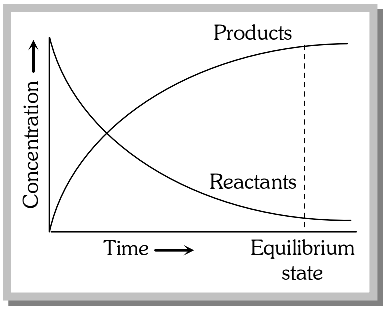
Chemical Equilibrium

Whenever we hear the word Equilibrium immediately a picture arises in our mind an object under the influence of two opposing forces. For chemical reactions also this is true. A reaction also can exist in a state of equilibrium balancing forward and backward reactions.

Equilibrium and its dynamic nature.



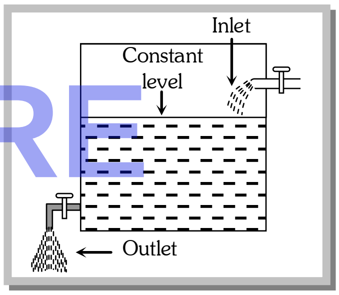
(1) **Definition** : *"**Equilibrium** is the state at which the concentration of reactants and products do not change with time. i.e. concentrations of reactants and products become constant."*

(2) **Characteristics** : Following are the important characteristics of equilibrium state,

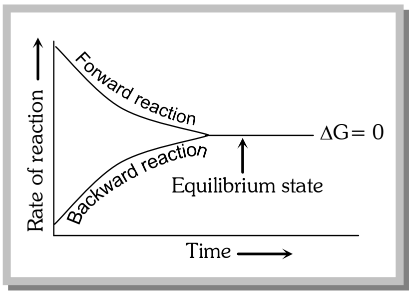
(i) Equilibrium state can be recognised by the constancy of certain measurable properties such as ***pressure, density, colour, concentration*** etc. by changing these conditions of the system, we can control the extent to which a reaction proceeds.

(ii) Equilibrium state can only be achieved in ***close vessel***, but if the process is carried out in an open vessel equilibrium state cannot be attained because in an open vessel, the reverse process will not take place.

(iii) Equilibrium state is ***reversible*** in nature.



(iv) Equilibrium state is also ***dynamic*** in nature. Dynamic means *moving* and at a microscopic level, the system is in motion. The dynamic state of equilibrium can be compared to water tank having an inlet and outlet. Water in tank can remain at the same level if the rate of flow of water from inlet (compared to rate of forward reaction) is made equal to the rate of flow of water from outlet (compared to rate of backward reaction). Thus, the water level in the tank remains constant, though both the inlet and outlet of water are working all the time.



(v) At equilibrium state,

Rate of forward reaction = Rate of backward reaction

(vi) At equilibrium state, $\Delta G = 0$, so that $\Delta H = T\Delta S$.

(3) **Types** : Equilibrium in a system implies the existence of the following types of equilibria simultaneously,

(i) ***Thermal equilibrium*** : There is no flow of heat from one part to another *i.e. T = constant.*

(ii) ***Mechanical equilibrium*** : There is no flow of matter from one part to another *i.e. P = constant.*

(iii) ***Physical equilibrium*** : There is the substance exist in three states: solid, liquid and gaseous.

(iv) ***Chemical equilibrium*** : There is no change in composition of any part of the system with time.

Physical equilibrium.

The physical equilibrium is a state of equilibrium between the same chemical species in different phases (solid, liquid and gaseous). The various equilibria which can exist in any physical system are,

Solid	$\rightleftharpoons$	***Liquid***
Liquid	$\rightleftharpoons$	**Vapour**
Solid	$\rightleftharpoons$	**Gas(vapour)**
Solid	$\rightleftharpoons$	**Saturated solution of solid in a liquid**
Gas(vapour)	$\rightleftharpoons$	**Saturated solution of gas in a liquid**

(1) **Solid-liquid equilibrium**

Rate of transfer of molecules from ice to water = Rate of transfer of molecules from water to ice

Rate of melting of ice = Rate of freezing of water

Free energy change and solid-liquid equilibrium in water : *For ice-water system free energy change* (ΔG), at 273 K, and one atmosphere pressure is zero *i.e.*, $\Delta G = 0$; Ice $\rightleftharpoons$ Water; $H_2O(s) \rightleftharpoons H_2O(l)$

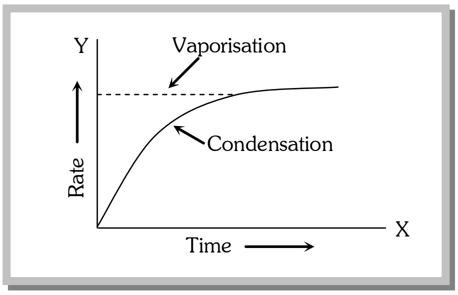
(i) At temperature higher than 273 K, and 1 *atm* pressure, $\Delta G < 0$. Thus, the process in the forward direction would become favourable and ice will melt to give more water.

(ii) At temperature less than 273 K, and 1 *atm* pressure, $\Delta G > 0$. Thus, the reverse reaction will become favourable, and more ice will be formed from liquid water.

(2) **Liquid-vapour equilibrium :** A liquid placed in an open container disappears completely. After some time vapours of the liquid held in an open container can escape out to the atmosphere. Thus, when vapour of liquid exists in equilibrium with the liquid, then

Rate of vaporisation = Rate of condensation,

$$H_2O(l) \rightleftharpoons H_2O(v)$$



Conditions necessary for a liquid-vapour equilibrium

(i) The system must be a closed system *i.e.*, the amount of matter in the system must remain constant.

(ii) The system must be at a constant temperature.

(iii) The visible properties of the system should not change with time.

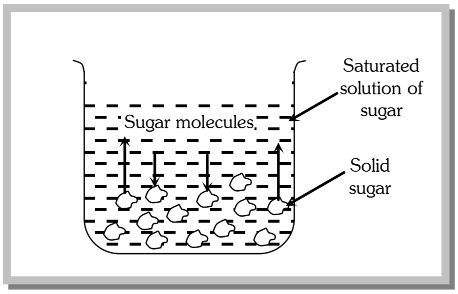
(3) **Solid-vapour equilibrium :** Certain solid substances on heating get converted directly into vapour without passing through the liquid phase. This process is called ***sublimation.*** The vapour when cooled, gives back the solid, it is called ***disposition***.

$$\text{Solid} \rightleftharpoons \text{Vapour}$$

The substances which undergo sublimation are camphor, iodine, ammonium chloride etc.

For *exampie*, Ammonium chloride when heated $\underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}}$ sublimes.

$$NH_4Cl(s) \qquad NH_4Cl(v)$$



(4) **Equilibrium between a solid and its solution :** When a saturated solution is in contact with the solid solute, there exists a dynamic equilibrium between the solid and the solution phase.

Solid substance ⇌ Solution of the substance

Example : Sugar and sugar solution. In a saturated solution, a dynamic equilibrium is established between dissolved sugar and solid sugar.

Sugar (*s*) ⇌ Sugar (aq)

At the equilibrium state, the number of sugar molecules going into the solution from the solid sugar is equal to the number of molecules precipitating out from the solution, *i.e.*, at equilibrium,

Rate of dissolution of solid sugar = Rate of precipitation of sugar from the solution.

