according to the reaction*

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$$

(a) Starting with 1·00 mol of acetic acid and 0·180 mol of ethanol at 293 K, the equilibrium mixture is found to contain 0·171 mol of ethyl acetate. Calculate the equilibrium constant.

(b) Starting with 0·500 mol of ethanol and 1·000 mol of acetic acid again at 293 K, the mixture is found to contain 0·214 mol of ethyl acetate. Has equilibrium been attained ? **(N.C.E.R.T.)**

Solution. (*a*)

	$CH_3COOH +$	$C_2H_5OH \rightleftharpoons$	$CH_3COOC_2H_5 +$	H_2O
Initial	1·00 mol	0·180 mol		
At eqm.	1−0·171 = 0·829 mol	0·180−0·171 = 0·009 mol	0·171 mol	0·171 mol
Molar concs.	0·829/V	0·009/V	0·171/V	0·171/V

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$= \frac{(0 \cdot 171/V)\,(0 \cdot 171/V)}{(0 \cdot 829/V)\,(0 \cdot 009/V)} = 3 \cdot 92$$

(*b*) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial	1·000 mol	0·500 mol		
At eqm.	1−0·214 = 0·786 mol	0·500−0·214 = 0·286 mol	0·214 mol	0·214 mol

Reaction quotient (Q_c)

$$= \frac{(0\cdot214/V)\,(0\cdot214/V)}{(0\cdot786/V)\,(0\cdot286/V)} = 0\cdot204$$

As $Q_c \neq K_c$, equilibrium has not been attained.

EXAMPLE 8. *The equilibrium constant at 278 K for*

$$Cu\,(s) + 2Ag^+\,(aq) \rightleftharpoons Cu^{2+}\,(aq) + 2Ag\,(s)$$

is 2.0×10^{15}. *In a solution in which copper has displaced some silver ions from the solution, the concentration of* Cu^{2+} *ions is* 1.8×10^{-2} *mol* L^{-1} *and the concentration of* Ag^+ *ions is* 3.0×10^{-9} *mol* L^{-1}. *Is this system at equilibrium ?*

Solution. Applying the law of chemical equilibrium to the given reaction, we have

$$K = \frac{[Cu^{2+}\,(aq)]\,[Ag\,(s)]^2}{[Cu(s)]\,[Ag^+\,(aq)]^2}$$

By convention, putting $[Ag\,(s)] = 1$

and $[Cu\,(s)] = 1$,

$$K = \frac{[Cu^{2+}\,(aq)]}{[Ag^+\,(aq)]^2}$$

With respect to standard state concentration of 1 mol L^{-1}, we put $[Cu^{2+}] = 1\cdot8 \times 10^{-2}$

and $[Ag^+] = 3\cdot0 \times 10^{-9}$

We get $K = \dfrac{1\cdot8 \times 10^{-2}}{(3\cdot0 \times 10^{-9})^2} = 2 \times 10^{15}$

which is same as for the reaction in equilibrium. Hence the given system is in equilibrium.

EXAMPLE 9. *In the equilibrium* $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$, *at 1073 K, the pressure of* CO_2 *is found to be* $2\cdot5 \times 10^4$ *Pa. What is the equilibrium constant of this reaction at 1073 K ?*

Solution. With reference to the standard state pressure of 1 bar *i.e.* 10^5 Pa,

$$K_p = p_{CO_2} = \frac{2\cdot5 \times 10^4\ \text{Pa}}{p^0}$$

$$= \frac{2\cdot5 \times 10^4\ \text{Pa}}{10^5\ \text{Pa}} = \mathbf{0\cdot25}$$

EXAMPLE 10. AB_2 *dissociates as*

$$AB_2\,(g) \rightleftharpoons AB\,(g) + B\,(g).$$

If the initial pressure is 500 mm of Hg and the total pressure at equilibrium is 700 mm of Hg, calculate K_p *for the reaction.*

Solution. After dissociation, suppose the decrease in the pressure of AB_2 at equilibrium is p mm. Then

	$AB_2\,(g) \rightleftharpoons$	$AB\,(g)$ +	$B\,(g)$
Initial pressure	500 mm	0	0
Pressures at eqm.	$(500-p)$ mm	p mm	p mm

∴ Total pressure at equilibrium

$= 500 - p + p + p = 500 + p$ mm

$500 + p = 700$ (*Given*) or $p = 200$ mm

Hence at equilibrium

$$p_{AB_2} = 500 - 200 = 300\ \text{mm},$$

$$p_{AB} = 200\ \text{mm},\quad p_B = 200\ \text{mm}$$

$$\therefore\ K_p = \frac{p_{AB} \times p_B}{p_{AB_2}} = \frac{200 \times 200}{300} = \mathbf{133\cdot3\ mm}$$

Note. With respect to standard state pressure of 1 bar *i.e.* 0·987 atm *i.e.* 750 mm,

$$K_p = \frac{133\cdot3}{750} = \mathbf{0\cdot178.}$$

EXAMPLE 11. *Under what pressure must an equimolar mixture of* PCl_3 *and* Cl_2 *be placed at 250°C in order to obtain* PCl_5 *at 1 atm ? (*K_p *for dissociation of* $PCl_5 = 1\cdot78$*).*

Solution. Suppose partial pressure of PCl_3 at equilibrium $= p$ atm

Then partial pressure of Cl_2 at equilibrium $= p$ atm

Partial pressure of PCl_5 at equilibrium $=$ 1 atm

For dissociation of PCl_5,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$K_p = 1\cdot78 = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{p \times p}{1} = p^2$$

$$\therefore\quad p = \sqrt{1\cdot78} = 1\cdot33\ \text{atm}$$

$$\therefore\quad \text{Total pressure} = p_{PCl_5} + p_{PCl_3} + p_{Cl_2}$$

$$= 1 + 1\cdot33 + 1\cdot33$$

$$= \mathbf{3\cdot66\ atm}$$

EXAMPLE 12. *At 448°C, the equilibrium constant (K_c) for the reaction*

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 50·5. Predict the direction in which the reaction will proceed to reach equilibrium at 448°C, if we start with $2 \cdot 0 \times 10^{-2}$ mol of HI, $1 \cdot 0 \times 10^{-2}$ mol of H_2 and $3 \cdot 0 \times 10^{-2}$ mol of I_2 in a 2·0 L container.

Solution. The initial concentrations are

$$[HI] = \frac{2 \cdot 0 \times 10^{-2}}{2} \text{ mol L}^{-1} = 1 \cdot 0 \times 10^{-2} \text{ mol L}^{-1}$$

$$[H_2] = \frac{1 \cdot 0 \times 10^{-2}}{2} \text{ mol L}^{-1} = 0 \cdot 5 \times 10^{-2} \text{ mol L}^{-1}$$

$$[I_2] = \frac{3 \cdot 0 \times 10^{-2}}{2} \text{ mol L}^{-1} = 1 \cdot 5 \times 10^{-2} \text{ mol L}^{-1}$$

$$\text{Reaction quotient, } Q = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(1 \cdot 0 \times 10^{-2})^2}{(0 \cdot 5 \times 10^{-2}) \times (1 \cdot 5 \times 10^{-2})} = 1 \cdot 3$$

Since Q < K, the reaction will proceed in the forward direction to attain equilibrium so that Q becomes equal to K.

EXAMPLE 13. *The degree of dissociation of PCl_5 at a certain temperature and atmospheric pressure is 0·2. Calculate the pressure at which it will be half (50%) dissociated at the same temperature.*

Solution. Suppose α is the degree of dissociation, then

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial conc.	1 mole		0		0
At. eqm.	$1-\alpha$		α		α

$\therefore$ Total number of moles at equilibrium

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

If P is the total pressure at equilibrium, then partial pressures will be

$$p_{PCl_3} = \frac{\alpha}{1+\alpha} P, \quad p_{Cl_2} = \frac{\alpha}{1+\alpha} P, \quad p_{PCl_5} = \frac{1-\alpha}{1+\alpha} P$$

$$\therefore \quad K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

$$= \frac{\left(\frac{\alpha}{1+\alpha} P\right) \times \left(\frac{\alpha}{1+\alpha} P\right)}{\left(\frac{1-\alpha}{1+\alpha} P\right)} = \frac{\alpha^2}{1-\alpha^2} \cdot P$$

We are given that at P = 1 atm, $\alpha = 0 \cdot 2$. Hence

$$K_p = \frac{(0 \cdot 2)^2}{1 - (0 \cdot 2)^2} \times 1 = \frac{0 \cdot 04}{0 \cdot 96} = 0 \cdot 0417.$$

When dissociation is 50%, *i.e.* $\alpha = 0 \cdot 5$, suppose total pressure is P′. Then

$$0 \cdot 0417 = \frac{(0 \cdot 5)^2}{1 - (0 \cdot 5)^2} \times P' = \frac{0 \cdot 25}{0 \cdot 75} \times P'$$

or $\quad$ **P′ = 0·125 atm**

EXAMPLE 14. *Determine the concentration of CO_2 which will be in equilibrium with $2 \cdot 5 \times 10^{-2}$ mol L^{-1} of CO at 100°C for the reaction*

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g), \quad K_c = 5 \cdot 0$$

Solution. $K_c = \frac{[CO_2]}{[CO]}$ *i.e.* $5 = \frac{[CO_2]}{2 \cdot 5 \times 10^{-2}}$

or $\quad [CO_2] = 5 \times 2 \cdot 5 \times 10^{-2}$

$$= \mathbf{12 \cdot 5 \times 10^{-2} \text{ mol L}^{-1}}$$

EXAMPLE 15. *At a certain temperature and a total pressure of 10^5 Pa, iodine vapour contain 40% by volume of iodine atoms [$I_2(g) \rightleftharpoons 2I(g)$]. Calculate K_p for the equilibrium.* **(N.C.E.R.T.)**

Solution. Partial pressure of I atoms

$$(p_I) = \frac{40}{100} \times 10^5 \text{ Pa} = 0 \cdot 4 \times 10^5 \text{ Pa}$$

Partial pressure of I_2 $(p_{I_2}) = \frac{60}{100} \times 10^5$ Pa

$$= 0 \cdot 60 \times 10^5 \text{ Pa}$$

$$K_p = \frac{p_I^2}{p_{I_2}} = \frac{(0 \cdot 4 \times 10^5)^2}{0 \cdot 60 \times 10^5} = \mathbf{2 \cdot 67 \times 10^4}$$

EXAMPLE 16. *The equilibrium constant for the reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ at 1024 K is $1 \cdot 6 \times 10^5$. Find the equilibrium pressure of all gases if 10·0 bar of HBr is introduced into a sealed container at 1024 K.* **(N.C.E.R.T.)**

Solution.

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g), \quad K = \frac{1}{(1 \cdot 6 \times 10^5)}$$

	$2HBr(g)$	$H_2(g)$	$Br_2(g)$
Initial	10 bar		
At eqm.	$10-p$	$p/2$	$p/2$

$$K_p = \frac{(p/2)(p/2)}{(10-p)^2} = \frac{1}{1 \cdot 6 \times 10^5}$$

$$\frac{p^2}{4(10-p)^2} = \frac{1}{1 \cdot 6 \times 10^5}$$

Taking square root of both sides, we get

$$\frac{p}{2\,(10-p)} = \frac{1}{4 \times 10^2}$$

or $4 \times 10^2\, p = 2\,(10 - p)$

or $402\, p = 20$

or $p = \frac{20}{402} = 4 \cdot 98 \times 10^{-2}$ bar

Hence at equilibrium

$$p_{H_2} = p_{HBr} = p/2 = 2 \cdot 5 \times 10^{-2}\ \textbf{bar},$$

$$p_{HBr} = 10 - p \approx 10\ \textbf{bar}$$

EXAMPLE 17. *At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90·55% CO by mass in the reaction*

$$C\,(s) + CO_2\,(g) \rightleftharpoons 2\,CO\,(g)$$

Calculate K_c for this reaction at the above temperature. (N.C.E.R.T.)

Solution. If total mass of the mixture of CO and CO_2 is 100 g, then

CO = 90·55 g and CO_2 = 100−90·55 = 9·45 g

∴ Number of moles of CO = 90·55/28 = 3·234

Number of moles of CO_2 = 9·45/44 = 0·215

$$\therefore\ p_{CO} = \frac{3 \cdot 234}{3 \cdot 234 + 0 \cdot 215} \times 1\ \text{atm} = 0 \cdot 938\ \text{atm}$$

$$p_{CO_2} = \frac{0 \cdot 215}{3 \cdot 234 + 0 \cdot 215} \times 1\ \text{atm} = 0 \cdot 062\ \text{atm}$$

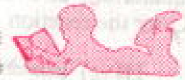
$$K_p = \frac{p^2_{CO}}{p_{CO_2}} = \frac{(0 \cdot 938)^2}{0 \cdot 062} = 14 \cdot 19.$$

$$\Delta n_g = 2 - 1 = 1$$

$$\therefore\quad K_p = K_c\,(RT)$$

$$\text{or}\ K_c = \frac{K_p}{RT} = \frac{14 \cdot 19}{0 \cdot 0821 \times 1127} = 0 \cdot 153.$$

PROBLEMS FOR PRACTICE



1. In a reaction between hydrogen and iodine, 6.34 moles of hydrogen and 4.02 moles of iodine are found to be in equilibrium with 42.85 moles of hydrogen iodide at 350°C. Calculate the equilibrium constant. **[Ans. 72.042]**
2. Calculate the equilibrium constants K_p and K_c for the reaction

   $$CO\,(g) + 1/2\,O_2\,(g) \rightleftharpoons CO_2\,(g)$$

   Given that the partial pressures at equilibrium in a vessel at 3000 K are

   p_{co} = 0.4 atm. p_{co_2} = 0.6 atm and p_{O_2} = 0.2 atm

   [Ans. K_p = 3.354, K_c = 52.64]
3. 1.5 moles of PCl_5 are heated at constant temperature in a closed vessel of 4 litre capacity. At the equilibrium point, PCl_5 is 35% dissociated into PCl_3 and Cl_2. Calculate the equilibrium constant. **[Ans. 0·071]**
4. The equilibrium composition for the reaction is

   $$\underset{0.20}{PCl_3} + \underset{0.10}{Cl_2} \rightleftharpoons \underset{0.40\ \text{moles/litre}}{PCl_5}$$

   What will be the equilibrium concentration of PCl_5 on adding 0.10 mole of Cl_2 at the same temperature ? **[Ans. 0·45 mol L^{-1}]**
5. If 1 mole of acetic acid and 1 mole of ethyl alcohol are mixed and the reaction proceeds to equilibrium, the concentrations of acetic acid and water are found to be 1/3 and 2/3 mole respectively. If 1 mole of ethyl acetate and 3 moles of water are mixed, how much ester is present when equilibrium is reached ? **[Ans. 0.465 mole]**
6. Calculate the degree of dissociation of HI at 450°C if the equilibrium constant for the dissociation reaction is 0.263. **[Ans. 0·51]**
7. One mole of pure ammonia was injected into a one litre flask at a certain temperature. The equilibrium mixture was then analysed and found to contain 0.30 mole of H_2. Calculate (*i*) the concentration of N_2 and (*ii*) the concentration of NH_3 at equilibrium. **[Ans. (*i*) 0.10 mol L^{-1} (*ii*) 0.80 mol L^{-1}]**
8. How much PCl_5 must be added to a one litre vessel at 250° C in order to obtain a concentration of 0.1 mole of chlorine ? Equilibrium constant for the dissociation of PCl_5 at 250°C is 0.0414. **[Ans. 0.3415 mole]**
9. In an experiment, 2 moles of HI are taken into an evacuated 10.0 litre container at 720K. The equilibrium constant equals to 0.0156 for the gaseous reaction $2\,HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$

   Calculate the amounts of HI, H_2 and I_2 at equilibrium.

   [Ans. HI = 1.6 mole H_2 = 0.2 mole I_2 = 0.2 mole]
10. For the reaction

    $$Cu\,(s) + 2\,Ag^+\,(aq) \rightleftharpoons Cu^{2+}\,(aq) + 2\,Ag\,(s)$$

fill in the blanks in the following table for the three solutions at equilibrium

Solution	$[Cu^{2+}(aq)]$ /mol lit^{-1}	$[Ag^{+}(aq)]$ /mol lit^{-1}	K/litre mol^{-1}
1	(*a*)	1.0×10^{-9}	2.0×10^{15}
2	2.0×10^{-7}	1.0×10^{-11}	(*b*)
3	2.0×10^{-2}	(*c*)	2.0×10^{15}

[Ans. (*a*) = 2.0×10^{-3} mol lit^{-1} (*b*) = 2.0×10^{15} (*c*) = 3.16×10^{-9} mol lit^{-1}]

11. When PCl_5 is heated in a closed vessel at 575 K, the total pressure at equilibrium is found to be 1 atm and partial pressure of Cl_2 is found to the 0·324 atm. Calculate the equilibrium constant (K_p) for the decomposition reaction. **[Ans. 0·298]**

12. In the dissociation of HI, 20% HI is dissociated at equilibrium at a certain temperature. Calculate K_p for the reaction

$$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g).$$

[Ans. $K_p = K_c = 0·125$]

13. A reaction mixture containing N_2 at 0·50 atm, H_2 at 3·0 atm and NH_3 at 0·50 atm is heated to 450°C. In which direction the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ will go if K_p is $4·28 \times 10^{-5}$? **[Ans. Backward direction]**

14. Reaction between nitrogen and oxygen takes place as follows :

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

If a mixture of 0·482 mol of N_2 nd 0·933 mol of O_2 is placed in a reaction vessel of volume 10 L and allowed to form N_2O at a temperature for which $K_c = 2·0 \times 10^{-37}$. Determine the composition of the equilibrium mixture. (*N.C.E.R.T.*)

[Ans. $[N_2] = 0·0482$ mol L^{-1}, $[O_2] = 0·0933$ mol L^{-1}, $[N_2O] = 6·6 \times 10^{-21}$ mol L^{-1}]

15. Nitric oxide reacts with bromine and gives nitrosyl bromide as per reaction given below :

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

When 0·087 mol of NO and 0·0437 mol of Br_2 are mixed in a closed container at constant temperature, 0·0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of nitric oxide and bromine. (*N.C.E.R.T.*)

[Ans. NO = 0·0352 mol, Br_2 = 0·0178 mol]

16. One mole of H_2O and one mole of CO are taken in a 10 litre vessel and heated at 725 K. At equilibrium 40 per cent of water (by mass) reacts with CO according to the equation

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

Calculate the equilibrium constant for the reaction. **[Ans. 0·444]**

17. At 700 K, equilibrium constant for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54·8. If 0·5 mol L^{-1} of HI (*g*) is present at equilibrium at 700 K, what are the concentrations of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI (*g*) and allowed it to reach equilibrium at 700 K.

(*N.C.E.R.T.*) **[Ans. $[H_2] = [I_2] = 0·068$ mol L^{-1}]**

18. The equilibrium constant for the reaction

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

is 4·0 at 25°C. Calculate the weight of ethyl acetate that will be obtained when 120 *g* of acetic acid are reacted with 92 *g* of alcohol. **[Ans. 117·04 *g*]**

19. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be $0·5 \times 10^{-1}$ mol L^{-1}. If value of K_c is $8·3 \times 10^{-3}$, what are the concentrations of PCl_3 and Cl_2 at equilibrium ? (*N.C.E.R.T.*)

[Ans. $[PCl_3] = [Cl_2] = 0·02$ mol L^{-1}]

20. Bromine monochloride (BrCl) decomposes into bromine and chlorine and attains the equilibrium

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

for which $K_c = 32$ at 500 K. If initially pure BrCl is present at a concentration of $3·30 \times 10^{-3}$ mol L^{-1}, what is its molar concentration in the mixture at equilibrium ? (*N.C.E.R.T.*)

[Ans. $3·0 \times 10^{-4}$ mol L^{-1}]

21. For the reaction $CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$, at 1173 K, the magnitude of the equilibrium constant, K_c is 3·6. For the following composition, decide whether reaction mixture is at equilibrium. If it is not, decide to which direction, the reaction should go

$[CH_4] = 1·07$ M, $[H_2S] = 1·20$ M,

$[CS_2] = 0·90$ M, $[H_2] = 1·78$ M. (*N.C.E.R.T.*)

[Ans. Backward direction]

HINTS FOR DIFFICULT PROBLEMS

1.

	H_2 +	I_2 ⇌	2 HI
Moles at eqm :	6·34	4·02	42·85
Molar concs. :	6·34/V	4·02/V	42·85/V moles L^{-1}

$$K_c = \frac{(42 \cdot 85 / V)^2}{(6 \cdot 34 / V)\,(4 \cdot 02 / V)} = 70 \cdot 042$$

2.

	CO +	$\frac{1}{2}O_2$ ⇌	CO
At. eqm.	0·4 atm	0·2 atm	0·6 atm

$$K_p = \frac{p_{CO_2}}{p_{CO} \times p_{O_2}^{1/2}} = \frac{0 \cdot 6}{0 \cdot 4 \times (0 \cdot 2)^{1/2}}$$

$$= 3 \cdot 354$$

$$K_p = K_c\,(RT)^{\Delta n} \quad \text{or} \quad K_c = K_p / (RT)^{\Delta n}$$

$$= 3 \cdot 354 / (0 \cdot 0821 \times 3000)^{-\,1/2} = 52 \cdot 64$$

3.

	PCl_5 ⇌	PCl_3 +	Cl_2
Initial moles	1·5		
At. eqm.	$\left(1 \cdot 5 - \frac{35}{100} \times 1 \cdot 5\right)$ = 1·5—0·525 = 0·975	0·525	0·525
Molar concs.	0·975/4	0·525/4	0·525/4

$$K_c = \frac{(0 \cdot 525 / 4)\,(0 \cdot 525 / 4)}{(0 \cdot 975 / 4)} = 0 \cdot 071$$

4. $K_c = \frac{0 \cdot 40}{0 \cdot 20 \times 0 \cdot 10} = 20$

New initial conc. of Cl_2 = $0 \cdot 10 + 0 \cdot 10$

$= 0 \cdot 20$ mol L^{-1}

New initial concs. of PCl_3 and PCl_5 remain the same

Supposing x mole of PCl_3 reacts, the new equilibrium concs. will be $[PCl_3] = 0 \cdot 20 - x$,

$[Cl_2] = 0 \cdot 20 - x$ and $[PCl_5] = 0 \cdot 40 + x$

Putting the values in $K_c = \frac{[PCl_5]}{[PCl_3]\,[Cl_2]}$

$$\frac{(0 \cdot 40 + x)}{(0 \cdot 20 - x)\,(0 \cdot 20 - x)} = 20$$

or $(0 \cdot 40 + x) = 20\,(0 \cdot 04 + x^2 - 0 \cdot 40\,x)$

or $20x^2 - 9x + 0 \cdot 40 = 0$

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

$$= \frac{9 \pm \sqrt{81 - 4 \times 20 \times 0 \cdot 4}}{2 \times 20} = \frac{9 \pm 7}{40}$$

$= 0 \cdot 4$ or $0 \cdot 05$ ($0 \cdot 4$ is impossible because x cannot be greater than $0 \cdot 2$)

Hence $[PCl_5] = 0 \cdot 40 + 0 \cdot 05 = 0 \cdot 45$ mol L^{-1}

5.

