12. Chemical Equilibrium

Can you recall?

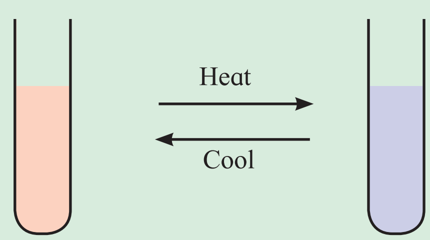
What are the types of the following changes? Natural waterfall, spreading of smoke from burning inscence stick, diffusion of fragrance of flowers. Can the above changes take place in the opposite direction ?

12.1 Introduction : You have learnt earlier that changes can be physical or chemical and reversible or irreversible. All the changes listed above are **irreversible physical changes**. You have also learnt earlier that chemical changes can be represented by chemical reactions when the exact chemical composition of reactants and products is known. In this chapter we are going to look at **reversible chemical reactions**. On allowing the reaction for a very long time so that the concentrations of the reactants or products do not vary, the reaction is said to have attained equilibrium.

12.1.1 Reversible reaction

Try this

Dissolve 4 g cobalt chloride in 40 ml water. It forms a redish pink solution. Add 60 ml concentrated HC1 to this. It will turn violet. Take 5 ml of this solution in a test tube and place it in a beaker containing ice water mixture. The colour of solution will become pink. Place the same test tube in a beaker containing water at 90^0 C. The colour of the solution turns blue.



$Co(H_2O)_6^{2\oplus}$ $CoCl_4^{2\ominus}$

Test tube in cold water Test tube in hot water

In the above activity, the change in colour of the solution is caused by the chemical reaction which reverses its direction with change of temperature.

$$\underset{\text{(Pink)}}{Co(H_2O)_6^{2\oplus}(aq)} + 4Cl^{\ominus}(aq) \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \underset{\text{(Blue)}}{CoCl_4^{2\ominus}(aq)} + 6H_2O(l)$$

Can you tell?

What does violet colour of the solution in above indicate ?

The reaction in the above activity is an example of a **reversible reaction**. These are many chemical reactions which appear to proceed in a single direction. For example:

$C(s)+O_2(g) \xrightarrow{\text{Burn}} CO_2(g)$

$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$

These are called **irreversible reactions**. They proceed only in single direction until one of the reactants is exhausted. Their direction is indicated by an arrow ($\longrightarrow$) pointing towards the products in the chemical equation. On the contrary, reversible reactions proceed in both directions. The direction from reactants to products is the **forward reaction,** whereas the opposite reaction from products to reactants is called the **reverse or backward reaction**. A reversible reaction is denoted by drawing in between the reactants and product a double arrow, one pointing in the forward direction and other in the reverse direction ($\rightleftharpoons$ or $\rightleftarrows$).

For example :

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

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^{\ominus}(aq) + H_3O^{\oplus}$

Consider an example of decomposition of calcium carbonate. Calcium carbonate when heated strongly, decomposes to form calcium oxide and carbon dioxide. If this reaction is carried out in a closed container or open container, what do we observe ?

Do you know ?

What is a closed system ? In a closed system, there is no exchange of matter with the surroundings. In an open system, exchange of both matter and heat occurs with the surroundings.

If we perform the experiment at high temperature in a closed system, we find that after certain time, we have some calcium carbonate present. If we continue the experiment over a longer period of time at the same temperature, we find the concentrations of calcium carbonate, calcium oxide and carbon dioxide are unchanged. The reaction thus appears to have stopped and we say the system has attained the equilibrium. Actually, the reaction does not stop but proceeds in both the directions with equal rates. In other words calcium carbonate decomposes to give calcium oxide and carbon dioxide at a particular rate. Exactly at the same rate the calcium oxide and carbon dioxide recombine and form calcium carbonate.

Such reactions which do not go to completion and occur in both the directions simultaneously are **reversible reactions**. A reversible reaction may be represented in general terms as :

$$\underset{\text{reactants}}{A + B} \underset{\text{backward}}{\overset{\text{forward}}{\rightleftharpoons}} \underset{\text{products}}{C + D}$$

The double arrow indicates that the reaction is reversible.

Consider the reaction of decomposition of calcium carbonate occuring in an open system or container. Now what will happen ? We have seen that during decomposition of calcium carbonate, carbon dioxide can escape away. So, can we obtain back calcium carbonate ?

No !

Such a reaction is **irreversible reaction** which occurs only in one direction, namely, from reactants to products.

Reactions are chemically represented as follows

General representation :

(a) $CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$

This represents the irreversible reaction in open container

In closed container : reversible reaction

(b) $CaCO_3(s) \underset{\text{backward}}{\overset{\text{forward}}{\rightleftharpoons}} CaO(s) + CO_2(g)$

Do you know ?

Calcium oxide is also known as quicklime or lime. When heated strongly it glows bright white. This was used in theatre lighting, which gave rise to the phrase *'in the limelight'*.

Internet my friend

1. Equilibrium existing in the formation oxyhaemoglobin in human body.
2. Refrigeration system in equilibrium.

12.2 Equilibrium in physical processes

(a) Liquid - Vapour equilibrium

Let us now look at a reversible physical process of evaporation of liquid water into water vapour in a closed vessel (see Fig. 12.1).