(5) **Equilibrium between a gas and its solution in a liquid :** Gases dissolve in liquids. The solubility of a gas in any liquid depends upon the,

(i) Nature of the gas and liquid.

(ii) Temperature of the liquid.

(iii) Pressure of the gas over the surface of the solution.

Henry's law : "*At a certain temperature, the mass of a gas which dissolves in a definite volume of a liquid is proportional to the pressure of the gas in equilibrium with the solution*."

$m \propto P$ or $m = KP$; (where K is the proportionality constant)

Thus, at a constant temperature, the ratio of the molar concentration of the gas in the solution and into the atmosphere is constant.

Limitations of Henry's law

- Henry's law is applicable to ideal gases only. Henry's law should be applied only at low pressures because real gases behave like ideal gases at low pressures.
- Henry's law is not applicable to gases which react chemically with the solvent.
- Henry's law will not apply to the solution of gases like ammonia (NH_3) and hydrogen chloride (HCl) in water because these gases react chemically with water.

Note : ✹ *A chilled soda water bottle fizzes out when opened because, soda water is a solution of carbon dioxide gas, $CO_2(g)$ in water at high pressure. As soon as the bottle is opened under normal atmospheric conditions, the dissolved gas escapes out to reach a new equilibrium state, so that the pressure of the gas inside the bottle becomes equal to the atmospheric pressure. At low pressure, the solubility of the gas in water decreases.*

Chemical equilibrium.

The equilibrium between different chemical species present in the same or different phases is called ***chemical equilibrium***. There are two types of chemical equilibrium.

(1) **Homogeneous equilibrium :** The equilibrium reactions in which all the reactants and the products are in the same phase are called *homogeneous equilibrium reactions.*

Example : (i) $\underbrace{C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)}_{\text{liquid phase}}$

(ii) $\underbrace{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}_{\text{gas phase}}$

(iii) $\underbrace{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}_{\text{gas phase}}$

(2) **Heterogeneous equilibrium :** The equilibrium reactions in which the reactants and the products are present in different phases are called *heterogeneous equilibrium reactions.*

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

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

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

(iv) $Ca(OH)_2(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$

Note : ✹ *The equilibrium expression for heterogeneous reactions does not include the concentrations of pure solids because their concentrations remain constant.*

Reversible and irreversible reactions.

A chemical reaction is said to have taken place when the concentration of reactants decreases, and the concentration of the products increases with time. The chemical reactions are classified on the basis of the extent to which they proceed, into the following two classes;

(1) Reversible reactions : Reactions in which only a part of the total amount of reactants is converted into products are termed as *reversible reactions*.

(i) ***Characteristics of reversible reactions***

(a) *These reactions can be started from either side,*

(b) *These reactions are never complete,*

(c) These reactions have a tendency to attain a state of equilibrium,

(d) This sign ($\rightleftharpoons$) represents the reversibility of the reaction,

(e) Free energy change in a reversible reaction is zero ($\Delta G = 0$),

(ii) ***Examples of reversible reactions***

(a) *Neutralisation between an acid and a base either of which or both are weak e.g.,*

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

(b) *Salt hydrolysis, e.g.,* $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 6HCl$

(c) *Thermal decomposition, e.g.,* $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} - Q$

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \; ; \; 2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2\,(g)}$$

(d) *Esterification, e.g.,* $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

(e) *Evaporation of water in a closed vessel, e.g.,* $H_2O_{(l)} \rightleftharpoons H_2O_{(g)} - Q$

(f) *Other reactions, e.g.,* $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + Q$; $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} + Q$

(2) Irreversible reactions : Reactions in which the entire amounts of the reactants are converted into products are termed as *irreversible reactions*.

(i) ***Characteristics of irreversible reactions***

(a) These reactions proceed only in one direction (forward direction),

(b) These reactions can proceed to completion,

(c) The arrow ($\rightarrow$) is placed between reactants and products,

(d) In an irreversible reaction, $\Delta G < 0$,

(ii) ***Examples of irreversible reactions***

(a) *Neutralisation between strong acid and strong base e.g.* $NaOH + HCl \rightarrow NaCl + H_2O + 13.7\ kcal$

(b) *Double decomposition reactions or precipitation reactions e.g.*

$BaCl_{2(aq)} + H_2SO_{4(aq)} \rightarrow BaSO_{4(s)} \downarrow + 2HCl_{(aq)}$; $AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(g)} \downarrow + NaNO_{3(aq)}$

(c) *Thermal decomposition, e.g.* $2KClO_{3(s)} \xrightarrow{MnO_2, \Delta} 2KCl_{(s)} + 3O_2 \uparrow$

$2Pb(NO_3)_2 \xrightarrow{\text{heat}} 2PbO + 4NO_2 + O_2 \uparrow$; $NH_4NO_2 \xrightarrow{heat} N_2 \uparrow + 2H_2O \uparrow$

(d) *Redox reactions, e.g.,* $SnCl_{2(aq)} + 2FeCl_{3(aq)} \rightarrow SnCl_{4(aq)} + 2FeCl_{2(aq)}$

(e) *Other reactions, e.g.,* $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow$

Law of mass action.

On the basis of observations of many equilibrium reactions, two Norwegian chemists ***Guldberg*** and ***Waage*** suggested (1864) a quantitative relationship between the rates of reactions and the concentration of the reacting substances. This relationship is known as ***law of mass action***. It states that

"*The rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants at a constant temperature at any given time.*"

The molar concentration *i.e. number of moles per litre* is also called ***active mass***. It is expressed by enclosing the symbols of formulae of the substance in square brackets. For example, molar concentration of A is expressed as $[A]$.

Let us consider a simple reaction between the species A and B : $A + B \rightarrow$ Products

According to law of mass action, rate of reaction, $r \propto [A]\,[B] = k\,[A]\,[B]$

Where $[A]$ and $[B]$ are the molar concentrations of the reactants A and B respectively, k is a constant of proportionality for the forward reaction and is known as *rate constant*. The rate constant is also called *velocity constant*. Now, if the concentration of each of the reactants involved in the reaction is unity, *i.e.*, $[A] = [B] = 1$, then, rate of reaction, $r = k \times 1 \times 1$ or $r = k$

Thus, the rate constant of a reaction at a given temperature may be defined as "*the rate of the reaction when the concentration of each of the reactants is unity.*"

For a general reaction, $aA + bB + cC \rightarrow$ Products

The law of mass action may be written as : Rate of reaction, $r = k[A]^a[B]^b[C]^c$

Thus, the law of mass action may be restated as, "*The rate of a chemical reaction at any particular temperature is proportional to the product of the molar concentrations of reactants with each concentration term raised to the power equal to the number of molecules of the respective reactants taking part in the reaction.*"

The number of molecules of a reactant taking part in a reaction is also called its ***stoichiometric coefficient***. For example, a, b and c…. in the above equation are called stoichiometric coefficients of A, B and C…. respectively.

Equilibrium constant.

(1) Equilibrium constant in terms of law of mass action : The law of mass action may be applied to a reversible reaction to derive a mathematical expression for equilibrium constant known as ***law of chemical equilibrium***.