	CH_3COOH +	C_2H_5OH ⇌	$CH_3COOC_2H_5$ +	H_2O
Initial	1 mole	1 mole		
At. eq.	1/3 mole	1/3 mole	2/3 mole	2/3 mole
Molar concs. (mol L^{-1})	1/3 V	1/3 V	2/3 V	2/3 V

$$K_c = \frac{(2/3\,V)\,(2/3\,V)}{(1/3\,V)\,(1/3\,V)} = 4$$

For the reverse reaction

	$CH_3COOC_2H_5$ +	H_2O ⇌	CH_3COOH +	C_2H_5OH
Initial	1 mole	3 moles		
At. eqm.	$(1 - x)$	$(3 - x)$	x	x

$$\therefore \quad \frac{x^2}{(1 - x)\,(3 - x)} = \frac{1}{4}$$

or $4x^2 = x^2 + 3 - 4x$

or $3x^2 + 4x - 3 = 0$

or $x = \frac{-4 \pm \sqrt{16 + 4 \times 3 \times 3}}{2 \times 3}$

$= 0 \cdot 535$ mole

∴ Ester present at eqm. = 1—0·535

= 0·465 mole

6. Suppose we start with 1 mole of HI and x is the degree of dissociation. Then at equilibrium,

$[HI] = (1 - x)/V$, $[H_2] = x / 2V$.

$[I_2] = x / 2V$ moles per litre.

Put the values in the equation

$$K_c = \frac{[H_2]\,[I_2]}{[HI]^2}$$

and calculate x.

7.

	$2\,NH_3$ ⇌	N_2 +	$3\,H_2$
Initial	1 mole		
At. eqm.	(1—0·2) mole = 0·8 mole	0·1 mole	0·30 mole

Note that 2 moles of NH_3 dissociate to form 1 mole of N_2 and 3 moles of H_2.

8.

	PCl_5 ⇌	PCl_3 +	Cl_2
Initial	a mole		
At. eqm.	$(a—0 \cdot 1)$	0·1	0·1 mol L^{-1}

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$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

i.e. $0.0414 = \dfrac{0.1 \times 0.1}{a - 0.1}$.

This gives $a = 0.3415$ mole

9. Suppose x moles of H_2 are formed at eqm. Then concs. at equilibrium will be

$$[HI] = (2 - 2x)/10, \; [H_2] = x/10$$

and $[I_2] = x/10$ moles/litre.

11. $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

At eqm., $p_{Cl_2} = p_{PCl_3} = 0.324$ atm. Hence

$$p_{PCl_5} = 1 - (0.324 + 0.324) = 0.352 \text{ atm}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{0.324 \times 0.324}{0.352} = 0.298 \text{ atm}$$

12.

	HI	$\rightleftharpoons$	$\frac{1}{2}H_2$	+	$\frac{1}{2}I_2$
Initial	1 mole				
At. eqm.	1—0.20 = 0.80 mole		0.10 mole		0.10 mole

$$K_c = \frac{(0.1)^{1/2}(0.1)^{1/2}}{0.80} = 0.125,$$

$$K_p = K_c = 0.125$$

13. Concentration quotient (Q)

$$= \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} = \frac{(0.50)^2}{0.5 \times (3.0)^3} = 0.055$$

As $K_p << Q$, reaction will go in the backward direction.

14.

	$2N_2(g)$	$+ \; O_2(g) \rightleftharpoons$	$2N_2O(g)$
Initial	0.482 mol	0.933 mol	
At eqm.	0.482—x	0.933—$x/2$	x
Molar conc.	$\frac{0.482 - x}{10}$	$\frac{0.933 - x/2}{10}$	$\frac{x}{10}$

As $K = 2.0 \times 10^{-37}$ is very small, this means that the amount of N_2 and O_2 reacted (x) is very very small. Hence at equilibrium, we have

$$[N_2] = 0.0482 \text{ mol L}^{-1},$$

$$[O_2] = 0.0933 \text{ mol L}^{-1}, [N_2O] = 0.1x$$

$$\therefore \quad K_c = \frac{(0.1x)^2}{(0.0482)^2(0.0933)} = 2.0 \times 10^{-37} \textit{ (Given)}$$

On solving, this gives $x = 6.6 \times 10^{-20}$

$$\therefore \quad [N_2O] = 0.1x = 6.6 \times 10^{-21} \text{ mol L}^{-1}$$

15. 0.0518 mol of NOBr is formed from 0.0518 mol of NO and 0.0518/2 = 0.0259 mol of Br_2.

∴ At equilibrium,

Amount of NO = 0.087 − 0.0518 = 0.0352 mol

Amount of Br_2 = 0.0437—0.0259 = 0.0178 mol.

16. At equilibrium,

$$[H_2O] = \frac{1 - 0.40}{10} \text{ mol L}^{-1} = 0.06 \text{ mol L}^{-1}$$

$$[CO] = 0.06 \text{ mol L}^{-1},$$

$$[H_2] = \frac{0.4}{10} \text{ mol L}^{-1} = 0.04 \text{ mol L}^{-1},$$

$$[CO_2] = 0.04 \text{ mol L}^{-1}$$

$$K = \frac{[H_2][CO_2]}{[H_2O[CO]} = \frac{0.04 \times 0.04}{0.06 \times 0.06} = 0.444$$

17. $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, $\quad K = 1/54.8$

At equilibrium, $[HI] = 0.5 \text{ mol L}^{-1}$,

$$[H_2] = [I_2] = x \text{ mol L}^{-1}$$

$$\therefore \quad K = \frac{x \times x}{(0.5)^2} = \frac{1}{54.8} \text{ (Given).}$$

This gives $x = 0.068$

18. Initially, $CH_3COOH = \dfrac{120}{60}$ mol = 2 mol

$$C_2H_5OH = \frac{92}{46} \text{ mol} = 2 \text{ mol}$$

At equilibrium $[CH_3COOH] = (2 - x)/V \text{ mol L}^{-1}$

$$[C_2H_5OH] = (2 - x)/V \text{ mol L}^{-1},$$

$$[CH_3COOC_2H_5] = [H_2O] = x/V \text{ mol L}^{-1}$$

$$K = \frac{x \times x}{(2 - x)^2} = 4 \text{ (Given).}$$

This gives $x = 1.33$ mol

∴ Mass of ethyl acetate = 1.33 × 88
= 117.04 g

(Molar mass of $CH_3COOC_2H_5 = 88 \text{ g mol}^{-1}$)

19. Similar to Problem 17.

20.

	$2BrCl(g)$	$\rightleftharpoons$	$Br_2(g)$	$+ \; Cl_2(g)$
Initial	3.30×10^{-3} mol L^{-1}			
At eqm.	$(3.30 \times 10^{-3} - x)$		$x/2$	$x/2$

$$K_c = \frac{(x/2)(x/2)}{(3.30 \times 10^{-3} - x)^2} = 32 \text{ (Given)}$$

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$$\frac{x^2}{4\,(3{\cdot}30 \times 10^{-3} - x)} = 32$$

or $$\frac{x}{2\,(3{\cdot}30 \times 10^{-3} - x)} = \sqrt{32}$$

$$= 5{\cdot}66$$

$$x = 11{\cdot}32\,(3{\cdot}30 \times 10^{-3} - x)$$

or $$12{\cdot}32x = 11{\cdot}32 \times 3{\cdot}30 \times 10^{-3}$$

or $$x = 3{\cdot}0 \times 10^{-3}$$

$\therefore$ At eqm.

$$[BrCl] = (3{\cdot}30 \times 10^{-3} - 3{\cdot}0 \times 10^{-3})$$

$$= 0{\cdot}30 \times 10^{-3} = 3{\cdot}0 \times 10^{-4} \text{ mol L}^{-1}$$

21. $$Q_c = \frac{[CS_2]\,[H_2]^4}{[CH_4]\,[H_2S]^2} = \frac{0{\cdot}90 \times (1{\cdot}78)^4}{1{\cdot}07 \times (1{\cdot}20)^2} = 5{\cdot}86$$

As $Q_c > K_c$, equilibrium will go in the backward direction.

7.13. Factors Affecting Equilibrium

A system in equilibrium is affected by the following factors :

(1) Change of concentration of any reactant or product

(2) Change of temperature of the system

(3) Change of pressure on the system

(4) Addition of catalyst

(5) Addition of some inert gas.

The effect of change of concentration, pressure and temperature is predicted with the help of a principle known as Le Chatelier's principle, described in the next section. The effect of adding a catalyst or an inert gas is explained below :

Effect of adding Catalyst on the equilibrium. It may be summed up as follows :

The addition of a catalyst does not disturb the equilibrium. However, it helps in the attainment of equilibrium quickly.

For example, the following equilibrium exists :

$$2\,H_2\,(g) + O_2\,(g) \rightleftharpoons 2\,H_2O\,(g)$$

But this equilibrium is never attained under ordinary conditions because hydrogen and oxygen do not combine to form water under ordinary conditions. However, in the presence of a catalyst such as platinised asbestos, the reaction proceeds quite fast and equilibrium is attained quickly. Further the value of the equilibrium constant at 298 K is found to be same *i.e.* 1.2×10^{40} (which is quite large) irrespective of the speed at which the equilibrium is attained. This is obviously due to the fact that the addition of catalyst increases the speeds of the forward reaction and the backward reaction to the same extent.

Effect of adding an inert gas to a reaction mixture in equilibrium. Consider the dissociation equilibrium

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

Applying the law of chemical equilibrium, we get

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

(*a*) *If the reaction takes place* **at constant volume** (*i.e.* in a closed vessel), addition of an inert gas (like nitrogen, helium, argon etc.) will not change the molar concentrations of the reactants and products. Hence the state of equilibrium will remain unaffected.

(*b*) *If the reaction takes place* **at constant pressure**, addition of the inert gas will increase the total volume. Hence at equilibrium, the molar concentration of each of the reactants and products will decrease. Since there are two concentration terms in the numerator and only one in the denominator, therefore K_c should decrease. But K_c is constant at constant temperature. Hence to keep K_c constant, either $[PCl_5]$ should decrease or $[PCl_3]$ and $[Cl_2]$ should increase. This can happen only if more of PCl_5 dissociates to give PCl_3 and Cl_2. *Hence the dissociation increases with the addition of an inert gas.*

To sum up :

Addition of inert gas at constant volume has no effect on the state of equilibrium whereas at constant pressure the equilibrium shifts towards larger number of moles.

Note. In case of gaseous reactions of Type I, as $n_p = n_r$ *i.e.* there is no change in the number of moles, therefore there is no effect of adding an inert gas on the state of equilibrium.

7.14. Le Chatelier's Principle

The effect of concentration, temperature and pressure on a system in equilibrium can be predicted with the help of a generalization first proposed by a French chemist Le Chatelier in 1884. After his name, this generalization is known as Le Chatelier's principle. It states as follows :

If a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction that tends to undo the effect of the change imposed.

Let us now discuss the effect of the various factors one by one.

(1) Effect of change of concentration. Consider the general reaction

$$A + B \rightleftharpoons C + D$$

If to this reaction in equilibrium, more of A or B is added, then according to Le Chatelier's principle, the effect will be to decrease the concentrations of A and B. This is possible only if more of A and B react to form C and D, *i.e.* the equilibrium shifts in the forward direction. Similarly, the effect of adding more of C and D to the reaction in equilibrium will be to shift the equilibrium in the backward direction.

The effect of change of concentration on a reaction in equilibrium can be very easily seen in the laboratory with the help of the following reaction

$$\underset{\text{(Pale yellow)}}{Fe^{3+}(aq)} + \underset{\text{(Colourless)}}{(SCN)^-(aq)} \rightleftharpoons \underset{\text{(Reddish brown)}}{[Fe(SCN)^{2+}](aq)}$$

i.e. if to the solution of a ferric salt *e.g.* ferric nitrate (which is pale yellow), a solution of sulphocyanide salt *e.g.* KSCN (which is colourless) is added, a reddish brown colour is obtained due to the formation of ferric sulphocyanide complex ion. Now if to this solution, more of ferric salt solution or potassium sulphoncyanide solution is added, the colour of the solution becomes darker, showing the formation of more of $[Fe(SCN)]^{2+}$ ions. Again if to the solution, a small amount of potassium ferrosulphocyanide (capable of giving $[Fe(SCN)]^{2+}$ ions) is added, the darkness of the solution decreases, showing that the equilibrium has shifted in the backward direction. Similarly to study the effect of decrease in the concentration, a small amount of NaF may be added to the reaction mixture. It combines with the ferric ions as follows :

$$Fe^{3+}(aq) + F^-(aq) \longrightarrow FeF^{2+}(aq)$$
$$Fe^{3+}(aq) + 2F^-(aq) \longrightarrow FeF_2^+(aq)$$

Thus the concentration of Fe^{3+} ions decreases. The intensity of the colour of the solution is found to decrease indicating that the equilibrium shifts backward.

The effect of change of concentration can also be predicted by comparing the reaction quotient with the equilibrium constant. Let us a consider the general reaction

$$A + B \rightleftharpoons C + D$$

$$K_c = \frac{[C]\,[D]}{[A]\,[B]} \qquad ...(i)$$

Suppose concentration of the reactant [A] or [B] is increased, so that now we write Q_c in place of K_c

$$Q_c = \frac{[C]\,[D]}{[A]\,[B]} \qquad ...(ii)$$

As [A] or [B] has been increased, Q_c will become less than K_c. In order that equilibrium is re-established, Q_c will tend to increase till it becomes equal to K_c. This can happen only if [A] and [B] decrease and [C] and [D] increase *i.e.* equilibrium will shift in the forward direction. Similarly, it can be seen that the effect of removal of product [C] or [D] shifts the equilibrium in the forward direction. This has a great significance in the industrial processes because if the product is reovered side by side, the equilibrium will shift in the forward direction to form more product. The removal of product is especially easy if it is a gas. For example,

(*i*) in the manufacture of NH_3 by Haber's process, NH_3 gas is liquefied and hence removed side by side from the reaction mixture.

(*ii*) In the manufacture of quick lime (CaO), by decomposition of $CaCO_3$, the gaseous CO_2 which is one of the products is allowed to escape.

Looking at eqn. (*ii*), it may be noticed that continuous removal of the product keeps the value of Q_c less than K_c. As a result, the reaction continues to move in the forward direction.

Some examples from everyday life. If in a system in equilibrium, the concentration in any one part is disturbed, it no longer remains in equilibrium and readjusts its concentrations to re-establish the equilibrium. This is illustrated with the following examples :

(*i*) *Clothes dry quicker when there is a breeze or we keep on shaking it.* This is because water vapour of the nearby air are removed and cloth loses more water vapour to re-establish equilibrium with the surrounding air.

(*ii*) *We sweat more on a humid day but it evaporates when we sit under the fan*. More sweating takes place because the surrounding air has large amount of water vapour and our skin cannot lose more to it. The fan removes the humid air and evaporation starts from the skin.

(*iii*) *Transport of oxygen by haemoglobin in blood.* Oxygen breathed in combines with the haemoglobin in the lungs according to the equilibrium

$$\mathrm{Hb}\,(s) + \mathrm{O_2}\,(g) \rightleftharpoons \mathrm{HbO_2}\,(s)$$

When it reaches the tissues, the pressure of oxygen there is low. To readjust the equilibrium, oxyhaemoglobin gives up oxygen. When it returns to lungs where the pressure of oxygen is high, more of oxyhaemoglobin is formed.

(*iv*) *Removal of CO_2 from tissues by blood.* The equilibrium is

$$\mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H_2CO_3}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{HCO_3^-}\,(aq)$$

As partial pressure of CO_2 is high in the tissues, CO_2 dissolves in the blood. In the lungs, as partial pressure of CO_2 is low, it is released from the blood.

(*v*) *Tooth decay by sweets.* Our teeth are coated with an enamel of an insoluble substance known as hydroxypatite, $Ca_5(PO_4)_3(OH)$. It exists in equilibrium with its ions as follows : —

$$\mathrm{Ca_5(PO_4)_3(OH)}\,(s) \underset{\text{Remineralisation}}{\overset{\text{Demineralisation}}{\rightleftharpoons}} 5\,\mathrm{Ca^{2+}} + 3\mathrm{PO_4^{3-}} + \mathrm{OH^-}$$

The forward reaction involving dissocation is called demineralization and the backward reaction involving formation is called remineralization. If we do not brush our teeth after eating sweets, the sugar gets fermented on the teeth to produce H^+ ions which combine with the OH^- ions shifting the equilibrium in the forward direction thereby causing tooth decay.

Thus in general,

If in a reaction in equilibrium, the concentration of any reactant is increased, the equilibrium shifts in the forward direction. On the other hand, if the concentration of any product is increased, the equilibrium shifts in the backward direction. The reverse happens if the concentrations are decreased.

(2) Effect of change of temperature. The change of temperature alters the state of equilibrium for only those reactions in which either heat is evolved (exothermic) or heat is absorbed (endothermic). In fact, every such reaction is made up of two opposing reactions. If the forward reaction is exothermic, the backward reaction will be endothermic and vice-versa.

(*i*) Consider the exothermic reaction

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightleftharpoons 2\mathrm{NH_3}\,(g),\ \Delta H = -92\cdot4\ \mathrm{kJ}$$

or it may be written as

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}} 2\mathrm{NH_3}\,(g) + 92\cdot4\ \mathrm{kJ}$$

Obviously, the forward reaction is exothermic whereas the backward reaction is endothermic. Now, if the temperature is increased *i.e.* heat is supplied to the system, then according to Le Chatelier's principle, the equilibrium will shift to the side that absorbs heat *i.e.* in the backward direction. Similarly, decrease in temperature will shift the equilibrium in the forward direction.

(*ii*) Again, consider the endothermic reaction

$$\mathrm{N_2}\,(g) + \mathrm{O_2}\,(g) \rightleftharpoons 2\mathrm{NO}\,(g),\ \Delta H = +180.7\ \mathrm{kJ}$$

or it may be written as

$$\mathrm{N_2}\,(g) + \mathrm{O_2}\,(g) + 180.7\ \mathrm{kJ} \underset{\text{exo}}{\overset{\text{endo}}{\rightleftharpoons}} 2\,\mathrm{NO}\,(g)$$

Obviously, here the forward reaction is endothermic whereas the backward reaction is exothermic. Arguing as before, the increase of temperature will favour the forward reaction while the decrease of temperature will favour the backward reaction. Thus in general,

Exothermic reactions are favoured by low temperature whereas endothermic reactions are favoured by high temperature.

(3) Effect of change of pressure. This factor has a significant role to play only in case of gaseous reactions and those too which proceed with a change in the number of moles.

(*i*) Consider the dissociation of N_2O_4 into NO_2 :

$$\underset{1\text{ mole}}{N_2O_4\,(g)} \rightleftharpoons \underset{2\text{ moles}}{2NO_2\,(g)}$$

Here, the forward reaction occurs with increase in number of moles. Therefore, the backward reaction must proceed with decrease in number of moles. If now the pressure on the system is increased, then according to Le Chatelier's principle, the equilibrium will shift in a direction in which the pressure decreases or the number of moles decreases (because pressure is directly proportonal to the number of moles). Since backward reaction takes place with decrease in number of moles, so an increase in pressure will favour the combination of NO_2 molecules to produce N_2O_4 *i.e.* suppresses the dissociation of N_2O_4 into NO_2.

Conversely, if the pressure on the system is decreased, the equilibrium will shift in the forward direction which is accompanied by increase in total number of moles. In other words, decrease in pressure favours the dissociation of N_2O_4 into NO_2 *i.e.*, increases the dissociation of N_2O_4.

(*ii*) Now, consider another gaseous reaction involving *formation of ammonia*.

$$\underbrace{\underset{1\text{ mole}}{N_2\,(g)} + \underset{3\text{ moles}}{3H_2\,(g)}}_{4\text{ moles}} \rightleftharpoons \underset{2\text{ moles}}{2NH_3\,(g)}$$

In this equilibrium reaction, the forward reaction is accompanied by a decrease in the total number of moles. If the pressure on the system is increased, then according to Le Chatelier's principle, the equilibrium will shift in that direction in which decrease in the total number of moles takes place *i.e.*, in favour of formation of ammonia. Thus, higher the pressure, the better would be the yield of ammonia.

If, on the other hand, the pressure on the system is decreased, the equilibrium will shift in that direction in which increase in total number of moles occurs *i.e.*, in the backward direction. In other words, a decrease in pressure will favour the dissociation of NH_3 into N_2 and H_2.

(*iii*) Lastly, consider the following equilibrium reaction involving the formation of hydrogen iodide.

$$\underset{1\text{ mole}}{H_2\,(g)} + \underset{1\text{ mole}}{I_2\,(g)} \rightleftharpoons \underset{2\text{ moles}}{2HI\,(g)}$$

This reaction takes place in either direction without change in number of moles. So according to Le Chatelier's principle, pressure will have no effect on this equilibrium. In general,

Low pressure favours those reactions which are accompanied by increase in total number of moles and high pressure favours those reactions which take place with decrease in total number of moles. However, pressure has no effect on an equilibrium reaction which proceeds with no change in total number of moles.

The effect of change of pressure can also be predicted by comparing the reaction quotient with the equilibrium constant as done in the case of the study of effect of change of concentration. Let us consider the reaction

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

Suppose the reaction mixture is enclosed in a cylinder fitted with a piston at constant temperature and a definite pressure. When equilibrium is attained, for the equilibrium concentrations, we have $K_c = \dfrac{[NH_3]^2}{[N_2]\,[H_2]^3}$

Now suppose the reaction mixture is compressed to half the volume (Fig. 7.12) *i.e.* pressure is doubled (as PV = constant at constant temperature). The molar concentration of each of the reactants and products will be doubled so that now the reaction quotient is

$$Q_c = \frac{\{2\,[NH_3]\}^2}{\{2\,[N_2]\}\,\{2\,[H_2]\}^3} = \frac{1}{4}\,\frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{1}{4}\,K_c$$

Thus Q_c is less than K_c. To re-establish the equilibrium Q_c will increase till it becomes equal to K_c. This can happen only if $[NH_3]$ increases and $[N_2]$ and $[H_2]$ decrease *i.e.* equilibrium will shift in the forward direction.

It is important to mention here that in the study of effect of pressure on reactions involving heterogeneous equilibrium, the solids and liquid reactants or products are not taken into cnsideration, as the effect of pressure on them is negligible. For example, for the reaction

$$C\,(s) + O_2\,(g) \rightleftharpoons 2\,CO\,(g),$$

we write $Q_c = \dfrac{[CO]^2}{[O_2]}$

Effect of change in volume. If the volume of a gaseous reaction is decreased, the pressure exerted by the molecules will increase. Thus the effect of

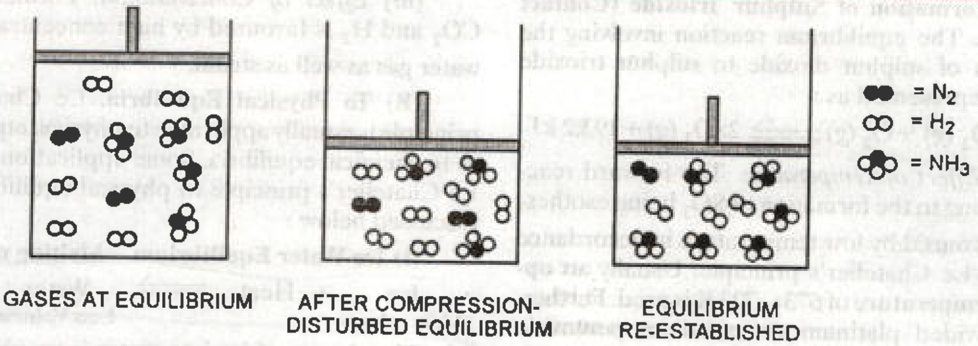


FIGURE 7.12. Demonstrating the effect of pressure on the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$

decrease of volume is equivalent to the effect of increase of pressure. As the effect of increase of pressure is to shift the equilibrium in the direction in which the number of moles decreases, hence the *effect of decrease in volume will be to shift the equilibrium in the direction in which the number of moles decreases*.