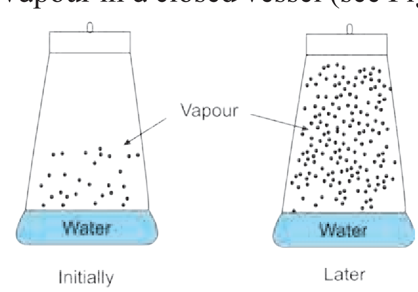


Fig. 12.1 : Water in a closed flask

Initially there is practically no vapour in the vessel. When a liquid evaporates in a closed container, the liquid molecules escape from the liquid surface into vapour phase building up vapour pressure. They also condense back into liquid state because the container is closed. In the beginning the rate of evaporation is high and the rate of condensation is low. But with time, as more and more vapour is formed, the rate of evaporation goes down and the rate of condensation increases. Eventually the two rates become equal. This gives rise to a constant vapour pressure. This state is known as an '**equilibrium state**'. In this state, the number of molecules leaving the liquid surface equals the number those return to liquid from the vapour state. Across the interface, there is a lot of activity between the liquid and the vapour. This state, when the rate of evaporation is equal to the rate of condensation is called equilibrium state. It may be represented as :

$$H_2O(l) \rightleftharpoons H_2O \text{ (vapour)}$$

At equilibrium, the pressure exerted by the gaseous water molecules at a given temperature remains constant, known as the equilibrium vapour pressure of water (or **saturated vapour pressure** of water or **aqueous tention**). The saturated vapour pressure increases with increase of temperature. In the case of water, the saturated vapour pressure is 1.013 bar (1atm) at 100 ^{0}C. Therefore, water boils at 100 ^{0}C when exposed to 1 atm pressure. For any pure liquid at 1 atm pressure the temperature at which its saturated vapour pressure equals to atmospheric pressure is called the normal boiling point of that liquid. The boiling point of water is 100° C at 1.013 bar pressure, whereas the boiling point of another liquid ethyl alcohol is 78 ^{0}C.

b. Solid - liquid equilibrium

Consider a mixture of ice and water in a perfectly insulated thermos flask at 273 K.

It is an example of solid-liquid equilibrium. Ice and water are at constant temperature. They remain in what is called solid-liquid equilibrium.

c. Solid - vapour equilibrium :

Try this

1. Place some iodine crystals in a closed vessel. Observe the change in colour intensity in it.

After some time the vessel gets filled up with violet coloured vapour.

The intensity of violet colour becomes stable after certain time.

What do you see in the flask (see Fig. 12.2)?

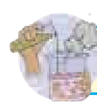
Fig. 12.2 Solid iodine in equilibrium with its vapour

We see both, that is, solid iodine and iodine vapour in the closed vessel. It means solid iodine sublimes to give iodine vapour and the iodine vapour condenses to form solid iodine. The stable intensity of the colour indicates a state of equilibrium between solid and vapour iodine. We can write the same as follows:

$$I_2\text{ (s)} \underset{\text{condensation}}{\overset{\text{sublimation}}{\rightleftharpoons}} I_2\text{(g)}$$

Other examples showing this kind of equilibrium are :

1. Camphor (s) $\rightleftharpoons$ Camphor (g)
2. Ammonium chloride (s) $\rightleftharpoons$ Ammonium chloride (g).



Try this

i. Dissolve a given amount of sugar in minimum amount of water at room temperature
ii. Increase the temperature and dissolve more amount of sugar in the same amout of water to make a thick sugar syrup solution.
iii. Cool the syrup to the room temperature.

Note the observation : Sugar crystals separate out.

In a saturated solution there exists dynamic equilibrium between the solute molecules in the solid state and in dissolved state.

$$\text{Sugar (aq)} \rightleftharpoons \text{Sugar (s)}$$

The rate of dissolution of sugar = The rate of crystallization of sugar

Do you know ?

1. What is a saturated solution ?
A saturated solution is the solution when additional solute can not be dissolved in it at the given temperature. The concentration of solute in a saturated solution depends on temperature.

12.3 Equilibrium in chemical process :

If a reaction takes place in a closed system so that the products and reactants cannot escape, we often find that reaction does not give a 100 % yield of products. Instead some reactants remain after the concentrations stop changing. **When there is no further change in concentration of reactant and product, we say that the reaction has attained equilibrium, with the rates of forward and reverse reactions being equal.** Chemical equilibrium at a given temperature is characterized by constancy of measurable properties such as pressure, concentration, density etc. Chemical equilibrium can be approached from either side.

Observe and Discuss

I. Colourless N_2O_4 taken in a closed flask is converted to NO_2 (a reddish brown gas) (See Fig. 12.3)

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

colourless   reddish brown

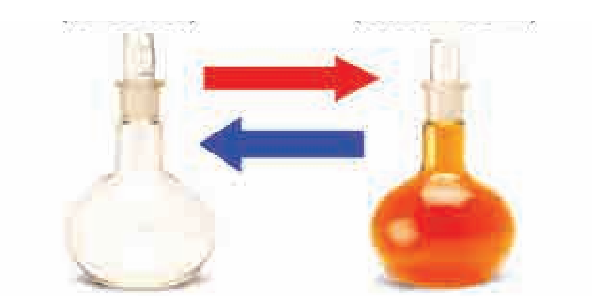


Figure 12.3 : N_2O_4 conversion to NO_2

The colour becomes lighter indicating the presence of NO_2 in the mixture. The formation of N_2O_4 from NO_2 is reversible. In such reaction the reactants combine to form the products and the products combine to give basic reactants.

As soon as the forward reaction produces any N_2O_4, the reverse reaction begins and N_2O_4 starts dissociating back to NO_2. At equilibrium, the concentrations of N_2O_4 and NO_2 remain unchanged and do not vary with time, because the rate of formation of N_2O_4 is equal to the rate of formation of NO_2 as shown in Fig. 12.3.

II. Consider the following dissociation reaction

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

Discuss

Colourless gas   Violet coloured gas

The reaction is carried out in a closed vessel starting with hydrogen iodide and following observations are noted

1. At first, there is an increase in the itensity of violet colour.
2. After certain time the increase in the intensity of violet colour stops.
3. When contents in a closed vessel are analysed at this stage, it is observed that reaction mixture contains the hydrogen iodide, hydrogen and iodine with their concentrations being constant over time.

The rate of decomposition of HI becomes equal to the rate of combination of H_2 and I_2. At equilibrium, no net change is observed and both reactions continue to occur.

Let us start with hydrogen and iodine vapour in a closed container at a certain temperature.