Let us consider a simple reversible reaction, $A + B \rightleftharpoons X + Y$ in which an equilibrium exists between the reactants (A and B) and the products (X and Y). The forward reaction is,

$$A + B \rightarrow X + Y$$

According to law of mass action,

$$Rate\ of\ forward\ reaction \propto [A][B] = k_f[A][B]$$

Where k_f is the rate constant for the forward reaction and $[A]$ and $[B]$ are molar concentrations of reactants A and B respectively.

Similarly, the backward reaction is ; $X + Y \rightarrow A + B$

$$Rate\ of\ backward\ reaction \propto [X][Y] = k_b[X][Y]$$

Where k_b is the rate constant for the backward reaction and $[X]$ and $[Y]$ are molar concentrations of products X and Y respectively.

At equilibrium, the rates of two opposing reactions become equal. Therefore, at equilibrium,

$$Rate\ of\ forward\ reaction = Rate\ of\ backward\ reaction$$

$$k_f[A][B] = k_b[X][Y]$$

$$\boxed{\frac{k_f}{k_b} = \frac{[X][Y]}{[A][B]} \quad \text{or} \quad K = \frac{[X][Y]}{[A][B]}}$$

The combined constant K, which is equal to k_f / k_b is called ***equilibrium constant*** and has a constant value for a reaction at a given temperature. The above equation is known as ***law of chemical equilibrium***.

For a general reaction of the type : $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant may be represented as : $K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

where the exponents a, b, c and d have the same values as those in the balanced chemical equation. Thus, ***the equilibrium constant*** may be defined as,

"The ratio between the products of molar concentrations of the products to that of the molar concentrations of the reactants with each concentration term raised to a power equal to its stoichiometric coefficient in the balanced chemical equation at a constant temperature."

(2) Characteristics of equilibrium constant

(i) *The value of equilibrium constant is independent of the original concentration of reactants.*

For example, the equilibrium constant for the reaction,

$$Fe^{3+}(aq) + SCN^-(aq) = FeSCN^{2+}(aq)\ ; \quad K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = 138.0\,L\,mol^{-1} \text{ (at 298 } K\text{)}$$

Whatever may be the initial concentrations of the reactants, Fe^{3+} and SCN^- ions, the value of K comes out to be 138.0 $L\ mol^{-1}$ at 298 K.

(ii) *The equilibrium constant has a definite value for every reaction at a particular temperature.* However, it varies with change in temperature.

For example, the equilibrium constant for the reaction between hydrogen and iodine to form hydrogen iodide is 48 at 717 *K*.

$$H_2(g)+I_2(g)=2HI(g); \quad K=\frac{[HI]^2}{[H_2][I_2]}=48$$

For this reaction, the value of *K* is fixed as long as the temperature remains constant.

(iii) *For a reversible reaction, the equilibrium constant for the forward reaction is inverse of the equilibrium constant for the backward reaction.*

For example, if equilibrium constant, *K*, for the reaction of combination between hydrogen and iodine at 717 *K* is 48

$$H_2(g)+I_2(g) \rightleftharpoons 2HI\ (g); \quad K'=\frac{[HI]^2}{[H_2][I_2]}=48$$

Then, the equilibrium constant for the decomposition of hydrogen iodide is the inverse of the above equilibrium constant.

$$2HI(g) \rightleftharpoons H_2(g)+I_2(g); \quad K=\frac{[H_2][I_2]}{[HI]^2}=\frac{1}{K'}=\frac{1}{48}=0.02$$

In general, $\boxed{K_{\text{forward reaction}}=\dfrac{1}{K'_{\text{backward reaction}}}}$

(iv) *The value of an equilibrium constant tells the extent to which a reaction proceeds in the forward or reverse direction*. If value of *K* is large, the reaction proceeds to a greater extent in the forward direction and if it is small, the reverse reaction proceeds to a large extent and the progress in the forward direction is small.

(v) *The equilibrium constant is independent of the presence of catalyst.* This is so because the catalyst affects the rates of forward and backward reactions equally.

(vi) *The value of equilibrium constant changes with the change of temperature*. Thermodynamically, it can be shown that if K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2. If ΔH is the heat of reaction at constant volume, then

$$\boxed{\log K_2-\log K_1=\frac{-\Delta H}{2.303\,R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]} \text{ (Van't Hoff equation)}$$

The effect of temperature can be studied in the following three cases

(a) When $\Delta H=0$ *i.e., neither heat is evolved nor absorbed*

$$\log K_2-\log K_1=0 \quad \text{or} \quad \log K_2=\log K_1 \ \text{or} \ K_2=K_1$$

Thus, equilibrium constant remains the same at all temperatures.

(b) When $\Delta H=+ve$ *i.e., heat is absorbed,* the reaction is ***endothermic***. The temperature T_2 is higher than T_1.

$$\log K_2-\log K_1=+ve \ \text{or} \ \log K_2>\log K_1 \ \text{or} \ K_2>K_1$$

The value of equilibrium constant is higher at higher temperature in case of endothermic reactions.

(c) When $\Delta H=-ve$, *i.e., heat is evolved,* the reaction is ***exothermic***. The temperature T_2 is higher than T_1.

$$\log K_2-\log K_1=-ve \ \text{or} \ \log K_1>\log K_2 \ \text{or} \ K_1>K_2$$

The value of equilibrium constant is lower at higher temperature in the case of exothermic reactions.

(vii) *The value of the equilibrium constant depends upon the stoichiometry of the chemical equation*.

Examples :

(a) If the equation (having equilibrium constant *K*) is divided by 2, then the equilibrium constant for the new equation is the square root of K *i.e.* $\sqrt{K}$. For example, the thermal dissociation of SO_3 can be represented in two ways as follows,

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \text{ and } SO_3(g) \rightleftharpoons SO_2(g) + 1/2O_2(g)$$

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2} \text{ and } K' = \frac{[SO_2][O_2]^{1/2}}{[SO_3]}; \quad \boxed{K' = \sqrt{K} \text{ or } (K)^{1/2}}$$

(b) Similarly, if a particular equation is multiplied by 2, the equilibrium constant for the new reaction (K') will be the square of the equilibrium constant (K) for the original reaction *i.e.*, $\boxed{K' = K^2}$

(c) If the chemical equation for a particular reaction is written in two steps having equilibrium constants K_1 and K_2, then the equilibrium constants are related as $\boxed{K = K_1 \times K_2}$

For example, the reaction $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ with equilibrium constant (K) can be written in two steps :

$$N_2(g) + O_2(g) \rightleftharpoons 2NO\ (g) \text{ ; (Equilibrium constant } = K_1\text{)}$$

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \text{ ; (Equilibrium constant } = K_2\text{)}$$

$$\text{Now, } K_1 = \frac{[NO]^2}{[N_2][O_2]} \text{ and } K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

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

(3) Types of equilibrium constant : Generally two types of equilibrium constants are used,

(i) K_c → It is used when the various species are generally expressed in terms of *moles/litre* or in terms of molar concentrations.

(ii) K_p → It is used when in gaseous reactions, the concentration of gases expressed in terms of their partial pressures.