7.15. Applications of Le Chatelier's Principle

(A) To Chemical Equilibria. Le Chatelier's principle is very useful in predicting the conditions of temperature, pressure and concentration to get higher yields in certain industrial reactions. A few examples are given below :

1. Formation of Ammonia (Haber's Process). The chemical equilibrium taking place in this process is

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g),\ \Delta H = -92.4\ \text{kJ}$$

(*i*) *Effect of temperature.* It has already been discussed above that lower the temperature, greater would be the yield of ammonia. However, if the temperature is kept low, the reaction will take a long time to attain equilibrium state. Therefore, a compromise is needed to make the process economical. Usually, a temperature of 750 K is employed. At this temperature, the yield of NH_3, of course, is less than that at a lower temperature. But from industry point of view, it is rather advisible to get a poorer yield than to waste time unnecessarily.

Finely divided iron is used as a catalyst to achieve the equilibrium rapidly and molybdenum (promoter) is used to increase the efficiency of the catalyst.

(*ii*) *Effect of Pressure.* It has already been discussed above that higher the pressure, greater would be the yield of ammonia. Usually a pressure of 350 atmospheres is employed.

(*iii*) *Effect of Concentration.* According to Le Chatelier's principle, an increase in the concentration of reactants (N_2 and H_2) would shift the equilibrium in that direction in which the reactants are consumed *i.e.*, in the forward direction. In other words, formation of NH_3 would be favoured. Moreover NH_3 formed should be continuously removed by liquefaction so that equilibrium shifts in the forward direction.

2. Formation of Nitric Oxide. Consider the formation of nitric oxide by direct combination of nitrogen and oxygen (as used in the Binkland-Eyde process for the manufacture of nitric acid). The thermochemical equation for this reaction is

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g),\ \Delta H = +180\cdot 7\ \text{kJ}$$

(*i*) *Effect of Temperature.* The forward reaction resulting in the formation of NO is endothermic. If the temperature of the system is increased, then according to Le Chatelier's principle, the equilibrium will shift in that direction in which absorption of heat occurs *i.e.*, in the forward direction. Therefore, the formation of NO will be favoured by high temperature. Usually, a temperature of 2773 K is employed.

(*ii*) *Effect of Pressure.* In this equilibrium reaction, no change in number of moles takes place since one mole of N_2 combines with one mole of O_2 to produce 2 moles of NO. Hence pressure has no effect on this equilibrium reaction.

(*iii*) *Effect of Concentration.* A high concentration of N_2 and O_2 will favour the formation of nitric oxide.

3. Formation of Sulphur Trioxide (Contact Process). The equilibrium reaction involving the oxidation of sulphur dioxide to sulphur trioxide may be represented as :

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) + 193.2 \text{ kJ}$$

(*i*) *Effect of Temperature.* The forward reaction leading to the formation of SO_3 being exothermic is favoured by low temperature in accordance with the Le Chatelier's principle. Usually an **optimum temperature** of 673 – 723 K is used. Further, finely divided platinum or vanadium pentoxide (V_2O_5) is used as a catalyst to attain the equilibrium state rapidly.

(*ii*) *Effect of Pressure.* The forward reaction favouring the formation of SO_3 takes place with decrease in number of moles. If pressure on the system is increased, the volume will decrease correspondingly. Hence, the total number of moles per unit volume will now be more than before. Therefore, according to Le Chatelier's principle, equilibrium will shift in that direction in which decrease in number of moles occurs *i.e.* in the forward direction. Therefore, *the formation of SO_3 is favoured by high pressure.* Usually, a pressure of 1.5 to 1.7 atmosphere serves the purpose.

(*iii*) *Effect of Concentration.* Higher the concentration of SO_2 and O_2, greater would be the yield of SO_3.

4. Bosch Process for the Manufacture of Hydrogen. In this process, H_2 is produced from water gas and steam according to the following equilibrium reaction :

$$\underbrace{\underbrace{H_2\,(g) + CO\,(g)}_{\text{Water gas}} + \underbrace{H_2O\,(g)}_{\text{Steam}}}_{\text{3 moles}} \rightleftharpoons \underbrace{2H_2(g) + CO_2\,(g)}_{\text{3 moles}}\,;\ \Delta H = +\,42{\cdot}0 \text{ kJ}$$

(*i*) *Effect of Temperature.* The forward reaction being endothermic is favoured by high temperature. Usually a temperature of 673-723 K is used.

(*ii*) *Effect of Pressure.* Since there is no change in the total number of moles in this reversible reaction, *pressure has no effect* on this equilibrium reaction.

(*iii*) *Effect of Concentration.* Formation of CO_2 and H_2 is favoured by high concentration of water gas as well as steam.

(B) To Physical Equilibria. Le Chatelier's principle is equally applicable to physical equilibria as to chemical equilibria. Some applications of the Le Chatelier's principle to physical equilibria are discussed below :

(i) Ice-Water Equilibrium – Melting of ice

$$\underset{\text{More volume}}{\text{Ice}} + \text{Heat} \rightleftharpoons \underset{\text{Less Volume}}{\text{Water}}$$

The change of ice into water is an endothermic (a heat absorbing), reversible process. The reaction involves decrease in volume *i.e.* when ice melts into water, volume decreases. Hence according to Le Chatelier's principle,

(*a*) On increasing the pressure on this system in equilibrium, the equilibrium tends to shift in a direction in which volume decreases *i.e.* equilibrium shifts to the right. Thus increasing pressure favours change of ice into water *i.e.* more of ice melts.

(*b*) Since the change of ice into water is an endothermic process, increase in temperature tends to shift the equilibrium to the right, *i.e.* on increasing the temperature, more ice melts into water.

(ii) Water-Vapour equilibrium – Vaporisation of water

$$\underset{\text{Less volume}}{\text{Water}} + \text{Heat} \rightleftharpoons \underset{\text{More volume}}{\text{Water vapour}}$$

The change of water to water vapour is a reversible endothermic (heat absorbing) process. The reaction involves increase in volume *i.e.* when water vaporises into water vapour, volume increases. Hence according to Le Chatelier's principle,

(*a*) On increasing the pressure on this system in equilibrium, the equilibrium tends to shift in a direction in which the volume decreases *i.e.* equilibrium shifts towards condensation of water vapour into water. In other words, the increase in pressure favours the condensation of water vapour into water and decreasing pressure favours vaporisation of water into water vapour.

(*b*) Since the vaporisation of water into water vapour is an endothermic reaction, increase in temperature shifts the equilibrium to the right *i.e* on increasing temperature, more water is changed into water vapour.

(iii) Solubility of Substances. Certain salts like ammonium chloride dissolve with the absorption of heat (endothermic). The solubility of such salts increases with increase in temperature.

On the other hand, certain salts like sodium hydroxide, calcium acetate etc. which dissolve with the evolution of heat, will have lower solubility at higher temperatures.

(iv) Gas-Solution System. Suppose there exists an equilibrium between a gas and its solution in a cylinder fitted with a piston. When pressure is increased by compressing the system with a piston, there occurs reduction of volume and, therefore, some of the gas dissolves in the solution. It means that increase of pressure increases the solubility of gas in liquids while decrease in pressure lowers it. For example, an aerated soda water bottle like Campa, Thums up etc., on opening bubbles out dissolved carbon dioxide as pressure is decreased.

ADD TO YOUR KNOWLEDGE

1. van't Hoff equation is

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

Assuming ΔH° to be constant over a small temperature range, integration of the above equation gives

$$\int d \ln K_p = \int \frac{\Delta H^\circ}{RT^2}\, dT$$

$$= \frac{\Delta H^\circ}{R} \int \frac{dT}{T^2}$$

or $$\ln K_p = -\frac{\Delta H^\circ}{RT} + I$$

where I is constant of integration. Thus a plot of $\ln K_p$ versus 1/T gives a straight line with slope $= -\Delta H^\circ / R$.

2. From the van't Hoff equation,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2 \cdot 303\, R}\left(\frac{T_2 - T_1}{T_1 T_2}\right),$$ we may conclude that

(*i*) If $\Delta H = 0$ *i.e.* no heat is evolved or absorbed in the reaction,

$$\log (K_2/K_1) = 0$$

i.e. $$K_2/K_1 = 1$$

or $$K_2 = K_1$$

i.e. equilibrium constant does not change with temperature

(*ii*) If $\Delta H = +\text{ve}$ *i.e.* heat is absorbed in the reaction, then

$$\log (K_2/K_1) = +\text{ve}$$

or $$\log K_2 > \log K_1$$

or $$K_2 > K_1.$$

i.e. equilibrium constant increases with increase in temperature.

(*iii*) If $\Delta H = -\text{ve}$ *i.e.* heat is evolved in the reaction, $\log (K_2/K_1) = -\text{ve}$

i.e. $\log K_2 < \log K_1$ or $K_2 < K_1$

i.e. equilibrium constant decreases with increase in temperature.

Conceptual Questions

Q. 1. Some sugar is added into a saturated solution of sugar in a beaker. What process/processes if any, do you expect to happen with the passage of time? What is this state called ?

Ans. Two processes namely dissolution and precipitation will continue to take place at equal rates. It is called a state of equilibrium.

Q. 2. Why gas fizzes out when soda water bottle is opened ?

Ans. The amount of the gas dissolved is very high due to high pressure. On opening the bottle, the pressure tends to decrease to atmospheric pressure. So the solubility decreases *i.e.* the dissolved gas escapes out.

Q. 3. Reaction between acetic acid and ethyl alcohol attains a state of equilibrium in an open vessel but decomposition of $CaCO_3$ does not. Why ?

Ans. Acetic acid and ethyl alcohol are liquids and their products ethyl acetate and water are also liquids but one of the products of decomposition of $CaCO_3$ is gaseous (CO_2) which escapes out and the reverse reaction cannot occur.

Q. 4. At equilibrium, the mass of each of the reactants and products remains constant. Does it mean that the reaction has stopped ? Explain.

Ans. No, the reaction does not stop. It continues to take place in the forward as wall as backward directions but at equal speeds.

Q. 5. What happens to a reversible reaction if a catalyst is added to it ?

Ans. The state of equilibrium is not disturbed but is attained quickly because both the rate of forward and backward reaction increase to the same extent.

Q. 6. The value of equilibrium constant depends on what ? ***(B.I.T. Ranchi 1990)***

Ans. The value of equilibrium constant depends upon (*i*) nature of the reaction (*ii*) temperature.

Q. 7. A cylinder fitted with an air tight piston contains a small amount of a liquid at a fixed temperature. The piston is moved out so that the volume increases.

(*a*) What will be the effect on the change of vapour pressure initially ?

(*b*) How will the rates of evaporation and condensation change initially ?

(*c*) What will happen when equilibrium is restored finally and what will be the final vapour pressure ? ***(N.C.E.R.T.)***

Ans. (*a*) Initially the vapour pressure will decrease.

(*b*) The rate of evaporation remains constant at constant temperature in a closed vessel. (discussed in unit 2 under vapour pressure) However, the rate of condensation will decrease because there are fewer molecules per unit volume in the vapour phase and hence the number of collisions per unit time with the liquid surface decreases.

(*c*) When equilibrium is restored, rate of evaporation = rate of condensation. The final vapour pressure will be same as it was originally.

Q. 8. Write expressions for the equilibrium constant K for each of the following reactions :

(*i*) $2\,NOCl\,(g) \rightleftharpoons 2\,NO\,(g) + Cl_2\,(g)$

(*ii*) $Na_2CO_3\,(s) + SO_3\,(g) + \frac{1}{2}O_2\,(g) \rightleftharpoons Na_2SO_4\,(s) + CO_2\,(g)$

(*iii*) $PbI_2\,(s) + aq \rightleftharpoons Pb^{2+}\,(aq) + 2\,I^-\,(aq)$ ***(N.C.E.R.T.)***

Ans. (*i*) $K = \dfrac{[NO\,(g)]^2\,[Cl_2\,(g)]}{[NOCl\,(g)]^2}$

(*ii*) $K = \dfrac{[Na_2SO_4\,(s)]\,[CO_2\,(g)]}{[Na_2CO_3\,(s)]\,[SO_2\,(g)]\,[O_2\,(g)]^{1/2}} = \dfrac{[CO_2\,(g)]}{[SO_2\,(g)]\,[O_2\,(g)]^{1/2}} = \dfrac{p_{CO_2}}{p_{SO_2} \times p_{O_2}^{1/2}}$

(*iii*) $K = \dfrac{[Pb^{2+}\,(aq)]\,[I^-\,(aq)]^2}{[PbI_2\,(s)]} = [Pb^{2+}\,(aq)]\,[I^-\,(aq)]^2$

Q. 9. **The concentration quotient of a reversible reaction is Q, and the equilibrium constant is K. What do you conclude if *(i)* Q = K *(ii)* Q > K *(iii)* Q < K.**

Ans. Refer to page 7/11.

Q. 10. **If concentrations are expressed in moles L^{-1} and pressures in atmospheres, what is the ratio of K_p to K_c for the reaction $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$ at 25°C ?**

Ans. $\Delta n_g = n_p - n_r = -1.$

Hence $K_p = K_c\,(RT)^{-1}$ or $K_p / K_c = 1 / RT = \dfrac{1}{0{\cdot}0821 \times 298} = 0{\cdot}04$

Q. 11. **The equilibrium constant for the reactions**

$$N_2 + O_2 \rightleftharpoons 2NO \quad \text{and} \quad 2\,NO + O_2 \rightleftharpoons 2NO_2$$

are K_1 and K_2 respectively, then what will be the equilibrium constant for the reaction

$$N_2 + 2O_2 \rightleftharpoons 2NO_2\ ?$$

Ans. For the required reaction, $K = K_1 \times K_2$.

Q. 12. **For the reaction $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$, at 400 K, $K_p = 41$. Find the value of K_p for each of the following reactions at the same temperature :**

(i) $2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g)$ *(ii)* $\frac{1}{2}\,N_2\,(g) + \frac{3}{2}\,H_2\,(g) \rightleftharpoons NH_3\,(g)$

(iii) $2\,N_2\,(g) + 6\,H_2\,(g) \rightleftharpoons 4\,NH_3\,(g)$ *(N.C.E.R.T.)*

Ans. *(i)* $K_p = \frac{1}{41}$ *(ii)* $\sqrt{41}$ *(iii)* $(41)^2$.

Q. 13. **What does the equilibrium constant K < 1 indicate ?**

Ans. The reaction does not proceed much in the forward direction.

Q. 14. **For an exothermic reaction, what happens to the equilibrium constant if temperature is increased ?**

Ans. $K = k_f / k_b$. In exothermic reaction, with increase of temperature k_b increases much more than k_f. Hence K decreases.

Q. 15. **Write expressions for K_p and K_c for the reaction $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$.**

Ans. $K_c = \dfrac{[CaO\,(s)]^2\,[CO_2\,(g)]}{[CaCO_3\,(s)]}$. Taking active masses of solids as unity, $K_c = [CO_2\,(g)]$. Similarly $K_p = p_{CO_2}$.

Q. 16. **The equilibrium constant expression for a gas reaction is $K_c = \dfrac{[NH_3]^4\,[O_2]^5}{[NO]^4\,[H_2O]^6}$**

Write the balanced chemical equation corresponding to this expression. *(N.C.E.R.T.)*

Ans. $4\,NO\,(g) + 6\,H_2O\,(g) \rightleftharpoons 4\,NH_3\,(g) + 5\,O_2\,(g)$

Q. 17. **What happens to the equilibrium $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$, if nitrogen gas is added to it *(i)* at constant volume *(ii)* at constant pressure ? Give reasons.**

Ans. *(i)* The state of equilibrium remains unaffected

(ii) Dissocation increases (*i.e.* equilibrium shifts forward). For reason, refer to the text (page 7/27).

Q. 18. **The equilibrium constant of a reaction is 2×10^{-3} at 25°C and 2×10^{-2} at 50°C. Is the reaction exothermic or endothermic ?**

Ans. As equilibrium constant has increased with temperature, the reaction is endothermic (in the forward direction).

Q. 19. **What two changes on the equilibrium $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$, $\Delta H = -92{\cdot}4$ kJ. can keep its state undisturbed ?**

Ans. Increase of temperature alongwith suitable increase of pressure or increase of pressure alongwith suitable increase of temperature.

Q. 20. **Some processes are given below. What happens to the process if it subjected to a change given in the brackets ?**

(*i*) Ice $\overset{\text{M. pt}}{\rightleftharpoons}$ Water (Pressure is increased)

(*ii*) Dissolution of NaOH in water (Temperature is increased)

(*iii*) $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) - 180 \cdot 7$ kJ (Pressure is increased and temperature is decreased).

Ans. (*i*) Equilibrium will shift in the forward direction *i.e.* more of ice will melt.

(*ii*) Solubility will decrease because it is an exothermic process.

(*iii*) Pressure has no effect. Decrease of temperature will shift the equilibrium in the backward direction.

Q. 21. **Explain why pure liquids and solids are ignored while writing the equilibrium constant expression.** *(N.C.E.R.T.)*

Ans. $[\text{Pure liquid}]$ or $[\text{Pure solid}] = \dfrac{\text{No. of moles}}{\text{Volume of L}} = \dfrac{\text{Mass/mol. mass}}{\text{Volume}}$

$$= \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Mol. mass}} = \frac{\text{Density}}{\text{Mol. mass}}$$

As density of a pure liquid or pure solid is constant at constant temperature and molecular mass is also constant, therefore their molar concentrations are constant and included into the equilibrium constant.

Q. 22. **What qualitative information can you obtain from the magnitude of equilibrium constant ?** *(N.C.E.R.T.)*

Ans. (*i*) Large value of equilibrium constant ($> 10^3$) shows that forward reaction is favoured *i.e.* concentration of products is much larger than that of the reactants at equilibrium.

(*ii*) Intermediate value of K (10^{-3} to 10^3) shows that the concentration of the reactants and products are comparable.

(*iii*) Low value of K ($< 10^{-3}$) shows that backward reaction is favoured *i.e.* concentration of reactants is much larger than that of the products.

Q. 23. **The following reaction has attained equilibrium**

$$CO\,(g) + 2\,H_2\,(g) \rightleftharpoons CH_3OH\,(g), \quad \Delta H^\circ = -92 \cdot 0 \text{ kJ mol}^{-1}$$

What will happen if (*i*) Volume of the reaction vessel is suddenly reduced to half ?

(*ii*) the partial pressure of hydrogen is suddenly doubled ?

(*iii*) an inert gas is added to the system ? *(N.C.E.R.T.)*

Ans. $K_c = \dfrac{[CH_3OH]}{[CO]\,[H_2]^2}, \quad K_p = \dfrac{p_{CH_3OH}}{p_{CO} \times p_{H_2}^2}$

(*i*) When volume of the vessel is reduced to half, the concentration of each reactant or product becomes double. Thus

$$Q_c = \frac{2\,[CH_3OH]}{2\,[CO] \times \{2\,[H_2]\}^2} = \frac{1}{4} K_c$$

As $Q_c < K_c$, equilibrium will shift in the forward direction, producing more of CH_3OH to make $Q_c = K_c$.

(*ii*) $$Q_p = \frac{p_{CH_3OH}}{p_{CO}} \times (2\,p_{H_2})^2 = \frac{1}{4} K_p.$$

Again $Q_p < K_p$, equilibrium will shift in the forward direction to make $Q_p = K_p$.

(*iii*) As volume remains constant, molar concentrations will not change. Hence there is no effect on the state of equilibrium.

Q. 24. Which of the following will be affected by increase of pressure ? Also mention whether the change will cause the reaction to go into right or left direction ?

(i) $CH_4\,(g) + 2\,S_2\,(g) \rightleftharpoons CS_2\,(g) + 2\,H_2S\,(g)$

(ii) $CO_2\,(g) + C\,(s) \rightleftharpoons 2\,CO\,(g)$

(iii) $4\,NH_3\,(g) + 5\,O_2\,(g) \rightleftharpoons 4\,NO\,(g) + 6\,H_2O\,(g)$

(iv) $C_2H_4\,(g) + H_2\,(g) \rightleftharpoons C_2H_6\,(g)$ **(N.C.E.R.T.)**

Ans. All except (i) will be affected by pressure (For (i) $n_p = n_r = 3$)

In (ii), $n_r = 1, n_p = 2$ i.e. $n_p > n_r$, equilibrium will go to left.

In (iii), $n_r = 9, n_p = 10$ i.e. $n_p > n_r$, equilibrium will go to left.

In (iv), $n_r = 2, n_p = 1$ i.e. $n_p < n_r$, equilibrium will go to right.

Q. 25. Hydrogen gas is obtained from natural gas by partial oxidation with steam according to the following endothermic reaction

$$CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3\,H_2\,(g)$$

(a) Write an expression for K_p for the above reaction.

(b) How will the value of K_p and composition of the equilibrium mixture be affected by

(i) increasing the pressure ?

(ii) increasing the temperature ?

(iii) using a catalyst ? **(N.C.E.R.T.)**

Ans. (a) $K_p = \dfrac{p_{CO} \times p^3_{H_2}}{p_{CH_4} \times p_{H_2O}}$

(b) (i) By Le Chatelier's principle, equilibrium will shift in the backward direction.

(ii) By Le Chatelier's principle, equilibrium will shift in the backward direction.

(iii) Equilibrium composition will not be disturbed but equilibrium will be attained quickly.

Q. 26. The following system is in equilibrium

$$SO_2Cl_2 + \text{Heat} \rightleftharpoons SO_2 + Cl_2,$$

What will happen to the temperature of the system if some Cl_2 is added into it at constant volume ? Give reason.

Ans. Temperature of the system will increase because on adding Cl_2, equilibrium will shift in the backward direction producing more heat.

Q. 27. In which one of the following reactions, the yield of the product will be maximum ?

$$2\,A + B \rightleftharpoons C, K = 10^{-5}$$

$$C + 2\,D \rightleftharpoons E, K = 10^5$$

$$D + 3\,B \rightleftharpoons F, K = 10^3$$

Ans. Higher the value of equilibrium constant K, greater is the yield of products. Hence yield of E will be maximum.

Q. 28. The equilibrium $H_2O\,(l) \rightleftharpoons H_2O\,(v)$ is attained in a closed container at 40°C. The aqueous tension of water at 40° C is 23 mm. What is K_p for the said equilibrium ?

Ans. $K_p = p_{H_2O} = 23$ mm

Very Short Answer Questions CARRYING 1 MARK

Q. 1. Which measurable property becomes constant in water $\rightleftharpoons$ water vapour equilibrium at constant temperature ?

Ans. Vapour pressure.

Q. 2. Give one example of everyday life in which there is gas $\rightleftharpoons$ solution equilibrium.

Ans. soda-water bottle.

Q. 3. Under what condition, a reversible process becomes irreversible ?

Ans. If one of the products (gaseous) is allowed to escape out (*i.e.* in open vessel)

Q. 4. What happens if ferric salt is added to the equilibrium of the reaction between Fe^{3+} and SCN^- ions ?

Ans. Red colour deepens.

Q. 5. What is the effect on the value of equilibrium constant on adding catalyst ?

Ans. No effect.

Q. 6. Write the expression for equilibrium constant K_p for the reaction

$$3\,Fe\,(s) + 4\,H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s) + 4\,H_2\,(g)$$

Ans. $K_p = p_{H_2} / p_{H_2O}$

Q. 7. What is the effect of increasing pressure on the equilibrium

$$N_2 + 3H_2 \rightleftharpoons 2NH_3\ ?$$

Ans. Equilibrium will shift in the forward direction forming more of ammonia.

