

Chemical Equilibrium

Irreversible and Reversible reactions

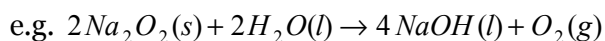
The chemical reactions are primarily classified as : (1) Irreversible and (2) reversible reactions.

(1) **Irreversible reactions** : These are chemical reactions in which the products are not capable of giving back the reactants. For example- $2KClO_3 \rightarrow 2KCl + 3O_2$; $AgNO_3 + HCl \rightarrow AgCl + HNO_3$

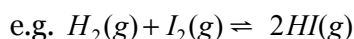
(2) **Reversible reactions** : These are chemical reactions in which the products are capable of reacting to give back the reactants. Such reactions can be made to occur in either direction by suitable variations in the conditions. For example : $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Reversible chemical reactions are classified into two types:

(i) **Heterogeneous reactions** : The reversible reactions in which more than one phase is present.



(ii) **Homogenous reactions** : The reversible reactions in which only one phase is present.

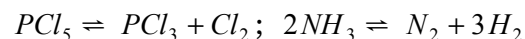


Homogenous reversible reactions are further classified into three types:

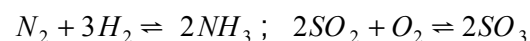
(a) **First type** : When there is no change in number of molecules, i.e. $\Delta n = 0$



(b) **Second type** : When there is increase in number of molecules, i.e., $\Delta n = +ve$



(c) **Third type** : When there is a decrease in number of molecules, i.e., $\Delta n = -ve$



Chemical equilibrium

When a reversible reaction is carried out in a closed vessel then it is observed that a constancy in properties like intensity of colour, pressure concentration etc. It is achieved under a given set of condition. Such a state is referred as an equilibrium state.

A chemical equilibrium is a state at which the composition of the chemical system become constant under given set of conditions. It must be noted that at equilibrium, the chemical reaction does not stop but both the forward as well as backward reactions takes place at the same rate. The following are the Characteristics of the equilibrium state

(1) It can be attained from either side.

(2) It is dynamic in nature i.e. both forward and backward reactions are in progress at equilibrium state.

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(3) It readjusts with the changing conditions and goes back to the original state spontaneously when the factors responsible for the change are removed.

(4) At constant temperature certain observable properties like pressure, concentration, density and colour remain unchanged at equilibrium.

(5) The state of equilibrium continues indefinitely until it is disturbed by external factors like variation of concentration, temperature, pressure etc.

(6) Catalyst does not affect the final state of the equilibrium. However, it enables the system to attain equilibrium state quickly by providing an alternative path which involves lower energy of activation.

Law of mass action

The law of mass action given by Guldberg and Waage in 1864. According to this law,

“At a constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants each raised to a power equal to its corresponding stoichiometric coefficient that appears in the balanced chemical equation”.

For example, let us consider a reaction : $aA + bB \longrightarrow \text{Products}$

According to law: rate of reaction (R) $\propto [A]^a \cdot [B]^b$ or $R = K[A]^a \cdot [B]^b$

Here a and b represent the stoichiometric coefficients of the reactants A and B . K is the rate constant while square bracket indicates the molar concentration of the species involved in it.

Molar concentration means the number of moles of the substance dissolved per litre of the solution. It is also called active mass. The active mass of a substance is normally written by enclosing its formula in square brackets e.g. $[NaOH]$.

$$\text{Active mass (molar concentration)} = \frac{\text{Number of moles (n)}}{\text{Volume in litres (V)}}$$

Law of chemical equilibrium

The law of mass action is applicable to the individual single step reactions. We can apply the law of mass action to both the forward and the backward reactions in a reversible reaction in a state of equilibrium.

For example : Let us consider the reaction. $A + B \rightleftharpoons C + D$

Rate of forward reaction (R_f) $\propto [A][B] = K_f[A][B]$, here K_f is the rate constant for the forward reaction.

Rate of backward reaction (R_b) $\propto [C][D] = K_b[C][D]$, here K_b is the rate constant for the backward reaction.

At the equilibrium $R_f = R_b$. Therefore, $K_f[A][B] = K_b[C][D]$ or $\frac{K_f}{K_b} = \frac{[C][D]}{[A][B]} = K_c$

Here K_c represents the equilibrium constant for the reversible reaction.