K_p is not always equal to K_c. K_p and K_c are related by the following expression, $\boxed{K_p = K_c(RT)^{\Delta n}}$

where, R = Gas constant = $0.0831\ bar\ dm^3\ mol^{-1}\ k^{-1}$; T = Temperature in Kelvin

Δn = number of moles of gaseous products – number of moles of gaseous reactants in chemical equation

(4) Unit of equilibrium constant : Equilibrium constant K has no units *i.e.*, dimensionless if the total number of moles of the products is exactly equal to the total number of moles of reactants. On the other hand if the number of mioles of products and reactants are not equal, K has specific units.

Units of K_p and K_c and the value of Δn

Value of Δn	*Relation between K_p and K_c*	*Units of K_p*	*Units of K_c*
0	$K_p = K_c$	**No unit**	**No unit**
>0	$K_p > K_c$	$(atm)^{\Delta n}$	$(mole\ l^{-1})^{\Delta n}$
<0	$K_p < K_c$	$(atm)^{\Delta n}$	$(mole\ l^{-1})^{\Delta n}$

(5) Applications of equilibrium constant : Knowing the value of the equilibrium constant for a chemical reaction is important in many ways. For example, it judge the extent of the reaction and predict the direction of the reaction.

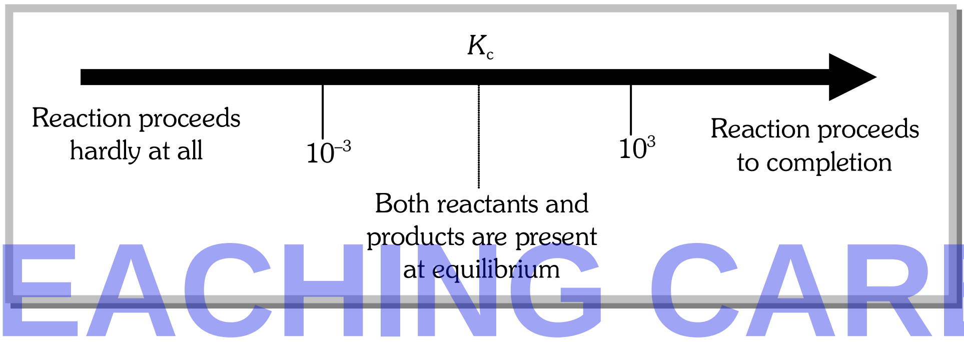
(i) ***Judging the extent of reaction***

We can make the following generalisations concerning the composition of equilibrium mixture.

(a) If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds almost all the way to completion.

(b) If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction proceeds hardly at all.

(c) If K_c is in the range 10^{-3} to 10^3, appreaciable concentration of both reactants and products are present. This is illustrated as follows,



(ii) ***Reaction quotient and predicting the direction of reaction*** **:** The concentration ratio, *i.e.*, ratio of the product of concentrations of products to that of reactants is also known as ***concentration quotient*** and is denoted by ***Q***.

Concentration quotient, $Q = \dfrac{[X][Y]}{[A][B]}$.

It may be noted that Q becomes equal to equilibrium constant (K) when the reaction is at the equilibrium state. At equilibrium, $Q = K = K_c = K_p$. Thus,

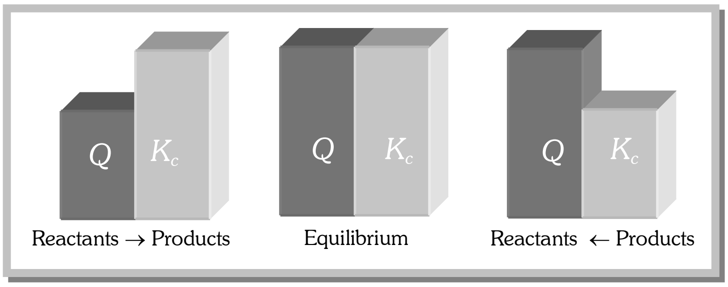
(a) If $Q > K$, the reaction will proceed in the direction of reactants (*reverse reaction*).

(b) If $Q < K$, the reaction will proceed in the direction of the products (*forward reaction*).

(c) If $Q = K$, the reaction mixture is already *at equilibrium*.

Thus, a reaction has a tendency to form products if $Q < K$ and to form reactants if $Q > K$.

This has also been shown in figure,



(6) **Calculation of equilibrium constant :** We have studied in the characteristics of the equilibrium constant that its value does not depend upon the original concentrations of the reactants and products involved in the reaction. However, its value depends upon their concentrations at the equilibrium point. Thus, if the equilibrium concentrations of the species taking part in the reaction be known, then the value of the equilibrium constant and *vice versa* can be calculated.

Homogeneous equilibria and equations for equilibrium constant (Equilibrium pressure is *P atm* in a V L flask)

	$\Delta n = 0;\ K_p = K_c$			$\Delta n < 0$; $K_p < K_c$						$\Delta n > 0;\ K_p > K_c$		
	$H_{2\,(g)}$ +	$I_{2\,(g)}$ ⇌	$2HI_{(g)}$	$N_{2\,(g)}$ +	$3H_{2\,(g)}$ ⇌	$2NH_{3\,(g)}$	$2SO_{2\,(g)}$ +	$O_{2\,(g)}$ ⇌	$2SO_{3\,(g)}$	$PCl_{5\,(g)}$ ⇌	$PCl_{3\,(g)}$ +	$Cl_{2\,(g)}$
Initial mole	1	1	0	1	3	0	2	1	0	1	0	0
Mole at Equilibrium	**(1–x)**	**(1– x)**	**2x**	**(1–x)**	**(3–3x)**	**2x**	**(2–2x)**	**(1–x)**	**2x**	**(1–x)**	**x**	**x**
Total mole at equilibrium	**2**			**(4 – 2x)**			**(3 – x)**			**(1 + x)**		
Active masses	$\left(\frac{1-x}{V}\right)$	$\left(\frac{1-x}{V}\right)$	$\frac{2x}{V}$	$\left(\frac{1-x}{V}\right)$	$3\left(\frac{1-x}{V}\right)$	$\left(\frac{2x}{V}\right)$	$\left(\frac{2-2x}{V}\right)$	$\left(\frac{1-x}{V}\right)$	$\left(\frac{2x}{V}\right)$	$\left(\frac{1-x}{V}\right)$	$\left(\frac{x}{V}\right)$	$\left(\frac{x}{V}\right)$
Mole fraction	$\left(\frac{1-x}{2}\right)$	$\left(\frac{1-x}{2}\right)$	$\frac{2x}{2}$	$\frac{1-x}{2(2-x)}$	$\frac{3}{2}\left(\frac{1-x}{2-x}\right)$	$\frac{x}{(2-x)}$	$\left(\frac{2-2x}{3-x}\right)$	$\left(\frac{1-x}{3-x}\right)$	$\left(\frac{2x}{3-x}\right)$	$\left(\frac{1-x}{1+x}\right)$	$\left(\frac{x}{1+x}\right)$	$\left(\frac{x}{1+x}\right)$
Partial pressure	$p\left(\frac{1-x}{2}\right)$	$p\left(\frac{1-x}{2}\right)$	$p\left(\frac{2x}{2}\right)$	$P\left(\frac{1-x}{2(2-x)}\right)$	$P\left(\frac{3(1-x)}{2(2-x)}\right)$	$\frac{Px}{(2-x)}$	$P\left(\frac{2-2x}{3-x}\right)$	$P\left(\frac{1-x}{3-x}\right)$	$P\left(\frac{2x}{3-x}\right)$	$P\left(\frac{1-x}{1+x}\right)$	$P\left(\frac{x}{1+x}\right)$	$P\left(\frac{x}{1+x}\right)$
K_c	$\frac{4x^2}{(1-x)^2}$			$\frac{4x^2V^2}{27\,(1-x)^4}$			$\frac{x^2V}{(1-x)^3}$			$\frac{x^2}{(1-x)V}$		
K_p	$\frac{4x^2}{(1-x)^2}$			$\frac{16x^2\,(2-x)^2}{27(1-x)^4P^2}$			$\frac{x^2\,(3-x)}{P\,(1-x)^3}$			$\frac{Px^2}{(1-x^2)}$		