Q. 8. What are the conditions for getting maximum yield of NH_3 by Haber's process ?

Ans. High concentrations of N_2 and H_2, low temperature, high pressure.

Q. 9. If the equilibrium constant for a reaction is 4·0, what will be the equilibrium constant for the reverse reaction.

Ans. $1/4 = 0{\cdot}25$.

Q. 10. What happens to the dissociation of PCl_5 in a closed vessel if helium gas is introduced into it at the same temperature ?

Ans. No effect.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 7.1. to 7.3.

1. What do you understand by term 'Equilibrium' ? Explain physical equilibrium with one suitable example.
2. Give one example of each of the following equilibria :
   (*i*) Solid-Liquid Equilibira
   (*ii*) Liquid-Gas Equilibrium
   (*iii*) Solid-Solution Equilibrium
3. Define the terms 'Vapour pressure and 'Solubility'.
4. Define Henry Law. Why the gas fizzes out when a soda water bottle is opened ?
5. Under what condition each of the following equilibria can exist :
   (*i*) Solid-Liquid equilibrium
   (*ii*) Liquid-gas equilibrium
   (*iii*)Solid-solution equilibrium
   (*iv*) Gas-solution equilibrium.

Sec. 7.4. **6.** What do you understand by Rerversible and Irreversible reactions ? Ilustrate your answer with two examples. Under what conditions a reversible reaction becomes irreversible ?

7. What do you understand by chemical equilibrium? Explain with one suitable example.

8. What do you understand by dynamic nature of chemical equilibrium ? Give one experiment to prove that equilibrium is dynamic in nature.

9. List any four important characteristics of a chemical equilibrium.

Sec. 7.5. **10.** State and explain the Law of Mass Action.

Sec. 7.6. **11.** State and explain the 'Law of Chemical Equilibrium.'

12. Derive a general expression for the equilibrium constant.

Sec. 7.7. **13.** What do you understand by K_c and K_p ? Derive a relationship between them.

14. Under what conditions $K_c = K_p$ for a gaseous reaction ?

Sec. 7.8. **15.** List the important characteristics of equilibrium constant.

16. How does the magnitude of equilibrium constant give an idea of the relative amounts of the reactants and products ?

17. The equilibrium constant for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2\,NH_3$$

is K. What will be the equilibrium constant for the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3\ ?$$

Sec. 7.9. **18.** Discuss the effect of temperature on the equilibrium constant. How does it change for (*a*) exothermic reaction (*b*) endothermic reaction (*c*) reaction having zero heat of reaction ?

Sec. 7.10. **19.** Define 'Homogeneous Equilibria and Heterogeneous Equilibria'. Give three examples of each of them.

Sec. 7.11. **20.** Write the equilibrium constant expression for the following reactions :

(*i*) $HCl\,(aq) \rightleftharpoons H^+\,(aq) + Cl^-\,(aq)$

(*ii*) $NH_3\,(aq) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$

(*iii*) $Ag_2CrO_4\,(s) + (aq) \rightleftharpoons 2Ag^+\,(aq) + CrO_4^{2-}\,(aq)$

(*iv*) $Al\,(s) + 3H^+\,(aq) \rightleftharpoons Al^{3+}\,(aq) + 3/2\,H_2\,(g)$

(*v*) $CH_3\,COCH_3\,(l) \rightleftharpoons CH_3COCH_3\,(g)$

21. Applying the law of chemical equilibrium explain why vapour pressure of water is constant at constant temperature.

Sec. 7.12. **22.** Why strictly speaking equilibrium constant has no units ?

Sec. 7.13. to 7.15. **23.** The equilibrium constant for the reaction.

$$2H_2\,(g) + O_2\,(g) \rightleftharpoons 2H_2O\,(g)$$

is 1.2×10^{40} at 298 K *i.e.* quite large while H_2 and O_2 do not react under ordinary conditions. How do you explain it ?

24. What is the effect of adding a catalyst on a reaction which is (*a*) in equilibrium (*b*) not in equilibrium ?

25. What is the effect of adding 1 mole of He (*g*) to a flask containing SO_2, O_2 and SO_3 in equilibrium at constant temperature ?

26. Name the factors which influence the equilibrium state. Explain influence of each factor with the help of examples.

27. State Le Chatelier's principle. Give two examples of its applications in chemical industries.

28. The following represents a gaseous system at equilibrium.

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) + \text{Heat}$$

Indicate the direction in which the equilibrium will shift when the following changes are made :

(*i*) Temperature of the system is decreased

(*ii*) Total pressure is decreased

(*iii*) Volume of the container is increased

(*iv*) A catalyst is added.

29. What is chemical equilibrium ? How does Le Chatelier's principle enable us to predict the effect of change in external conditions on a system in equilibrium ?

30. Consider the following reaction

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g) \quad \Delta H = 58{\cdot}6\ \text{kJ}$$

What will be the effect of the following changes on the concentration of N_2O_4 at equilibrium ?

(*i*) Increasing the pressure

(*ii*) Increasing the temperature

(*iii*) Increasing the volume

(*iv*) Adding more NO_2 (*g*) to the system without changing temperature and pressure

(*v*) Adding catalyst.

31. What will be the effect of increased pressure on the following equilibria ?

(*i*) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

(*ii*) $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

(*iii*) $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_2\,(g)$

(*iv*) $2O_3\,(g) \rightleftharpoons 3O_2\,(g)$

(*v*) $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

32. Using Le Chatelier's principle, predict the effect of

(*i*) decreasing the temperature and

(*ii*) increasing the pressure on each of the following equilibria :

A. $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + \text{Heat}$

B. $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g) + \text{Heat}$

C. $H_2O\,(g) + \text{Heat} \rightleftharpoons H_2\,(g) + \frac{1}{2}\,O_2\,(g)$

D. $2CO\,(g) + O_2\,(g) \rightleftharpoons 2CO_2\,(g) + \text{Heat}$

33. In the reaction equilibrium $A + B \rightleftharpoons C + D$, what will happen to concentration of A, B and D if the concentration of C is increased ?

34. Mention at least three ways by which the concentration of SO_3 can be increased after the equilibrium is established in the following reaction :

$$2SO_2\,(g) + O_2(g) \rightleftharpoons 2SO_3 + \text{Heat}$$

35. What is Le Chatelier's principle ? Under what conditions is it applicable ? How does it differ from the Law of Mass Action ?

36. Why does manufacture of ammonia by Haber's process require higher pressure, low temperature, use of catalyst and pure gases ?

37. State Le Chatelier-Braun principle. Discuss its application in the manufacture of NH_3 by Haber's process.

38. With the help of Le Chatelier's principle, explain the following :

(*i*) Effect of temperature on the solubility of sugar in water, given that dissolution of sugar in water is an endothermic process.

(*ii*) Effect of temperature and pressure on the solubility of gases in liquids.

(*iii*) Effect of pressure on the boiling point of a liquid.

(*iv*) Effect of pressure on the freezing point of liquid.

Long Answer Questions CARRYING 5 or more MARKS

Sec. 7.1. to 7.3. **1.** What do you understand by 'Equilibrium' ? Discuss one example of each of the following physical equilibria :

(*i*) Solid-liquid equilibrium

(*ii*) Liquid-gas equilibrium

(*iii*) Solid-solution equilibrium

(*iv*) Gas-solution equilibrium

Give one important characteristic of each of the above equilibria.

Sec. 7.4. **2.** Briefly explain the following :—

(*i*) Reversible and Irreversible reaction

(*ii*) Dynamic nature of chemical equilibrium

3. Briefly explain the important characteristics of chemical equilibrium.

Sec. 7.5. to 7.6. **4.** State and explain the Law of Mass Action. Derive the Law of chemical equilibrium and hence define equilibrium constant.

Sec. 7.7. **5.** What are K_c and K_p ? Derive a relationship between them.

Sec. 7.8. to 7.9. **6.** Explain the effect of the following on the equilibrium constant.

(*i*) Concentrations of the reactants are doubled

(*ii*) The reaction is reversed

(*iii*) Catalyst is added to the reaction

(*iv*) Temperature is increased.

Sec. 7.10. to 7.12. **7.** What are Homogeneous and Heterogeneous equilibria ? Give three examples of each. Write expressions for their equilibrium constant and give its units in each case.

Sec. 7.13. to 7.15. **8.** State and explain Le-Chatelier's principle. Discuss its application to the manufacture of

(*i*) NH_3 by Haber's process

(*ii*) H_2SO_4 by contact process

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

Calculation of degree of dissociation from vapour density measurements

Degree of dissociation of a substance at a particular temperature is defined as the fraction of the total number of molecules dissociated into simpler molecules at that particular temperature i.e.

$$\text{Degree of dissociation} \quad (\alpha) = \frac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}}$$

Degree of dissociation can be calculated from vapour density measurements for those substances which are accompanied by change in the number of moles *e.g.*

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad \text{or} \qquad N_2O_4 \rightleftharpoons 2\,NO_2 \text{ etc.}$$

Taking the example of dissociation of PCl_5, suppose we start with 1 mole of PCl_5 and α is its degree of dissociation at the exeperimental temperature. Then we have

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

	PCl_5	PCl_3	Cl_2
No. of moles before dissociation	1	0	0
No. of moles after dissociation	$1-\alpha$	α	α

Suppose the volume occupied by the vapour per mole = V litres. Then

Before dissociation. Total no. of moles = 1. Hence total volume = V litres. If D is the vapour density of PCl_5 before dissociation (called *theoretical vapour density*), then

$$D \propto \frac{1}{V} \qquad \left(\because \text{ Density} \propto \frac{1}{\text{Volume}}\right) \qquad \text{...(}i\text{)}$$

After dissociation. Total no. of moles = $(1-\alpha) + \alpha + \alpha = 1 + \alpha$

$\therefore$ Total volume occupied by the reaction mixture = $(1 + \alpha)$ V litres

Now, if d is the density of the vapour (called *observed density*), then

$$d \propto \frac{1}{(1+\alpha)V} \qquad \text{...(}ii\text{)}$$

Dividing eqn. (*i*) by eqn. (*ii*), we get

$$\frac{D}{d} = \frac{\dfrac{1}{V}}{\dfrac{1}{(1+\alpha)V}} = 1 + \alpha \quad \text{or} \quad \alpha = \frac{D}{d} - 1$$

or

$$\boxed{\alpha = \frac{D-d}{d}} \qquad \text{...(}iii\text{)}$$

ADDITIONAL USEFUL INFORMATION contd.

As Mol. mass = 2 × Vapour density, eqn. (*iii*) can also be written as

$$\alpha = \frac{M_t - M_0}{M_0} \qquad ...(iv)$$

where M_t = theoretical (calculated) molecular mass

M_0 = observed (experimental) molecular mass

Alternatively, observed molecular mass can be calculated from the mass of a definite volume of the vapour at a particular temperature, using the relation

$$PV = \frac{w}{M} RT \quad \text{or} \quad M_0 = \frac{w\,RT}{PV} \quad \left(\text{as } n = \frac{w}{M}\right)$$

In case of dissociation of N_2O_4, we can write

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

	$N_2O_4\,(g)$	$2\,NO_2\,(g)$
No. of moles before dissociation	1	0
No. of moles after dissociation	$1-\alpha$	2α, Total $= 1+\alpha$

Hence the same formulae will apply as for the dissociation of PCl_5.

In general, if one mole dissociates to give *n* moles of products

i.e.	A	⟶	*n*B	
Initial moles	1		0	
Moles after disso.	$1-\alpha$		$n\alpha$	Total $= 1 - \alpha + n\alpha = 1 + (n-1)\alpha$

Then $\frac{D}{d} = 1 + (n-1)\alpha$ or $\alpha = \frac{1}{n-1}\left(\frac{D-d}{d}\right)$

PROBLEMS ON CALCULATION OF DEGREE OF DISSOCIATION FROM V.D.

The vapour density of PCl_5 at 473 K is found to be 70·2. Find the degree of dissociation of PCl_5 at this temperature.

Solution. Theoretical vapour density of PCl_5 is

$$D = \frac{\text{Mol. mass of } PCl_5}{2} = \frac{31 + 5 \times 35{\cdot}5}{2}$$

$$= \frac{208{\cdot}5}{2} = 104{\cdot}25$$

Observed vapour density is, $d = 70{\cdot}2$

∴ Degree of dissociation (α)

$$= \frac{104{\cdot}25 - 70{\cdot}2}{70{\cdot}2} = 0{\cdot}485$$

At 523 K, 1 litre of partially dissociated PCl_5 at 1 atm weighs 2·695 g. Calculate the percentage dissociation of PCl_5 at 523 K.

Solution. Applying the relation,

$$PV = \frac{w}{M} RT$$

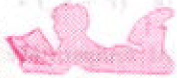
$$M_0 = \frac{w\,RT}{PV} = \frac{2{\cdot}695 \times 0{\cdot}0821 \times 523}{1 \times 1} = 115{\cdot}7$$

For PCl_5, $M_t = 31 + 5 \times 35{\cdot}5 = 208{\cdot}5$

$$\therefore\ \alpha = \frac{M_t - M_0}{M_0} = \frac{208{\cdot}5 - 115{\cdot}7}{115{\cdot}7} = 0{\cdot}80$$

$$= 80\%$$

PROBLEMS FOR PRACTICE



1. At a certain temperature, the vapour density of N_2O_4 is 24·8. Calculate its percentage dissociation at this temperature. [Ans. 85·5%]

2. 1·588 g of N_2O_4 gives a total pressure of 760 mm when partially dissociated in a 500 ml vessel at 298 K. What is its degree of dissociation at this temperature ? [Ans. 0·185]

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS

Q. 1. **Prove that the pressure necessary to obtain 50% dissociation of PCl_5 at 500 K is numerically equal to three times the value of the equilibrium constant, K_p.**

Ans. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
Initial moles	1	0	0
Moles at eqm.	$1 - 0{\cdot}5 = 0{\cdot}5$	$0{\cdot}5$	$0{\cdot}5$

Total = $1{\cdot}5$ moles

If P is the total required pressure, then

$$p_{PCl_5} = \frac{0{\cdot}5}{1{\cdot}5} \times P = \frac{P}{3},\ p_{PCl_3} = \frac{0{\cdot}5}{1{\cdot}5} \times P = \frac{P}{3},$$

$$p_{Cl_2} = \frac{0{\cdot}5}{1{\cdot}5} \times P = \frac{P}{3}$$

$$\therefore\ K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{(P/3)(P/3)}{(P/3)} = \frac{P}{3}$$

or $P = 3\,K_p$.

Q. 2. **Show that the degree of dissociation (α) for the dissociation of PCl_5 into PCl_3 and Cl_2 at pressure P is given by $\alpha = \left(\frac{K_p}{P + K_p}\right)^{1/2}$**

Ans. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
Initial moles	1	0	0
Moles after disso.	$1 - \alpha$	α	α, Total = $1 + \alpha$

$$\therefore\ p_{PCl_5} = \frac{1-\alpha}{1+\alpha} \times P, p_{PCl_3} = \frac{\alpha}{1+\alpha} \times P, p_{Cl_2} = \frac{\alpha}{1+\alpha} \times P$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{\alpha}{1+\alpha} P\right)\left(\frac{\alpha}{1+\alpha} P\right)}{\left(\frac{1-\alpha}{1+\alpha} P\right)} = \frac{\alpha^2 P}{1 - \alpha^2}$$

or $(1 - \alpha^2) K_p = \alpha^2 P$

or $(P + K_p)\,\alpha^2 = K_p$ or $\alpha = \left(\frac{K_p}{P + K_p}\right)^{1/2}$

Q. 3. **At temperature T, a compound $AB_2\,(g)$ dissociates according to the reaction**

$$2AB_2 \rightleftharpoons 2AB\,(g) + B_2\,(g)$$

with a degree of dissociation, x, which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant, K_p and the total pressure, P.

(I.I.T. 1994)

Ans. $2AB_2\,(g) \rightleftharpoons 2AB\,(g) + B_2\,(g)$

	$2AB_2\,(g)$	$2AB\,(g)$	$B_2\,(g)$
Initial	1 mole	0	0
At equilibrium	$1 - x$	$2x$	x

Total number of moles at equilibrium

$= 1 - x + 2x + x = 1 + 2x$

$$p_{AB_2} = \frac{1 - x}{1 + 2x} \times P$$

$$p_{AB} = \frac{2x}{1 + 2x} \times P$$

$$p_{B_2} = \frac{x}{1 + 2x} \times P$$

$$\therefore\ K_p = \frac{p^2_{AB} \times p_{B_2}}{p^2_{AB_2}}$$

$$= \left(\frac{2x \times P}{1 + 2x}\right)^2 \times \left(\frac{x \times P}{1 + 2x}\right)\left(\frac{1 - x}{1 + 2x} \times P\right)^2$$

$$\text{or}\quad K_p = \frac{4x^3 P}{(1 - x)(1 + 2x)}$$

Neglecting x in comparison to unity

$$K_p = 4x^3 P \quad \text{or} \quad x = \left(\frac{K_p}{4P}\right)^{1/3}$$

Q. 4. **Giving reasons in brief, indicate whether the following statement is TRUE or FALSE :**

The rate of an exothermic reaction increases with increasing temperature. ***(I.I.T. 1990)***

Ans. False because in an exothermic reaction, heat is evolved. Increase of temperature will shift the equilibrium in the backward direction *i.e.* the rate of reaction decreases.

Q. 5. **What is the effect of reducing the volume on the system described below ?**

$$2\,C\,(s) + O_2\,(g) \rightleftharpoons 2\,CO\,(g)$$

(B.I.T. Ranchi 1990)

Ans. On reducing the volume, the pressure will increase. By Le Chatelier's principle, equilibrium will shift to the side accompanied by decrease of pressure *i.e.* decrease in the number of gaseous moles *i.e.* backward direction.

Q. 6. **Nitrogen and hydrogen react to form ammonia as per the reaction**

$$1/2\,N_2 + 3/2\,H_2 \rightleftharpoons NH_3$$

When the mixture of the three gases is in equilibrium, predict whether the amount of ammonia increases or decreases if

(*i*) the pressure on the system is increased.

***(ii)* the temperature of the system is raised.**
***(iii)* the concentration of hydrogen is increased.**
(B.I.T. Ranchi 1991)

Ans. *(i)* When pressure is increased, equilibrium shifts to that direction in which pressure decreases *i.e.* number of moles decreases which is in the forward direction. Hence the amount of NH_3 increases.

(ii) As the forward reaction is exothermic, increase of temperature will shift the equilibrium in the backward direction *i.e.* the amount of NH_3 decreases.

(iii) On increasing the concentration of H_2, equilibrium will shift in the forward direction *i.e.* the amount of NH_3 increases.

Q. 7. Express K_p and K_c for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

What is the relation between these equilibrium constants for the above reaction ?

(I.S.M. Dhanbad 1991)

Ans. $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$, $K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}}$,

$\Delta n = 2 - (1+3) = -2$

$\therefore K_p = K_c (RT)^{\Delta n} = K_c (RT)^{-2} = K_c / (RT)^2$

Q. 8. A reaction $A(g) + B(g) \rightleftharpoons 2C(g)$ is in equilibrium at a certain temperature. Can we increase the amount of products by *(i)* adding catalyst *(ii)* increasing pressure ?

Ans. *(i)* No, because catalyst does not disturb the state of equilibrium. *(ii)* No, because $n_p = n_r$

Q. 9. The reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is being carried out in a closed vessel at 373 K. At a particular instant, concentration of N_2O_4 as well as NO_2 is 1 mol L^{-1}. In which direction the reaction will go to establish the equilibrium ? The equilibrium constant for the reaction at 373 K is 0·36.

Ans. Concentration quotient, Q (at 373 K)

$$= \frac{[NO_2]^2}{[N_2O_4]} = 1. \text{ But } K_c = 0{\cdot}36.$$

Thus to establish the equilibrium, Q should decrease. This can happen if $[NO_2]$ decreases or $[N_2O_4]$ increases *i.e.* equilibrium shifts in the backward direction.

Q. 10. In the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at equilibrium, gas is injected into the vessel without disturbing the overall pressure of the system. What will be the effect on the equilibrium ?

Ans. $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

As pressure is kept constant, volume will increase. Hence molar concentraton of NH_3, N_2 and H_2 will decrease. As there are two concentration terms in numerator and four concentration terms in the denominator, to keep K_c constant, decrease in NH_3 should be more *i.e. equilibrium will shift in the backward direction.*

Q. 11. At a particular temperature, the number of moles of different constituents for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ are $(1-\alpha)$ for N_2, $3(1-\alpha)$ for H_2 and 2α for NH_3. Find out K_p in terms of α and the total pressure. Show that α will increase with the increase of the total pressure. Assume that $\alpha << 1$.

(West Bengal J.E.E. 2001)

Ans. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Moles at eqm. $1-\alpha$ $\quad 3(1-\alpha)$ $\quad 2\alpha$,

Total $= 4 - 2\alpha = 2(2-\alpha)$

$$p_{N_2} = \frac{1-\alpha}{2(2-\alpha)} P, \quad p_{H_2} = \frac{3(1-\alpha)}{2(2-\alpha)} P,$$

$$p_{NH_3} = \frac{2\alpha}{2(2-\alpha)} P$$

$$K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}}$$

$$= \frac{[\alpha^2/(2-\alpha)^2]P^2}{[(1-\alpha)/2(2-\alpha)]P \times [9(1-\alpha)^3/8(2-\alpha)^3]P^3}$$

$$= \frac{16\alpha^2(2-\alpha)^2}{9(1-\alpha)^4} \frac{1}{P^2}$$

Taking $\alpha << 1$,

$$K_p = \frac{16\alpha^2 \times (2)^2}{9} \times \frac{1}{P^2} = \frac{64\alpha^2}{9P^2}$$

If P is increased, to keep K_p constant, α will increase.

Q. 12. Mention two different ways of drawing the following equilibrium towards right

$$CH_3COOH + CH_3CH_2OH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O \text{ (all are liquids)}$$

(West Bengal J.E.E. 2003)

Ans. *(i)* By adding more of CH_3COOH or CH_3CH_2OH.

(ii) By removing the ester or water formed.

Q. 13. The equilibrium constant for the reaction : $A_2 + B_2 \rightleftharpoons 2AB$ is K_p. What will be the equilibrium constant for the reaction, $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$? [A, B and AB, all are gases]

(West Bengal J.E.E 2004)

Ans. For $A_2 + B_2 \rightleftharpoons 2AB$, equilibrium constant $= K_p$

For the reverse reaction, $2\,AB \rightleftharpoons A_2 + B_2$, equilibrium constant $= 1/K_p$

On dividing by 2, $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$, equilibrium constant $= 1/\sqrt{K_p}$

B. PROBLEMS

Problem 1. **Ammonium carbamate decomposes as $NH_2COONH_4\,(s) \rightleftharpoons 2\,NH_3\,(g) + CO_2\,(g)$**

In a closed vessel containing ammonium carbamate in equilibrium, NH_3 is added such that the partial pressure of NH_3 now equals original total pressure. Calculate the ratio of total pressure now to the original pressure.