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

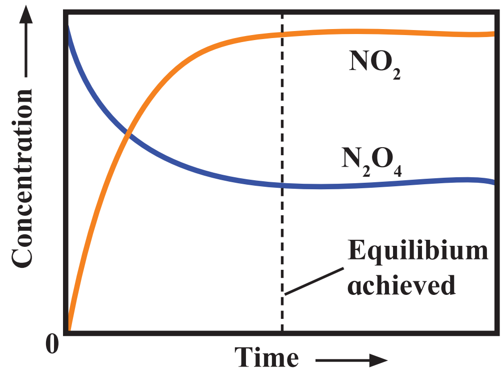


Fig. 12.4 (a) : Graph of forward and reverse reaction rates versus time for conversion of NO_2 to N_2O_4

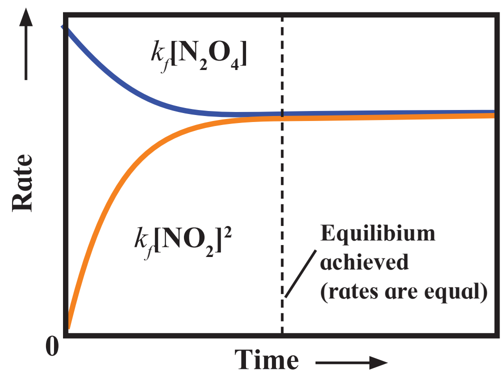


Fig. 12.4 (b) : Changes in reaction rates during a reversible reaction developing a chemical equilibrium. (Forward rate represented by upper curve in red and reverse reaction rate lower curve in blue)

Remember

For any reversible reaction in a closed system whenever the opposing reactions (forward and reaction) are occurring at different rates, the forward reaction will gradually become slower and the reverse reaction will become faster. Finally the rates become equal and equilibrium is established.

12.4 Law of mass action and equilibrium constant : The chemical equilibrium is mathematically described in terms of what is called the **equilibrium constant (K_C)**. We noted earlier that an equilibrium state is attained when the rate of the forward and reverse reactions become equal (refer Fig. 12.4).

12.4.1 Rate of chemical reaction : As any reaction proceeds the concentration of the reactants decreases and the concentration of the products increases. The rate of reaction thus can be determined by measuring the extent to which the concentration of a reactant decreases in the given time interval, or extent to which the concentration of a product increases in the given time interval. Mathematically, the rate of reaction is expressed as:

$$\text{Rate} = -\frac{d[\text{Reactant}]}{dT} = \frac{d[\text{Product}]}{dT}$$

Where d [reactant] and d [product] are the small decrease or increase in concentration during the small time interval dT.

12.4.2 Law of mass action : The law of mass action states that **the rate of a chemical reaction at each instant is proportional to the concentration product of all the reactants**. In case the balanced chemical equation shows more molecules of reactants, the concentration is raised to a power equal to the number of molecules of that reactant. A rate equation can be written for a reaction by applying the law of mass action as follows :

Consider a reaction $A + B \longrightarrow C$

Here A and B are the reactants and C is the product. The concentrations of chemical species are expressed in mol L^{-1} and denoted by putting the formula in square brackets. By applying the law of mass action to this reaction we write a proportionality expression as :

Rate α [A] [B]

This proportionality expression is transformed into an equation by introducing a proportionality constant, k, as follows:

$$\text{Rate} = k\,[A]\,[B] \qquad \ldots(12.1)$$

The Eq. (12.1) is called the **rate equation** and the proportionality constant, **k**, is called the **rate constant** of the reaction.

Problem 12.1 : Write the rate equation for the following reaction:

i. $C + O_2 \longrightarrow CO_2$

ii. $2KClO_3 \longrightarrow 2KCl + 3O_2$

Solution : the rate equation is written by applying the law of mass action.

i. The reactants are C and O_2

Rate α $[C]\,[O_2]$

$\therefore$ Rate = k $[C]\,[O_2]$

ii. The reactant is $KClO_3$ and its 2 molecules appear in the balanced equation.

$\therefore$ Rate α $[KClO_3]^2$

$\therefore$ Rate = k $[KClO_3]^2$

12.4.3 Equilibrium constant : Consider a hypothetical reversible reaction $A + B \rightleftharpoons C + D$. As we have noted earlier, two reactions, namely forward and reverse reactions occur simultaneously in a reversible chemical reaction. We, therefore, write rate equations for the forward and reverse reactions :

$\text{Rate}_{\text{forward}} \;\alpha\; [A][B]$

$$\therefore \text{Rate}_{\text{forward}} = k_f\,[A]\,[B] \qquad \text{....... (12.2)}$$

$\text{Rate}_{\text{reverse}} \;\alpha\; [C]\,[D]$

$$\therefore \text{Rate}_{\text{reverse}} = k_r\,[C]\,[D] \qquad \text{....... (12.3)}$$

At equilibrium, the rates of forward and reverse reactions are equal. Thus,

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

$\therefore k_f[A]\,[B] = k_r\,[C]\,[D]$

$$\therefore \frac{k_f}{k_r} = K_C = \frac{[C][D]}{[A][B]} \qquad \text{....... (12.4)}$$

Remember

At equilibrium the ratio of product multiplicative term denoting the concentraton of products to that of the reactants is unchanged and equals K_C. The value of K_C depends upon the temperature. It is interesting to note that though the concentration ratio remains unchanged, both the forward as well as reverse reactions do proceed at equilibrium, but at the same rate. Therefore the chemical equilibrium is a **dynamic equilibrium**.