Heterogeneous equilibria and equation for equilibrium constant (Equilibrium pressure is P atm)

	$NH_4HS(s)$ ⇌	$NH_3(g)$ +	$H_2S(g)$	$C(s)+$	$CO_2(g)$ ⇌	$2CO(g)$	$NH_2CO_2NH_4(s)$ ⇌	$2NH_3(g)+$	$CO_2(g)$
Initial mole	1	0	0	1	1	0	1	0	0
Mole at equilibrium	**(1–x)**	**x**	**x**	**(1–x)**	**(1–x)**	**2x**	**(1–x)**	**2x**	**x**
Total moles at equilibrium (solid not included)		**2x**			**(1 +x)**			**3x**	
Mole fraction		$\frac{x}{2x}=\frac{1}{2}$	$\frac{1}{2}$		$\left(\frac{1-x}{1+x}\right)$	$\left(\frac{2x}{1+x}\right)$		$\frac{2}{3}$	$\frac{1}{3}$
Partial pressure		$\frac{P}{2}$	$\frac{P}{2}$		$P\left(\frac{1-x}{1+x}\right)$	$P\left(\frac{2x}{1+x}\right)$		$\frac{2P}{3}$	$\frac{P}{3}$
K_p		$\frac{P^2}{4}$			$\frac{4P^2x^2}{(1-x^2)}$			$\frac{4P^3}{27}$	

(7) Equilibrium constant and standard free energy change : Standard free energy change of a reaction and its equilibrium constant are related to each other at temperature T by the following relation,

$$\boxed{\Delta G^o = -2.303\, RT \log K}$$

when, $\Delta G^o = -ve$, the value of equilibrium constant will be large positive quantity and

when, $\Delta G^o = +ve$, the value of equilibrium constant is less than 1 *i.e.*, low concentration of products at equilibrium state.

Example : 1 In the reversible reaction $A + B \rightleftharpoons C + D$, the concentration of each C and D at equilibrium was 0.8 *mole/litre*, then the equilibrium constant K_c will be **[MP PET 1986]**

(a) 6.4 (b) 0.64 (c) 1.6 (d) 16.0

Solution: (d) Suppose 1 *mole* of A and B each taken then 0.8 *mole/litre* of C and D each formed remaining concentration of A and B will be (1 – 0.8) = 0.2 *mole/litre* each.

$$K_c = \frac{[C][D]}{[A][B]} = \frac{0.8 \times 0.8}{0.2 \times 0.2} = 16.0$$

Example : 2 For the system $A(g) + 2B(g) \rightleftharpoons C(g)$, the equilibrium concentrations are (A) 0.06 *mole/litre* (B) 0.12 *mole/litre* (C) 0.216 *mole/litre*. The K_{eq} for the reaction is **[CPMT 1983]**

(a) 250 (b) 416 (c) 4×10^{-3} (d) 125

Solution: (a) For reaction $A + 2B \rightleftharpoons C$; $K_{eq} = \frac{[C]}{[A][B]^2} = \frac{0.216}{0.06 \times 0.12 \times 0.12} = 250$

Example : 3 Molar concentration of O_2 is 96 *gm*, it contained in 2 *litre* vessel, active mass will be

(a) 16 *mole/litre* (b) 1.5 *mole/litre* (c) 4 *mole/litre* (d) 24 *mole/litre*

Solution: (b) Active mass $= \frac{\frac{\text{weight}}{\text{M.wt.}}}{\text{Volume}} = \frac{\text{weight}}{\text{M.wt.} \times \text{Volume}} = \frac{96}{32 \times 2} = \frac{3}{2} = 1.5\, mol / litre$

Example : 4 2 moles of PCl_5 were heated in a closed vessel of 2 litre capacity. At equilibrium, 40% of PCl_5 is dissociated into PCl_3 and Cl_2. The value of equilibrium constant is **[MP PMT 1989]**

(a) 0.266 (b) 0.53 (c) 2.66 (d) 5.3

Solution: (a) At start, $\underset{2}{PCl_5} \rightleftharpoons \underset{0}{PCl_3} + \underset{0}{Cl_2}$

At equilibrium. $\frac{2 \times 60}{100}$ $\frac{2 \times 40}{100}$ $\frac{2 \times 40}{100}$

Volume of cantainer = 2 litre

$$\therefore\ K_c = \frac{\frac{2 \times 40}{100 \times 2} \times \frac{2 \times 40}{100 \times 2}}{\frac{2 \times 60}{100 \times 2}} = 0.266$$

Example : 5 A mixture of 0.3 mole of H_2 and 0.3 mole of I_2 is allowed to react in a 10 litre evacuated flask at $500^o C$. The reaction is $H_2 + I_2 \rightleftharpoons 2HI$ the K_c is found to be 64. The amount of unreacted I_2 at equilibrium is **[KCET 1990]**

(a) 0.15 *mole* (b) 0.06 *mole* (c) 0.03 *mole* (d) 0.2 *mole*

Solution: (b) $K_c = \frac{[HI]^2}{[H_2][I_2]}$; $64 = \frac{x^2}{0.03 \times 0.03}$

$x^2 = 64 \times 9 \times 10^{-4}$; $x = 8 \times 3 \times 10^{-2} = 0.24$

x is the amount of HI at equilibrium. Amount of I_2 at equilibrium will be

$0.30 - 0.24 = 0.06\, mole$

Example : 6 The rate constant for forward and backward reactions of hydrolysis of ester are 1.1×10^{-2} and 1.5×10^{-3} per minute respectively. Equilibrium constant for the reaction,

$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$ is **[AIIMS 1999]**

(a) 4.33 (b) 5.33 (c) 6.33 (d) 7.33

Solution: (d) $K_f = 1.1 \times 10^{-2}$, $K_b = 1.5 \times 10^{-3}$; $K_c = \frac{K_f}{K_b} = \frac{1.1 \times 10^{-2}}{1.5 \times 10^{-3}} = 7.33$

Example : 7 For the reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5$ at $250^\circ C$, the value of K_c is 26, then the value of K_p on the same temperature will be **[MNR 1990; MP PET 2001]**

(a) 0.61 (b) 0.57 (c) 0.83 (d) 0.46

Solution: (a) $\Delta n_g = 1 - 2 = -1$

$\therefore K_p = K_c(RT)^{\Delta n}$; $\because K_p = K_c(RT)^{-1}$

Since $R = 0.0821$ *litre atm* k^{-1} mol^{-1}, $T = 250^\circ C = 250 + 273 = 523$ $K_p = 26(0.0821 \times 523)^{-1} = 0.61$