Solution. Suppose the total pressure of the mixture initially is P. This is due to NH_3 and CO_2 which are present in the ratio of 2 : 1. Thus $p_{NH_3} = \frac{2}{3}P$, $p_{CO_2} = \frac{1}{3}P$

$$\therefore K_p = (p_{NH_3})^2\,(p_{CO_2})^2 = \left(\frac{2}{3}P\right)^2\left(\frac{1}{3}P\right) = \frac{4}{27}P^3$$

After adding NH_3, $p_{NH_3} = P$ *(Given)*

$$\therefore \quad P^2 \times p_{CO_2} = K_p = \frac{4}{27}P^3 \text{ or } p_{CO_2} = \frac{4}{27}P$$

$$\therefore \text{ Total pressure now} = p_{NH_3} + p_{CO_2}$$

$$= P + \frac{4}{27}P = \frac{31}{27}P$$

$\therefore$ Ratio of total pressure now to the original pressure $= \frac{31}{27}$

Problem 2. **The equilibrium constant of a reaction doubles on increasing the temperature of the reaction from 25°C to 35°C. Calculate enthalpy change of the reaction, assuming it to be constant in this temperature range.**

Solution. According to integrated van't Hoff equaton (page 7/16)

$$\log\frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H°}{2{\cdot}303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Putting $(K_p)_2/(K_p)_1 = 2$, $T_1 = 25°C = 298\ K$, $T_2 = 35°C = 308\ K$

$R = 8{\cdot}314\ JK^{-1}\ mol^{-1}$, we get

$$\log 2 = \frac{\Delta H°}{2{\cdot}303 \times 8{\cdot}314\ JK^{-1}\,mol^{-1}} \times \frac{(308 - 298)\ K}{298\ K\ 308\ K}$$

or $\Delta H° = 52898\ J\,mol^{-1} = \mathbf{52{\cdot}898\ kJ\,mol^{-1}}$

Problem 3. **An equilibrium mixture $CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$ present in a vessel of one litre capacity at 1000 K was found to contain 0·4 mole of CO, 0·3 mole of H_2O, 0·2 mole of CO_2 and 0·6 mole of H_2. If it is desired to increase the concentration of CO to 0·6 mole by adding CO_2 into the vessel, how many moles of it must be added into equilibrium mixture at constant temperature in order to get this change.**

Solution. **Step 1.** *To calculate K_c of the reaction.*

$$K_c = \frac{[CO_2\,(g)]\,[H_2\,(g)]}{[CO\,(g)]\,[H_2O\,(g)]} = \frac{0{\cdot}2 \times 0{\cdot}6}{0{\cdot}4 \times 0{\cdot}3} = 1$$

Step 2. *To calculate extra CO_2 to be added*

Suppose extra CO_2 to be added $= x$ mole. Then writing the reverse reaction, we have

	CO_2	+ H_2 $\rightleftharpoons$	CO	+ H_2O
Initial moles after addition	$0{\cdot}2 + x$	$0{\cdot}6$	$0{\cdot}4$	$0{\cdot}3$
Moles (Molar conc.) at new equilibrium	$(0{\cdot}2 + x - 0{\cdot}2)$ $= x$	$(0{\cdot}6 - 0{\cdot}2)$ $= 0{\cdot}4$	$0{\cdot}6$ *(Given)*	$(0{\cdot}3 + 0{\cdot}2)$ $= 0{\cdot}5$

(V = 1 L)

$$K_c' = \frac{1}{K_c} = \frac{0{\cdot}6 \times 0{\cdot}5}{x \times 0{\cdot}4} = 1 \text{ or } x = \mathbf{0{\cdot}75\ mole}$$

Problem 4. **The degree of dissociation of N_2O_4 into NO_2 at one atmospheric pressure and 313 K is 0·310. Calculate K_p of the dissociation reaction at this temperature. What will be the degree of dissociation at 10 atmospheric pressure at the same temperature ?**

Solution. For the dissociation reaction

	$N_2O_4\,(g) \rightleftharpoons$	$2\,NO_2\,(g)$
Initial moles	1	0
Moles at eqm.	$1 - 0{\cdot}310$ $= 0{\cdot}69$	$2 \times 0{\cdot}310$ $= 0{\cdot}62$

($\alpha = 0{\cdot}310$, Given)

Total $= 0{\cdot}69 + 0{\cdot}62 = 1{\cdot}31$ moles

At one atmospheric pressure,

$$p_{N_2O_4} = \frac{0{\cdot}69}{1{\cdot}31} \times 1\ atm, \quad p_{NO_2} = \frac{0{\cdot}62}{1{\cdot}31} \times 1\ atm.$$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{(0{\cdot}62/1{\cdot}31\ atm)^2}{(0{\cdot}69/1{\cdot}31\ atm)} = 0{\cdot}425\ atm$$

At 10 atmospheric pressure, suppose degree of dissociation $= \alpha$. Then

	$N_2O_4 \rightleftharpoons$	$2\,NO_2$	
Initial moles	1	0	
Moles at eqm.	$1 - \alpha$	2α,	Total $= 1 + \alpha$

$$p_{N_2O_4} = \frac{1 - \alpha}{1 + \alpha} \times 10\ atm, \quad p_{NO_2} = \frac{2\alpha}{1 + \alpha} \times 10\ atm$$

$$K_p = \frac{[20\,\alpha/(1 + \alpha)]^2}{[10\,(1 - \alpha)/(1 + \alpha]} = \frac{40\,\alpha^2}{(1 - \alpha\,(1 + \alpha)} = \frac{40\,\alpha^2}{1 - \alpha^2}$$

$$\therefore \quad \frac{40\,\alpha^2}{1-\alpha^2} = 0\cdot425$$

Neglective α^2 in comparison to 1, $40\,\alpha^2 = 0\cdot425$

or $\quad \alpha = 0\cdot103 = 10\cdot3\%$

Problem 5. **When α – D glucose is dissolved in water, it undergoes mutarotation to form an equilibrium mixture of α – D glucose and β – D glucose containing 63·6% of the latter. Calculate K_c for the mutarotation.**

Solution. α – D glucose $\rightleftharpoons$ β – D glucose

At equilibrum	36·4%	63·6%

$$K_c = \frac{63\cdot6}{36\cdot4} = 1\cdot747$$

Problem 6. **At 77°C and one atmospheric pressure, N_2O_4 is 70% dissociated into NO_2. What will be the volume occupied by the mixture under these conditions if we start with 10 g of N_2O_4 ?**

Solution. Molar mass of N_2O_4

$= 28 + 64 = 92\,g\,mol^{-1}$

	$N_2O_4 \rightleftharpoons$	$2\,NO_2$
Initial moles	$\frac{10}{92}$	0
After dissociation	$\frac{10}{92} - \frac{70}{100} \times \frac{10}{92}$	$2 \times 0\cdot076$
	$= 0\cdot109 - 0\cdot076$	$= 0\cdot152$
	$= 0\cdot033$	

$\therefore$ Total moles after dissociation

$= 0\cdot033 + 0\cdot152 = 0\cdot185$

$T = 77°C = 77 + 273\,K = 350\,K$

$PV = nRT$ or $V = \frac{n\,RT}{P}$

$$= \frac{0\cdot185 \text{ mole} \times 0\cdot0821 \text{ L atm K}^{-1}\text{ mol}^{-1} \times 350\text{ K}}{1 \text{ atm}}$$

= 5·32 L.

Problem 7. **Some solid NH_4HS is placed in a flask contaning 0·5 atm of NH_3. What would be the pressure of NH_3 and H_2S when equilibrium is reached ?**

$$NH_4HS\,(s) \rightleftharpoons NH_3\,(g) + H_2S\,(g),\ K_p = 0\cdot11$$

(M.L.N.R. Allahabad 1994)

Solution. NH_3 and H_2S produced by the decomposition of NH_4HS will be same. Suppose at equilibrium each has pressure $= p$ atm due to decomposition of NH_4HS. Then $p_{H_2S} = p$ atm

$p_{NH_3} = p + 0\cdot5$ atm

Applying law of chemical equilibrium to the given reaction

$$p_{NH_3} \times p_{H_2S} = K_p$$

$\therefore \quad p \times (p + 0\cdot5) = 0\cdot11$

or $\quad p^2 + 0\cdot5\,p = 0\cdot11$

or $\quad p^2 + 0\cdot5\,p - 0\cdot11 = 0$

$$\therefore \quad p = \frac{-0\cdot5 \pm \sqrt{(0\cdot5)^2 - 4\,(-0\cdot11)}}{2}$$

$$= \frac{-0\cdot5 \pm \sqrt{0\cdot25 + 0\cdot44}}{2}$$

$$= -\frac{0\cdot5 \pm \sqrt{0\cdot69}}{2}$$

$$= \frac{-0\cdot5 \pm 0\cdot83}{2} = \frac{0\cdot33}{2} = 0\cdot165$$

$\therefore \quad p_{H_2S} = 0\cdot165$ **atm,** $\quad p_{NH_3} = 0\cdot665$ **atm**

(Neglecting —ve value)

Problem 8. **One mole of H_2 and three moles of HI are injected in a litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 490°C ? The equilibrium constant for the reaction at 490° C is 45.9.**

(M.L.N.R. Allahabad 1995)

Solution.	H_2 +	$I_2 \rightleftharpoons$	2HI
Initial conc.	1	2	3
			moles L^{-1}
Concs at eqm.	$(1 - x)$	$(2 - x)$	$(3 + 2x)$
			mole L^{-1}

$$K = \frac{(3 + 2x)^2}{(1 - x)\,(2 - x)} = \frac{9 + 4\,x^2 + 12\,x}{2 + x^2 - 3\,x} = 45\cdot9$$

(Given)

$\therefore \quad 9 + 4x^2 + 12x = 91\cdot8 + 45\cdot9x^2 - 137\cdot7x$

or $\quad 41\cdot9x^2 - 149\cdot7x + 82\cdot8 = 0$

$$x = \frac{149\cdot7 \pm \sqrt{(149\cdot7)^2 - 4 \times 41\cdot9 \times 82\cdot8}}{2 \times 41\cdot9}$$

$$= \frac{149\cdot7 \pm \sqrt{22410\cdot09 - 13877\cdot28}}{83\cdot8}$$

$$= \frac{149\cdot7 \pm 92\cdot4}{83\cdot8} = 2\cdot89 \text{ and } 0\cdot68$$

But $\quad x = 2\cdot89$ is impossible. Hence $x = 0\cdot684$

$\therefore$ Concentrations at equilibrium will be

$[H_2] = 1 - x = 1 - 0\cdot684 = $ **0·316 mol L^{-1}**

$[I_2] = 2 - x = 2 - 0\cdot684 = $ **1·316 mol L^{-1}**

$[HI] = 3 + 2x = 3 + 2 \times 0\cdot684$

= 4·368 mol L^{-1}

Problem 9. **A mixture of H_2 and I_2 (vapour) in molecular proportion of 2 : 3 was heated at 440°C till the reaction $H_2 + I_2 \rightleftharpoons 2HI$ reached equilibrium**

state. Calculate the percentage of iodine converted into HI (K_c at 440°C is 0·02). ***(Bihar 1997)***

Solution.	$H_2(g)$	$+ I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial	2	3		0 moles
At eqm.	$2-x$	$3-x$		$2x$
Molar concs	$\frac{2-x}{V}$	$\frac{3-x}{V}$		$\frac{2x}{V}$

$$K_c = \frac{(2x/V)^2}{[(2-x)/V]\,[(3-x)/V]}$$

$$= \frac{4x^2}{(2-x)(3-x)} = 0\cdot02 \text{ (Given)}$$

This on solving gives $x = 0\cdot1615$

$\therefore$ % of iodine converted into HI

$$= \frac{0\cdot1615}{3} \times 100 = 5\cdot38\%.$$

Problem 10. **0·1 mole of N_2O_4 (g) was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of moles of NO_2 (g) present if the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is reached after some time (K_p = 0·14)** ***(M.L.N.R. 1997)***

Solution.	$N_2O_4(g)$	$\rightleftharpoons 2NO_2(g)$
Initial amounts	$0\cdot1$ mole	0
At equilibrium	$(0\cdot1-x)$	$2x$,

Total = $0\cdot1 + x$ moles

As P = 1 atm,

$$p_{N_2O_4} = \frac{0\cdot1-x}{0\cdot1+x},\quad p_{NO_2} = \frac{2x}{0\cdot1+x}\text{ atm.}$$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}$$

$$= \frac{(2x/(0\cdot1+x))^2}{(0\cdot1-x)/(0\cdot1+x)} = \frac{4x^2}{(0\cdot1-x)(0\cdot1+x)}$$

$$= \frac{4x^2}{0\cdot01-x^2}$$

$$\therefore \frac{4x^2}{0\cdot01-x^2} = 0\cdot14 \text{ or } 4\cdot14x^2 = 0\cdot0014$$

or $\qquad x = 0\cdot018$

$\therefore$ No. of moles of NO_2 at equilibrium

$= 2x = 2 \times 0\cdot018 =$ **0·036 mole**

I.I.T. (MAINS) SPECIAL

Problem 1. **The degree of dissociation of HI at a particular temperature is 0·8. Calculate the volume of 2 M $Na_2S_2O_3$ solution required to neutralize the iodine present in the equilibrium mixture of a reaction when 2 mole each of H_2 and I_2 are heted in a closed vessel of 2 litre capacity.**

Solution. Step 1. *Calculation of K_c.*

Degree of dissociation of HI (α) = 0·8

	$2HI$	$\rightleftharpoons$ H_2	$+ I_2$
Before dissociation	1	0	0
Moles after disso.	$1-\alpha$	$\alpha/2$	$\alpha/2$

$$K_c = \frac{(\alpha/2)(\alpha/2)}{(1-\alpha)^2} = \frac{\alpha^2}{4(1-\alpha)^2} = \frac{(0\cdot8)^2}{4(1-0\cdot8)^2} = 4$$

Step 2. *Calculation of I_2 in equilibrium mixture.*

	H_2	$+ I_2$	$\rightleftharpoons$ $2HI$
Initial moles	2	2	0
Moles after reaction	$(2-x)$	$(2-x)$	$2x$
Molar conc.	$(2-x)/2$	$(2-x)/2$	$2x/2$

$$K_c' = \frac{1}{K_c} = \frac{(2x/2)^2}{\left(\frac{2-x}{2}\right)\left(\frac{2-x}{2}\right)} = \frac{4x^2}{(2-x)^2}$$

$$\therefore \frac{4x^2}{(2-x)^2} = \frac{1}{4} \text{ or } \frac{2x}{2-x} = \frac{1}{2} \text{ or } x = \frac{2}{5}$$

Thus I_2 left $= 2 - \frac{2}{5} = \frac{8}{5}$ mole.

Step 3. *Calculation of volume of hypo used.*

$$2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

2 moles $\quad$ 1 mole

$\therefore$ Moles of $Na_2S_2O_3$ reacted $= 2 \times \frac{8}{5}$ mole

$= \frac{16}{5}$ mole

Volume of 2 M $Na_2S_2O_3$ reacted

$$= \frac{1000}{2} \times \frac{16}{5} = 1600 \text{ mL} = 1\cdot6 \text{ L}$$

Problem 2. **At 627° C and one atmosphere pressure, SO_3 is partially dissociated into SO_2 and O_2 as**

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g).$$

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*These being original problems as asked in the competitive examinations, at many places units of K_p and K_c have been included as per old convention.

The density of the equilibrium mixture is found to be 0·925 g L^{-1}. Calculate the degree of dissociation of SO_3 under the given conditions.

Solution. Observed molar mass can be calculated from the given density as follows :

$$PV = nRT = \frac{w}{M}RT$$

$$\text{or} \quad M_{obs} = \frac{w\,RT}{VP} = \frac{d\,RT}{P}$$

$$= \frac{0\cdot925\,gL^{-1} \times 0\cdot0821\text{ L atm }K^{-1}\text{mol}^{-1} \times (627+273)K}{1\text{ atm}}$$

$= 68\cdot35$ g mol^{-1}

Theoretical molar mass of SO_3 ($M_{theoretical}$)

$= 32 + 48 = 80$ g mol^{-1}

If α is the degree of dissociation,

$$SO_3\,(g) \rightleftharpoons SO_2\,(g) + \frac{1}{2}O_2\,(g)$$

	$SO_3\,(g)$	$SO_2\,(g)$	$\frac{1}{2}O_2\,(g)$
Initial moles	1	0	0
At equilirbium	$1-\alpha$	α	$\frac{1}{2}\alpha$,

Total $= 1 + \frac{\alpha}{2}$

Theoretical V.D. (D) $\propto \frac{1}{V}$ (V = Molar volume)

Observed V.D. $(d) \propto \frac{1}{\left(1+\frac{\alpha}{2}\right)V}$

$$\therefore \quad \frac{D}{d} = 1 + \frac{\alpha}{2} \quad \text{or} \quad \alpha = 2\left(\frac{D-d}{d}\right)$$

$$\text{or} \quad \alpha = 2\left(\frac{M_{theretical} - M_{observed}}{M_{observed}}\right)$$

$$= 2\left(\frac{80-68\cdot35}{68\cdot35}\right) = \mathbf{0\cdot3409.}$$

Problem 3. **NH_3 is heated at 15 atm from 27°C to 347°C keeping the volume constant. The new pressure becomes 50 atm at equilibrium of the reaction**

$$2\,NH_3 \rightleftharpoons N_2 + 3\,H_2.$$

Calculate % of mole of NH_3 actually decomposed.

Solution. $2\,NH_3 \rightleftharpoons N_2 + 3\,NH_2$

	$2\,NH_3$	N_2	$3\,NH_2$
Initial moles	a	0	0
Moles at eqm.	$a-2x$	x	$3x$, Total$=a+2x$

Pressure of a moles of NH_3 at 27°C = 15 atm.

Pressure of a moles of NH_3 at 347°C

= P atm *(say)*

As volume remains constant, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{15}{300} = \frac{P}{620} \quad \text{or} \quad P = 31 \text{ atm.}$$

Now at 327°C and constant volume,

Pressure $\propto$ No. of moles

$\therefore \quad 31 \propto a$

$50 \propto a + 2x$

$$\therefore \quad \frac{a+2x}{a} = \frac{50}{31} \quad \text{or} \quad x = \frac{19}{62}a$$

% of NH_3 decomposed

$$= \frac{2x}{a} \times 100 = 2 \times \frac{19a}{62} \times \frac{1}{a} \times 100 = 61\cdot3\%$$

Problem 4. **The equilibrium constant of the reaction**

$$A_2\,(g) + B_2\,(g) \rightleftharpoons 2AB\,(g)$$

at 100°C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2, how many moles of AB will be formed at 373 K ? ***(I.I.T. 1985)***

Solution. $A_2 + B_2 \rightleftharpoons 2AB$

	A_2	B_2	$2AB$
Initial amounts :	1 mole	2 moles	0
Amounts at eqm:	$1-x$	$2-x$	$2x$
Molar concs at eqm.	$\frac{1-x}{3}$	$\frac{2-x}{3}$	$\frac{2x}{3}$ mol L^{-1}

$$K = \frac{[AB]^2}{[A_2]\,[B_2]}$$

$$\text{or} \quad 50 = \frac{(2x)^2}{\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)}$$

On solving, we get $x = 0\cdot955$ mole

Hence no. of moles of AB formed at eqm.

$= 2 \times 0\cdot955$

$= \mathbf{1\cdot91}$ **moles**

Problem 5. **A mixture of SO_3, SO_2 and O_2 gases is maintained at equilibrium in 10 litre flask at a temperature at which K_c for the reaction, $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$ is 100 mol^{-1} litre. At equilirbium.**

(a) If no. of moles of SO_3 and SO_2 in the flask are same, how many moles of O_2 are present ?

(b) If no. of moles of SO_3 in the flask are twice the number of moles of SO_2, how many moles of O_2 are present. ***(Roorkee 1987)***

Solution. $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = 100\,(\textit{Given})$$

(*a*) As $[SO_3] = [SO_2]$,

$$\therefore 100 = \frac{1}{[O_2]} \quad \text{or} \quad [O_2] = \frac{1}{100} \text{ mol L}^{-1}$$

$$\therefore O_2 \text{ present in 10 litre} = \frac{1}{100} \times 10 = \mathbf{0 \cdot 1 \text{ mole}}$$

(*b*) If $[SO_3] = 2\,[SO_2]$, *i.e.* $\frac{[SO_3]}{[SO_2]} = 2$, then

$$100 = \frac{4}{[O_2]} \quad \text{or} \quad [O_2] = \frac{4}{100} \text{ mol L}^{-1}$$

$$\therefore O_2 \text{ present in 10 litre} = \frac{4}{100} \times 10 = \mathbf{0 \cdot 4 \text{ mole}}$$

Problem 6. **The equilirbium constant K_p of the reaction $2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$ is 900 atm^{-1} at 800 K. A mixture containing SO_3 and O_2 having initial pressure of 1 atm and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K at equilibrium.** ***(I.I.T. 1989)***

Solution. Considering the reverse reaction, we have

$$\begin{array}{llll} & 2\,SO_3 \rightleftharpoons & 2\,SO_2 + & O_2, \; K_p = \frac{1}{900} \text{ atm} \\ \text{Initial pressure} & 1 \text{ atm} & 0 & 2 \text{ atm} \\ \text{Pressure at eqm.} & 1 - x & x & 2 + \frac{x}{2} \end{array}$$

$$K_p = \frac{p^2_{SO_2} \times p_{O_2}}{p^2_{SO_3}} = \frac{x^2 \times (2 + \frac{x}{2})}{(1-x)^2} = \frac{1}{900}$$

As K_p for this reaction is very small, $x << 1$. Taking $2 + \frac{x}{2} \approx 2$ and $(1 - x) \approx 1$, we get

$$x^2\,(2) = \frac{1}{900} \quad \text{or} \quad x^2 = \frac{1}{1800} \quad \text{or} \quad x = 0 \cdot 0236$$

Hence at equilibrium

$$p_{SO_3} = 1 - x = 1 - 0 \cdot 0236 \text{ atm} = \mathbf{0 \cdot 9764 \text{ atm}}$$

$$p_{SO_2} = x = \mathbf{0 \cdot 0236 \text{ atm}}$$

$$p_{O_2} = 2 + \frac{x}{2} = 2 + \frac{0 \cdot 0236}{2} = \mathbf{2 \cdot 0118 \text{ atm}}$$

Problem 7. **When sulphur in the form of S_8 is heated at 900 K, the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of S_8 to S_2. Calculate the equilibrium constant for the reaction.** ***(Roorkee 1990)***

Solution.

$$\begin{array}{lll} & S_8(g) \rightleftharpoons & 4\,S_2(g) \\ \text{Initial} & 1 \text{ atm} & \\ \text{At eqm.} & 1 - 0 \cdot 29 & 4 \times 0 \cdot 29 \text{ atm} \\ & = 0 \cdot 71 \text{ atm} & = 1 \cdot 16 \text{ atm} \end{array}$$

$$K_p = \frac{p^4_{s_2\,(g)}}{p_{s_8\,(g)}} = \frac{(1 \cdot 16)^4}{0 \cdot 71} = \mathbf{2 \cdot 55 \text{ atm}^3}$$

Problem 8. **An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0·28 and 1·1 atm respectively. If the volume of the container is doubled, calculate the new equilibrium pressures of the two gases.** ***(Roorkee 1991)***

Solution. **Step 1.** *Calculate of K_p*

$$\begin{array}{lll} & N_2O_4 \rightleftharpoons & 2\,NO_2 \\ \text{Equilibrium pressures} & 0 \cdot 28 \text{ atm} & 1 \cdot 1 \text{ atm.} \end{array}$$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{(1 \cdot 1 \text{ atm})^2}{0 \cdot 28 \text{ atm}} = 4 \cdot 32 \text{ atm.}$$

Step 2. *Calculation of new equilibrium pressures.* On doubling the volume, pressure will decrease to half. Hence equilibrium will shift to the side accompanied by increase in the number of moles *i.e.* forward direction. This means that pressure of N_2O_4 will decrease while that of NO_2 will increase. Suppose decrease in pressure of $N_2O_4 = p$. Then

$$\begin{array}{lll} & N_2O_4 \rightleftharpoons & 2\,NO_2 \\ \text{Initial pressures} & 0 \cdot 28/2 \text{ atm} & 1 \cdot 1/2 \text{ atm} \\ \text{New eqm. pressures} & \left(\frac{0 \cdot 28}{2} - p\right) \text{atm} & \left(\frac{1 \cdot 1}{2} + 2\,p\right) \text{atm.} \\ & = (0 \cdot 14 - p) \text{ atm} & = (0 \cdot 55 + 2\,p) \text{ atm} \end{array}$$

$$K_p = \frac{(0 \cdot 55 + 2p)^2}{(0 \cdot 14 - p)} = 4 \cdot 32 \text{ atm } (\textit{Calculated above})$$

$$0 \cdot 3025 + 4p^2 + 2 \cdot 2p = 0 \cdot 6048 - 4 \cdot 32\,p$$

$$4\,p^2 + 6 \cdot 52\,p - 0 \cdot 3023 = 0$$

$$p = \frac{-6 \cdot 52 \pm \sqrt{42 \cdot 51 + 4 \cdot 84}}{8} = 0 \cdot 045 \text{ atm.}$$

(minus value is neglected)

(For quadratic equation $ax^2 + bx + c = 0$

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

$\therefore$ New equilibrium pressures

$$p_{N_2O_4} = 0 \cdot 14 - 0 \cdot 045 = \mathbf{0 \cdot 095 \text{ atm}}$$

$$p_{NO_2} = 0 \cdot 55 + 2 \times 0 \cdot 045 = \mathbf{0 \cdot 64 \text{ atm}}$$

Problem 9. **K_c for $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at 986°C is 0·63. A mixture of 1 mol of $H_2O(g)$ and 3 moles CO(g) is allowed to react to an equilibrium. The equilibrium pressure is 2·0 atm**

(*a*) How many moles of H_2 are present at equilibrium ?

