5. CHEMICAL EQUILIBRIUM

1. INTRODUCTION

Attainment of equilibrium in a system indicates a balanced condition of a system.

Balanced condition includes:

(a) Concentration of the components remain constant. It is not necessary for the concentrations to be equal.

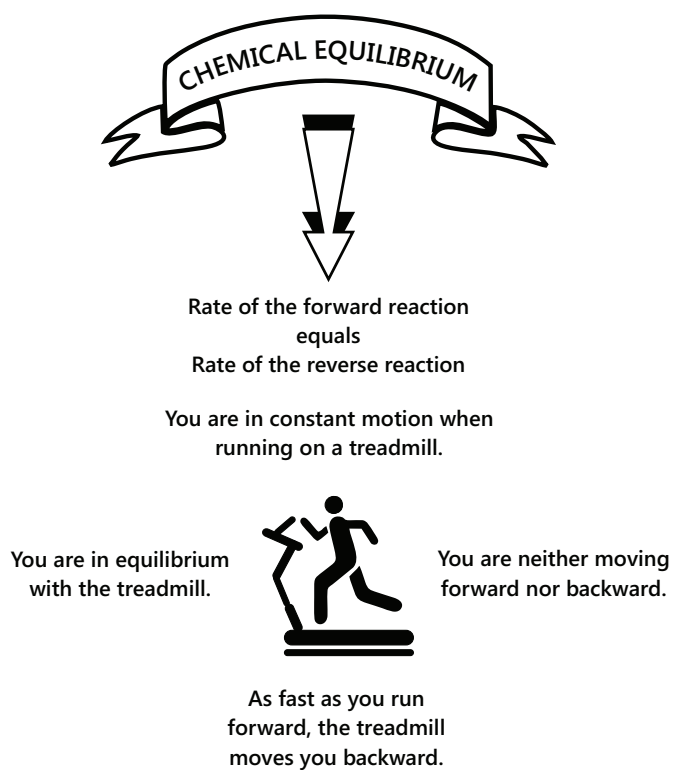**(b)** Rate of forward reaction=Rate of backward reaction.

CHEMICAL EQUILIBRIUM

Rate of the forward reaction
equals
Rate of the reverse reaction

You are in constant motion when
running on a treadmill.

You are in equilibrium
with the treadmill.

You are neither moving
forward nor backward.

As fast as you run
forward, the treadmill
moves you backward.

Figure 5.1: Everyday example of equilibrium

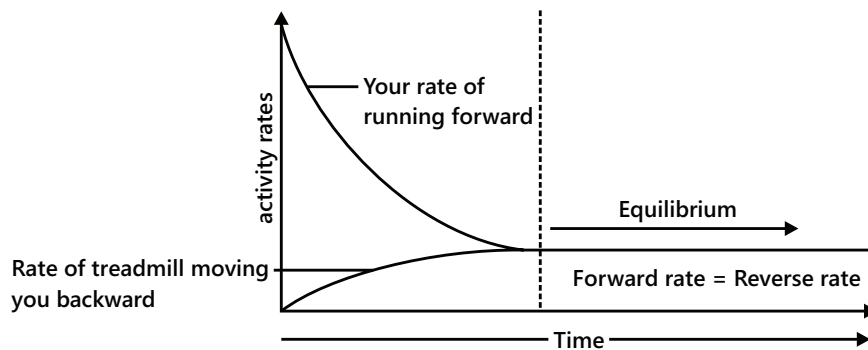If we plot the above condition on a graph, we get,
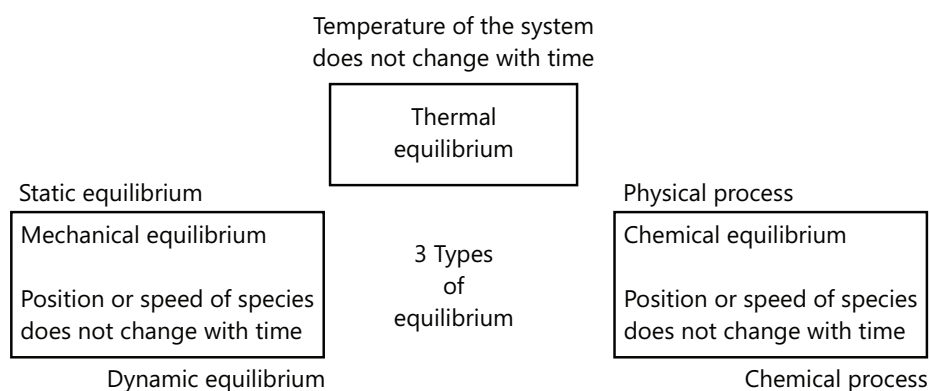

Figure 5.2: Attainment of equilibrium

Figure 5.3: Types of equilibrium

Various examples of equilibrium-

(a) Inside a bottle of fizzy cold drink

    (i) There is carbon dioxide (CO_2) dissolved in the liquid

    (ii) The space between the liquid and the cap also contains CO_2 gas CO_2 moves constantly from the liquid to the gas phase, and from the gas phase into the liquid maintaining the equilibrium $CO_2(g) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq)$

(b) While learning to ride a bicycle, one applies a large amount of force on the pedals in order to balance. This itself imposes a backward pressure on the leg muscles in the form of pain. But, once the balance is attained, the magnitude of the force to be applied becomes less and constant at one point, thereby easing the pain. Thus, equilibrium is maintained.

(c) Running needs a lot of energy and to produce energy, one's body needs to consume a lot of oxygen, for which the heart pumps/beats more than the normal. Once we stop running, our heart beats slow down and come to normal, but do not stop. There is a constant beating rate maintained and thus energy-oxygen equilibrium is maintained.

(d) A staircase which is built against a wall remains so with the passage of time posing as a good example of Static equilibrium.
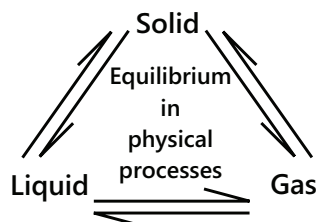
2. EQUILIBRIUM IN PHYSICAL PROCESSES

The equilibrium involving physical processes are referred to as physical equilibrium. The physical equilibrium involving change in state may be of the following three types.

2.1 Solid-Liquid Equilibrium

Process: Melting of a crystalline solid attains equilibrium under 1 atmospheric pressure at a certain temperature, wherein the temperature is termed as the melting or freezing point of that solid.

Changes: On application of constant heat to the equilibrium mixture, solid gets converted to liquid. But if the mixture is kept in an insulated thermos flask, a dynamic equilibrium, (i.e. both the states would be constant) would be maintained.

Example: Let us consider ice and water at 273 K (melting point of ice), taken in a perfectly insulated thermos flask. The temperature as well as the masses of ice and water remains constant. Since there is no change in mass of ice and water, the number of molecules going from ice into water, is equal to the number of molecules of water going into ice.

Rate of melting = Rate of freezing

2.2 Liquid – Gas Equilibrium

Process: Evaporation of water in an evacuated vessel gives vapour formation with a gradual decrease in the water level.

Changes: Equilibrium is attained wherein a constant level is observed after a certain time. This is dynamic in nature. In beginning, rate of evaporation is more and hence water vapour concentration increases, which in turn condenses back into the liquid. As the concentration of water vapours increases, rate of condensation also increases. At equilibrium, rate of evaporation is equal to rate of condensation.
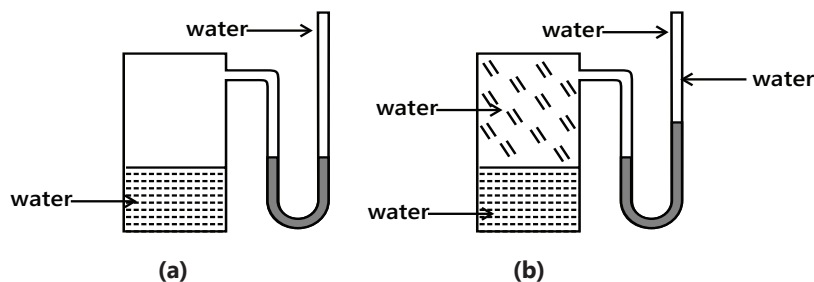
∴ Rate of evaporation = Rate of condensation.

Figure 5.4: Evaporation of water in a closed vessel (a) initial stage (b) equilibrium stage
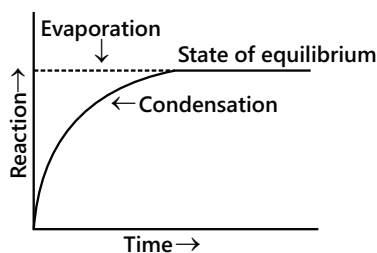
Figure 5.5: Attainment of liquid - vapour equilibrium
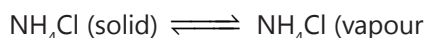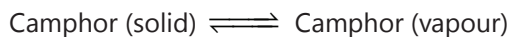
2.3 Solid – Vapour Equilibrium

Process: Sublimation occurs when solid turns into vapour phase.

Example: (with explanation of changes): A piece of solid iodine kept in a closed vessel, fills with violet vapour in sometime. Intensity of colour goes on increasing with time and attains a constant violet shade which indicates the equilibrium position. This point gives the sublimation and condensation processes in balance.

Represented as:

I_2 (solid) $\rightleftharpoons$ I_2 (vapour)
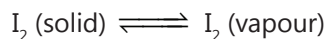
Other examples showing this kind of equilibrium are:

Camphor (solid) $\rightleftharpoons$ Camphor (vapour)

NH_4Cl (solid) $\rightleftharpoons$ NH_4Cl (vapour

2.4 Equilibrium Involving Dissolution of Solids or Gases in Liquids
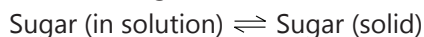
Solids in Liquids

Condition: A saturated solution is the one in which no more solute can be dissolved in a given amount of solvent. The added solute poses as a precipitate.

The amount of solute required to prepare a saturated solution in a given quantity of solvent is known as solubility of the solute at a particular temperature.