Example : 8 If K_p for reaction $A_{(g)} + 2B_{(g)} \rightleftharpoons 3C_{(g)} + D_{(g)}$ is 0.05 *atm* at 1000K its K_c in term of R will be **[CBSE PMT 1989]**

(a) $\frac{5 \times 10^{-4}}{R}$ (b) $\frac{5}{R}$ (c) $\frac{5 \times 10^{-5}}{R}$ (d) None of these

Solution: (c) $K_p = K_c(RT)^{\Delta n} \Rightarrow 5 \times 10^{-2} = K_c(R \times 1000)^1 \Rightarrow K_c = \frac{5 \times 10^{-5}}{R}$

Example : 9 If the equilibrium constant of the reaction $2HI \rightleftharpoons H_2 + I_2$ is 0.25, then the equilibrium constant of the reaction $H_2 + I_2 \rightleftharpoons 2HI$ would be **[MP PMT 1989, 95]**

(a) 1.0 (b) 2.0 (c) 3.0 (d) 4.0

Solution: (d) K_c for the IInd reaction is reverse of Ist for reaction $2HI \rightleftharpoons H_2 + I_2$ is $0.25 K'_c$ for reaction, $H_2 + I_2 \rightleftharpoons 2HI$ will be $K'_c = \frac{1}{K_c} = \frac{1}{0.25} = 4$.

Example : 10 If equilibrium constant for reaction $2AB \rightleftharpoons A_2 + B_2$, is 49, then the equilibrium constant for reaction $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$, will be **[MP PMT 2003; EAMCET 1998]**

(a) 7 (b) 20 (c) 49 (d) 21

Solution: (a) $2AB \rightleftharpoons A_2 + B_2$

$$K_c = \frac{[A_2][B_2]}{[AB]^2} = 49$$

For reaction $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$

$$K'_c = \frac{[A_2]^{1/2}[B_2]^{1/2}}{[AB]}$$

$$K'_c = \sqrt{K_c} = \sqrt{49} = 7$$

Example : 11 For the reaction $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$ $K_c = 1.8 \times 10^{-6}$ at $185^\circ C$. At $185^\circ C$, the value of K'_c for the reaction $NO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NO_{2(g)}$ is **[UPSEAT 2000]**

(a) 0.9×10^6 (b) 7.5×10^2 (c) 1.95×10^{-3} (d) 1.95×10^3

Solution: (b) Reaction is reversed and halved.

$$\therefore\ K'_c = \frac{1}{\sqrt{K_c}};\quad K'_c = \frac{1}{\sqrt{1.8 \times 10^{-6}}} = 7.5 \times 10^2$$

Example : 12 In an equilibrium reaction for which $\Delta G^0 = 0$ the equilibrium constant K_p should be **[BHU 1987]**

(a) 0 (b) 1 (c) 2 (d) 10

Solution: (b) If $\Delta G^0 = 0$ and $\Delta G^0 = -2.303RT\log K_p$

$$\log K_p = 0,\ K_p = 1$$

Example : 13 ΔG^0 for $HI_{(g)} \cong +1.7 kJ/mole$ what is the equilibrium constant at $25^\circ C$ for $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ **[KCET 1992]**

(a) 24.0 (b) 3.9 (c) 2.0 (d) 0.5

Solution: (d) $\Delta G^0 = -2.303RT\log K_p = -2.303 \times 8.314 \times 10^{-3} \times 298 \log K_p$

$$1.7 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log K_p$$

$$K_p = 0.5$$

Example : 14 It is found that the equilibrium constant increases by a factor of four when the temperature is increased from $25^\circ C$ to $40^\circ C$. The value of ΔH° is

(a) $25.46\, kJ\, mol^{-1}$ (b) $171.67\, kJ\, mol^{-1}$ (c) $89.43\, kJ\, mol^{-1}$ (d) $71.67\, kJ\, mol^{-1}$

Solution: (d) Using the equation,

$$\log\frac{(K_p)_{40^\circ C}}{(K_p)_{25^\circ C}} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

we get $\log 4 = \frac{\Delta H}{2.303 \times 8.314}\left(\frac{1}{273+25} - \frac{1}{273+40}\right)$

$$\therefore\ \Delta H = 71.67\, kJ\, mol^{-1}$$

Example : 15 K_c for the reaction $A(g) + B(g) \rightleftharpoons 2C(g)$ is 3.0 at 400*K*. In an experiment "*a*" *mol* of *A* is mixed with 3 *mol* of *B* in a 1-*L* vessel. At equilibrium 3 *mol* of *C* is formed. The value of '*a*' will be,

(a) 4.5 *mol* (b) 9.5 *mol* (c) 2.5 *mol* (d) 3.5 *mol*

Solution: (d)

$$\begin{array}{ccccc} A(g) & + & B(g) & \rightleftharpoons & 2C(g) \\ a & & 3 & & 0 \\ a-x & & 3-x & & 2x \end{array}$$

From the equation, $2x = 3 \Rightarrow x = 1.5$

$$K_c = \frac{4x^2}{(a-x)(b-x)}\,;\; 3 = \frac{4\times(1.5)^2}{(a-1.5)(3-1.5)}\,;\; 3 = \frac{4\times 2.25}{(a-1.5)(1.5)} \Rightarrow a = 3.5$$

Example : 16 For the reaction $AB(g) \rightleftharpoons A(g)+B(g)$, AB is 33% dissociated at a total pressure of P. Then

(a) $P = K_p$ (b) $P = 4K_p$ (c) $P = 3K_p$ (d) $p = 8K_p$

Solution: (d)

$$\begin{array}{ccccc} AB(g) & \rightleftharpoons & A(g) & + & B(g) \\ 1 & & 0 & & 0 \\ -1/3 & & +1/3 & & +1/3 \\ 2/3 & & 1/3 & & 1/3 \end{array}$$

$$(\Sigma n)_{eq/m} = \frac{2}{3}+\frac{1}{3}+\frac{1}{3} = \frac{4}{3}$$

$$K_p = \frac{P_A P_B}{P_{AB}} = \frac{\frac{1/3}{4/3}P\,\frac{1/3}{4/3}P}{\frac{2/3}{4/3}P} = \frac{1}{8}P$$

$$P = 8K_p$$

Example : 17 The total pressure observed at equilibrium in the dissociation of solid ammonium carbamate at a certain temperature is 2.0 *atm*. The equilibrium constant K_p is

(a) 4.185 (b) 1.185 (c) 2.276 (d) 1.072

Solution: (b)

$$NH_4COONH_2(s) \rightleftharpoons \underset{\frac{2}{3}P}{2NH_3(g)} + \underset{\frac{1}{3}P}{CO_2(g)}$$

$$K_p = P_{NH_3}^2 P_{CO_2} = \left(\frac{2}{3}P\right)^2\left(\frac{1}{3}P\right) = \frac{4}{27}P^3 = \frac{4}{27}\times(2)^3 = 1.185$$

Example : 18 At the equilibrium of the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the observed molar mass of N_2O_4 is 77.70 *g*. The percentage dissociation of N_2O_4 is