For the reaction : $aA + bB \rightleftharpoons cC + dD$, $\Rightarrow K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

The expression is according to the law of chemical equilibrium which states that:

“For a reversible reaction in a state of equilibrium, the ratio of the product of the molar concentrations of the products to that of the molar concentrations of the Reactants each concentration term raised to a power equal to its stoichiometric coefficient in the balanced chemical equation, is a constant known as the equilibrium constant provided the temperature is constant”.

Here $[C], [D], [A]$ and $[B]$ represents the molar concentrations of C, D, A and B respectively at the equilibrium.

For gaseous reactions, the equilibrium constant can be calculated from the respective partial pressure of the gaseous species. The equilibrium constant determined from the partial pressures is represented by K_p .

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

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

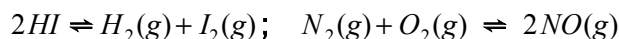
Relation between K_p and K_c : $K_p = K_c (RT)^{\Delta n}$

Where, K_p = Equilibrium constant when partial pressures are considered.

K_c = equilibrium constant when molar concentrations are considered.

R = Gas constant , T = Temperature in Kelvin, Δn = Change in the number of gaseous moles.

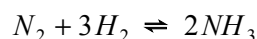
(i) If $\Delta n = 0$ then , $K_p = K_c$



(ii) If $\Delta n = +ve$ then $K_p > K_c$



(iii) If $\Delta n = -ve$ then, $K_p < K_c$



The units of K_c and K_p are $mol L^{-1}$ and KPa respectively. The unit of R is $0.082 L atm k^{-1} mol^{-1}$.

Factors affecting the K_c and K_p

(i) The value of K_c is independent of initial concentration of reactants. It depends only on the concentration at equilibrium.

(ii) Equation constant $K_{Forward} = \frac{1}{K_{Backward}}$.

(iii) The value of K_c depends on the stoichiometry of reactants and products at the point of equilibrium.

For Example : $2NO + O_2 \rightleftharpoons 2NO_2 \dots\dots\dots K_1$

and $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2 \dots\dots\dots K_2$

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are related as, $K_1 = (K_2)^2$

(iv) The numerical value of K_c depends on the equation for the reaction.

(v) If the reaction is multiplied by 2, the equilibrium constant is squared.

(vi) The value of K_c gives us a relative idea about the extent to which a reaction proceeds.

(vii) The value of K_c and K_p depends on concentration, temperature, pressure and volume.

(viii) Equilibrium constant varies with temperature. It's variation with temperature can be described by the following relation : $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$; Where, ΔH = Enthalpy change, R = Universal gas constant.

K_1 and K_2 = Equilibrium constants at temperatures T_1 and T_2 respectively.

When $\Delta H = 0$; $K_2 = K_1$ (i.e., heat of reaction at constant volume is zero)

When $\Delta H = +ve$; $K_2 > K_1$ (i.e., endothermic reaction)

When $\Delta H = -ve$; $K_2 < K_1$ (i.e., exothermic reaction)

Reaction quotient (Q)

The ratio of molar concentrations or the partial pressures of the product species to that of the reacting species at any stage in the reaction.

If molar concentration of the species are considered, the reaction quotient is called concentration quotient (Q_c). It is known as partial pressure quotient (Q_p) in case the partial pressures of the different species are considered.

For a reversible reaction, $aA + bB \rightleftharpoons cC + dD$

$$Q_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}; \quad Q_p = \frac{pC^c \times pD^d}{pA^a \times pB^b};$$

Relation between Q and K :

(1) If $Q = K$, the reaction is in a state of equilibrium, i.e. molar conc. or partial pressures of reactants = that of product

(2) If $Q > K$, the reaction is not in a state of equilibrium. i.e. The products are present in large amount as compared to the reactants.

Therefore, the reaction has proceeded more in the forward direction.

(3) If $Q < K$, the reaction is not in a state of equilibrium. i.e. the products are present in smaller amount as compared to the reactants.

Therefore, the reaction has proceeded more in back ward direction.

Le Chatelier's principle

This principle given by French scientist, Le chatelier is applicable to all systems in equilibrium. It deals with the effect of change in concentration, temperature or pressure on the equilibrium state.

The principle states that, “If a system in equilibrium is subjected to a change of temperature, pressure or concentration, the equilibrium is disturbed and shifts in the direction in which the effect of the change is imposed”.