(*b*) Calculate partial pressure of each gas at equilibrium. ***(Roorkee 1992)***

Solution. $CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$

Initial moles	3	1	0	0
Moles at eqm.	$3-x$	$1-x$	x	x

Total no. of moles at equilibrium

$$= 3 - x + 1 - x + x + x = 4$$

$$K_c = \frac{x \times x}{(3-x)(1-x)} \quad i.e.\ 0{\cdot}63 = \frac{x^2}{3 + x^2 - 4x}$$

On solving, it gives $x = 0{\cdot}681$

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

∴ Moles of H_2 present at eqm. = **0·681 mole**

Total pressure at eqm. = 2 atm (*Given*)

Total moles at eqm. = 4

$$\therefore \quad p_{CO} = \frac{3 - 0{\cdot}681}{4} \times 2 = \mathbf{1{\cdot}16\ atm}$$

$$p_{H_2O} = \frac{1 - 0{\cdot}681}{4} \times 2 = \mathbf{0{\cdot}16\ atm}$$

$$p_{CO_2} = p_{H_2} = \frac{0{\cdot}681}{4} \times 2 = \mathbf{0{\cdot}34\ atm.}$$

Problem 10. **0·15 mole of CO taken in 2·5 *l* flask is maintained at 750 K alongwith a catalyst so that the following reaction can take place.**

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

Hydrogen is introduced until the total pressure of the system is 8·5 atmosphere at equilibrium and 0·08 mole of methanol is formed. Calculate

(*i*) K_p and K_c and (*ii*) the final pressure if the same amount of CO and H_2 as before are used but with no catalyst so that the reaction does not take place. ***(I.I.T. 1993)***

Solution. (*i*) $CO + 2H_2 \rightleftharpoons CH_3OH$

	CO		CH_3OH
Initially :	0·15 mole		
At eqm. :	0·15—0·08 mole = 0·017 mole		0·08 mole

Total volume, $V = 2{\cdot}5$ L,

Total pressure $P = 8{\cdot}5$ atm, $T = 750$ K.

Applying $PV = nRT$,

we get $8{\cdot}5 \times 2{\cdot}5 = n \times 0{\cdot}0821 \times 750$

or $n = 0{\cdot}345$ mole

∴ No. of moles of H_2 at equilibrium

$$= 0{\cdot}345 - (0{\cdot}017 + 0{\cdot}08) = 0{\cdot}248 \text{ mol}$$

$$P_{co} = \frac{0{\cdot}017}{0{\cdot}345} \times 8{\cdot}5 \text{ atm} = 0{\cdot}42 \text{ atm}$$

$$P_{H_2} = \frac{0{\cdot}248}{0{\cdot}345} \times 8{\cdot}5 \text{ atm} = 6{\cdot}11 \text{ atm}$$

$$P_{CH_3OH} = \frac{0{\cdot}08}{0{\cdot}345} \times 8{\cdot}5 \text{ atm} = 1{\cdot}97 \text{ atm}$$

$$K_p = \frac{P_{CH_3OH}}{P_{co} \times P_{H_2}} = \frac{1{\cdot}97}{0{\cdot}42 \times (6{\cdot}11)^2} = 0{\cdot}1256$$

$$K_c = \frac{[CH_3OH]}{[CO]\,[H_2]^2}$$

$$= \frac{0{\cdot}08 / 2{\cdot}5}{(0{\cdot}017/2{\cdot}5)\,(0{\cdot}248/2{\cdot}5)^2} = 478{\cdot}2$$

(*ii*) **No. of moles of H_2 taken initially**

$$= 0{\cdot}248 + 2 \times 0{\cdot}08 = 0{\cdot}308$$

No. of moles of CO taken initially = 0·15

∴ Total no. of moles = 0·308 + 0·15

= 0·458

Applying $PV = nRT$,

$$P \times 2{\cdot}5 = 0{\cdot}458 \times 0{\cdot}0821 \times 750$$

or $\mathbf{P = 11{\cdot}28\ atm}$

Problem 11. **A vessel at 1000 K contains carbon dioxide with a pressure of 0·5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K if the total pressure at equilibrium is 0·8 atm.** ***(Roorkee 1993)***

Solution. The reaction is

$$CO_2\,(g) + C\,(s) \rightleftharpoons 2CO\,(g)$$

Suppose decrease in pressure of CO_2 after reaction $= p$ atm

Then increase in pressure due to CO $= 2p$

∴ Final pressure $= (0{\cdot}5 - p) + 2p$

$= 0{\cdot}5 + p = 0{\cdot}8$ atm (Given)

∴ $p = 0{\cdot}3$ atm. Hence we have

$$p_{CO_2} = 0{\cdot}5 - 0{\cdot}3 = 0{\cdot}2 \text{ atm}$$

and $$p_{CO} = 2 \times 0{\cdot}3 = 0{\cdot}6 \text{ atm}$$

$$\therefore \quad K = \frac{P^2_{CO}}{P_{CO_2}} = \frac{(0{\cdot}6)^2}{0{\cdot}2} = \mathbf{1{\cdot}8}$$

Problem 12. **Calculate the percent dissociation of $H_2S\,(g)$ if 0·1 mole of H_2S is kept in 0·4 litre vessel at 1000 K. For the reaction**

$$2H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S\,(g)$$

the value of K_c is $1{\cdot}0 \times 10^{-6}$ ***(Roorkee 1994)***

Soluton. Molar conc. of $H_2S = \frac{0{\cdot}1}{0{\cdot}4}$ mol L^{-1}

$= 0{\cdot}25$ mol L^{-1}

Suppose degree of dissociation of $H_2S = \alpha$. Then

	H_2S	$\rightleftharpoons$	$2H^+$	+	S^{2-}
Initial conc.	0·25 M				
Conc. at eqm.	$0{\cdot}25\,(1-\alpha)$		$2 \times 0{\cdot}25\,\alpha$ $= 0{\cdot}5\,\alpha$		$0{\cdot}25\,\alpha$

$$K_c = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$10^{-6} = \frac{(0\cdot5\,\alpha)^2\,(0\cdot25\,\alpha)}{0\cdot25\,(1-\alpha)} = \frac{0\cdot25\,\alpha^2}{1-\alpha}$$

Neglecting α in comparison to 1, we get

$$10^{-6} = 0\cdot25\,\alpha^2 \quad \text{or} \quad \alpha^2 = 4 \times 10^{-6}$$

or $\alpha = 2 \times 10^{-3} = 0\cdot002$

$\therefore$ % age dissociation = **0·2%**

Problem 13. **For the reaction $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2\,CN^-$, K_c at 25°C is 4×10^{-19}. Calculate $[Ag^+]$ in solution which was originally 0·1 M in KCN and 0·03 M in $AgNO_3$.** ***(I.I.T. 1994)***

Solution. Originally on mixing KCN and $AgNO_3$, the reaction is

	$2\,KCN$ +	$AgNO_3 \longrightarrow$
Initial amounts	0·1 M	0·03 M
Amounts after reaction	$(0\cdot1-0\cdot06)$ $= 0\cdot04$ M	0

	$Ag(CN)_2^-$ +	KNO_3 +	K^+
Initial amounts	0	0	0
Amounts after reaction	0·03 M	0·03 M	0·03 M

Thus in the solution, now we have $Ag(CN)_2^- = 0\cdot03$ M, $CN^- = 0\cdot04$ M. Suppose x is the amount of $Ag(CN)_2^-$ dissociated at equilibrium. Then

	$Ag(CN)_2^- \rightleftharpoons$	Ag^+ +	$2\,CN^-$
Initial amounts	0·03	0	0·04
Amounts at eqm	$(0\cdot03-x)$	x	$0\cdot04+2x$

$$K_c = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = \frac{x\,(0\cdot04+2x)^2}{(0\cdot03-x)}$$

$= 4 \times 10^{-19}$ *(Given)*

As K_c is very small, dissociation of $Ag(CN)_2^-$ is very small *i.e.* x is very small. Hence $0\cdot04 + 2x \approx 0\cdot04$ and $0\cdot03 - x \approx 0\cdot03$.

$$\therefore \frac{x\,(0\cdot04)^2}{0\cdot03} = 4 \times 10^{-19} \quad \text{or} \quad x = 7\cdot5 \times 10^{-18}$$

Thus at equilibrium, $[Ag^+] = \mathbf{7\cdot5 \times 10^{-18}\ M}$

Problem 14. **At 700 K, hydrogen and bromine react to form hydrogen bromide. The value of equilibrium constant for this reaction is 5×10^8. Calculate the amount of the H_2, Br_2 and HBr at equilibrium if a mixture of 0·6 mole of H_2 and 0·2 mole of Br_2 is heated to 700 K.** ***(Roorkee 1995)***

Solution.	H_2 +	$Br_2 \rightleftharpoons$	$2HBr$
Initial amounts	0·6 mole	0·2 mole	
Amounts at eqm.	$(0\cdot6-x)$	$(0\cdot2-x)$	$2x$ moles
Molar concs at eqm.	$\frac{0\cdot6-x}{V}$	$\frac{0\cdot2-x}{V}$	$\frac{2x}{V}$ moles L^{-1}

(V = Volume of reaction mixture)

$$K = \frac{(2x/V)^2}{\frac{(0.6-x)}{V} \times \frac{(0.2-x)}{V}}$$

$$= \frac{4x^2}{(0\cdot6-x)(0\cdot2-x)} = 5 \times 10^8$$

or $$\frac{4x^2}{0\cdot12 - 0\cdot8x + x^2} = 5 \times 10^8$$

or $(x^2 - 0\cdot8x - 0\cdot12) \times 5 \times 10^8 = 4x^2$

Neglecting $4x^2$ in comparison to $5 \times 10^8 x^2$, we get

$$x^2 - 0\cdot8x - 0\cdot12 = 0$$

$$x = \frac{0\cdot8 \pm \sqrt{(0\cdot8)^2 - 4 \times 0\cdot12}}{2}$$

$$= \frac{0\cdot8 \pm 0\cdot693}{2} = 0\cdot7465 \text{ and } 0\cdot0535$$

$x = 0\cdot7465$ is impossible. Hence $x = 0\cdot0535$

$\therefore$ Amounts at equlibrium will be

$H_2 = 0\cdot6 - 0\cdot0535 =$ **0·5465 mole**

$Br_2 = 0\cdot2 - 0\cdot0535 =$ **0·1465 mole**

$HBr = 2 \times 0\cdot0535 =$ **0·1070 mole**

Problem 15. **At some temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated, temperature remaining same.** ***(Roorkee 1996)***

Solution. 1st case. *When PCl_5 is 10% dissociated*

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
At eqm.	$1 - 0\cdot1$ $= 0\cdot9$ mole	0·1 mole	0·1 mole

Total no. of moles = 0·9 + 0·1 + 0·1 = 1·1 mole

$$p_{PCl_5} = \frac{0\cdot9}{1\cdot1} \times 4 \text{ atm}, \quad p_{PCl_3} = \frac{0\cdot1}{1\cdot1} \times 4 \text{ atm},$$

$$p_{Cl_2} = \frac{0\cdot1}{1\cdot1} \times 4 \text{ atm}$$

$$\therefore K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\frac{0\cdot4}{1\cdot1} \times \frac{0\cdot4}{1\cdot1}}{\frac{0\cdot9 \times 4}{1\cdot1}} = 0\cdot0404$$

2nd case. *When PCl_5 is 20% dissociated.* Suppose total pressure = P atm. Then

$$\begin{array}{lccc} & PCl_5 & \rightleftharpoons PCl_3 & + \quad Cl_2 \\ \text{Initial} & 1 \text{ mole} & & \\ \text{At equilibrium} & 1-0{\cdot}2 & 0{\cdot}2 \text{ mole} & 0{\cdot}2 \text{ mole} \\ & = 0{\cdot}8 \text{ mole} & & \end{array}$$

Total no. of moles $= 0{\cdot}8 + 0{\cdot}2 + 0{\cdot}2$
$= 1{\cdot}2$ moles

$$p_{PCl_5} = \frac{0{\cdot}8}{1{\cdot}2} \times \text{P atm}, \; p_{PCl_3} = \frac{0{\cdot}2}{1{\cdot}2} \times \text{P atm},$$

$$p_{Cl_2} = \frac{0{\cdot}2}{1{\cdot}2} \times \text{P atm}$$

$$K_p = \frac{\frac{0{\cdot}2\,P}{1{\cdot}2} \times \frac{0{\cdot}2\,P}{1{\cdot}2}}{\frac{0{\cdot}8\,P}{1{\cdot}2}} = \frac{0{\cdot}2}{1{\cdot}2} \times \frac{0{\cdot}2}{0{\cdot}8} P = 0{\cdot}0404$$

(calculated above)

which gives $P = 0{\cdot}97$ atm

Problem 16. **20% of N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of the equilibrium mixture.** ***(Roorkee 1996)***

Solution.

$$\begin{array}{lcc} & N_2O_4\,(g) \rightleftharpoons & 2\,NO_2\,(g) \\ \text{Initial} & 1 \text{ mole} & \\ \text{At. eqm.} & 1-0{\cdot}2 = 0{\cdot}8 \text{ mole} & 0{\cdot}4 \text{ mole.} \end{array}$$

Total = 1·2 moles

If V is the volume of the vapour per mole, volume of vapour before dissociation = V

Hence density (D) $\propto \frac{1}{V}$

But density before dissciation

$$D = \frac{\text{Mol. wt. of } N_2O_4}{2} = \frac{92}{2} = 46$$

(Theoretical density)

Volume after dissociation = 1·2 V

$\therefore$ Density $(d) \propto \frac{1}{1{\cdot}2\,V}$

$$\therefore \quad \frac{D}{d} = \frac{1}{V} \times 1{\cdot}2\,V = 1{\cdot}2$$

or $\quad d = \frac{D}{1{\cdot}2} = \frac{46}{1{\cdot}2} = \mathbf{38{\cdot}3}$

Alternatively, use the formula directly,

$$\alpha = \frac{D-d}{d}.$$

Problem 17. **A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium**

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$$

was established with an equilibrium constant $K_c = 2{\cdot}1 \times 10^{-3}$. At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of the air in mole fraction of N_2 and O_2. ***(I.I.T. 1997)***

Solution. In the given reaction, there is no change in the number of moles. Suppose total no. of moles initially present in the air = 100. Then no. of moles after attainment of equilibrium = 100. We have

$$\begin{array}{lccc} & N_2\,(g) & + \quad O_2\,(g) \rightleftharpoons & 2NO \\ \text{Initial} & a & b & 0 \end{array}$$

$$a + b = 100 \quad \text{...}(i)$$

$$\begin{array}{lccc} \text{At eqm.} & a - x & b - x & 2x \end{array}$$

$$K_c = \frac{(2x)^2}{(a-x)\,(b-x)} = \frac{4x^2}{(a-x)\,(b-x)}$$

In the question, we are given $2x = 1{\cdot}8$

or $x = 0{\cdot}9$ and $K_c = 2{\cdot}1 \times 10^{-3}$

$$\therefore \quad 2{\cdot}1 \times 10^{-3} = \frac{(1{\cdot}8)^2}{(a-0{\cdot}9)\,(b-0{\cdot}9)}$$

$$ab - 0{\cdot}9\,a - 0{\cdot}9\,b + 0{\cdot}81 = 1620$$

$$ab - 0{\cdot}9\,(a+b) + 0{\cdot}81 = 1620$$

$$ab - 0{\cdot}9 \times 100 + 0{\cdot}81 = 1620$$

or $\quad ab = 1709{\cdot}19 = 1709$

Now $\quad (a-b)^2 = (a+b)^2 - 4\,ab$

$$= (100)^2 - 4 \times 1709 = 3164$$

or $\quad a - b = \sqrt{3164} = 56{\cdot}2 \quad \text{...}(ii)$

Solving (*i*) and (*ii*), $a = 78{\cdot}1$ moles,

$$\text{Mole fraction of } N_2 = \frac{78{\cdot}1}{100} = \mathbf{0{\cdot}781}$$

$$\text{Mole fraction of } O_2 = 1 - 0{\cdot}781 = \mathbf{0{\cdot}219}$$

Problem 18. **The K_p for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is 640 mm at 775 K. Calculate the percentage dissocation of N_2O_4 at equilibrium pressure of 160 mm. At what pressure the dissociation will be 50% ?** ***(Roorkee 1997)***

Solution. Suppose initially N_2O_4 taken = 1 mole and its degree of dissociation = α

$$\begin{array}{lcc} & N_2O_4 \rightleftharpoons & 2NO_2 \\ \text{Initial} & 1 \text{ mole} & \\ \text{At eqm.} & 1-\alpha & 2\,\alpha \end{array}$$

Total $= 1 - \alpha + 2\,\alpha = 1 + \alpha$

If P is the total pressure at equilbrium, then

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times P \text{ and } p_{NO_2} = \frac{2\,\alpha}{1+\alpha} \times P$$

$$\text{Now} \quad K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{\left(\frac{2\,\alpha}{1+\alpha} \cdot P\right)^2}{\frac{1-\alpha}{1+\alpha} \cdot P}$$

$$= \frac{4\,\alpha^2}{(1+\alpha)\,(1-\alpha)} = \frac{4\,\alpha^2}{1-\alpha^2} \times P$$

Putting $K_p = 640$ mm (*Given*) and equilibrium pressure, P = 160 mm, we get $640 = \frac{4\alpha^2}{1-\alpha^2} \times 160$

or $\frac{\alpha^2}{1-\alpha^2} = 1$ or $\alpha^2 = 1 - \alpha^2$

or $2\alpha^2 = 1$ or $\alpha^2 = 0{\cdot}5$ or $\alpha = 0{\cdot}707 = \mathbf{70{\cdot}7\%}$

For dissocation to be 50%, $\alpha = 0{\cdot}50$, $K_p = 640$ mm (constant) $\therefore$ $640 = \frac{4(0{\cdot}5)^2}{1-(0{\cdot}5)^2} \times P$

or $640 = \frac{1}{1-\frac{1}{4}} P = \frac{4}{3} P$ or $\mathbf{P = 480\ mm}$

Problem 19. **The degree of dissociation is 0·4 at 400 K and 1·0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of the equilibrium mixture at 400 K and 1·0 atmosphere. (Atomic mass of P = 31·0 and Cl = 35·5)** ***(I.I.T. 1998)***

Solution. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
At eqm.	0·6	0·4	0·4 moles

Average molecular mass of the mixture

$$= \frac{0{\cdot}6\,(31+5\times35{\cdot}5) + 0{\cdot}4\,(31+3\times35{\cdot}5) + 0{\cdot}4\,(2\times35{\cdot}5)}{0{\cdot}6+0{\cdot}4+0{\cdot}4}$$

$$= \frac{125{\cdot}1 + 55 + 42{\cdot}6}{1{\cdot}4} = 148{\cdot}92$$

For ideal gases, $PV = nRT = \frac{w}{M} RT$

or $PM = \frac{w}{V} RT = d\,RT$

$\therefore$ $d = \frac{PM}{RT} = \frac{1 \times 148{\cdot}92}{0{\cdot}08205 \times 400} = \mathbf{4{\cdot}5374\ g\ L^{-1}}$

Problem 20. **At 540 K, 0·10 mol of PCl_5 are heated in a 8·0 L flask. The pressure of the equilibrium mixture is found to be 1·0 atm. Calculate K_p and K_c for the reaction.** ***(Roorkee 1998)***

Solution. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
Initial	0·1 mol		
At eqm.	$0{\cdot}1 - x$	x	x

Total no. of moles at eqm. = $0{\cdot}1 + x$

$PV = nRT$

i.e. $n = \frac{PV}{RT} = \frac{1 \times 8}{0{\cdot}0821 \times 540} = 0{\cdot}18$

$\therefore$ $0{\cdot}1 + x = 0{\cdot}18$ or $x = 0{\cdot}08$

$\therefore$ $K_c = \frac{(0{\cdot}08/8)\,(0{\cdot}08/8)}{(0{\cdot}02/8)} = \mathbf{0{\cdot}04}$

$K_p = K_c (RT)^{\Delta n} = 0{\cdot}04\,(0{\cdot}0821 \times 540)^1 = \mathbf{1{\cdot}77}$

Problem 21. **When 3·06 g of solid NH_4HS is introduced into a two-litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.**

(*i*) Calculate K_c and K_p for the reaction at 27°C.

(*ii*) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask ? ***(I.I.T. 1999)***

Solution. (*i*) $NH_4HS\,(s) \rightleftharpoons NH_3\,(s) + H_2S\,(g)$

	$NH_4HS\,(s)$	NH_3	H_2S
Initial amount	3·06 g = 3·06/51 mole = 0·06 mole		
At. eqm.	$0{\cdot}06 - \frac{30}{100} \times 0{\cdot}06$ $= 0{\cdot}06 - 0{\cdot}018$ $= 0{\cdot}042$ mole	**0·018** mole	**0·018** mole
Eqm. concs.	1 (being solid)	0·018/2 =0·009	0·018/2 = 0·009 mol L^{-1}

$K_c = \frac{[NH_3]\,[H_2S]}{[NH_4HS]} = \frac{0{\cdot}009 \times 0{\cdot}009}{1}$

$= \mathbf{8{\cdot}1 \times 10^{-5}}$ $([NH_4HS\,(s)] = 1)$

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

$= 8{\cdot}1 \times 10^{-5} \times (0{\cdot}082 \times 300)^2$

$= \mathbf{0{\cdot}049}$ $(\Delta n_g = 2 - 0 = 2)$

(*ii*) As $K_c = [NH_3]\,[H_2S]$ and does not depend upon the amount of $NH_4HS\,(s)$. Hence there will be no effect on equilibrium when more solid NH_4HS is added.