(a) 28.4 (b) 46.7 (c) 22.4 (d) 18.4

Solution: (d) $\alpha = \frac{M_{Th}-M_{obs}}{M_{obs}(n-1)}$; Molar mass of $N_2O_4 = 92\,g\,mol^{-1}$

Here, $n = 2$; $\alpha = \frac{92.00-77.70}{77.70(2-1)} = 0.184 = 18.4\%$

Example : 19 In the equilibrium $H_2O(g) \rightleftharpoons H_2(g)+\frac{1}{2}O_2(g)$, the extent of dissociation of water when $p = 1$ *atm* and $K = 2.08\times 10^{-3}$ is approximately

(a) 2% (b) 0.2% (c) 20% (d) 1%

Solution: (a) For the equilibrium $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$

$$K_p = \frac{\alpha^{3/2} P^{1/2}}{\sqrt{2}} P = 1\,atm$$

$$\alpha = (\sqrt{2}.K_p)^{2/3} = 0.0205 \approx 2\%$$

Factors which Change the State of Equilibrium : Le-Chatelier's Principle.

Le-Chatelier and Braun (1884), French chemists, made certain generalizations to explain the effect of changes in concentration, temperature or pressure on the state of system in equilibrium. When a system is subjected to a change in one of these factors, the equilibrium gets disturbed and the system readjusts itself until it returns to equilibrium. The generalization is known as ***Le-Chatelier's principle.*** It may stated as :

"Change in any of the factors that determine the equilibrium conditions of a system will shift the equilibrium in such a manner to reduce or to counteract the effect of the change."

The principle is very helpful in predicting ***qualitatively*** the effect of change in concentration, pressure or temperature on a system in equilibrium. *This is applicable to all physical and chemical equilibria*.

(1) **Effect of change of concentration** : According to Le-Chatelier's principle, *"If concentration of one or all the reactant species is increased, the equilibrium shifts in the forward direction and more of the products are formed. Alternatively, if the concentration of one or all the product species is increased, the equilibrium shifts in the backward direction forming more reactants."*

Thus,

Increase in concentration of any of the reactants $\xrightarrow[\text{equilibrium to}]{\text{Shifts the}}$ **Forward direction**

Increase in concentration of any of the products $\xrightarrow[\text{equilibrium to}]{\text{Shifts the}}$ **Backward direction**

(2) **Effect of change of temperature** : According to Le-Chatelier's principle, *"If the temperature of the system at equilibrium is increased (heat is supplied), the equilibrium will shift in the direction in which the added heat is absorbed. In other words, the equilibrium will shift in the direction of* ***endothermic reaction*** *with increase in temperature. Alternatively, the decrease in temperature will shift the equilibrium towards the direction in which heat is produced and, therefore, will favour* ***exothermic reaction.****"*

Thus,

Increase in temperature $\xrightarrow[\text{in the direction of}]{\text{Shifts the equilibrium}}$ **Endothermic reaction**

Decrease in temperature $\xrightarrow[\text{in the direction of}]{\text{Shifts the equilibrium}}$ **Exothermic reaction**

(3) **Effect of change of pressure** : Pressure has hardly effect on the reactions carried in solids and liquids. However, it does influence the equilibrium state of the reactions that are carried in the gases. The effect of pressure depends upon the number of moles of the reactants and products involved in a particular reaction. According to Le-Chatelier's principle, *"Increase in pressure shifts the equilibrium in the direction of decreasing gaseous moles.*

Alternatively, decrease in pressure shifts the equilibrium in the direction of increasing gaseous moles and pressure has no effect if the gaseous reactants and products have equal moles."

Thus,

Increase in pressure $\xrightarrow[\text{in the direction of}]{\text{Shifts the equilibrium}}$ **Decreasing gaseous moles**

Decrease in pressure $\xrightarrow[\text{in the direction of}]{\text{Shifts the equilibrium}}$ **Increasing gaseous moles**

(4) **Effect of volume change** : We know that increase in pressure means decrease in volume, so the effect of change of volume will be exactly reverse to that of pressure. Thus, "*decreasing the volume of a mixture of gases at equilibrium shifts the equilibrium in the direction of decreasing gaseous moles while increasing the volume shifts the equilibrium in the direction of increasing gaseous moles."*

Thus,

Increase in volume $\xrightarrow[\text{in the direction of}]{\text{Shifts the equilibrium}}$ **Increasing gaseous moles**

Decrease in volume $\xrightarrow[\text{in the direction of}]{\text{Shifts the equilibrium}}$ **Decreasing gaseous moles**

(5) **Effect of catalyst** : Catalyst has no effect on equilibrium. This is because, catalyst favours the rate of forward and backward reactions equally. Therefore, the ratio of the forward to reverse rates remains same and no net change occurs in the relative amount of reactants and products present at equilibrium. Thus, a **catalyst does not affect the position of the equilibrium**. It simply helps to achieve the equilibrium quickly. It may also be noted that a catalyst has no effect on the equilibrium composition of a reaction mixture.

Thus, **Catalyst does not shift the equilibrium in any direction**

(6) **Effect of addition of inert gas** : The addition of an inert gas (like helium, neon, etc.) has the following effects on the equilibrium depending upon the conditions :

(i) ***Addition of an inert gas at constant volume :*** When an inert gas is added to the equilibrium system at constant volume, then the total pressure will increase. But the concentrations of the reactants and products (ratio of their moles to the volume of the container) will not change. Hence, under these conditions, *there will be no effect on the equilibrium.*

(ii) ***Addition of an inert gas at constant pressure :*** When an inert gas is added to the equilibrium system at constant pressure, then the volume will increase. As a result, the number of moles per unit volume of various reactants and products will decrease. Hence, *the equilibrium will shift in a direction in which there is increase in number of moles of gases.*

Thus,

Addition of an inert gas $\xrightarrow{V = \text{constant}}$ **No effect on the equilibrium.**

Addition of an inert gas $\xrightarrow[\text{Shifts the equilibrium in the direction of}]{P = \text{constant}}$ **Increasing gaseous moles.**

Applications of Le-Chatelier's Principle.

The Le-Chateliers principle has a great significance for the chemical, physical systems and in every day life in a state of equilibrium. Let us discuss in brief a few applications.

(1) **Applications to the chemical equilibrium** : With the help of this principle, most favourable conditions for a particular reaction can be predicted.

(i) ***Synthesis of ammonia*** *(Haber's process)*: $\underset{1\,vol}{N_2} + \underset{3\,vol}{3H_2} \rightleftharpoons \underset{2\,vol}{2NH_3} + 23 kcal$ (exothermic)

(a) High pressure $(\Delta n < 0)$ (b) Low temperature (c) Excess of N_2 and H_2 (d) Removal of NH_3 favours forward reaction.

(ii) ***Formation of sulphur trioxide :*** $\underset{2\,vol}{2SO_2} + \underset{1\,vol}{O_2} \rightleftharpoons \underset{2\,vol}{2SO_3} + 45\ kcal$ (exothermic)

(a) High pressure $(\Delta n < 0)$ (b) Low temperature (c) Excess of SO_2 and O_2, favours the reaction in forward direction.