Thus according to this principle :

(1) Increase in the concentration of a substance at equilibrium shifts the equilibrium in that direction in which the added substance is consumed. Thus addition of a reactant at equilibrium favours forward reaction. i.e. more of products will be formed.

Change mode at equilibrium

Any reactant added
Any product removed
Any reactant removed
Any product added

Shift of equilibrium

Forward direction, product formed
Forward direction, product formed.
Backward direction, product consumed.
Backward direction, product consumed, reactant formed

Order of ease of removal of substance is:

Gases > Liquid > Solid
(Most easily removed) (Most difficult to remove)

(2) The increase of temperature will make the reaction go in that direction in which heat is absorbed i.e., towards endothermic reaction. Thus, higher yields of products are obtained at higher temperatures in endothermic reactions. Exothermic reversible reactions are favoured at low temperature, because the effect of lowering of temperature is annulled by evolution of heat, i.e., when the reaction goes towards the products. In exothermic reactions, higher yields of products are obtained at low temperature.

(3) The increase of pressure at equilibrium shifts the system in that direction in which there is a decrease in volume, i.e. number of moles.

Applications of Le-Chatelier's principle

(1) To Physical equilibria

(i) **Effect of temperature on solubility :** Some solids dissolve in water with absorption of heat while some evolve heat on dissolution. Hence according to Le-chatelier's principle, solubility of those substances which dissolve with absorption of heat, increases with rise in temperature. Solids which evolve heat on dissolution, dissolve less at higher temperature. Their solubility increases with decrease in temperature.

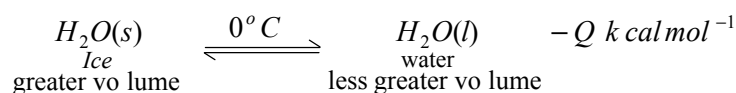
Example : (a) $KNO_3(s) \rightleftharpoons KNO_3(aq.) - Q \text{ kcal mol}^{-1}$

Thus, when KNO_3 dissolves in water, heat is absorbed, i.e. the solution cools down. So, with rise of temperature, solubility of KNO_3 increases.

(b) $Ca(OH)_2(s) + aq. \rightleftharpoons Ca(OH)_2(aq.) + Q \text{ kcal mol}^{-1}$. Dissolution of $Ca(OH)_2$ in water is accompanied by evolution of heat, So it's solubility decreases with rise in temperature.

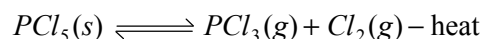
(ii) **Effect of pressure on solubility of gases :** When a gas dissolves in a liquid. It's volume decreases, hence on increasing pressure solubility of a gas increases solubility of a gas in water is increased by rise in pressure and lowering of temperature.

(iii) Effect of temperature and pressure on melting of Ice :

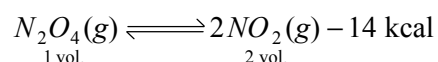


Extent of dissociation of PCl_5 will be more at: (a) Low pressure (b) High temperature (c) Excess of $PCl_5(g)$

Extent of dissociation of $PCl_5(s)$ will not be affected by adding more of $PCl_5(s)$ in the equilibrium.



(vii) **Dissociation of Dinitrogen tetra oxide** $N_2O_4(g)$



N_2O_4 will undergo dissociation to a greater extent at: (a) High temperature (b) Low pressure (c) Excess of $N_2O_4(g)$

Some important points

(1) If any chemical reaction, equilibrium is supposed to be established when velocity of mutual reactions become equal.

$$(2) K_p = K_c(RT)^{1-\frac{1}{2}}; K_p = K_c(RT)^{-\frac{1}{2}}; \frac{K_p}{K_c} \sqrt{\frac{1}{RT}}$$

(3) Equilibrium constant does not change with change in concentration of reactants.

(4) Law of mass action cannot be applied on irreversible reaction.

(5) Introduction of inert gas at constant volume has no effect on the position of equilibrium.

(6) Catalyst does not affect equilibrium constant.

(7) Le-chatelier principle is not applicable to solid-solid equilibrium.

(8) $n_p = n_r$ the $K_p = K_c$; Where $n_p =$ no. of moles of product; $n_r =$ no. of moles of reactants.