This state is dynamic equilibrium.

Figure 5.6: Equilibrium involving dissolution of solid or gases in liquids

Example: Addition of sugar to water remains undissolved in a saturated sugar solution.

Sugar (in solution) $\rightleftharpoons$ Sugar (solid)

The dynamic nature of equilibrium can be demonstrated by adding radioactive sugar into a saturated solution of non-radioactive sugar.

It is observed that the solution dissolves some radioactive sugar. This shows that even at equilibrium, the process of dissolution and precipitation are taking place. This means that equilibrium is dynamic in nature. However, at equilibrium:

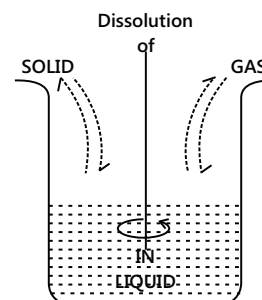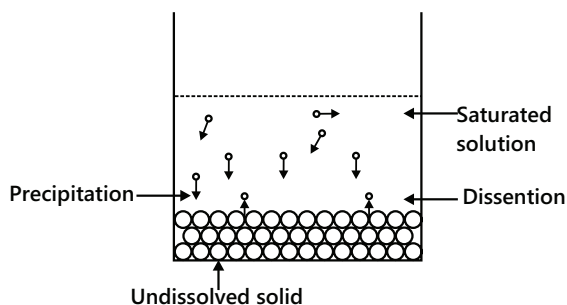Rate of dissolution = Rate of precipitation.

Figure 5.7: Attainment of solid - liquid equilibrium

Gases in Liquids

Condition: Certain liquids dissolve gases at a particular temperature to a certain extent. This suggests that a state of equilibrium exists between molecules in the gaseous state and the molecules dissolved in the liquid.

Example: Carbon dioxide dissolved in soda water.

The following equilibrium exists:
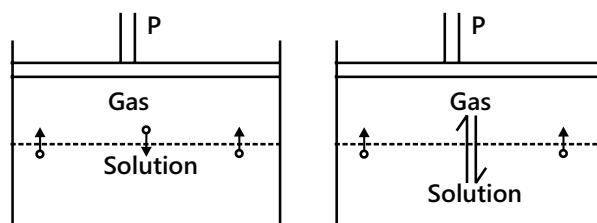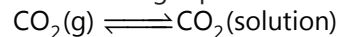$$CO_2(g) \rightleftharpoons CO_2(solution)$$

Figure 5.8: Attainment of equilibrium in a gas-liquid system

At equilibrium, the rate at which gas molecules pass into the solution becomes equal to the rate at which dissolved gas molecules come back into the gaseous phase. This is shown in the Fig.

General Characteristics of Physical equilibria:

(a) The system should be closed wherein no exchange of matter takes place with the surroundings.

(b) Irrespective of the side from which a process starts, a stable dynamic condition exists.

(c) The constant concentration keeps the other measurable properties of the system constant.

(d) On reaching the equilibrium at a particular temperature, the concentration of the reacting species reaches a constant value.

(e) The extent of the reaction before reaching equilibrium is given by the magnitude of concentration related expressions.

MASTERJEE CONCEPTS

Table 5.1: Examples of physical equilibrium and their constants

Physical Equilibrium	Constant
1. Liquid $\rightleftharpoons$ Vapour equilibrium	Vapour pressure
2. Solid $\rightleftharpoons$ Liquid equilibrium - Coexist at only one temperature (1 atm) i.e. the melting point, without any heat exchange with the surroundings.	Mass
3. Dissolution	
a. Solids in Liquids b. Gases in Liquids - Concentration of a gas in liquid proportionately changes with the pressure of the gas above the liquid.	Solubility at a given temperature Concentration of a gas in liquid proportionately changes with the pressure of the gas above the liquid.

Nikhil Khandelwal (JEE 2009, AIR 94)

2.5 Equilibrium in our Daily Life

(a) On a windy day, the clothes dry quickly since the moving breeze takes away the water vapour, making the clothes lose more water to the surroundings, in order to re-establish the equilibrium.

(b) Perspiration is seen more on a humid day which evaporates on sitting under a fan. The presence of water vapour in the surroundings prevents the loss of water from the skin while the moving air of the fan carries away the humid air enabling the loss of water from the skin and maintaining the equilibrium.

(c) Transport of oxygen by haemoglobin in blood. Oxygen breathed in combines with the haemoglobin according to the equilibrium: $Hb\ (s) + O_2(g) \rightleftharpoons HbO_2(s)$

When it reaches the tissues, the pressure of oxygen is low over there. 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.
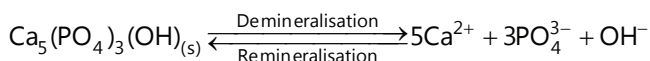
(d) Removal of CO_2 from tissues by blood. The equilibrium is:

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO^-_3(aq)$$
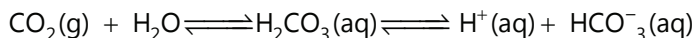
As partial pressure of CO_2 is high in the tissues, CO_2 dissolves in the blood. In the lungs, as partial pressure of CO_2 is low, it is released from the blood.

(e) Sweets cause tooth decay. Enamel coatings on the teeth consist of an insoluble substance called as hydroxyapatite, $Ca_5(PO_4)_3(OH)$.

The following equation shows the equilibrium between the substance and its ions.

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

3. EQUILIBRIA IN CHEMICAL PROCESS

3.1 Irreversible Reactions

Irreversible reactions: The chemical reactions which proceed in such a way that reactants are completely converted into products, i.e. the reactions which move in one direction, i.e. forward direction only are called irreversible reactions.

(a) **(i)** Thermal decomposition of ammonium nitrite, $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(b) Precipitation reaction,

  (ii) $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

  (iii) $Pb(NO_3)_2 + 2KI \longrightarrow PbI_2 + 2KNO_3$
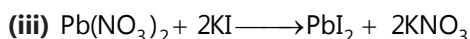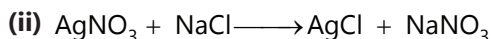
(c) Neutralisation reactions: $\underset{\text{Strong acid}}{H_2SO_4} + \underset{\text{Strong base}}{2NaOH} \longrightarrow Na_2SO_4 + 2H_2O$

3.2 Reversible Reactions

Reactions which thus proceed in both the directions and do not reach to completion are known as reversible reactions. The reaction proceeding from left to right is conventionally called the forward reaction and the opposite one proceeding from right to left is called the reverse or backward reaction. In such reactions the arrow ($\longrightarrow$) or sign of equality (=) is replaced by two half arrow ($\rightleftharpoons$) pointing the reaction in both the directions. This sign ($\rightleftharpoons$) represents the reversibility of the reaction

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$
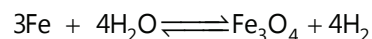
Some examples of reversible reactions are given below:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$
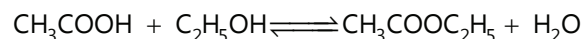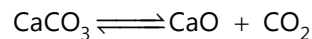
Steamed Iron!!!

Q. When steam is passed over heated iron fillings in an open tube, Iron is completely converted into its oxide but when the tube is closed, some Iron remains unreacted. Why?

Sol: Iron reacts with steam to form an oxide of iron (Fe_3O_4) and H_2 gas. When the tube is open, H_2 escapes and reverse reaction cannot occur but when the tube is closed, reverse reaction, i. e., reaction between Fe_3O_4 and H_2 also occurs forming iron and H_2O vapour and ultimately equilibrium is attained.
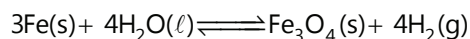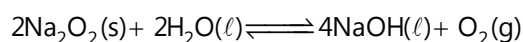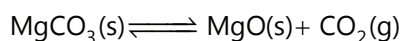

MASTERJEE CONCEPTS

Student's prior experience of reactions that proceed to completion appears to have influenced their conception of equilibrium reactions; many students failed to discriminate clearly between the characteristics of completion reactions and reversible reactions. Try to change your mind set in this case.

Saurabh Gupta (JEE 2010, AIR 443)

3.2.1 Heterogeneous Reactions

The reversible reaction in which more than one phase is present is called heterogeneous reaction.

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

$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$

$2Na_2O_2(s) + 2H_2O(\ell) \rightleftharpoons 4NaOH(\ell) + O_2(g)$

$3Fe(s) + 4H_2O(\ell) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
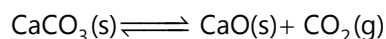
3.2.2 Homogeneous Reactions

The reversible reaction in which only one phase is present, i.e. all the reactions and products are in the same physical state is called homogeneous reaction.

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

$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$
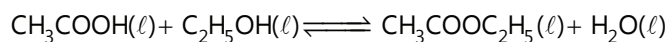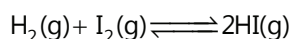
MASTERJEE CONCEPTS

A reaction is said to be irreversible when

• Either of the product separates out as solid, e.g.

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

$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4\downarrow + 2KNO_3$

• Either of the product escapes out as gas, e.g. $CaCO_3 \longrightarrow CaO + CO_2\uparrow$

However, if the above reaction is carried out in closed container i.e., leaving no scope for gas to escape out, the reaction shows reversible nature.

Neeraj Toshniwal (JEE 2009, AIR 94)

3.3 Dynamic Nature of Chemical Equilibrium

Dynamic nature is characterized by constant change, activity, or progress.

Thus, chemical equilibrium is dynamic in nature.

In a reversible reaction, the state in which both forward and backward reactions or two opposing reactions occur at the same speed is called as chemical equilibrium.

The measurable properties of the system such as pressure, density, colour or concentration remain constant under a certain set of conditions.