Problem 22. **The K_p value for the reaction $H_2 + I_2 \rightleftharpoons 2\,HI$ at 460°C is 49.**

If the initial pressure of H_2 and I_2 is 0·5 atm respectively, determine the partial pressure of each gas at equilibrium. ***(Roorkee 1999)***

Solution. $H_2 + I_2 \rightleftharpoons 2\,HI$

	H_2	I_2	$2\,HI$
Initial	0·5	0·5	0
At. eqm.	$0{\cdot}5 - x$	$0{\cdot}5 - x$	$2x$

$K_p = \frac{(2x)^2}{(0{\cdot}5-x)^2} = 49$ or $\frac{2x}{0{\cdot}5-x} = 7$

or $2x = 3{\cdot}5 - 7x$ or $9x = 3{\cdot}5$

or $x = \frac{3{\cdot}5}{9} = 0{\cdot}39$

$\therefore$ Pressure of H_2 and I_2 at eqm. = $0{\cdot}5 - 0{\cdot}39$

$= \mathbf{0{\cdot}11\ atm}$

Problem 23. **A mixture in which the mole ratio of H_2 and O_2 is 2 : 1 is used to prepare water by the reaction**

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(g)$$

The total pressure of the container is 0·8 atm at 20°C before the reaction. Determine the final pressure at 120°C after reaction assuming 80% yield of water. ***(Roorkee 1999)***

Solution. $2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(g)$

Initial moles $\quad 2a \quad a \quad 0$

As pressures are in the ratio of their moles

$$\therefore\ 2a + a = 0\cdot 8 \text{ atm or } 3a = 0\cdot 8 \text{ or } a = \frac{0\cdot 8}{3} \text{ atm}$$

Theoretically expected yield of $H_2O = 2a$

$$\text{Actual yield} = 2a \times \frac{80}{100} = 1\cdot 6\,a$$

$\therefore$ H_2 reacted $= 1\cdot 6\,a$ moles,

O_2 reacted $= 0\cdot 8\,a$ moles

Moles after reaction : $H_2 = 2a - 1\cdot 6\,a = 0\cdot 4\,a$,

$O_2 = a - 0\cdot 8\,a = 0\cdot 2\,a$

Total no. of moles

$$= 0\cdot 4\,a + 0\cdot 2\,a + 1\cdot 6\,a = 2\cdot 2\,a$$

$$\text{Hence final pressure} = 2\cdot 2 \times \frac{0\cdot 8}{3} = \mathbf{0\cdot 59\ atm}$$

Problem 24. **At 817°C, K_p for the reaction between $CO_2\,(g)$ and excess hot graphite (s) is 10 atm**

(*a*) What are the equilibrium concentrations of the gases at 817°C and a total pressure of 5 atm ?

(*b*) At what total pressure, the gas contains 50% CO_2 by volume ? ***(Roorkee 2000)***

Solution. (*a*) $CO_2\,(g) + C\,(g) \rightleftharpoons 2\,CO\,(g)$

Suppose at equilibrium, pressure of

$CO\,(p_{CO}) = p$ atm

Then pressure of $CO_2\,(p_{CO_2}) = 5 - p$ atm

$$K_p = \frac{p_{CO}}{p_{CO_2}} = \frac{p^2}{(5-p)} = 10$$

$$\text{or } p^2 + 10\,p - 50 = 0$$

$$\text{or } \quad p = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-10 \pm \sqrt{100 - (-200)}}{2} = 3\cdot 66 \text{ atm}$$

Thus at eqm., $p_{CO} = 3\cdot 66$ *atm*,

$p_{CO_2} = 5 - 3\cdot 66 = 1\cdot 34$ atm

Applying $\quad PV = nRT$

$$\text{or} \quad \frac{n}{V} = \frac{P}{RT}$$

$$\textit{i.e. } \text{molar conc.} = \frac{P}{RT}$$

$$\text{Molar conc. of CO} = \frac{3\cdot 66}{0\cdot 0821 \times (817 + 273)}$$

$$= \mathbf{0\cdot 041\ mol\ L^{-1}}$$

$$\text{Molar conc. of } CO_2 = \frac{1\cdot 34}{0\cdot 0821 \times 1090}$$

$$= \mathbf{0\cdot 015\ mol\ L^{-1}}$$

(*b*) When the gas contains 5% CO_2 by volume, this means that pressure exerted by CO_2 is also 5% of the total pressure. Thus if P is the total pressure, then at equilibrium, $\quad p_{CO_2} = 0\cdot 05$ P $\quad$ and $\quad p_{CO} = 0\cdot 95$ P

$$K_p = \frac{p^2_{CO}}{p_{CO_2}} = \frac{(0\cdot 95\,P)^2}{(0\cdot 05\,P)} = 10 \text{ or } 18\cdot 05\,P = 10$$

or $\qquad$ **P = 0·554 atm.**

Problem 25. **The value of K_p is 1×10^{-3} atm^{-1} at 25°C for the reaction : $2\,NO + Cl_2 \rightleftharpoons 2\,NOCl$. A flask contains NO at 0·02 atm and at 25°C. Calculate the mol of Cl_2 that must be added if 1% of the NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0·2 mol of the gas produce 1 atm pressure at 25°C.**

(Ignore the probable association of NO to N_2O_2)

(Roorkee 2001)

Solution. Suppose initial pressure of Cl_2 added is p atm. Then

$$2\,NO \quad + \quad Cl_2 \quad \rightleftharpoons \quad 2\,NOCl$$

Initial $\quad 0\cdot 02$ atm $\qquad p$ atm

$$\text{At eqm.} \left(0\cdot 02 - \frac{0\cdot 02}{100}\right) \quad \left(p - \frac{0\cdot 01}{100}\right) \quad \frac{0\cdot 02}{100}$$

$$= 2 \times 10^{-2} - 2 \times 10^{-4} \quad = p - 10^{-4} \quad = 2 \times 10^{-4}$$

$$= 2 \times 10^{-4}\,(100 - 1) \qquad \text{atm}$$

$$= 198 \times 10^{-4} \text{ atm}$$

$$K_p = \frac{p^2_{NOCl}}{p^2_{NO} \times p_{Cl_2}}$$

$$10^{-3} = \frac{(2 \times 10^{-4})^2}{(198 \times 10^{-4})^2 \times (p - 10^{-4})}$$

$$\text{or } (p - 10^{-4}) = \frac{4}{(198)^2} \times \frac{1}{10^{-3}} = 0\cdot 102$$

$$\text{or} \quad p = 0\cdot 102 + 0\cdot 0001 = 0\cdot 1021 \text{ atm}$$

Volume of the vessel can be calculated as follows:

$$PV = nRT \text{ or } V = \frac{nRT}{P} = \frac{0\cdot 2 \times 0\cdot 082 \times 273}{1} \text{ L}$$

$$= 4\cdot 887 \text{ L}$$

To calculate the number of moles of Cl_2, again apply

$$PV = nRT \text{ or } n = \frac{PV}{RT} = \frac{0\cdot 1021 \times 4\cdot 887}{0\cdot 082 \times 298}$$

$$= \mathbf{0\cdot 0204\ mol}$$

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. Reaction between iron and steam is reversible if it is carried out

(*a*) at constant temperature

(*b*) at constant pressure

(*c*) in an open vessel

(*d*) in a closed vessel.

2. The relationship between K_p and K_c is

(*a*) $K_c = K_p (RT)^{\Delta n}$ (*b*) $K_c = K_p (RT)^{-\Delta n}$

(*c*) $K_p = K_c (RT)^{-\Delta n}$ (*d*) None of these is correct.

3. The equilibrium constant for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is K. The equilibrium constant for

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftharpoons NH_3 \text{ will be}$$

(*a*) K / 2 (*b*) 2K

(*c*) $\sqrt{K}$ (*d*) K^2.

4. If an inert gas is added to the equilibrium mixture of the dissociation of PCl_5 in a closed vessel,

(*a*) the concentration of Cl_2 will increase

(*b*) the concentration of PCl_3 will increase

(*c*) the concentration of PCl_5 will increase

(*d*) the equilibrium concentrations will remain unaffected.

5. If pressure is increased on the equilibrium $N_2 + O_2 \rightleftharpoons 2\,NO$, the equilibrium will

(*a*) shift in the forward direction

(*b*) shift in the backward direction

(*c*) remain undisturbed

(*d*) may shift in the forward or backward direction.

6. For the reaction

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

the value of K_c at 250°C is 26. The value of K_p at this temperature will be

(*a*) 0·61 (*b*) 0·57

(*c*) 0·83 (*d*) 0·46.

(M.L.N.R. Allahabad 1990)

7. According to Le Chatelier's principle adding heat to a solid and liquid in equilibrium will cause the

(*a*) amount of solid to decrease

(*b*) amount of liquid to decrease

(*c*) temperature to rise

(*d*) temperature to fall.

(M.L.N.R. Allahabad 1990)

8. In a reaction $A_2\,(g) + 4\,B_2\,(g) \rightleftharpoons 2\,AB_4\,(g)$, $\Delta H < 0$. The formation of $AB_4\,(g)$ will be favoured by

(*a*) low temperature and high pressure

(*b*) high temperature and low pressure

(*c*) low temperature and low pressure

(*d*) high temperature and high pressure.

(I.I.T. 1990)

9. The reaction which proceeds in the forward direction is

(*a*) $Fe_3O_4 + 6\,HCl = 2\,FeCl_3 + 3\,H_2O$

(*b*) $NH_3 + H_2O + NaCl = NH_4Cl + NaOH$

(*c*) $SnCl_4 + Hg_2Cl_2 = SnCl_2 + 2\,HgCl_2$

(*d*) $2\,CuI + I_2 + 4\,K^+ = 2\,Cu^{2+} + 4\,KI$.

(I.I.T. 1991)

10. For which of the following reaction, $K_p = K_c$?

(*a*) $2\,NOCl\,(g) \rightleftharpoons 2\,NO\,(g) + Cl_2\,(g)$

(*b*) $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$

(*c*) $H_2\,(g) + Cl_2\,(g) \rightleftharpoons 2\,HCl\,(g)$

(*d*) $2\,N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$

(I.I.T. 1991)

11. In a vessel containing SO_3, SO_2 and O_2 at equilibrium some helium gas is introduced so that the total pressure increases while temperature and volume remain constant. According to Le Chatelier's principle, the dissociation of SO_3

(*a*) increases (*b*) decreases

(*c*) remains unaltered (*d*) changes unpredictably.

(M.L.N.R. Allahabad 1991)

ANSWERS

1. *d* **2.** *b* **3.** *c* **4.** *d* **5.** *c* **6.** *a* **7.** *a* **8.** *a* **9.** *a* **10.** *c*
11. *b*

12. In a reversible reaction, two substances are in equilibrium. If the concentration of each one is doubled, the equilibrium constant will be
(*a*) Reduced to half its original value
(*b*) Reduced to one fourth of its original value
(*c*) Doubled (*d*) Constant.
(M.L.N.R. Allahabad 1992, B.I.T. Ranchi 1992)

13. An equilibrium mixture for the reaction
$$2\,H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$$
had 1 mole of H_2S, 0·2 mole of H_2 and 0·8 mole of S_2 in a 2 litre flask. The value of K_c in mol L^{-1} is
(*a*) 0·004 (*b*) 0·08
(*c*) 0·016 (*d*) 0·160. *(I.I.T. 1992)*

14. In what manner will increase of pressure affect the following equilibrium ?
$$C\,(s) + H_2O\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$$
(*a*) Shift in the forward direction
(*b*) Shift in the reverse direction
(*c*) Increase in the yield of hydrogen
(*d*) No effect. *(I.I.T. 1994)*

15. The reaction, $SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$ is exothermic and reversible. A mixture of $SO_2\,(g)$, $Cl_2\,(g)$ and $SO_2Cl_2\,(g)$ is at equilibrium in a closed container. Now a certain quantity of extra SO_2 is introduced into the container, the volume remaining the same. Which of the following is/are true ?
(*a*) The pressure inside the container will not change
(*b*) The temperature will not change
(*c*) The temperature will increase
(*d*) The temperature will decrease.
(I.S.M. Dhanbad, 1994)

16. The equilibrium constant for the reaction, $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$ is 4×10^{-4} at 2000 K.

In presence of a catalyst, equilibrium is attained ten times faster. Therefore, the equilibrium constant, in presence of the catalyst, at 2000 K is :
(*a*) 40×10^{-4} (*b*) 4×10^{-4}
(*c*) 4×10^{-3}
(*d*) difficult to compute without more data.
(M.L.N.R. Allahabad, 1994)

17. In $2HI \rightleftharpoons H_2 + I_2$, the forward reaction is affected by change in
(*a*) Catalyst (*b*) Pressure
(*c*) Volume (*d*) Temperature.
(Haryana C.E.E.T. 1994)

18. 64 g of HI are present in a 2 litre vessel. The active mass of HI is
(*a*) 0·5 (*b*) 0·25
(*c*) 1·0 (*d*) None of the three.
(Haryana C.E.E.T. 1994)

19. The equilibrium constant (K_p) for the reaction
$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$ is 16. If the volume of the container is reduced to one-half of its original volume, the value of K_p for the reaction at the same temperature will be
(*a*) 32 (*b*) 64
(*c*) 16 (*d*) 4.
(Haryana C.E.E.T. 1996, 2000)

20. In a reaction, $A + 2B \rightleftharpoons 2C$, 2·0 mole of 'A' 3·0 mole of 'B' and 2·0 mole of 'C' are placed in a 2·0 L flask and the equilibrium concentration of 'C' is 0·5 mole/L. The equilibrium constant (K) for the reaction is
(*a*) 0·073 (*b*) 0·147
(*c*) 0·05 (*d*) 0·026.
(Haryana C.E.E.T. 1996)

21. One mole of $N_2O_4\,(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_4\,(g)$ decomposes to $NO_2\,(g)$. The resultant pressure is
(*a*) 1·2 atm (*b*) 2·4 atm
(*c*) 2·0 atm (*d*) 1·0 atm. *(I.I.T. 1996)*

22. If the concentration of the reactants is increased by *x*, then equilibrium constant K becomes
(*a*) $\ln \frac{K}{x}$ (*b*) $\frac{K}{x}$
(*c*) $K + x$ (*d*) K
(A.F.M.C. Pune 1997)

23. In which case K_p is less than K_c ?
(*a*) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.
(*b*) $H_2 + Cl_2 \rightleftharpoons 2HCl$
(*c*) $2SO_2 + O_2 \rightleftharpoons 2SO_3$
(*d*) All of these *(A.F.M.C. Pune 1997)*

ANSWERS

12. *d* 13. *c* 14. *b* 15. *c* 16. *b* 17. *d* 18. *b* 19. *c* 20. *c* 21. *b*
22. *d* 23. *c*

24. If K_1 and K_2 are the respective equilibrium constants for the two reactions

$XeF_6(g) + H_2O(g) \rightleftharpoons XeOF_4(g) + 2HF(g)$

$XeO_4(g) + XeF_6(g) \rightleftharpoons XeOF_4(g) + XeO_3F_2(g)$

the equilibrium constant of the reaction

$XeO_4(g) + 2HF(g) \rightleftharpoons XeO_3F_2(g) + H_2O(g)$

will be

(a) K_1/K_2^2 (b) $K_1 . K_2$

(c) K_1/K_2 [✓ (d) K_2/K_1]

(C.B.S.E. P.M.T. 1998)

25. For the homogeneous gas reaction

$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$

the equilibrium constant, K_c has the dimensions of

(a) $conc^{+10}$ [✓ (b) $conc^{+1}$]

(c) $conc^{-1}$ [✓ (d) It is dimensionless]

(M.P. P.M.T. 1998)

26. Formation of SO_3 takes place according to the reaction

$2SO_2 + O_2 \rightleftharpoons 2SO_3$, $\Delta H = -45 \cdot 2$ kcal

Which of the following factors favours the formation of SO_3 ?

(a) Increase in temperature

[✓ (b) Increase in pressure]

(c) Removal of oxygen

(d) Increase in volume *(M.P. P.M.T. 1998)*

27. K_p/K_c for the reaction

$CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ is

(a) 1 (b) RT

[✓ (c) $1/\sqrt{RT}$] (d) $(RT)^{1/2}$

(M.P. P.M.T. 1998, A.I.E.E.E. 2002)

28. For the reaction

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

at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by

(a) adding a suitable catalyst

(b) adding an inert gas

(c) decreasing the volume of the container

(d) increasing the amount of CO(g).

(I.I.T. 1998)

29. For the chemical reaction

$3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by

[✓ (a) temperature and pressure]

(b) temperature only

(c) pressure only

(d) temperature , pressure. and catalyst

30. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ + Heat.

[✓ (a) $K_p = K_c(RT)^{-2}$] (b) $K_p = K_c$

(c) $K_p = K_c RT$ (d) $K_p = K_c(RT)^{-1}$.

(D.C.E.E.E. 1999)

31. What would happen to a reversible dissociation reaction at equilibrium when an inert gas is added while the pressure remains unchanged ?

(a) Less of the product will be formed

[✓ (b) More of the product will be formed]

(c) More of the reactants will be formed

(d) It remains unaffected. *(D.C.E.E.E. 1999)*

32. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant K_p changes with

[✓ (a) temperature] (b) total pressure

(c) catalyst (d) amount of H_2 and I_2.

(D.C.E.E.E. 1999)

33. In the gaseous reaction A + 2 B $\rightleftharpoons$ C + heat, the forward reaction is favoured by

(a) low temperature and low pressure

(b) low pressure

(c) high temperature and high pressure

[✓ (d) high pressure and low temperature.]

(D.C.E.E.E. 1999)

34. For a reversible reaction, if the concentrations of the reactants are doubled, the equilibrium constant will be

(a) halved (b) doubled

[✓ (c) the same] (d) one fourth.

(C.B.S.E. P.M.T. 2000)

35. For the equilibrium

$MgCO_3(s) \overset{\Delta}{\rightleftharpoons} MgO(s) + CO_2(g)$

which of the following expressions is correct ?

(a) $K_p = \frac{p_{MgO} \times p_{CO_2}}{p_{MgCO_3}}$ (b) $K_p = \frac{[MgO][CO_2]}{[MgCO_3]}$

ANSWERS

24. d **25.** b **26.** b **27.** c **28.** d **29.** a **30.** a **31.** b **32.** a **33.** d
34. c

(*c*) $K_p = \dfrac{p_{MgO} \times p_{CO_2}}{p_{MgCO_3}}$ (*d*) $K_p = p_{CO_2}$.

(C.B.S.E. P.M.T. 2000)

36. What happens to the yield of this reaction when temperature is increased ?

$$N_2 + O_2 \rightleftharpoons 2\,NO \,;\, 43 \cdot 2 \text{ kcal}$$

(*a*) increases (*b*) decreases
(*c*) remains same (*d*) None of these.

(A.F.M.C. 2000)

37. 500 ml vessel contains 1·5 M each of A, B, C and D at equilibrium. If 0·5 M each of C and D are taken out, the value of K_c for $A+B \rightleftharpoons C+D$ will be

(*a*) 1·0 (*b*) 1/9
(*c*) 4/9 (*d*) 8/9.

(D.C.E.E.E. 2000)

38. At 25°C the value of K_c for the reaction $\frac{1}{2}N_2 + O_2 \rightleftharpoons NO_2$ is 2×10^4. What will be the value of K_c' for $2\,NO_2 \rightleftharpoons N_2 + 2\,O_2$?

(*a*) $\sqrt{2} \times 10^2$ (*b*) $\dfrac{1}{4 \times 10^8}$
(*c*) 2×10^4 (*d*) 10^4. *(C.P.M.T. 2000)*

39. Which of the following is not affected by increase in pressure ?

(*a*) $2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g)$
(*b*) $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$
(*c*) $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$
(*d*) $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$.

(J.I.P.M.E.R. 2000)

40. For the reversible reaction, $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$ at 500°C, the value of K_p is $1 \cdot 44 \times 10^{-5}$ when partial pressure is measured in atmospheres. The corresponding value of K_c, with concentration in mole litre^{-1}, is

(*a*) $1 \cdot 44 \times 10^{-5} / (0 \cdot 082 \times 500)^{-2}$
(*b*) $1 \cdot 44 \times 10^{-5} / (8 \cdot 314 \times 773)^{-2}$
(*c*) $1 \cdot 44 \times 10^{-5} / (0 \cdot 082 \times 773)^{2}$
(*d*) $1 \cdot 44 \times 10^{-5} / (0 \cdot 082 \times 773)^{-2}$.

(I.I.T. 2000)

41. When two reactants A and B are mixed to give products C and D, the reaction quotient, Q, at the initial stages of the reaction

(*a*) is zero (*b*) decreases with time
(*c*) is independent of time
(*d*) increases with time. *(I.I.T. 2000)*

42. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2\,NO_2$ is expressed by $K_p = (4x^2\,P)/(1 - x^2)$ where P = pressure, x = extent of decomposition. Which one of the following statements is true ?

(*a*) K_p increases with increase of P
(*b*) K_p increases with increase of x
(*c*) K_p increases with decrease of x
(*d*) K_p remains constant with change in P and x.

(I.I.T. 2001)

43. 5 moles of SO_2 and 5 moles of O_2 are allowed to react to form SO_3 in a closed vessel. At the equilibrium stage, 60% SO_2 is used up. The total number of moles of SO_2, O_2 and SO_3 in the vessel now is

(*a*) 3·9 (*b*) 10·5
(*c*) 8·5 (*d*) 10·0 *(K.C.E.T. 2001)*

44. A quantity of PCl_5 was heated in a 10 dm^3 vessel at 250°C : $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$. At equilibrium, the vessel contains 0·1 mole of PCl_5 and 0·2 mole of Cl_2. The equilibrium constant of the reaction is

(*a*) 0·04 (*b*) 0·025
(*c*) 0·02 (*d*) 0·05

(K.C.E.T. 2001)

45. 9·2 grams of $N_2O_4\,(g)$ is taken in a closed one litre vessel and heated till the following equilibrium is reached

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

At equilibrium, 50% $N_2O_4\,(g)$ is dissociated. What is the equilibrium constant (in mol lit^{-1}) (Molecular weight of N_2O_4 = 92)

(*a*) 0·1 (*b*) 0·2
(*c*) 0·4 (*d*) 2

(E.A.M.C.E.T. 2001)

ANSWERS

35. *d* **36.** *a* **37.** *a* **38.** *b* **39.** *c* **40.** *d* **41.** *d* **42.** *d* **43.** *c* **44.** *a*
45. *b*

46. If $N_2 + 3H_2 \rightleftharpoons 2NH_3$—K, then
$2N_2 + 6H_2 \rightleftharpoons 4NH_3$—K' ?

(*a*) K^2 (*b*) $\sqrt{K}$ (*c*) $1/\sqrt{K}$ (*d*) $1/K^2$

(Rajasthan P.M.T. 2002)

47. In the case of a gaseous homogeneous reaction, the active mass of the reactant is obtained by the expression

(*a*) $\frac{PV}{RT}$ (*b*) $\frac{P}{RT}$ (*c*) $\frac{RT}{P}$ (*d*) $\frac{n}{V}RT$

(Tamil Nadu C.E.T. 2002)

48. In which of the following equilibrium, change in the volume of the system does not alter the number of moles ?

(*a*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

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

(*c*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(*d*) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

(A.I.E.E.E. 2002)

49. 1 mole of N_2 and 2 moles of H_2 are allowed to react in a 1 *dm*^{3} vessel. At equilibrium, 0·8 mole of NH_3 is formed. The concentration of H_2 in the vessel is

(*a*) 0·6 mole (*b*) 0·8 mole

(*c*) 0·2 mole (*d*) 0·4 mole

(Manipal P.M.T. 2002)

50. The rate of forward reaction is two times that of the reverse reaction at a given temperature and identical concentration. $K_{equilibrium}$ is

(*a*) 0·5 (*b*) 1·5

(*c*) 2·5 (*d*) 2·0 *(K.C.E.T. 2002)*

51. Consider the following equilibrium in a closed container : $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements, holds true regarding the equilibrium constant (K_p) and degree of dissociation (α) ?