K_C is called the **equilibrium constant.**

The equilibrium constant depends on the form of the balanced chemical equation. Consider reversible reaction :

$$aA + bB \rightleftharpoons cC + dD$$

$$\text{The equilibrium constant } K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \text{........ (12.5)}$$

If the equilibrium is written as

$$cC + dD \rightleftharpoons aA + bB,$$

$$K'_C = \frac{[A]^a[B]^b}{[C]^c[D]^d} = \frac{1}{K_C}$$

Thus equilibrium constant of the reverse chemical reaction is K'_C, is the reciprocal of the equilibrium constant K_C

Let us consider the equilibrium that occurs in the Haber process for synthesis of ammonia:

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

$$K_C = \frac{[NH_3]^2 \leftarrow \text{coefficient of } NH_3}{[N_2][H_2]^3 \leftarrow \text{coefficient of } H_2}$$

and for the equilibrium reaction written as

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

$$K'_C = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

12.4.3 Equilibrium constant with respect to partial pressure (K_P) : For reactions involving gases, it is convenient to express the equilibrium constant in terms of partial pressure.

$\therefore$ For the reaction,

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g),$$

the equilibrium constant can be expressed using partial pressures (Kp) as given by

$$K_P = \frac{(P_C)^c(P_D)^d}{(P_A)^c(P_B)^d} \qquad \text{........ (12.6)}$$

where P_A, P_B, P_C and P_D are equilibrium partial pressures of A, B, C and D, respectively.

Can you recall?

Ideal gas equation with significance of each term involved in it (refer Chapter 10, section 10.5.5).
PV = nRT, where P is pressure in pascal
n is number of moles of gas
V is volume in dm^3
R is molar gas constant in L atm K^{-1} mol^{-1}
T is absolute temperature

For a mixture of ideal gases, the partial pressure of each component is directly proportional to its concentration at constant temperature.

For component A,

$P_AV = n_ART$ .... (I)

$\frac{n_A}{V}$ is molar concentration of A in mol dm^{-3}

$P_A = \frac{n_A}{V} \times RT$, where $[A] = \frac{n_A}{V}$

$\therefore P_A = [A]RT$ .... (II)

Similarly for component B, $P_B = [B]RT$ ... (III)

For a chemical equilibrium reaction, both equilibrium constants are equal.

$P_B = [B]RT$
$P_C = [C]RT$
$P_D = [D]RT$

12.2.4 Relationship between K_P and K_C

Consider a general reversible reaction:

$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

Now substituting equations for P_A, P_B, P_C, P_D in Eq. (12.2)

$$K_P = \frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b} = \frac{[C]^c(RT)^c[D]^d(RT)^d}{[A]^a(RT)^a[B]^b(RT)^b}$$

$$K_P = \frac{[C]^C[D]^d(RT)^{c+d}}{[A]^a[B]^b(RT)^{a+b}}$$

$$\therefore K_P = \frac{[C]^c[D]^d}{[A]^a[B]^b} \times (RT)^{(c+d)-(a+b)}$$

$$\therefore K_P = \frac{[C]^C[D]^d}{[A]^a[B]^b} \times (RT)^{\Delta n}$$

But $K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ from equation (12.5)

$\therefore$ **$K_P = K_C (RT)^{\Delta n}$,** .... (12.7)

where Δn = (number of moles of gaseous products) - (number of moles of gaseous reactants) in balanced chemical equation.

R = 0.08206 L atm $K^{-1}mol^{-1}$

While calculating the value of Kp, pressure should be expressed in bar, because standard state of pressure is 1 bar. [1 pascal (Pa) = 1 Nm^{-2} and 1 bar = 10^5 Pa]

Problem 12.2 :

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

Write expressions for K_P and substitute expressions for P_{N_2}, and P_{NH_3}.

Solution : $K_P = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

$$\therefore K_P = \frac{[NH_3(g)]^2[RT]^2}{[N_2(g)]RT.[H_2(g)]^3[RT]^3}$$

$$\therefore K_P = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} \times \frac{[RT]^2}{[RT][RT]^3}$$

$\therefore K_P = K_C \times RT^{(2-4)}$

$\therefore K_P = K_C \times RT^{-2}$

Problem 12.3 : For a chemical equilibrium reaction

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

write an expression for K_P.

Solution : $K_P = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})}$

$$\therefore K_P = \frac{[HI(g)]^2[RT]^2}{[H_2(g)]RT.[I_2(g)]RT}$$

$$\therefore K_P = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} \times \frac{[RT]^2}{[RT][RT]}$$

$\therefore K_P = K_C \times RT^{2-(1+1)}$

$\therefore K_P = K_C$

12.5 Homogeneous and Heterogenous equilibria

12.5.1 Homogeneous reactions and Heterogeneous reactions : In a homogeneous equilibrium state all the reactants are in the same phase. An example of homogeneous gas phase equilibrium is dissociation of HI.

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

While Heterogenous equilibrium results from a reversible reaction involving reactants and products those are in different phases.

$NH_3\ (g) + Cl_2\ (g) \rightleftharpoons NH_4Cl\ (s)$

Just think

Two processes which are taking place in opposite directions in equilibrium.

How to write equilibrium constant expression for heterogenous equilibrium ?

12.3.2 Equilibrium constant for heterogeneous equilibria : As stated earlier, equilibrium in a system having more than one phase is called heterogeneous equilibrium. Consider,

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

If ethanol is placed in a conical flask, liquid vapour equilibrium is established.

$C_2H_5OH(l) \rightleftharpoons C_2H_5OH(g)$

For a given temperature

$$K_C = \frac{[C_2H_5OH(g)]}{[C_2H_5OH(l)]}$$

But $[C_2H_5OH(l)] = 1$

$\therefore K_C = [C_2H_5OH(g)]$

Thus, at any given temperature density is constant irrespective of the amount of liquid, and the term in the denominator is also constant.

Similarly $I_2(s) \rightleftharpoons I_2(g)$

Can you recall?

For any pure liquid and solid, the concentration is simply its density and this will not change no matter how much solid or liquid you use.

In an experiment of sublimation of iodine

$K_C = [I_2(g)]$

Solids are pure substances with unchanging concentrations and thus equilibria including solids are simplified.