Figure 5.9: Dynamic nature of chemical equilibrium

3.4 Characteristics of Equilibrium State

(i) A system needs to be always closed to achieve equilibrium since an open system allows the escape of the formed products which prevents the backward reaction.
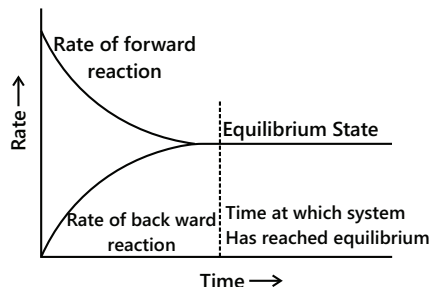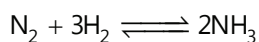
(ii) Chemical equilibrium, at a given temperature, is characterized by constancy of certain properties such as pressure, concentration, density or colour.

(iii) Chemical equilibrium can be attained from either side, i.e., from the side of reactants or products.

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

At equilibrium, each reactant and each product has a fixed concentration and this is independent of the fact whether we start the reaction with the reactants or with the products.

This reaction can be graphically represented as,
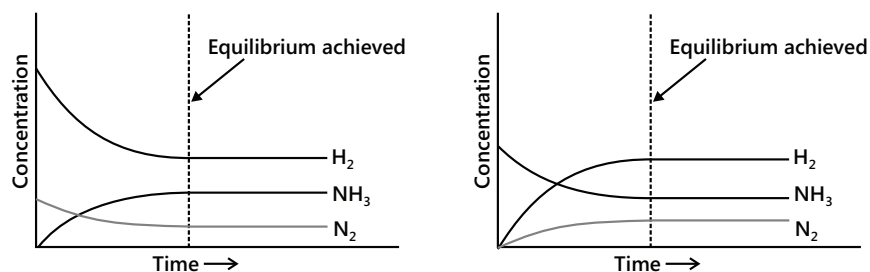
Figure 5.10: Attainment of equilibrium from either side of the reaction

(iv) Presence of catalyst never affects the equilibrium but it helps in attaining it rapidly.

(v) The reactions move with the same speed exhibiting the dynamic nature.

MASTERJEE CONCEPTS

- Chemical equilibrium is the state at which concentration of either of reactants or products do not change with time. It is attained when the rate of forward reaction becomes equal to the rate of backward reaction.

- Chemical equilibria are dynamic in nature. It can be approached from either side.

- The gaseous phase chemical equilibrium is attained only if a reaction is made in a closed container, either at constant pressure or at constant volume.

Misconception: Equilibrium is the state where the rates of the forward and reverse reactions are equal, not when the rates reach zero. (Common misconception: Nothing happens at equilibrium.

Aman Gour (JEE 2012, AIR 230)

4. LAW OF MASS ACTION

The term active mass (a) is directly proportional to concentration (in molarity or molality), i.e. $a \propto c_M$ or $a \propto c_m$

Active mass refers to the actual mass of reactants which takes part in a particular reaction.

$\therefore a = f \times c_{molarity}$ and $a = \gamma \times c_{molality}$

where, f and γ are activity coefficients; Also in terms of mole fraction, activity = activity coefficient (γ) × mole fraction.

Thus, if rate $\propto$ active mass also, rate $\propto$ concentration in mol/litre.

Consider a general reaction at equilibrium, $n_1 A + n_2 B \rightleftharpoons m_1 Z + m_2 Y + \ldots$

Therefore, rate of forward reaction $\propto [A]_0^{n_1} [B]_0^{n_2} \ldots$

$r_f = K_f [A]_0^{n_1} [B]_0^{n_2} \ldots$ . . . (i)

where, K_f is rate constant for forward reaction.

Similarly, rate of backward reaction $\propto [Z]_0^{m_1} [Y]_0^{m_2}$

$r_b = K_b [Z]_0^{m_1} [Y]_0^{m_2}$ . . . (ii)

where, K_b is rate constant for backward reaction.

At equilibrium, rate of forward reaction = rate of backward reaction, i.e. $r_f = r_b$

$$K_f [A]_{eq.}^{n_1} [B]_{eq.}^{n_2} \ldots = K_b [Z]_{eq.}^{m_1} [Y]_{eq.}^{m_2} \ldots \quad \text{or} \quad K_c = \frac{K_f}{K_b} = \frac{[Z]_{eq.}^{m_1} [Y]_{eq.}^{m_2} \ldots}{[A]_{eq.}^{n_1} [B]_{eq.}^{n_2}} \qquad \text{. . . (iii)}$$

Remember: By convention, the active masses of the products are written in the numerator and those of the reactants in the denominator.

MASTERJEE CONCEPTS

The value of an equilibrium constant is independent of the following factors:

- Initial concentration of the reactants involved.

- The presence of a catalyst.

- The direction from which the equilibrium has been attained.

- The presence of inert materials.

- The equilibrium expression for a given reaction is independent of the reaction mechanism.

- The equilibrium state is one of minimum Gibbs energy (G) (free energy). Gibbs energy is the energy associated with a chemical reaction that can be used to do work.

- K_c does not change with time. It has one unique or definite value for a given reaction at a given temperature and it depends only on temperature.

- If a reversible reaction has an exceedingly small value of Kc, adding a catalyst would be of little help.

- The concentrations of pure solid and liquid must be ignored while writing the equilibrium constant expression.

Vaibhav Krishnan (JEE 2009, AIR 22)

Misconception

(a) Many students confuse rate of reaction with extent of reaction.

    (i) Rate of Reaction: The **reaction rate** (rate of reaction) or **speed of reaction** for a reactant or product in a particular reaction is intuitively defined as how fast or slow a reaction takes place.

    (ii) Extent of Reaction: The **extent of reaction** is a quantity that measures the extent in which the reaction proceeds. It is usually denoted by the Greek letter ξ. The extent of a reaction has units of amount (moles).

(b) Equilibrium constants can change with temperature when the activation energies of forward and reverse reactions are different. (Common misconception: Equilibrium constants are constant under all conditions.)

(c) The rate of the forward reaction increases with time from the mixing of the reactants until equilibrium is established. But note that this is not so.

Key Concepts

(a) The magnitude of K equilibrium constant is a measure of the extent to which a given reaction has taken place at equilibrium.

(b) The higher value of equilibrium constant ($\simeq 10^3$) for a reaction indicates that the reaction proceeds more in forward direction. A very high value of equilibrium constant ($> 10^3$) such as:

$H_2 + Br_2 \rightleftharpoons 2HBr; \ K_c = 5.4 \times 10^{18}$ or $H_2 + Cl_2 \rightleftharpoons 2HCl; \ K_c = 4.0 \times 10^{31}$ shows that reaction has gone almost to completion.

(c) The lower values of equilibrium constant ($< 10^{-3}$) for a reaction indicates that the reaction proceeds more in backward direction. A way low value of such as

$N_2 + O_2 \rightleftharpoons 2NO; \ K_c = 4.8 \times 10^{-31}$ shows that reaction does not proceed significantly in forward direction,

(d) The intermediate value of K_c (10^3 to 10^{-3}) shows that concentrations of products and reactants are comparable.
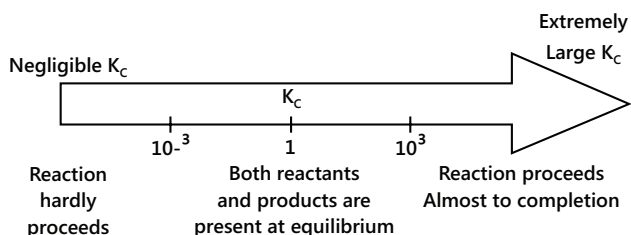
Figure 5.11: Dependence of extent of reaction on K_c

5. RELATIONSHIP BETWEEN K_P AND K_C

A gaseous reaction consists of particle gaseous species which exert an individual pressure, called as partial pressure which is taken into account for the measure of the equilibrium constant called K_p.

Consider gaseous reaction, $nA(g) + mB(g) \rightleftharpoons aY(g) + bZ(g)$

where,

P_A = partial pressure of A

P_B = partial pressure of B

P_Y = partial pressure of Y

P_Z = partial pressure of Z

$$K_p = \frac{(P_Y)^a (P_Z)^b}{(P_A)^n (P_B)^m}$$

Considering the gas equation, $PV = nRT$ or $P = \dfrac{n}{V} RT$

$\therefore P = CRT \quad \left[\dfrac{n}{V} = C \text{ i.e. concentration} \right]$

Substituting in the K_p expression, we get,

$$K_p = \frac{(C_Y RT)^a (C_Z RT)^b}{(C_A RT)^n (C_B RT)^m} = \frac{(C_Y)^a (C_Z)^b RT^{(a+b)-(n+m)}}{(C_A)^n (C_B)^m}$$

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

Δn = total no. of molecules of gaseous products − total no. of molecules of gaseous reactants.

MASTERJEE CONCEPTS

Equilibrium constant in terms of mole fractions (K_x)

Consider the general gaseous reaction: $aA + bB \rightleftharpoons cC + dD$

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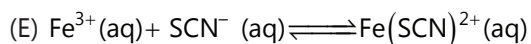
$$K_x = \frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b}.$$

Similar to the relation between K_p and K_c, we have $K_p = K_x(P)^{\Delta n}$

Nikhil Khandelwal (JEE 2009, AIR 94)

Illustration 1: Write equilibrium constant for the each **(JEE MAIN)**

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

(B) $KClO_3(s) \rightleftharpoons KCl(s) + (3/2)O_2(g)$

(C) $CaC_2(s) + 5O_2(g) \rightleftharpoons 2CaCO_3(s) + 2CO_2(g)$

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

(E) $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$
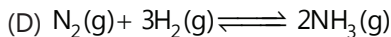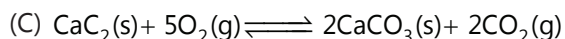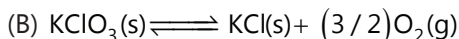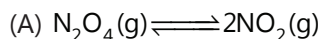
Sol: Use K_p and K_c expression wherever necessary.