(*a*) neither K_p nor α changes

(*b*) both K_p and α change

(*c*) K_p changes but α does not change

(*d*) K_p does not change but α changes *(I.I.T. 2002)*

52. The reaction quotient (Q) for the reaction
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
is given by $Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$
The reaction will proceed from right to left if

(*a*) $Q = K_c$ (*b*) $Q < K_c$ (*c*) $Q > K_c$ (*d*) $Q = 0$

(C.B.S.E. P.M.T. 2003)

53. The following equilibria are given

$N_2 + 3H_2 \rightleftharpoons 2NH_3, K_1$

$N_2 + O_2 \rightleftharpoons 2NO, K_2$

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O, K_3$

The equilibrium constant of the reaction

$2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$

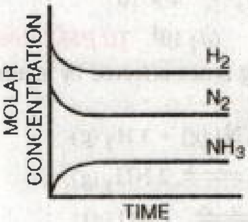
in terms of K_1, K_2 and K_3 is

(*a*) $K_1K_2K_3$ (*b*) K_1K_2/K_3

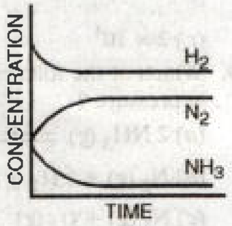
(*c*) $K_1K_3^2/K_2$ (*d*) $K_2K_3^3/K_1$

(C.B.S.E. P.M.T. 2003)

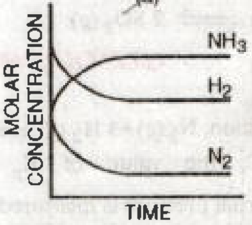
54. For the synthesis of ammonia by the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ in the Haber's process, the attainment of equilibrium is correctly predicted by the curve



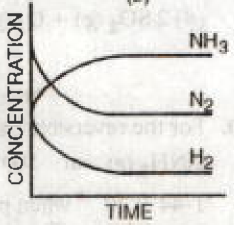
(a)



(b)

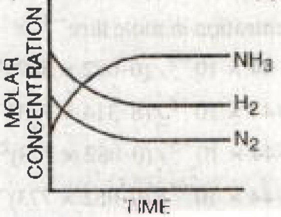


(c)



(d)

(e)



(Kerala M.E.E. 2003)

ANSWERS

46. *a* **47.** *b* **48.** *a* **49.** *b* **50.** *d* **51.** *d* **52.** *c* **53.** *d* **54.** *a*

55. In the reaction $PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$, the equilibrium concentrations of PCl_5 and PCl_3 are 0·4 and 0·2 mole/litre respectively. If the value of K_c is 0·5, what is the concentration of Cl_2 in moles/litre ?

(*a*) 2·0 (*b*) 1·5
(*c*) 1·0 (*d*) 0·5

(E.A.M.C.E.T. 2003)

56. In a given system, water and ice are in equilibrium. If pressure is applied to the above system then

(*a*) More of ice is formed
(*b*) Amount of ice and water will remain same
(*c*) More of ice is melted
(*d*) Either (*a*) or (*c*) *(Bihar C.E.C.E. 2004)*

57. Of the following which change will shift the reaction towards the product ?

$I_2 (g) \rightleftharpoons 2 I (g), \Delta H^\circ_r (298 K) = + 150 kJ$

(*a*) increase in concentration if I
(*b*) decrease in concentration of I_2
(*c*) increase in temperature
(*d*) increase in total pressure *(A.I.I.M.S. 2004)*

58. For the reaction $CO (g) + Cl_2 (g) \rightleftharpoons COCl_2 (g)$, K_p / K_c equal to

(*a*) 1/RT (*b*) RT
(*c*) $\sqrt{RT}$ (*d*) 1·0

(A.I.E.E.E. 2004)

59. 56 *g* of nitrogen and 8 *g* of hydrogen gas are heated in a closed vessel. At equilibrium, 34 *g* of ammonia are present. The equilibrium number of moles of nirogen, hydroen and ammonia are respectively

(*a*) 1, 2, 2 (*b*) 2, 2, 1
(*c*) 1, 1, 2 (*d*) 2, 1, 2

(Karnataka C.E.T. 2004)

60. Calculate the partial pressure of carbon monoxide from the following data :

$CaCO_3 (s) \xrightarrow{\Delta} CaO (s) + CO_2 \uparrow, K_p = 8 \times 10^{-2}$

$CO_2 (g) + C (s) \longrightarrow 2 CO (g), K_p = 2$

(*a*) 0·2 (*b*) 0·4
(*c*) 1·6 (*d*) 4

(Orissa J.E.E. 2004)

61. The equilibrium $P_4 (s) + 6 Cl_2 (g) \rightleftharpoons 4 PCl_3 (g)$ is attained by mixing equal moles of P_4 and Cl_2 in an evacuated vessel. Then at equilibrium

(*a*) $[Cl_2] > [PCl_3]$ (*b*) $[Cl_2] > [P_4]$
(*c*) $[P_4] > [Cl_2]$ (*d*) $[PCl_3] > [P_4]$

(J & K C.E.T. 2004)

62. In the given reaction $2 X (g) + Y (g) \rightleftharpoons 2 Z (g) + 80$ kcal, which combination of pressure and temperature will give the highest yield of Z at equilibrium ?

(*a*) 1000 atm and 200°C
(*b*) 500 atm and 500°C
(*c*) 1000 atm and 200°C
(*d*) 500 atm and 100°C
(*e*) 1000 atm and 500°C *(Kerala C.E.T. 2004)*

63. A mixture of NO_2 and N_2O_4 has a vapour density of 38·3 at 300 K. What is the number of moles of NO_2 in 100 *g* of the mixture ?

(*a*) 0·043 (*b*) 4·4
(*c*) 3·4 (*d*) 3·86
(*e*) 0·437 *(Kerala P.M.T. 2004)*

64. Ammonium carbamate when heated to 200°C gives a mixture of NH_3 and CO_2 vapours with a density of 16·0. What is the degree of dissociation of ammonium carbamate ?

(*a*) 3/2 (*b*) 1/2
(*c*) 2 (*d*) 1
(*e*) 5/2 *(Kerala P.M.T. 2004)*

65. 2 mol of N_2 is mixed with 6 mol of H_2 in a closed vessel of one litre capacity. If 50% of N_2 is converted into NH_3 at equilibrium, the value of K_c for the reaction $N_2 (g) + 3 H_2 (g) \rightleftharpoons 2 NH_3 (g)$ is

(*a*) 4/27
(*b*) 27/4
(*c*) 1/27
(*d*) 27
(*e*) 9 *(Kerala P.M.T. 2004)*

66. K_p for the following reaction will be equal to

$Fe (s) + 4 H_2O (g) \rightleftharpoons Fe_3O_4 (s) + 4 H_2 (g)$

(*a*) $(p_{H_2})^4 (p_{Fe_3O_4})$ (*b*) $\frac{p_{H_2}}{p_{H_2O}}$

(*c*) $\frac{(p_{H_2})^4}{(p_{H_2O})^4}$ (*d*) $\frac{(p_{H_2}) (p_{Fe_3O_4})}{p_{Fe}}$

(U.P. C.P.M.T. 2004)

ANSWERS

55. *c* **56.** *c* **57.** *c* **58.** *a* **59.** *c* **60.** *b* **61.** *c* **62.** *c* **63.** *e* **64.** *d*
65. *a* **66.** *c*

HINTS/EXPLANATIONS to Multiple Choice Questions

1. As otherwise the H_2 gas will escape.

2. $K_p = K_c (RT)^{\Delta n}$ or $K_c = K_p (RT)^{-\Delta n}$

4. In a closed vessel, concentrations of reactants and products do not change on adding inert gas.

6. $K_p = K_c (RT)^{\Delta n} = 26 \times (0 \cdot 0821 \times 523)^{-1} = 0 \cdot 61$.

7. Solid + Heat $\rightleftharpoons$ Liquid. Adding heat will shift the equilibrium in the forward direction.

8. The given reaction is exothermic ($\Delta H < 0$) and accompanied by decrease in the number of moles. Hence it will be favoured by low temperature and high pressure.

9. $FeCl_3$ and H_2O do not react to give back Fe_3O_4 and HCl.

11. See Hint to Q. 4.

12. Equilibrium constant of a reaction does not depend upon concentrations. It is constant at constant temperature.

14. The forward reaction is accompanied by the increase in the number of gaseous moles. Hence increase of pressure will favour the reverse reaction.

15. $SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$ + Heat. On adding SO_2, the equilibrium will shift forward *i.e.* more heat will be evolved. So temperature will increase.

16. Equilibrium constant of a reaction is constant at constant temperature.

17. It is an endothermic reaction. Hence equilibrium is affected by temperature.

18. Mol. mass of HI = 130,

$$\therefore \quad [HI] = \frac{64}{130} \times \frac{1}{2} = 0 \cdot 25.$$

19. K_p does not depend upon volume or concentrations. It is constant at constant temperature.

20.

	A +	2 B $\rightleftharpoons$	2 C
Initial concs.	1 mol L^{-1}	1·5 mol L^{-1}	1 mol L^{-1}
At eqm.	(1 + 0·25) = 1·25 mol L^{-1}	(1·5 + 0·5) = 2·0 mol L^{-1}	0·5 mol L^{-1}

$$K = \frac{(0 \cdot 5)^2}{1 \cdot 25 \times (2 \cdot 0)^2} = 0 \cdot 05$$

21.

	N_2O_4 $\rightleftharpoons$	2 NO_2
Initial	1 mole	
At. eqm.	1—0·20 = 0·80 mole	0·40 mole, Total = 1·2 mole

1 mole vapour have pressure = 1 atm at 300 K.

Applying PV = *n*RT, 1 × V = 1 × R × 300 ...(*i*)

When *n* = 1·2 mole, T = 600 K,

P × V = 1·2 × R × 600 ...(*ii*)

Dividing (*ii*) by (*i*), P = 2·4 atm.

22. Equilibrium constant is constant at constant temperature.

23. $K_p = K_c (RT)^{\Delta n}$. K_p is less than K_c if Δn = – ve *i.e.* $n_p < n_r$

24. $K_1 = \frac{[XeOF_4][HF]^2}{[XeF_6][H_2O]}$, $K_2 = \frac{[XeOF_4][XeO_3F_2]}{[XeO_4][XeF_6]}$

Aim : $\frac{[XeO_3F_2][H_2O]}{[XeO_4][HF]^2} = \frac{K_2}{K_1}$

25. $K_c = \frac{[NO]^4 [H_2O]^6}{[NH_3]^4 [O_2]^5} = \frac{(conc)^{10}}{(conc.)^9}$ = conc.

But with respect to standard state concentration of 1 mol L^{-1}, it is dimensionless.

27. $\Delta n_g = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$

$K_p / K_c = (RT)^{\Delta n} = (RT)^{-1/2} = 1 / \sqrt{RT}$

29. Backward reaction is dissociation reaction and hence endothermic. The forward reaction will, therefore, be exothermic. Further, it is accompanied by decrease in the number of gaseous moles. Hence its equilibrium will be affected by temperature and pressure.

31. On adding inert gas at constant pressure, dissociation increases i.e. more of the products will be formed.

32. Equilibrium constant changes only with temperature.

35. [Solid] = 1.

37. $K_c = \frac{1 \cdot 5 \times 1 \cdot 5}{1 \cdot 5 \times 1 \cdot 5} = 1$. On changing concentrations, equilibrium constant does not change.

38. The reaction is reversed and multiplied by 2, therefore equilibrium constant = $1 / K^2$

$$= 1 / (2 \times 10^4)^2 = \frac{1}{4 \times 10^8}$$

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

$$= 1 \cdot 44 \times 10^{-5} / (0 \cdot 082 \times 773)^{-2}$$

41. $A + B \rightleftharpoons C + D$, $Q = \frac{[C][D]}{[A][B]}$. With time, [C] and [D] increase and so does Q.

HINTS CONTD.

42. K_p is constant at constant temperature.

43. $2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$

Initial moles $5 \quad 5$

At eqm. $5 - \frac{60}{100} \times 5 \quad 5 - 1 \cdot 5 \quad 3$

$= 5 - 3 = 2 \quad = 3 \cdot 5$

Total $= 2 + 3 \cdot 5 + 3 = 8 \cdot 5$

44. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Moles at eqm. $0 \cdot 1$ mole $\quad 0 \cdot 2$ mole $\quad 0 \cdot 2$ mole

Molar concs. $0 \cdot 1/10 \quad 0 \cdot 2/10 \quad 0 \cdot 2/10$ mol dm^{-3}

$$K = \frac{0 \cdot 02 \times 0 \cdot 02}{0 \cdot 01} = 0 \cdot 04$$

45. Initial $[N_2O_4] = 9 \cdot 2 / 92$ mol L^{-1}

$= 0 \cdot 1$ mol L^{-1}

At. eqm. (after 50% dissociation),

$[N_2O_4] = 0 \cdot 05$ M, $[NO_2] = 0 \cdot 1$ M

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0 \cdot 1)^2}{0 \cdot 05} = 0 \cdot 2$$

47. Active mass = Molar conc. $= \frac{n}{V}$

From $PV = nRT, \frac{n}{V} = \frac{P}{RT}$

48. Change in volume changes the molar concentration. In (*a*), $n_p = n_r$. Change in volume will not alter the number of moles in this case.

49. $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$

Formation of $0 \cdot 8$ mole of NH_3 means that $\frac{3}{2} \times 0 \cdot 8$ mole of H_2 have reacted. Hence concentration of $H_2 = 2 - \frac{3}{2} \times 0 \cdot 8 = 2 - 1 \cdot 2 = 0 \cdot 8$ mole

50. $K_{eqm.} = \frac{k_f}{k_b} = \frac{2}{1} = 2.$

51. K_p is constant at constant temperature. As volume is halved, pressure will be doubled. Hence equilibrium will shift in the backward direction *i.e.* degree of dissociation decreases.

52. The reaction proceeds from right to left when $Q > K_c$ so that Q tends to decrease to become equal to K_c.

53. $K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}, K_2 = \frac{[NO]^2}{[N_2][O_2]},$

$$K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}}$$

Aim : $K = \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = \frac{K_2 K_3^3}{K_1}$.

54. (*a*) is correct because concentrations of H_2 and N_2 decrease with time while that of NH_3 increases with time and after equilibrium, all of them remain constant.

55. $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

i.e. $0 \cdot 5 = \frac{0 \cdot 2 \times [Cl_2]}{0 \cdot 4}$ or $[Cl_2] = 1 \cdot 0$ mol L^{-1}.

56. Ice $\rightleftharpoons$ Water.

More vol. Less vol.

On applying pressure, equilibrium shifts to the side in which volume is less.

57. The given reaction is endothermic. So on increasing temperature, it will shift in the forward direction

58. $\Delta n_g = 1 - 2 = -1$

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^{-1} = K_c/RT$$

or $K_p/K_c = 1/RT$

59. $56\,g\ N_2 = 56/28 = 2$ moles,

$8\,g\ H_2 = 8/2 = 4$ moles,

$34\,g\ NH_3 = 34/17 = 2$ moles

$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$

Initial 2 moles 4 moles

At. eqm. $2 - 1$ mole $\quad 4 - 3 \quad$ 2 moles

$= 1$ mole $\quad = 1$ mole

60. For reaction (*i*), $K_p = p_{CO_2} = 8 \times 10^{-2}$ (*Given*)

For reaction (*ii*), $K_p = \frac{p^2_{CO}}{p_{CO_2}} = 2$ (*Given*)

$\therefore\ 2 = \frac{p^2_{CO}}{8 \times 10^{-2}}$ or $p_{CO} = 0 \cdot 4$

61. $P_4(s) + 6\,Cl_2(g) \rightleftharpoons 4\,PCl_3(g)$

Initial 1 mole 1 mole

At eqm. $1 - x \quad 1 - 6x \quad 4x$

As $(1 - x) > (1 - 6x)$, hence $[P_4] > [Cl_2]$

62. As $n_p < n_r$, higher the pressure, greater will be yield of Z. As reaction is exothermic in the forward direction, lower the temperature, greater is the yield of Z (As at low temperature the reaction is slow, usually optimum temperature is used).

63. Suppose $NO_2 = x\,g$. Then $N_2O_4 = (100 - x)\,g$

HINTS CONTD.

Moles of $NO_2 = \frac{x}{46}$, Moles of $N_2O_4 = \frac{100-x}{92}$

Mole fraction of $NO_2 = \frac{x/46}{x/46 + (100-x)/92}$

$$= \frac{x}{46} \times \frac{92}{100+x} = \frac{2x}{100+x}$$

Mole fraction of $N_2O_4 = 1 - \frac{2x}{100+x}$

$$= \frac{100-x}{100+x}$$

Molar mass of mixture

$$= \frac{2x}{100+x} \times 46 + \frac{100-x}{100+x} \times 92 = \frac{9200}{100+x}$$

$$\therefore \quad \frac{9200}{100+x} = 2 \times 38{\cdot}3 = 76{\cdot}6$$

or $76{\cdot}6x = 9200 - 7660 = 1540$

or $x = 20{\cdot}10\,g$

$\therefore$ Moles of $NO_2 = \frac{20{\cdot}10}{46} = 0{\cdot}437$

64. $NH_2COONH_4 \longrightarrow 2NH_3 + CO_2$

	NH_2COONH_4	$2NH_3$	CO_2
Initial	1 mole		
After disso.	$1-\alpha$	2α	α,

Total $= 1 + 2\alpha$

Theoretical density (D) $\propto \frac{1}{V}$

Observed density (d) $\propto \frac{1}{(1+2\alpha)V}$

$$\therefore \quad \frac{D}{d} = 1 + 2\alpha$$

or $\alpha = \frac{1}{2}\left(\frac{D-d}{d}\right) = \frac{1}{2}\left(\frac{48-16{\cdot}0}{16{\cdot}0}\right) = 1{\cdot}0$

65. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

	N_2	$3H_2$	$2NH_3$
Initial	2 mol	6 mol	
At. eqm.	1 mol	3 mol	2 mol
Molar conc.	1	3	2 mol L^{-1}

$$K_c = \frac{(2)^2}{1 \times (3)^3} = \frac{4}{27}$$

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of two statements, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(*a*) If both Assertion and Reason are true and the Reason is the correct explanation of the Assertion.

(*b*) If both Assertion and Reason are true but reason is not a correct explanation of the 'Assertion'.

(*c*) If Assertion is true but Reason is false.

(*d*) If Assertion is false but Reason is true.

(*e*) If both Assertion and Reason are false.

	Assertion	Reason
1.	The equilibrium constant is fixed and characteristic for any given chemical reaction at a specified temperature.	The composition of the final equilibrium mixture at a particular temperature depends upon the starting amount of reactants.
2.	When a catalyst is added to a reaction mixture in equilibrium, the amount of the products increases.	The forward reaction becomes faster on adding the catalyst.
3.	Adding inert gas to dissociation equilibrium of N_2O_4 at constant pressure and temperature increases the dissociation.	Molar concentrations of the reactants and products decrease.
4.	K_p is always greater than K_c.	The effect of pressure is greater on the rate of reaction than the effect of concentration.
5.	Equilibrium constant of a reaction increases if temperature is increased.	The forward reaction becomes faster with increase of temperature.

True/False Statements

Which of the following statements are false ?

1. When equilibrium is attained, the concentration of each of the reactants and products becomes equal.
2. Burning of magnesium to form MgO is an irreversible process.
3. Equilibrium is disturbed if catalyst is added to it.
4. The equilibrium constant of a reaction is independent of the concentrations of the reactants.
5. There is no effect on the equilibrium constant of $H_2 + I_2 \rightleftharpoons 2HI$, if some inert gas is added to it.
6. There is no effect of pressure on the dissociation of N_2O_4.

Fill In The Blanks

1. When equilibrium is attained, the concentration of each of the reactants and products becomes ..... .
2. Chemical equilibrium is ..... in nature.
3. Solid $\rightleftharpoons$ liquid equilibrium exists only at ..... .
4. The rate at which a substance reacts is proportional to its ..... .
5. The value of equilibrium constant is constant at constant ..... .
6. The value of equilibrium constant of an endothermic reaction ..... with rise in temperature.
7. Temperature has no effect on the equilibrium constant for reactions for which ΔH is ..... .
8. If an inert gas is added to the equilibrium mixture of the dissociation of PCl_5 at constant pressure, the dissociation of PCl_5 will ..... .
9. Exothermic reactions are favoured by........ temperature.
10. For a given reaction at a fixed temperature, equilibrium constants K_p and K_c are related as........ . *(I.I.T. 1994)*
11. A ten-fold increase in pressure on the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium results in........ in K_p. *(I.I.T. 1996)*
12. For a gaseous reaction $2B \longrightarrow A$, the equilibrium constant K_p is........ to/than K_c. *(I.I.T. 1997)*

Matching Type Questions

1. Match the entries of column A with appropriate entries of column A.

Column A	**Column B** (New eqm. const.)
(*a*) Reaction is reversed	(*a*) $\sqrt{K}$
(*b*) Reaction is divided by 2	(*b*) K^2
(*c*) Reaction is multiplied by 2	(*c*) $1/K$

where K is the equilibrium constant of the original reaction.

2. Match the entries of column A with appropriate entries of columns B and C.

Column A	**Column B**	**Column C**
(*a*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta H = -92{\cdot}5$ kJ	(*a*) Increase of pressure shifts the equilibrium in the forward direction.	(*a*) Increase of temp. shifts the equilibrium in the forward direction.
(*b*) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$, $\Delta H = 0$	(*b*) Increase of pressure shifts the equilibrium in the backward direction.	(*b*) Increase in temp. shifts the equilibrium in the backward direction.
(*c*) $N_2O_4 \rightleftharpoons 2NO_2$ $\Delta H = +58{\cdot}6$ kJ	(*c*) Increase of pressure has no effect on equilibrium.	(*c*) Increase of temp. has no effect on the equilibrium.

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*a*) **2.** (*e*) **3.** (*a*) **4.** (*e*) **5.** (*e*)

TRUE/FALSE STATEMENTS

1, 3, 6.

FILL IN THE BLANKS

1. constant **2.** dynamic **3.** melting point **4.** active mass **5.** temperature **6.** increases **7.** zero **8.** increase **9.** low **10.** $K_p = K_c (kT)^{\Delta n}$ **11.** no change **12.** less.

MATCHING TYPE QUESTIONS

1. (*a*) — (*c*), (*b*)—(*a*), (*c*)—(*b*) **2.** (*a*) — (*a*) — (*b*), (*b*) — (*c*) — (*a*), (*c*) — (*b*) — (*c*).

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

1. If the starting amounts are changed, the composition of the equilibrium mixture changes in such a way that K remains constant at constant temperature.
2. Both the forward and backward reaction become faster and equilibrium is not disturbed.
4. $K_p = K_c (RT)^{\Delta n}$. If $\Delta n = 0$, $K_p = K_c$. If $\Delta n = +ve$, $K_p > K_c$. If $\Delta n = -ve$, $K_p < K_c$. Both pressure and concentration affect the rate of reaction.
5. Effect of temperature on equilibrium constant K depends upon whether the reaction is exothermic or endothermic.