Remember

When writing an equilibrium constant expression use only the concentrations of gases (g) and dissolved substances (aq).

12.3.3 Units of equilibrium constant

The unit of equilibrium constant depends upon the expression of K_C which is different for different equilibria. Therefore, the unit of K_C is also different.

To calculate units of equilibrium constant

Equilibrium Reaction (I)	Equilibrium Reaction (II)
$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$ $K_C = \frac{[HI(g)]^2}{[H_2(g)]\ [I_2(g)]}$ ..... (I) Units of $K_C = \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}]\ [mol\ dm^{-3}]}$ $= \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}]^2}$ As all the units cancel out For (I), K_C has no units	$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3(g)$ $K_C = \frac{[NH_3(g)]^2}{[N_2(g)]\ [H_2(g)]^3}$ ..... (II) Units of $K_C = \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}]\ [mol\ dm^{-3}]^3}$ $= \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}]^4}$ $= [mol\ dm^{-3}]^{-2}$ $= mol^{-2}\ dm^6$

Hint : Simplest way to calculate units of K_C is difference between number of moles in the numerator and number of moles at the denominator in equilibrium constant expression.

With reference to expression (II) to above, difference between number of moles =

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

$\therefore \Delta n = 2 - 4$

$\therefore \Delta n = -2$

$\therefore$ units of $K_C = (mol\ dm^{-3})^{\Delta n}$
$\therefore$ units of $K_C = (mol\ dm^{-3})^{-2}$
$\therefore$ units of $K_C = mol^{-2}dm^{6}$
Similarly with reference to expression (I) \ units of $K_C = (mol\ dm^{-3})^{\Delta n} = (mol\ dm^{-3})^{0}$
$\therefore$ K_C has no unit.

Problem 12.4 : Write the equilibrium constant expression for the decomposition of baking soda. Deduce the unit of K_C from the above expression.

Solution :

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$K_C = \frac{[Na_2CO_3(s)][CO_2(g)][H_2O(g)]}{[NaHCO_3(s)]^2}$$

$\therefore K_C = [CO_2(g)][H_2O(g)]$
$\therefore K_C$ has no unit.

12.6 Characteristics of equilibrium constant

1. The value of equilibrium constant is independent of initial concentrations of either the reactants or products.
2. Equilibrium constant is temperature dependent. Hence K_C, K_P change with change in temperature.
3. Equilibrium constant has a characteristic value for a particular reversible reaction represented by a balanced equation at a given temperature.
4. Higher value of K_C or K_P means more concentration of products is formed and the equilibrium point is more towards right hand side and vice versa.

12.7 Application of equilibrium constant

Some applications of equilibrium constant are discussed below.

12.7.1 Prediction of the direction of the reaction : For the reaction, $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant is

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b},$$

where all concentrations are equilibrium concentrations.

The ratio is called reaction quotient, Q_C, when the concentrations are not necessarily equilibrium concentrations.

$$Q_C = \frac{[C]^c[D]^d}{[A]^a[B]^b},$$

The reaction quotient has same form as that of equilibrium constant, but involves concentrations that are not necessarily equilibrium concentrations. This concept is very useful and we compare Q_C with K_C for a reaction under given conditions. We can decide whether the forward or the reverse reaction should occur to establish the equilibrium. It is shown diagramatically in Fig. 12.4.

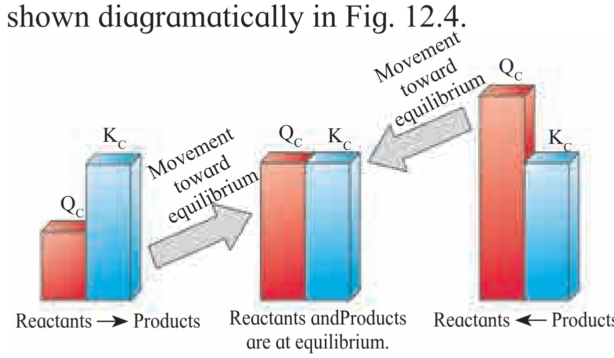


Fig. 12.4 : Predicting direction of reaction

If $Q_C < K_C$, the reaction will proceed from left to right, in forward direction, generating more product to attain the equilibrium.

If $Q_C = K_C$ the reaction is at equilibrium and hence no net reaction occurs.

If $Q_C > K_C$, the reaction will proceed from right to left, requiring more reactants to attain equilibrium.

A comparison of Q_C with K_C indicates the direction in which net reaction proceeds as the system tends to attain the equilibrium.

Note : The prediction of the direction of the reaction on the basis of Q_C and K_C values makes no comment on the time required for attaining the equilibrium.

12.7.2 : To know the extent of reaction :

Let us recall an expression for equilibrium constant K_C. (See Fig. 12.5). It indicates that the magnitude of K_C is

i. directly proportional to concentrations of the product.

ii. inversely proportional to the concentrations of the reactants.

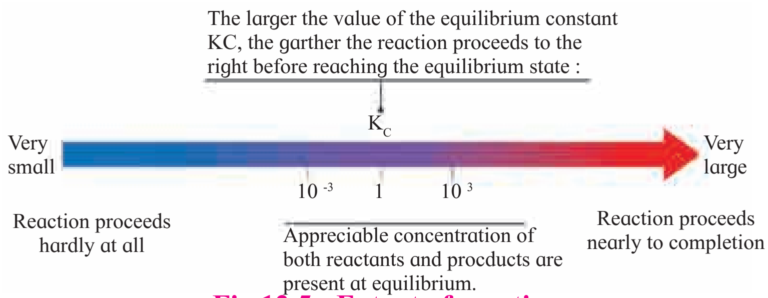


Fig 12.5 : Extent of reaction

Consider, for example, following two eqilibrium reactions :