(A) $K_c = \frac{[NO_2]^2}{[N_2O_4]}; K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})}$

(B) $K_c = [O_2]^{3/2}; K_p = (P_{O_2})^{3/2}$

(C) $K_c = \frac{[CO_2]^2}{[O_2]^5}; k_p = \frac{P_{CO_2}}{P_{O_2}^5}$

(D) $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}; K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

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

Illustration 2: The equilibrium constant K_c for the gaseous phase reaction at 523 K: $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ is 23.10 litre mol^{-1}. Calculate K_p at 503 K. **(JEE MAIN)**

Sol: $PCl_3 + Cl_2 \rightleftharpoons PCl_5$;
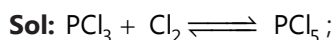
Use $K_p = K_c(RT)^{\Delta n}$ using the given K_c.

The formula to calculate K_p is as follows,

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

Values of K_c, R and T is known, we have to calculate Δn

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

$K_p = K_c(RT)^{-1}$;

Substituting the values in above equation,

$$k_p = \frac{23.10}{0.0821 \times 503} = 0.5593 \text{ atm}^{-1}$$

Illustration 3: The rate of reversible reaction (change in concentration per second):

$PtCl_4^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3]^- + Cl^-$; was observed at 0.3 ionic strength at 25°C and noticed that

$$\frac{\Delta[PtCl_4^{2-}]}{\Delta t} = 3.0 \times 10^{-5}[PtCl_4^{2-}] - 1.1 \times 10^{-3} \ [Pt(H_2O)Cl_3]^-[Cl^-] \qquad \textbf{(JEE ADVANCED)}$$

Calculate

(A) Rate constant for forward and backward reaction.

(B) The equilibrium constant for the complexation of fourth Cl⁻ at 0.3 ionic strength.

Sol: Observe the data properly and use the rate constants to find equilibrium constant.

(A) Rate constant for forward reaction $\Rightarrow K_f = 3.0 \times 10^{-5} \text{ sec}^{-1}$

   Rate constant for backward reaction $\Rightarrow K_b = 1.1 \times 10^{-3} \text{ litre mol}^{-1} \text{ sec}^{-1}$

(B) Equilibrium constant for the complexation of fourth Cl– is equilibrium, i.e. K_c for backward reaction is:

$$K_c = \frac{K_b}{K_f} = \frac{1.1 \times 10^{-3}}{3.0 \times 10^{-5}} = 36.66 \ \text{ litre mol}^{-1}$$

Illustration 4: Determine K_c for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2^2}Br(g) \rightleftharpoons NOBr(g)$ from the following data at 298 K.

The equilibrium constant for the following reactions, $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ and

$NO(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$ are 2.6 × 10³⁰ and 1.2 respectively. **(JEE MAIN)**

Sol: Frame a net reaction for the formation of NOBr from the given data and apply K_c.

The net reaction is, $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br(g) \rightleftharpoons NOBr(g)$

Equilibrium constant is given by, $K_{C_{(net)}} = \frac{[NOBr]}{[N_2]^{1/2}[O_2]^{1/2}[Br_2]^{1/2}}$

Considering the given equations:

$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; Equilibrium constant = 2.6 × 10³⁰

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; Equilibrium constant = $\frac{1}{2.6 \times 10^{30}}$

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$;

Equilibrium constant = $\left(\frac{1}{2.6 \times 10^{30}}\right)^{1/2}$ = 6.2 × 10⁻¹⁶

$\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} = K_c' = 6.2 \times 10^{-16}$ . . . . (i)

$$NO(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$$
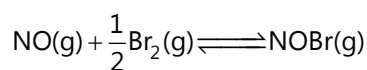
$$\frac{[NOBr]}{[NO][Br_2]^{1/2}} = K_c^{"} = 1.2 \qquad \qquad \text{... (ii)}$$

Multiplying i and ii equations

$$\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} \times \frac{[NOBr]}{[NO][Br_2]^{1/2}} = K_c^{'} \times K_c^{"} = 6.2 \times 10^{-16} \times 1.2$$

$$\text{or } \frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}[Br_2]^{1/2}} = K_{c_{(net)}} = 7.68 \times 10^{-16}$$

6. EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

According to the Arrhenius equation, $\qquad k = Ae^{-E/RT} \qquad \qquad$ ... (i)

where, k = rate constant, E = activation energy, R = gas constant, T = absolute temperature and e = exponential constant.

$$\log\frac{k_2}{k_1} = -\frac{E}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \qquad \text{... (ii)}$$

when, $T_2 > T_1$

for forward reaction, $\log\left(\frac{k_{f_2}}{k_{f_1}}\right) = -\frac{E_f}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \qquad$ ... (iii)

for backward reaction, $\log\left(\frac{k_{b_2}}{k_{b_1}}\right) = -\frac{E_b}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \qquad$ ... (iv)

Subtracting eq.(iv) from eq.(iii) we get

$$\log\left(\frac{k_{f_2}/k_{b_2}}{k_{f_1}/k_{b_1}}\right) = -\frac{(E_f - E_b)}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{ or } \log\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (v)}$$

where, ΔH is the heat of reaction at constant volume and K_1 and K_2 are the equilibrium constants of a reaction at temperatures T_1 and $T_2(T_2 > T_1)$. This equation is known as integrated form of van't Hoff isochore.

The differential form of van't Hoff isochore is: $\frac{d}{dt}\ln K_c = \frac{\Delta H}{RT^2} \qquad \qquad$ ... (12)

MASTERJEE CONCEPTS

Equilibrium constants can change with temperature when the activation energies of forward and reverse reactions are different.

(Common misconception: Equilibrium constants are constant under all conditions.)

Aman Gour (JEE 2012, AIR 230)
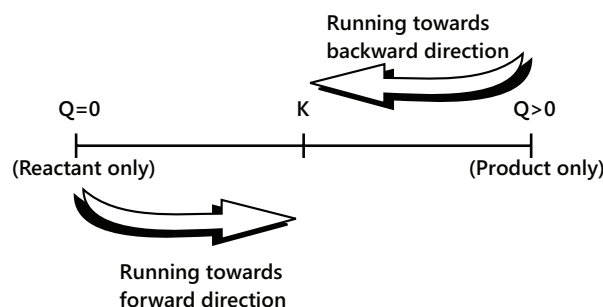
Figure 5.12: Relation between reaction quotient and equilibrium constant

7. REACTION QUOTIENT OR MASS ACTION RATIO

Table 5.2: Prediction of direction of reaction by using reaction quotient

Assume the reaction: A + B $\rightleftharpoons$ C + D	
$Q = \dfrac{[C][D]}{[A][B]}$	Q can be Q_c or Q_p
	Q_c = Concentration in moles/litre
	Q_p = Concentration in partial pressure
$Q_c = K_c$ or $Q_p = K_p$	Reaction attains equilibrium
$Q_c < K_c$ or $Q_p < K_p$	Forward reaction proceeds faster
$Q_c > K_c$ or $Q_p > K_p$	Backward reaction proceeds faster

Illustration 5: The equilibrium constant, K_p, for the reaction. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.6×10^{-4} atm^{-2} at 300°C. What will be the equilibrium constant at 500°C if heat of reaction in this temperature range is −25.14 kcal

(JEE MAIN)

Sol: Apply $\log\dfrac{K_{p_2}}{K_{p_1}} = \dfrac{\Delta H}{2.303R}\left[\dfrac{T_2 - T_1}{T_2 T_1}\right]$ i.e. the modified Arrhenius equation.

Given,

$K_{p_1} = 1.0 \times 10^{-4}$;

$\Delta H = -22$ kcal

$R = 2 \times 10^{-3}$ kcal deg^{-1} mol^{-1}

$T_1 = 300 + 273 = 573$ K,

$T_2 = 500 + 273 = 773$ K

Using the following relation, new equilibrium constant can be calculated.

Substituting the values,

$$\log\frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log\frac{K_{p_1}}{(1.0 \times 10^{-4})} = \frac{-22}{2.303 \times 2 \times 10^{-3}}\left[\frac{773 - 573}{773 \times 573}\right] = -4 - 2.1567 = -6.1567$$

$K_{p_2} = 6.97 \times 10^{-7}$ atm^{-2}

Illustration 6: For the reaction, A + B $\rightleftharpoons$ 3C at 25°, a 3 litre vessel contains 1, 2, 5 moles of A, B and C respectively. Predict the direction of reaction if: (a) K_c for the reaction is 10; (b) K_c for the reaction is 20.83 **(JEE MAIN)**

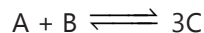**Sol:** Remember $\text{Concentration} = \dfrac{\text{no. of moles}}{\text{Volume}}$. Use this expression and calculate Q, reaction quotient. Compare with the given K_c and predict the direction.

A + B $\rightleftharpoons$ 3C

Before reaction, $[A]_0 = 1/3$

Thus, $Q = \dfrac{[C]_0^3}{[A]_0[B]_0} = \dfrac{4^5 \times 3 \times 3}{3^3 \times 1 \times 2} = \dfrac{5^3}{3 \times 1 \times 2} = \dfrac{125}{6} = 20.83$

(a) Since, $K_c = 10$, thus Q must decreases to attain K_c value and thus, [C] must decrease or [A] and [B] should increase. Thus, reaction will occur in backward direction.

(b) $Q = K_c$, thus reaction is in equilibrium

Illustration 7: A graph plotted between log10 K_c and 1/T is straight line with intercept 10 and slope equal to 0.5. **(JEE ADVANCED)**
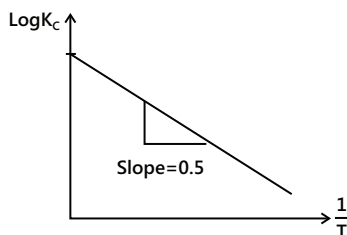
Calculate:

(i) Pre-exponential factor A.

(ii) Heat of reaction at 298 K.

(iii) Equilibrium constant at 298 K.

(iv) Equilibrium constant at 800 K assuming ΔH remains constant between 298 K and 800 K.