(iii) ***Synthesis of nitric oxide :*** $\underset{1\,vol}{N_2} + \underset{1\,vol}{O_2} \rightleftharpoons \underset{2\,vol}{2NO} - 43.2\ kcal$ (endothermic)

(a) High temperature (b) Excess of N_2 and O_2 (c) Since reaction takes place without change in volume i.e., $\Delta n = 0$, pressure has no effect on equilibrium.

(iv) ***Formation of nitrogen dioxide :*** $\underset{2\,vol}{2NO} + \underset{1\,vol}{O_2} \rightleftharpoons \underset{2\,vol}{2NO_2} + 27.8\ Kcal$

(a) High pressure (b) Low temperature (c) Excess of NO and O_2 favours the reaction in forward direction.

(v) ***Dissociation of phosphours pentachloride :*** $\underset{1\,vol}{PCl_5} \rightleftharpoons \underset{1\,vol}{PCl_3} + \underset{1\,vol}{Cl_2} - 15\ kcal$

(a) Low pressure or high volume of the container, $\Delta n > 0$ (b) High temperature (c) Excess of PCl_5.

(2) **Applications to the physical equilibrium** : Le-Chatelier's principle is applicable to the physical equilibrium in the following manner;

(i) ***Melting of ice*** *(Ice – water system)* : $\underset{\text{(Greater Volume)}}{\text{Ice}} \rightleftharpoons \underset{\text{(Lesser Volume)}}{\text{Water}} - x\ kcal$

(In this reaction volume is decreased from 1.09 *c.c.* to 1.01 *c.c. per gm.*)

(a) At high temperature more water is formed as it absorbs heat.(b) At high pressure more water is formed as it is accompanied by decrease in volume.(c) At higher pressure, melting point of ice is lowered, while boiling point of water is increased.

(ii) ***Melting of sulphur :*** $S_{(s)} \rightleftharpoons S_{(l)} - x\ kcal$

(This reaction accompanies with increase in volume.)

(a) At high temperature, more liquid sulphur is formed. (b) At higher pressure, less sulphur will melt as melting increases volume.(c) At higher pressure, melting point of sulphur is increased.

(iii) ***Boiling of water*** *(water- water vapour system)* : $\underset{\text{(Low volume)}}{\text{Water}} \rightleftharpoons \underset{\text{(Higher volume)}}{\text{Water Vapours}} - x\ kcal$

(It is accompanied by absorption of heat and increase in volume.)

(a) At high temperature more vapours are formed.(b) At higher pressure, vapours will be converted to liquid as it decreases volume.(c) At higher pressure, boiling point of water is increased (principle of pressure cooker).

(iv) ***Solubility of salts*** : If solubility of a salt is accompanied by absorption of heat, its solubility increases with rise in temperature; e.g., NH_4Cl, K_2SO_4, KNO_3 etc. $KNO_{3(s)} + (aq) \longrightarrow KNO_{3(aq)} - x\ kcal$

On the other hand if it is accompanied by evolution of heat, solubility decreases with increase in temperature; e.g., $CaCl_2, Ca(OH)_2, NaOH, KOH$ etc. $Ca(OH)_{2(s)} + (aq) \longrightarrow Ca(OH)_{2\,(aq)} + x\ kcal$

(3) **Application in every day life** : We have studied the application of the Le-Chatelier's principle to some equilibria involved in the physical and chemical systems. In addition to these, the principle is also useful to explain certain observations which we come across in every day life. A few out of them are discussed below,

(i) ***Clothes dry quicker in a windy day*** **:** When wet clothes are spread on a stand, the water evaporates and the surrounding air tends to get saturated thus hampering the process of drying. On a windy day when breeze blows, the nearby wet air is replaced by dry air which helps the process of evaporation further. Thus, clothes dry quicker when there is a breeze.

(ii) ***We sweat more on a humid day*** **:** The explanation is the same as given above. In a humid day, the air is already saturated with water vapours. This means that the water that comes out of the pores of the body as sweat does not vaporise. This will result in greater sweating in a humid day.

(iii) ***Carriage of oxygen by haemoglobin in blood*** **:** The haemoglobin (Hb) in red corpuscles of our blood carries oxygen to the tissues. This involves the equilibrium, $Hb(s) + O_2(g) \rightleftharpoons HbO_2(s)$

The blood that is in equilibrium with the oxygen of the air in the lungs finds a situation in the tissues where the partial pressure of oxygen is low. According to Le-Chatelier's principle, the equilibrium shifts towards the left so that some of the oxyhaemoglobin changes to haemoglobin giving up the oxygen. When the blood returns to the lungs, the partial pressure of the oxygen is higher and the equilibrium favours the formation of more oxyhaemoglobin.

(iv) ***Removal of carbon dioxide from the tissues by blood*** **:** Blood removes CO_2 from the tissues. The equilibrium is, $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

Carbon dioxide dissolves in the blood in the tissues since the partial pressure of CO_2 is high. However in the lungs, where the partial pressure of CO_2 is low, it is released from the blood.

(v) ***Sweet substances cause tooth decay*** **:** Tooth enamel consists of an insoluble substance called hydroxyapatite, $Ca_5(PO_4)_3OH$. The dissolution of this substance from the teeth is called *demineralization* and its formation is called *remineralization*. Even with the healthy teeth, there is an equilibrium in the mouth as

$$Ca_5(PO_4)_3OH(s) \underset{endothermic}{\overset{exothermic}{\rightleftharpoons}} 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

When sugar substances are taken, sugar is absorbed on teeth and gets fermented to give H^+ ions. The H^+ ions produced distrub the equilibrium by combining with OH^- to form water and with PO_4^{3-} to form HPO_4^{2-}. Removal of products cause the equilibrium to shift towards right and therefore, $Ca_5(PO_4)_3OH$ dissolves causing tooth decay.

Relation between vapour density and degree of dissociation.

In the following reversible chemical equation.

	A	$\rightleftharpoons$	yB	
Initial mol	1		0	
At equilibrium	(1–x)		yx	x = degree of dissociation

Number of moles of A and B at equilibrium $= 1 - x + yx = 1 + x(y-1)$

If initial volume of 1 mole of A is V, then volume of equilibrium mixture of A and B is, $= [1 + x(y-1)]V$

Molar density before dissociation, $\boxed{D = \frac{molecular\ weight}{volume} = \frac{m}{V}}$

Molar density after dissociation, $d = \frac{m}{[1 + x(y-1)]V}$; $\frac{D}{d} = [1 + x(y-1)]$; $x = \frac{D-d}{d(y-1)}$

y is the number of moles of products from one mole of reactant. $\frac{D}{d}$ is also called ***Van't Hoff factor.***

In terms of molecular mass,

$x = \frac{M-m}{(y-1)m}$; Where $M =$ Initial molecular mass, $m =$ molecular mass at equilibrium

Thus for the equilibria

(I) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}, y = 2$ (II) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}, y = 2$ (III) $2NO_2 \rightleftharpoons N_2O_4, y = \frac{1}{2}$

$\therefore\ x = \frac{D-d}{d}$ (for I and II) and $x = \frac{2(d-D)}{d}$ (for III)

Also $D \times 2 =$ Molecular weight (theoretical value)

$d \times 2 =$ Molecular weight (abnormal value) of the mixture

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