$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$	$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$
Equilibrium constant values $K_C = \dfrac{[H_2O(g)]^2}{[H_2(g)]^2[O_2(g)]}$ $K_C = 2.4 \times 10^{47}$ At 500 K	$K'_C = \dfrac{[H_2(g)]^2[O_2(g)]}{[H_2O(g)]^2}$ $K'_C = \dfrac{1}{K_C} = \dfrac{1}{2.4 \times 10^{47}}$ $K'_C = 4.1 \times 10^{-48} = 0.41 \times 10^{-47}$ at 500 K
1. Value of K_C is very high ($K_C > 10^3$).	1. Value of K_C is very low ($K_C < 10^{-3}$).
2. At equilibrium there is a high proportion of products compared to reactants.	2. At equilibrium, only a small fraction of the reactants are converted into products.
3. Forward reaction is favoured.	3. Reverse reaction is favoured.
4. Reaction is in favour of products and nearly goes to completion.	4. Reaction hardly proceeds towards the products.
K_C >>>1. Reaction proceeds almost totally towards products.	K_C <<< 1. Rection hardly proceeds towards the products.

Can you tell?

Comment on the extent to which the forward reaction will proceed, from the magnitude of the equilibrium constant for the following reactions :

1. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $K_C = 20$ at 550 K
2. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$, $K_C = 10^{18}$ at 550 K

12.7.3 To calculate equilibrium concentrations : An equilibrium constant can be used to calculate the composition of an equilibrium mixture.

Consider an equilibrium reaction,

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

The equilibrium constant is 4.0 at a certain temperature.

Use your brain power

The value of K_C for the dissociation reaction $H_2(g) \rightleftharpoons 2H(g)$ is 1.2×10^{-42} at 500 K Does the equilibrium mixture contain mainly hydrogen molecules or hydrogen atoms ?

If we start with 2.0 mol of ethanoic acid and 2.0 mol of ethanol in 'V' litres. Let us find out the composition of equilibrium mixture. Consider *x* mol of ethyl ethanoate at equilibrium.

Internet my friend

Collect information about Chemical Equilibrium.

	CH_3COOH	+ C_2H_5OH $\rightleftharpoons$	$CH_3COOC_2H_5$	+ H_2O
Initial (No. of moles)	2.0	2.0	0	0
At equilibrium (No. of moles)	$(2.0 - x)$	$(2.0 - x)$	x	x
Equilibrium concentrations	$\frac{(2.0 - x)}{V}$	$\frac{(2.0 - x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

Equilibrium constant

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

$$\therefore 4.0 = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(2.0 - x)}{V} \times \frac{(2.0 - x)}{V}}$$

substituting the value of equilibrium concentration

$$\therefore 4.0 = \frac{x^2}{(2.0 - x)^2}$$

$$\therefore \sqrt{4} = \frac{x}{2.0 - x}$$

$$\therefore 2 = \frac{x}{2.0 - x}$$

$$\therefore 4 - 2x = x$$

$$\therefore x = \frac{4}{3}$$

$\therefore x = 1.33$

$\therefore (2.0 - x) = 0.67$

Therefore, equilibrium concentrations are 0.67 mol of ethanoic acid, 0.67 mol of ethanol and 1.33 mol of ethyl ethanoate.

Problem 12.5 : Equal concentrations of hydrogen and iodine are mixed together in a closed container at 700 K and allowed to come to equilibrium. If the concentraion of HI at equilibrium is 0.85 mol dm^{-3}, what are the equilibrium concentrations of H_2 and I_2 if $K_C = 54$ at this temperature ?

Solution : Balanced chemical reaction :

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

$$\therefore Kc = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

on substituting the values

$$\therefore 54 = \frac{(0.85)^2}{[H_2(g)]^2}$$

as initial concentrations of H_2(g) and I_2 (g) are equal.

(Refer to the balanced chemical equation : 1 mole of H_2 reacts with 1 mole of I_2)

Equilibrium concentration of I_2 (g) = Equilibrium concentration of H_2 (g)

$$\therefore 54 = \frac{(0.85)^2}{[H_2(g)]^2},$$

$\therefore [H_2(g)] = 0.12$ mol dm^{-3}

Equilibrium concentrations of H_2 and I_2 are equal to 0.12 mol dm^{-3}.

12.7.4 Link between chemical equilibrium and chemical kinetics :

We have deduced in section 12.4.3

$$K_C = \frac{k_f}{k_r} \quad \text{....... (12.7)}$$

Where $\mathbf{k_f}$ and $\mathbf{k_r}$ are velocity or **rate constants** of the forward and reverse reactions respectively. This equation can be used to determine the composition of the reaction mixture

$\mathbf{k_f > k_r}$	$\mathbf{k_f \approx k_r}$
$\therefore$ K_C is very large.	k_f and k_r have comparable values $\therefore$ K_C is nearly one.
$\therefore$Reaction goes almost to completion.	Reaction never goes to completion.
$\therefore$If k_f is much larger than K_C, the reaction may be irreversible (Reverse reaction is too slow to be detected).	Comparable concentrations of reactants and products are present at equilibrium.

Remember

The equilibrium refers to the relative amounts of reactants and products and thus a shift in equilibrium in a particular direction will imply the reaction in that direction will be favoured.

Problem 12.6 : The equilibrium constant K_C for the reaction of hydrogen with iodine is 54.0 at 700 K.

$$H_2(g) + I_2(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2HI(g)$$

K_C = 54.0 at 700 K

a. If k_f is the rate constant for the formation of HI and kr is the rate constant for the decomposition of HI, deduce whether kf is larger or smaller than kr.

Solution : As $K_C = \frac{k_f}{k_r} = 54.0$,

k_f is greater than k_r by a factor of 54.0

b. If the value of k_r at 700 K is 1.16 x 10^{-3}, what is the k_f ?

$K_P = K_C \times k_r = 54.0 \times (1.16 \times 10^{-3})$

$= 62.64 \times 10^{-3}$

12.8 Le Chaterlier's principle and factors altering the composition of equilibrium :

We have learnt that a reaction attains a state of equilibrium under a certain set of conditions (of temperature, pressure, concentration and catalyst).