Sol: Using the plotted graph and the graph related expressions, calculate the different parameters.

van't Hoff isochore is: $\log_{10}K = \log_{10}A - \dfrac{\Delta H}{2.303RT}$

(i) Thus, intercept $= \log_{10}A = 10$; $A = 10^{10}$

(ii) Also, slope $= \tan\theta = 0.5 = -\dfrac{\Delta H}{2.303R}$ ∴ $\Delta H = -9.573$ks mol

(iii) Also, $\log_{10}K = 10 + \dfrac{2.303}{2.303 \times 2 \times 298}$; $K \approx 1.0 \times 10^{10}$

Illustration 8: The following reaction has attained equilibrium $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, $\Delta H° = -92.0$ 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? **(JEE ADVANCED)**

Sol: Application of Le-Chatelier's principle and the use of Q_c will answer the conditions.

$K_c = \dfrac{[CH_3OH]}{[CO][H_2]^2}, K_p = \dfrac{p_{CH_3OH}}{p_{CO} \times p_{H_2}^2}$

(i) When volume of the vessel is reduced to half, the concentration of each reactant or product becomes double.

Thus, $Q_c = \dfrac{2[CH_3OH]}{2[CO] \times \{2[H_2]\}^2} = \dfrac{1}{4} K_c$

As $Q_c < K_c$, equilibrium will shift in the forward direction, producing more of CH_3OH to make $QC = K_c$.

(ii) As volume remains constant, molar concentrations will not change. Hence, there is no effect on the state of equilibrium.

8. STANDARD FREE ENERGY CHANGE OF A REACTION AND ITS EQUILIBRIUM CONSTANT

Energy is the driving force for reactions. The standard free energy of a substance represents the free energy change associated with the formation of the substance from the elements in their most stable forms as they exist under the standard conditions of 1 atm pressure and 298K.

$\Delta G°$ = Difference in free energy of the reaction when all the reactants and products are in the standard state (1 atmospheric pressure and 298 K)

K_c or K_p = Thermodynamic equilibrium constant of the reaction. Both are related to each other at temperature T by the following relation:

$\Delta G° = -2.303\ RT \log K_c$ and $\Delta G° = -2.303\ RT \log K_p$ (in case of ideal gases)

This equation represents one of the most important results of thermodynamics and relates to the equilibrium constant of a reaction to a thermochemical property. It is sometimes easier to calculate the free energy in Law reaction rather than to measure the equilibrium constant.

Standard free energy change can be thermodynamically calculated as:

$\Delta G° = \Delta H° - T\Delta S°$

Here, $\Delta H°$ = standard enthalpy change,

$\Delta S°$ = standard entropy change.

$-RT \log_e K_p = \Delta H° - T\Delta S°$

$\log_e K_p = \dfrac{\Delta S°}{R} - \dfrac{\Delta H°}{RT}$; $\log_{10} K_p = \dfrac{\Delta S°}{2.303R} - \dfrac{\Delta H°}{2.303RT}$
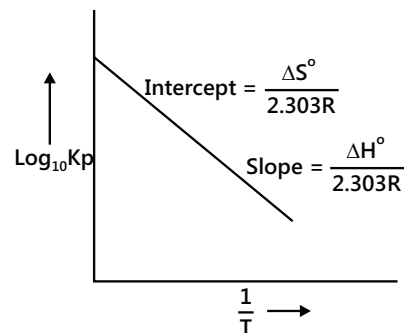
MASTERJEE CONCEPTS

(a) The catalyst never affects $\Delta G°$ of the reaction at equilibrium.

(b) (i) If $\Delta G° = 0$, then $K_c = 1$.

(ii) If $\Delta G° > 0$, (+ ve), then $K_c < 1$. So, reverse reaction is possible, i.e., less concentration of products of equilibrium state.

(iii) If $\Delta G° < 0$, (− ve), then $K_c > 1$.

So, forward reaction is possible where a large concentration of products is observed till the point of equilibrium is attained.

(c) A negative $\Delta G°$ never indicates the complete transformation of the reactants into products. Similarly, a positive $\Delta G°$ does not indicate the absence of product formation.

Neeraj Toshniwal (JEE 2009, AIR 21)

Illustration 9: For the equilibrium, $N_2O_4 \rightleftharpoons 2NO_2$; $(G^{\circ}_{N_2O_4})_{298} = 150\text{kJ / mol}$ and $(G^{\circ}_{NO_2})_{298} = 75\text{kJ / mol}$

(A) When 5 mole / litre of each is taken, calculate the value of ΔG for the reaction at 298 K.

(B) Find the direction of reaction and concentrations at equilibrium. **(JEE MAIN)**

Sol: Use the expression relating Gibb's free energy and the equilibrium constant. By observing the sign of ΔG, direction of the reaction can be predicted. The same values will be used to calculate the concentrations.

$$N_2O_4 \rightleftharpoons 2NO_2$$

(A) Concentration at $t = 0$ 5   5

$[G^{\circ}_{N_2O_4}]_{298K} = 100\text{kJmol}^{-1}, [G^{\circ}_{NO_2}]_{298K} = 50\text{kJmol}^{-1}$

ΔG° for reaction $= 2 \times G^{\circ}_{NO_2} - G^{\circ}_{N_2O_4} = 2 \times 75 - 150 = 0$

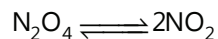Now, $\Delta G = \Delta G^{\circ} + 2.303 \text{ RT log Q}$

$\Delta G = 0 + 2.303 \times 8.314 \times 10^{-3} \times 298 \times \log \dfrac{5^2}{5}$; $\Delta G = + 3.99$ kJ

Since, $\Delta G = +$ ve and thus, reaction will not proceed in forward direction. It will take place in backward direction.

(B) Also for reverse reaction,

$$2NO_2 \rightleftharpoons N_2O_4$$
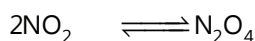
Conc. at $t = 0$ 5   5

Conc. at equilibrium $(5 - 2x)$ $(5 + x)$

At equilibrium, $\Delta G = 0$; Also, $\Delta G^{\circ} = 0$

$\therefore$ From $\Delta G^{\circ} = -2.303 \text{ RT log K}$; $K_c = 1$

Thus, $K_c = \dfrac{5 + x}{(5 - 2x)^2} = 1$ $\therefore$ x = 1.25

Thus, $[NO_2]_{at}$ eq.$= 5 - 2.50 = 2.5$ mol litre^{-1}

$[N_2O_4]_{at}$ eq. $= 5 + 1.25 = 6.25$ mol litre^{-1}

Illustration 10: Calculate K_p at 298 K for the gas-phase reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ from the following data. **(JEE MAIN)**

	CO	H_2O	CO_2	H_2
$\Delta H^{\circ}f$ (kJ/mole)	−120.5	−241.8	−383.5	0
S° (J/mole. K)	177.6	188.7	215.6	130.4

Sol: According to the given reaction, calculate $\Delta H^{\circ}f$ and ΔS° from the available data. Use it in the equation $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$. One gets ΔG°, through which one can calculate K_p by using the equation, $\Delta G^{\circ} = -2.303 \text{ RT log } K_p$.

For the given reaction,

$\Delta H^{\circ} = [\Delta H^{\circ}_f(CO_2) + \Delta H^{\circ}_f(H_2)] - [\Delta H^{\circ}_f(CO) + \Delta H^{\circ}_f(H_2O)] = (-383.5 + 0) - (-120.5 - 241.8) = -21.2$ kJ $= -21200$ J/mole.

$\Delta S^{\circ} = [S^{\circ}(CO_2) + H^{\circ}(H_2)] - [H^{\circ}(CO) + S^{\circ}(H_2O)] = (215.6 + 130.4) - (177.6 + 188.7) = -20.9$ J/mole.

Applying the thermodynamic equation,

$\Delta G° = \Delta H° - T\Delta S° = -21200 - 298 \times (-20.9) = -14978$ J.

Now, we have, $\Delta G° = -2.303$ RT log K_p

$-14978 = -2.303 \times 8.314 \times 298 \times \log K_p$

$\log K_p = 2.6254$

$\therefore K_p = 4.16 \times 10^2$

Illustration 11: The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g/litre at 288 K and 1.84 g/litre at 348 K. Calculate the enthalpy of reaction: $N_2O_4 \rightleftharpoons 2NO_2$. Also calculate the standard entropy change during the reaction at 348 K. **(JEE AVANCED)**

Sol: Use the density to calculate concentration; Arrhenius expression for enthalpy and free energy expression for entropy.

$N_2O_4 \rightleftharpoons 2NO_2$; $PV = \dfrac{w}{m}RT$
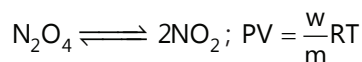
$\therefore m_{mix} = \dfrac{w}{m}.RT = \dfrac{dRT}{P} = \dfrac{3.62}{1\,atm} \times 0.08 \times 288 = 85.69$. Let a mole N_2O_4 and $(1 - a)$ mole of NO_2 exist at equilibrium

$\therefore a \times 82 + (1 - a) \times 46 = 85.6$; $a = 0.86$

$\therefore [n_{N_2O_4}] = 0.86$ mole and $[n_{NO_2}] = 0.14$ mole

$\therefore K_p = \dfrac{0.14 \times 0.14}{0.86} \times \left[\dfrac{1}{1}\right]^1 = 0.0228$ atm at 288 K

Case II: $m_{mix} = 1.84 \times 0.0821 \times 248 = 82.57$

Let a' mole of N_2O_4 and $(1 - a')$ mole of NO_2 exist at equilibrium

$\therefore a' \times 92 + (1 - a') \times 46 = 52.57$

$\therefore a' = 0.14$

$\therefore [n_{N_2O_4}] = 0.14$ $[n_{NO_2}] = 0.86$

$\therefore K_p = \dfrac{0.86 \times 0.86}{0.14} \times \left[\dfrac{1}{1}\right]^1 = 5.283$ atm at 348 K

Now, $2.303\log\dfrac{K_{p_2}}{K_{p_1}} = \dfrac{\Delta H°}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$\therefore 2.303\log\dfrac{5.283}{0.0228} = \dfrac{\Delta H°}{2} - \left[\dfrac{348 - 288}{348 \times 288}\right]$