In general, if we add more reactant, the system will react to remove it. If we remove a product, the system will react to replenish it. Under these changed condition, new equilibrium will be established with different composition from the earlier equilibrium mixture.

The principal goal of chemical synthesis is to achieve maximum conversion of reactants to products with minimum expenditure of energy. To achieve this goal, the reaction conditions must be adjusted.

The qualitative effect of various factors on the composition of equilibrium mixture are described through the Le Chatelier's principle.

If a stress is applied to a reaction mixture at equilibrium, reaction occurs in the direction which relieves the stress. Stress means any change in concentration, pressure, volume or temperature which disturbs the original equilibrium. The direction that the reaction takes is the one that reduces the stress. For example, if you increase concentration of the reactants, reaction goes in a direction that tends to decrease concentration.

Le Chatelier's Principle :

It states that, when a system at equilibrium is subjected to a change in any of the factors determining the equilibrium conditions of a system, system will respond in such a way as to minimize the effect of change.

12.8.1 Influencing factors of Le Chatelier's Principle :

a. Change of concentration

Consider reversible reaction representing production of ammonia (NH_3)

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$$

The reaction proceeds with decrease in number of moles ($\Delta n = -2$) and the forward reaction is exothermic. Iron (containing a small quantity of molybdenum) is the catalyst.

$$\text{At equilibrium } Q_C = K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} \text{ .... (I)}$$

Stage I : system at equilibrium

Stage II : If equilibrium disturbed by making $Q_C < K_C$ by adding H_2.

Due to addition of extra hydrogen, system is no longer at equilibrium.

How does a system regain its equilibrium ?

Stage III : Added hydrogen is to be used up and converted to more NH_3.

Sytem responds to any change in the concentration of the equilibrium mixture in order to restore the equilibrium.

Stage IV : System responds to restore equilibrium position.

According to Le-Chatelier's principle, the effect of addition of H_2 (or N_2 or both) is reduced by shifting the equilibrium from left to right so that the added N_2 or H_2 is consumed.

The forward reaction occurs to a large extent than the reverse reaction until the new equilibrium is established. This results in increased yield of NH_3.

Remember

In general, if the concentration of one of the species in equilibrium mixture is increased, the position of equilibrium shifts in the opposite so as to reduce the concentration of this species. However, the quilibrium constant remains unchanged.

b. Effect of Pressure

You know that : Ideal gas equation is

$PV = nRT$,

solving P at constant temperature gives,

$$P = RT\frac{n}{V}$$

$\therefore P \propto \frac{n}{V}$, where the ratio $\frac{n}{V}$ is an expression for the concentration of the gas in mol dm^{-3}

1. An equilibrium mixture of dinitrogen tetroxide (colourless gas) and nitrogen dioxide (brown gas) set up in a sealed flask at a particular temperature (refer Fig. 12.3). The effect of change of pressure on the gaseous equilibrium can be followed by observing the change in its colour intensity. See Table 12.1.

Table 12.1 : Change in colour intensity

Change in pressure	Change in colour intensity	Shift in equilibrium position
1. Decrease in pressure	The colour darkens	To the right, the side with more molecules
2. Increase in pressure	The colour lightens to almost colourless	To the left, the side with fewer molecules

You earlier noted that for equilibrium reaction

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

Forward reaction takes place with increase of number of molecules, whereas reverse reaction takes place with decrease in number of molecules.

2. Consider the reaction,

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

As there is the same number of molecules of gas on both sides, change of pressure has no effect on the equilibrium

Remember

1. There is no change in value of K_C during any change in pressure of the equilibrium reaction mixture.
2. A reaction in which decrease in volume takes place, reaction will be favoured by increasing pressure and increase in volume will be favoured with lowering pressure, temperature being constant.

Remember

In a reversible reaction, the reverse reaction has an energy change that is equal and opposite to that of the forward reaction.

c. Effect of Temperature :

Consider the equilibrium reaction,

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) + 92.5$ kJ

The forward reaction is exothermic. The reverse reaction is endothermic. An endothermic reaction consumes heat. Therefore, the equilibrium must shift in the reverse direction to use up the added heat (heat energy converted to chemical energy).

Now let us study the effect of change of temperature on the equilibrium constant.

1. Consider the equilibrium reaction :

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) +$ Heat

$\Delta H = -90$ kJmol^{-1}

Equilibrium constant K_C for the reaction, is given in Table 12.2.

$$K_C = \frac{[CH_3OH\ (g)]}{[CO\ (g)][H_2\ (g)]^2}$$

Table 12.2

Temperature (K)	K_C
298	1.7×10^{17}
500	1.1×10^{11}
1000	2.1×10^{6}

The forward reaction is exothermic. According to Le Chatelier's principle an increase in temperature shifts the position of equilibrium to the left. Therefore, the concentration of $[CH_3OH(g)]$ decreases and the concentration of $CO(g)$ and $H_2(g)$ increases.

$$K_C = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]^2}$$

Therefore, the value of K_C decreases as the temperature is increased.

d. Effect of Catalyst :

Rate of a chemical reaction, increases with the use of catalyst.

Consider an Esterification reaction :

$$\underset{\text{ethanoic acid}}{CH_3COOH(l)} + \underset{\text{ethanol}}{C_2H_5OH(l)} \rightleftharpoons \underset{\text{ethyl ethanoate}}{CH_3COOC_2H_5(l)} + \underset{\text{water}}{H_2O(l)}$$

If the above reaction is carried out without catalyst, it would take many days to reach equilibrium. However, the addition of hydrogen ions (H^+) as catalyst reduces the time only to a few hours.

Remember

In all the cases of change in concentration, pressure, temperature and presence of catalyst, once the equilibrium has been re-established after the change, the value of K_C will be unaltered

A catalyst does not affect equilibrium constant and equilibrium composition of a reaction mixture.

Do you know ?

Catalyst lowers activation energy for the forward and reverse reactions by exactly the same amount.

A catalyst does not appear in the balanced chemical equation and in the equilibrium constant expression.

Let us **summarize** effects of all four factors on the position of equilibrium and value of K_C.

Effect of	Position of equilibrium	Value of K_C
Concentration	Changes	No change
Pressure	Changes if reaction involves change in number of gas molecules	No change
Temperature	Change	Change
Catalyst	No change	No change

Making ammonia The Haber process

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

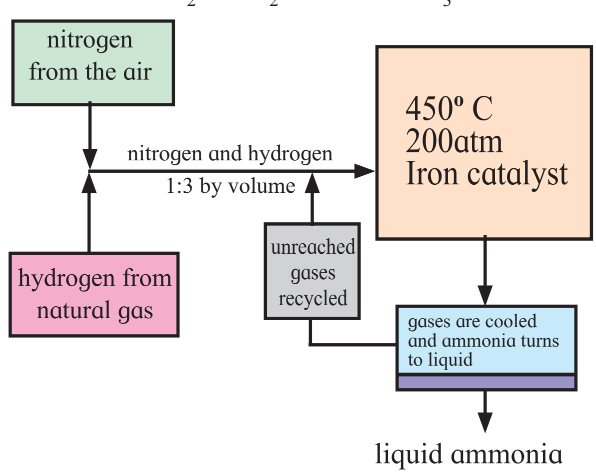


Fig. 12.6 The Haber process

12.9 Industrial Application :

The Haber process : (Industrial preparation of ammonia)

Industrial processes can be made efficient and profitable by applying ideas of rate of reaction and equilibrium.

The Haber process is the process of synthesis of ammonia gas by reacting together hydrogen gas and nitrogen gas in a particular stoichiometric ratio by volumes and at selected optimum temperature.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$$

The reaction proceeds with a decrease in number of moles ($\Delta n = -2$) and the forward reaction is exothermic. Iron (containing a small quantity of molybdenum) is used as catalyst.

We studied earlier in section 12.8.1 a. how the change in concentration of the reactants affects the yield of ammonia. Now let us consider the effect of temperature and pressure on the synthesis of ammonia.

a. Effect of temperature : The formation of ammonia is exothermic reaction. Hence, lowering of temperature will shift the equilibrium to right. At low temperature however, the rate of reaction is small and longer time would be required to attain the equilibrium. At high temperatures, the reaction occurs rapidly with appreciable decomposition of ammonia. Hence, the optimum temperature has to be used. The **optimum temperature** is about 773 K.

b. Effect of pressure : The forward reaction is favoured with high pressure as it proceeds with **decrease in number of moles**. At high pressure, the catalyst becomes inefficient. Therefore optimum pressure need to be used. The **optimum pressure is about 250 atm**.

Can you tell?

1. If NH_3 is added to the equilibrium system, in which direction will the eqilibrium shift to consume added NH_3 to reduce the effect of stress?
2. In this process, out of the reactions (reverse and forward reaction), which reaction will occur to a greater extent?
3. What will be the effect on yield of NH_3 ?

Internet my friend

1. Collect information about Haber Process in Chemical Equilibrium.
2. Youtube.Freesciencelessons The Haber Process.

Exercises

1. Choose the correct option

A. The equilibrium, $H_2O(l) \rightleftharpoons H^{\oplus}(aq) + OH(aq)$ is

a. dynamic   b. static
c. physical   d. mechanical

B. For the equlibrium, $A \rightleftharpoons 2B$ + Heat, the number of 'A' molecules increases if
a. volume is increased
b. temperature is increased
c. catalyst is added
d. concerntration of B is decreased

C. For the equlibrium $Cl_2\,(g) + 2NO(g) \rightleftharpoons 2NOCl(g)$ the concerntration of NOCl will increase if the equlibrium is disturbed by
a. adding Cl_2 b. removing NO
c. adding NOCl c. removal of Cl_2

D. The relation between K_c and K_p for the reaction $A\,(g) + B\,(g) \rightleftharpoons 2C\,(g) + D\,(g)$ is
a. Kc = Ykp   b. Kp = Kc²
c. $Kc = \frac{1}{\sqrt{Kp}}$ d. Kp/Kc = 1

E. When volume of the equilibrium reaction $C\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + H_2\,(g)$ is increased at constant temperature the equilibrium will
a. shift from left to right
b. shift from right to left
c. be unalered
d. can not be predicted

2. Answer the following

A. Write statement for Law of Mass action.
B. Write an expression for equilibrium constant with respect to concerntration.

C. Derive mathematically value of Kp for for $A(g) + B(g) \rightleftharpoons C(g) + D(g)$
D. Write expressions of K_c for following chemical reactions
i. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
ii. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
E. Mention various applications of equilibrium constant.
F. How does the change of pressure affect the value of equilibrium constant ?
J. Differentiate irreversible and reversible reaction.
K. Write suitable conditions of concentration, temperature and pressure used during manufacture of ammonia by Haber process.
L. Relate the terms reversible reactions and dynamic equilibrium.
M. For the equilibrium.
$BaSO_4(g) \rightleftharpoons Ba^{2\oplus}(aq) + SO_4^{\,2\ominus}(aq)$
state the effect of
a. Addition of $Ba^{2\oplus}$ ion.
b. Removal of $SO_4^{\,2\ominus}$ ion
c. Addition of $BaSO_4(s)$
on the equilibrium.

3. Explain :

A. Explain dynamic nature of chemical equilibrium with suitable example.
B. Relation between K_c and K_p.
C. State and explain Le Chatelier's principle suitably with reference to
1. Change in temperature
2. Change in concerntration.
D. a. Reversible reaction
b. Rate of reaction
E. What is the effect of adding chloride on the equilibrium ?
$AgCl(g) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$

Activity :

Prepare concepts maps of chemical equilibrium.