$\therefore \Delta H° = 18195.6$ cal $= 18.196$ kcal

Also, $-\Delta G° = 2.303 \times 2 \times 348 \times \log 5.283$

$\therefore \Delta G° = -2.303 \times 2 \times 348 \times \log 5.283 = -1158.7$ cal $= -1.1587$ kcal

$\therefore \Delta S° = \dfrac{\Delta H° - \Delta G°}{T} = \dfrac{18196 + 1158.7}{348} = 55.62$ cal

9. APPLICATIONS OF LAW OF MASS ACTION
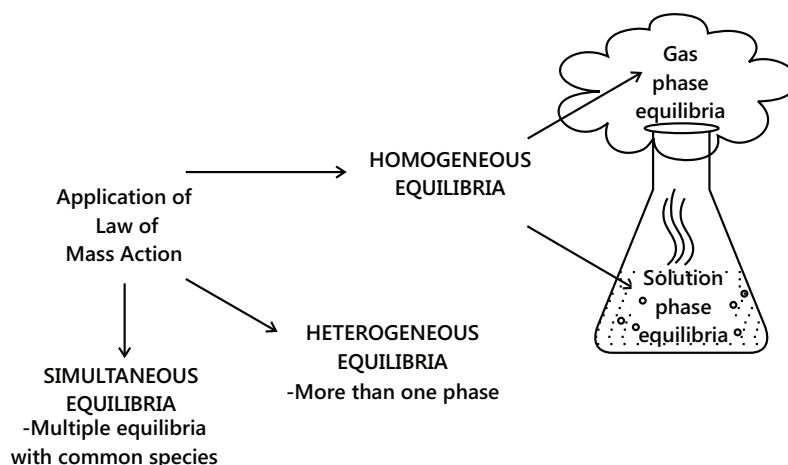
Figure 5.13: Application of law of mass action to different types of equilibria

9.1 Homogeneous Equilibria

These are of two types

(i) Gaseous phase equilibria: This type of equilibria involves following cases:

Table 5.3: Gaseous phase equilibria

Formation Equilibria							
$\Delta n = 0$ [vol.='V' L]				$\Delta n \neq 0$ [vol.='V' L]			
Cond.	No. of moles			Cond.	No. of moles		
	$H_2(g) \quad + \quad I_2(g) \rightleftharpoons 2HI(g)$				$N_2(g) \quad + 3H_2(g) \rightleftharpoons 2NH_3(g)$		
t = 0	a	b	0	t = 0	a	b	0
EQM	(a-x)	(b-x)	2x	EQM	(a-x)	(b-x)	2x
CONC.	$\dfrac{(a-x)}{V}$	$\dfrac{(b-x)}{V}$	$\dfrac{2x}{V}$	CONC.	$\dfrac{(a-x)}{V}$	$\dfrac{(b-x)}{V}$	$\dfrac{2x}{V}$
$K_c = \dfrac{4x^2}{(a-x)(b-x)}$				$K_c = \dfrac{4x^2V^2}{(a-x)(b-3x)^3}$			
Total Pressure of gases at eqm. = P_T				Eqm. Pressure = P Total moles at eqm.= (a-x)+(b-3x) + 2x $\quad$ = a+ b -2x			
Partial pressure =Tot. pressure × Mole fraction (P_T) $K_P = \dfrac{\left[\dfrac{n_{HI}}{\Sigma n}\right]^2 \times P_T^2}{\left[\dfrac{n_{H2}}{\Sigma n}\right] \times P_T \times \left[\dfrac{n_{I_2}}{\Sigma n}\right] \times P_T} = \dfrac{(n_{HI})^2}{nH_2 \times n_{I_2}}$ $K_P = \dfrac{4x^2}{(a-x)(b-x)}$				$K_P = \dfrac{(n_{NH_3})^2}{n_{N_2}(n_{H_2})^3} \times \left[\dfrac{P}{\Sigma n}\right]^{-2}$ $\quad = \dfrac{(2x)^2}{(a-x)(b-3x)^3}\left[\dfrac{P}{(a+b-2x)}\right]^{-2}$ $K_P = \dfrac{4x^2(a+b-2x)^2}{P^2(a-x)(b-3x)^3}$			

Dissociation Equilibria							
$\Delta n = 0$ [vol.='V' L]				$\Delta n \neq 0$ [vol.='V' L]			
Cond.	No. of moles			Cond.	No. of moles		
	$2HI(g) \rightarrow H_2(g) + I_2(g)$				$NH_3(g) \longrightarrow N_2 + 3H_2(g)$		
t = 0	1	0	0	t = 0	1	0	0
EQM	(1-x)	x/2	x/2	EQM	(1-x)	x/2	x/2
	X= Degree of Dissociation				X= Degree of Dissociation		
CONC.	$\dfrac{(1-x)}{V}$	$\dfrac{x}{2V}$	$\dfrac{x}{2V}$	CONC.	$\dfrac{(a-x)}{V}$	$\dfrac{(b-x)}{V}$	$\dfrac{2x}{V}$
$K_c = \dfrac{x^2}{4(1-x)^2}$				$K_c = \dfrac{\dfrac{x}{2V}\left(\dfrac{3x}{2V}\right)^3}{\left(\dfrac{1-x}{V}\right)^2} = \dfrac{27x^4}{16V^2(1-x)^2}$			
Eqm. Pressure = P Total moles = (1- x) + x/2 + x/2=1				Eqm. Pressure =P Total moles = (1- x) + x/2 + 3x/2v			
$K_P = \dfrac{n_{H_2} \times \left(n_{I_2}\right)^3}{(n_{HI})^2} \times \left[\dfrac{P}{\Sigma n}\right]^{-2} = \dfrac{x^2}{4(1-x)^2}$				$K_P = \dfrac{n_{N_2} \times \left(n_{H_2}\right)^3}{(n_{NH_3})^2} \times \left[\dfrac{P}{\Sigma n}\right]^{-2} = \dfrac{\dfrac{x}{2} \times \left(\dfrac{3x}{2}\right)^3}{(1-x)^2} \times \left[\dfrac{P}{(1+x)}\right]^2$ $K_P = \dfrac{27 \times P^2}{16(1-x^2)^2}$			

(ii) Solution phase equilibria: Here, the reactants and products are in the solution/aqueous phase, represented as follows,

$$CH_3COOH\ (l)\ +\ C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l)\ +\ H_2O$$
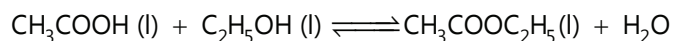
In such cases, only K_c exists.

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

9.2 Heterogeneous Equilibria

More than one phase existence is seen for the reactants and the products.

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

$$K_p = P'_{CO_2} = n_{CO_2} \times \left(\dfrac{P}{\Sigma n}\right)^1$$

$$3Fe(s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$
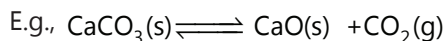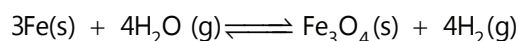
The constants in the multiple phases

(a) Pure solids and pure liquids do not undergo any change in their concentration, along with the progress of the reaction.

(b) Thus, in heterogeneous equilibria, their concentration is considered as unity.

9.3 Simultaneous Equilibria

When all the products that are not inert but present in the reacting mixture cannot be expressed in terms of one equilibrium reaction, we must consider simultaneous equilibrium reactions are occurring. In such cases, thermodynamic conditions remains same for all the equilibrium system.

Illustration 12: There occurs following equilibria in one container. If 100 mole/litre of but-1-yne is taken in flask, calculate the value of K_{c_1}, K_{c_2} and K_{c_3}.

$CH_3 . CH_2 . C \equiv CH(g) \rightleftarrows CH_3C \equiv C . CH_3(g)$; K_{c_1}

$CH_3 . CH_2 . C \equiv CH(g) \Longrightarrow CH_2 = CH - CH = CH_2(g)$; K_{c_2}

$CH_3 . C \equiv C . CH_3(g) \Longrightarrow CH_2 = CH - CH = CH_2(g)$; K_{c_3} **(JEE MAIN)**

Sol: Using the concentration of 100 mole/litre and the K_c expression, substitute the values.

The overall reaction may be written as

$$CH_3 \cdot CH_2C \equiv CH \quad \rightleftharpoons \quad CH_3 \cdot C \equiv C \cdot CH_3$$
$$CH_2 = CH - CH = CH_2$$
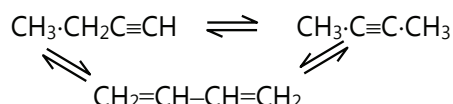
Let x mol/litre of 1,3-butadiene and y mole/litre of but-2-yne are formed then

$[CH_3CH_2 . C \equiv CH] = 100 - x - y$

$[CH_3 . C \equiv CH_3] = y$

$[CH_2 = CH - CH = CH_2] = x$

$$\therefore K_{c_1} = \frac{y}{100 - x - y}$$
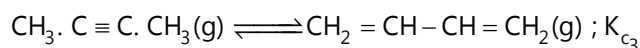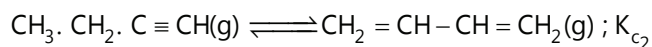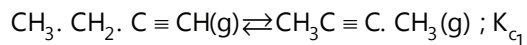
Illustration 13: The equilibrium concentration of A, B and C for the reaction are $A \Longrightarrow B + C$ 4.2, 2.1 and 2.1 moles/L respectively at 25°C. If 2 moles per-litre of A are removed, calculate the equilibrium concentration of A, B and C at the same temperature.   **(JEE MAIN)**

Sol: Using the expression of K and the given number of moles, calculate the case after deduction of the concentrations.

For equilibrium : $A \Longrightarrow B + C$
Concentration at equilibrium   4.2   2.1   2.1
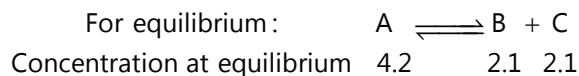
$$K = \frac{2.1 \times 2.1}{4.2} = 1.05$$

Now suppose the initial concentration is 'a' moles/L and 'x' moles/L of A changed to the products at equilibrium

conc. of A at eqb. = (a – x) = 4.2

and conc. of B or C at eqb = x = 2.1

∴ Initial conc. of A = a = (a – x) + x = 4.2 + 2.1 = 6.3 moles/L

Since 2 moles per litre of A are removed, the initial concentration of A will be (6.3 – 2) i. e., 4.3 moles per litre.

Suppose x' moles/L of a will change to the product when the new equilibrium is attained.

Initial concentration

$$A \rightleftharpoons B + C$$
$$(4.3 - x') \qquad x' \quad x' \text{ Concentration at equilibrium}$$

$$\therefore K = \frac{x' \cdot x'}{4.3 - x'} = 1.05 \text{ (K remains the same as the temperature is not change)}$$

On solving, we get x' = 1.48

∴ At equilibrium,

[A] = 4.3 − 1.48 = 2.81 moles/litre

[B] = 1.48 moles/litre,

[C] = 1.48 moles/litre.

Illustration 14: A flask containing 0.50 atm of ammonia contains some solid NH_4HS which undergoes dissociation according to $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$. Calculate the pressure of NH_3 and H_2S at equilibrium (K_p = 0. 11).

Also, calculate the total pressure. **(JEE ADVANCED)**

Sol: Apply law of mass action and using the partial pressure equation, calculate the total pressure. Since 1 mole of solid NH_4HS, on dissociation, produces 1 mole of NH_3 and 1 mole of H_2S, the partial pressure of NH_3 should be equal to that of H_2S if the flask contains no other substances. Let this be X atm.

But as the flask contains 0. 50 atm of NH_3 besides solid NH_4HS, the partial pressure of NH_3 will be (0.50 + X) atm.

Now, for the equilibrium, $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$K_p = p_{NH_3} \times p_{H_2S}$ As NH_4HS is solid, it includes the constant active mass of NH_4HS

0.11 = (0.5 + X) × X

X = 0.17

$\therefore p_{NH_3} = 0.50 + 0.17 = 0.67$ atm

$p_{H_2S} = 0.17$ atm

Total pressure = $p_{NH_3} + p_{H_2S} = 0.84$ atm.

10. LE CHATELIER'S PRINCIPLE

Temperature	Le-Chatelier's Principle	Concentration

Temperature

1. T increase
   -Endothermic $reac^n$ is favoured

2. - T decrease Exothermic $reac^n$ is favoured

Le-Chatelier's Principle

"On disturbing a system at equilibrium by changing the conditions, the position of equilibrium move to regain the balance."

Concentration

1. $R + x \rightarrow P$
   -Rate of forward $reac^n$ increase
   -More P is formed.

2. $R \rightarrow P + x$
   -Rate of backward $reac^n$ increase
   -More R is formed.

**Catalyst
"No difference"**

1. +ve catalyst
   -increase rate of both forward & reverse $reac^n$ s.

2. -ve catalyst

   T increase rate of both forward & reverse $reac^n$ s.

**(Applicable to gaseous $reac^{ns}$)
Pressure**

1. P increase
   -Space/Vol. decrease
   -Side with fewer moles is favoured.

2. P decrease
   -Space/Vol. increase
   -Side with more moles is favoured.

Flowchart 5.1: Le-Chatelier's principle

MASTERJEE CONCEPTS

- Equilibrium tends to oppose a change. (Misconception: The rate of the favoured reaction increases but the rate of the other reaction decreases.)

- Le Chatelier's Rule.

   (Misconception: Students sometimes have a hard time getting the idea that Le Chatelier's Rule is about perturbing an equilibrium state, driving the system to a new equilibrium state.)

- It doesn't matter how much of a solid is present when it is at equilibrium with a surrounding solution. The concentrations of the aqueous species will still end up being the same. (Misconception: Students usually think that if you add more solid, the equilibrium concentrations of the aqueous species will go up. This is a misapplication of Le Chatelier's Rule.)

Effect of adding an inert gas

An inert gas (or noble gas) such as helium is one that does not react with other elements or compounds. At constant volume, addition of this inert gas does not affect the equilibrium.

According to Dalton's law, the partial pressures of the other gases remains same, which itself is the reason for the unchanged equilibrium.

But on increasing the volume, the partial pressures of all gases would decrease, resulting in a shift towards the side with the greater number of moles of gas.

MASTERJEE CONCEPTS

Table 5.4: Summary of Le chateliers Rule

Conditions	Forward Direction	No Effect	Backward Direction
$\Delta v = 0$ v = constant	×	✓ $\Delta v = 0$ = + = -	×
$\Delta v \neq 0$ v ≠ constant	×	✓ $\Delta v = 0$	×
Δn = (no. of gaseous moles of product)	✓ $\Delta v = 0$	×	×
— (no. of gaseous moles of reat.)	×	×	$\Delta v < 0$

where, Δn = number of gaseous moles of product – number of gaseous moles of reactant

Table 5.5: Effect of temperature and pressure

Nature of Reaction	Effect of ↑ T	Δn	Side with fewer mole	Effect of ↑ P
Exothermic	Backward Shift	0	Neither	No Shift
		−ve	Right	Forward
		+ve	Left	Backward
		−ve	Right	Forward
Endothermic	Forward Shift	−ve	Right	Forward
		+ve	Left	Forward
		0	Neither	No Shift

Systems will tend to attain a state of lower potential energy i.e. enthalpy if nothing else is acting upon them. A chemical reaction will always favour the side (reactants or products) with minimum enthalpy if no other factors are considered.

Saurabh Gupta (JEE 2010, AIR 443)

10.1 Applications of Le Chatelier's Principle to Physical Equilibrium

(a) **Effect of Pressure on Boiling Point:** Water $\rightleftharpoons$ vapour; An increases in pressure will favour backward reaction, i.e., the reaction in which volume decreases ($V_{vapour} > V_w$). Thus more water will exist at equilibrium, i.e., boiling point of water (solvent) increases with increases in pressure.

(b) **Effect of Pressure on Melting Points**

   (i) For, Ice $\rightleftharpoons$ water equilibrium: An increase in pressure will favour forward reaction because V_{ice} is greater then V_{water}. Thus, more and more ice will melt or the m. pt. of ice is lowered with increases in pressure.

(ii) For, solid $\rightleftharpoons$ liquid equilibrium: An increases in pressure will favour backward reaction because $V_{(l)} > V_{(s)}$ and thus, more solid will exist at equilibrium, i.e., m. pt. of solid increases with increases in pressure.

(c) Effect of Pressure on Solubility of Gases: Gas + Solvent $\rightleftharpoons$ Solution (and $V_f > V_b$) where, V_f is volume of left hand side components and V_b is volume of right hand side components.

An increase in pressure will favour forward reaction and thus, solubility of gas increases with increase in pressure. Dissolution of water soluble gas in water is always exothermic ($\Delta H = -$ ve) and spontaneous ($\Delta G = -$ve). It is thus evident form $\Delta G = \Delta H - T\Delta S$, that ΔS will be $-$ ve or entropy decreases on dissolution or if $\Delta S = +$ ve then $T\Delta S < \Delta H$.

(d) Effect of Temperature on Solubility of Solids

(i) Solute + Solvent $\rightleftharpoons$ Solution ; $\Delta H = $ -ve

An increases in temperature always favours endothermic process and thus, solute having endothermic dissolution (e.g., urea, glucose) show an increases in their solubility with temperature, e.g., urea, glucose.

(ii) Solute + Solvent $\rightleftharpoons$ Solution ; $\Delta H = +$ ve

Accordingly, solute having exothermic dissolution (e.g., lime, acids) show a decrease in their solubility with temperature.

MASTERJEE CONCEPTS

- The critical temperature and critical pressure for liquid H_2O, i. e., water is 647.15 K and 218 atm respectively.   Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Vapour

  These three phases exist in equilibrium at a point called as triple point of water seen at 0.0098° C and 4.58 mm pressure.

- A solid-solid heterogeneous system cannot be studied using Le Chatelier's principle.

- Heat absorption takes place when hydrated salts like $CuSO_4$. $5H_2O$, CH_2O. $6H_2O$ are dissolved in water i.e. , $\Delta H_{sol} = +$ ve.

- An exceptional case of NaOH whose solubility increases with temperature but expels out heat.

Neeraj Toshniwal (JEE 2009, AIR)

11. CALCULATION OF DEGREE OF DISSOCIATION

Definition: Defined as the fraction of one molecule dissociated.

Expressed as: x or α having a value always less than 1. Complete dissociation is achieved when the value becomes 1.

General Reversible Reaction

	A $\rightleftharpoons$	nB
Initial moles	1	0
Equilibrium moles	(1 −x)	nx
Conc.	$\dfrac{1-x}{v}$	$\dfrac{nx}{v}$

Total no. of moles = 1 − x + nx

= 1 + x(n -1)

$D\alpha\dfrac{1}{v}$

$d\alpha\dfrac{1}{[1+(n-1)x]v}$

D = vapour density when no dissociation occurs

d = vapour density when

x = degree of dissociation

Dividing the above equations,

$\dfrac{D}{d}=1+(n-1)x$ or $\dfrac{D}{d}-1=(n-1)x$ or $\dfrac{D-d}{d}=(n-1)x$ or $x=\dfrac{D-d}{(n-1)d}$ 　　　　(iii)

$x=\dfrac{M-m}{(n-1)m}$ where,　　M = initial molecular mass and　　　　m = molecular mass at equilibrium

Calculation of Degree of Reaction Using Pressure-Temperature Determination

Consider the following gaseous reaction:

P_1 = Initial pressure　　　　At equilibrium,

T_1 = Initial temperature　　　Pressure = P_2

Volume of vessel = 'V'　　　　Temperature = T_2

$$PCl_5 \rightleftharpoons PCl_3 \quad Cl_2$$

(g)　　　　(g)　　　　(g)
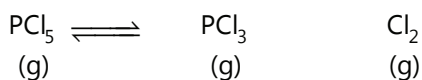
t=0　　　　a　　　　0　　　　0

t=eq.　　　a-ax　　　ax　　　ax

Initial P_1V= aRt_1 state　　　　　equilibrium

State $P_2V = (a + ax)\ RT_2$

Dividing the above equations, we get

$\dfrac{P_1}{P_2}=\dfrac{T_1}{(1+x)T_2}$

$(1+x)=\dfrac{P_2T_1}{P_1T_2}\Rightarrow x=\dfrac{P_2T_1-P_1T_2}{P_1T_2}$

Illustration 15: $2N_2O(g) +O_2(g)\rightleftharpoons 4NO\ (g)$; $\Delta H > 0$.

What will be the effect on equilibrium when　　　　　　　　　　　　　　　　　　　**(JEE ADVANCED)**

(A) Volume of the vessel increases?　　　(B) Temperature decreases?　　　　　　　**[AIPMT 2008]**
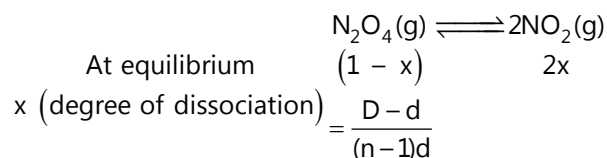
Sol: Apply Le-Chatelier's principle.

(A) For the given reaction, $K = \dfrac{[NO]^4}{[N_2O]^2[O_2]}$

- When volume of the vessel increases, number of moles per unit volume (i. e. molar concentration) of each reactant and product decreases. As there are 4 concentration terms in the numerator but 3 concentration terms in the denominator, to keep K constant, the decrease in [N2O] and [O2] should be more i. e. , equilibrium will shift in the forward direction.

- Alternatively, increases in volume of the vessel means decreases in pressure. As forward reaction is accompanied by increases in the number of moles (i. e., increase of pressure) decreases in pressure will favour forward reaction (according to Le Chatelier's principle.).

(B) As ΔH is + ve, i. e., reaction is endothermic, decrease of temperature will favour direction in which heat is absorbed, i. e., backward direction.

Illustration 16: The vapour density (hydrogen = 1) of a mixture containing NO_2 and N_2O_4 is 35.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 grams of the mixture. **(JEE ADVANCED) [MLNR 1993]**

Sol: Use vapour density to calculate molar mass and then calculate the individual concentration of the species.

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

At equilibrium $(1-x)$ $2x$

$x \text{ (degree of dissociation)} = \dfrac{D-d}{(n-1)d}$

Given, d = 35.3, D = $\dfrac{\text{Mol. mass of } N_2O_4}{2} = \dfrac{92}{2} = 46, n = 2$; So $x = \dfrac{46-35.3}{35.3} = 0.303$

At equilibrium, amount of N_2O_4 = 1 − 0.308 = 0.70 mol and amount of NO_2 = 2 × 0.308 = 0.606 mol

Mass of mixture = 0.7 × 92 + 0.606 × 46 = 64.4 × 27.9 = 92.3 g

Since, 92.3 gram of the mixture contains = 0.606 mol NO_2

So, 100 gram of the mixture contains = $\dfrac{0.606 \times 100}{92.3} \approx 0.65$ mole NO_2

Illustration 17: 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. **(JEE MAIN)**

(A) Calculate K_c and K_p for the reaction at 27°C.

(B) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

Sol: Use the stepwise calculation of the concentration of the reacting species following the decomposition and apply Le-Chatelier's principle.

$$NH_4HS(s) \rightleftharpoons NH_3(s) + H_2S(g)$$
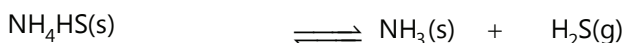
(A) Initial amt 3.06g = 3.06 / 51mole = 0.06mole

At eqm $0.06 - \frac{30}{100} \times 0.06$ 0.018 mole   0.018 mole

= 0.06 − 0.018

= 0.042mole

$$NH_4HS(s) \rightleftharpoons NH_3(s) + H_2S(g)$$

Eqm. conc.   1   0.018 / 2   0.018 / 2

(being solid)   = 0.009   = 0.009 mol L^{-1}

$K_c = \dfrac{[NH_3][H_2S]}{[NH_4HS]} = \dfrac{0.009 \times 0.009}{1} = 8.1 \times 10^{-5} \left(\left[NH_4HS(s) \right] = 1 \right)$

$K_p = K_c(RT)^{\Delta n_g} = 8.1 \times 10^{-5} \times (0.082 \times 500)^2 = 40.5$ $(\Delta n_g = 2 - 0 = 2)$

(B) 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.

Illustration 18: Ammonium carbamate when heated to 200°C gives a mixture of NH_3 and CO_2 vapours with a density of 15.0. What is the degree of dissociation of ammonium carbonate?

(a) 3/2   (b) 1/2   (c) 2   (d) 1   (e) 5/2   **(JEE MAIN)**

Sol: Write down the decomposition of ammonium carbamate, noting down the dissociated values of the reacting species. Using the vapour density, calculate degree of dissociation.

$$NH_2COONH_4 \longrightarrow 2NH_3 + CO_2$$
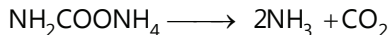
Initial 1 mole, After disso. $1 - \alpha$ 2α α

Total $= 1 + 2\alpha$

Theoretical density (D) $\propto \dfrac{1}{v}$; Observed density (d) $\propto \dfrac{1}{(1+2\alpha)V}$ $\therefore \dfrac{D}{d} = 1 + 2\alpha$ or $\alpha = \dfrac{1}{2}\left(\dfrac{D-d}{d}\right) = \dfrac{1}{2}\left(\dfrac{48-15.0}{15.0}\right) = 1.1$

PROBLEM-SOLVING TACTICS

(a) The equilibrium constant expression depends on the stoichiometry of the balanced reaction.

Table 5.6: Variation of Equilibrium Constant with Stoichiometric Coefficient

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	$K = K_1 \times K_2$

Case I: If $\Delta n(g) = 0$, $K_p = K_c$

Case II: If $\Delta n(g) = +ve$, $K_p > K_c$

Case III: If $\Delta n(g) = -ve$, $K_p < K_c$

Retain in Memory

For Δn, count only the gaseous species.

Δn may be positive, negative, zero, integer or a fraction. If $\Delta n = 0$, $K_p = K_c$.

Units of K_p and K_c

Unit of K_p = (unit of pressure)$^{\Delta n}$

Unit of K_c = (unit of concentration)$^{\Delta n}$

If $\Delta n = 0$; K_p or K_c have no units.

(b) If 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). If pressure is expressed in bars, R = 0.0831 litre bar K^{-1} mol^{-1}. (1 bar = 10^5 Pa = 10^5 Nm^{-2} = 0.987 atm). If the given value of K_p or K_c is dimensionless, use R = 0.0831 L bar K^{-1} mol^{-1}.

(c) Effect of temperature on equilibrium constant:

Case I: If $\Delta H = 0$, i.e. neither heat is evolved nor

absorbed, then $2.303\log_{10}\left(\dfrac{K_2}{K_1}\right) = 0$ or $\dfrac{K_2}{K_1} = 1$ or $K_2 = K_1$

i.e. equilibrium constant remains same at different temperature.

Case II: If ΔH = +ve, i.e., heat is absorbed during the course of reaction, then

$$2.303 \log \left(\frac{K_2}{K_1} \right) = +ve \quad or \quad \log K_2 > \log K_1 \ or \ K_2 > K_1$$

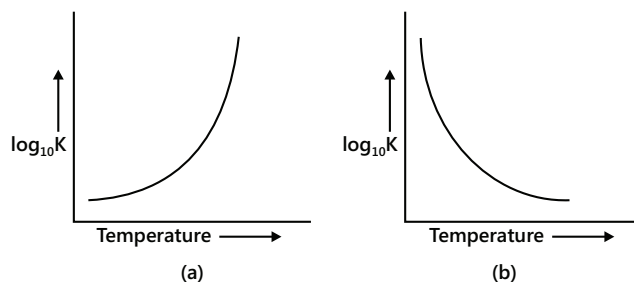i. e. , equilibrium constant increases with increase in temperature.

Case III: If ΔH = − ve, i.e.heat is evolved during the course of reaction, then

$$2.303 \log \left(\frac{K_2}{K_1} \right) = -ve \quad or \quad \log K_2 < \log K_1 \ or \ K_2 < K_1$$

i.e., equilibrium constant decreases with increase in temperature.

Figure 5.14: Plots of log K versus T
(a) Endothermic reaction (b) Exothermic reaction

POINTS TO REMEMBER

Effect of adding an inert gas:

• An inert gas (or noble gas) such as helium is one that does not react with other elements or compounds. At constant volume, addition of this inert gas does not affect the equilibrium.

• According to Dalton's law, the partial pressures of the other gases remains same, which itself is the reason for the unchanged equilibrium.

• But on increasing the volume, the partial pressures of all gases would decrease, resulting in a shift towards the side with the greater number of moles of gas.

Factors affecting the state of Equilibrium

Conditions	Shifts the Equilibrium
Increase in concentration of reactants	Forward direction
Increase in concentration of any product	Backward direction
Increase in temperature	In direction of endothermic reaction
Decrease in temperature	Direction of exothermic reaction
Increase in pressure	In direction of less number of gaseous moles
Decrease in pressure	In direction of large number of moles

Effect of temperature and Pressure :

Nature of Reaction	Effect of increase in T	Δn	Side with fewer mole	Side with fewer mole	Effect of increase on P
Exothermic concentration of reactants	Backward shift	0	Neither	neither	No shift
		-ve	Right	Forward	Forward
		+ve	Left	Backward	Backward
		-ve	Right	Forward	Forward
Endothermic concentration of any product	Forward shift	-ve	Right	Right	Forward
		+ve	Left	Forward	Forward
		0	Neither	No Shift	No shift