Equilibrium

- Equilibrium is the state of a process in which the properties like temperature, pressure, and concentration etc of the system do not show any change with passage of time.
- In all processes which attain equilibrium, two opposing processes are involved.
- Equilibrium is attained when the rates of the two opposing processes become equal.
- If the opposing processes involve only physical changes, the equilibrium is called **Physical Equilibrium.**
- If the opposing processes are chemical reactions, the equilibrium is called **Chemical Equilibrium**.

Physical Equilibrium

- **Solid – liquid Equilibrium:** $H_2O(s) \rightleftharpoons H_2O(l)$
- **Liquid – Gas Equilibrium:** $H_2O(l) \rightleftharpoons H_2O(g)$
- **Solid – Solution Equilibrium:** Salt(Solid) $\rightleftharpoons$ Salt(in solution)
- **Gas –Solution equilibrium:** $CO_2(g) \rightleftharpoons CO_2$(in solution)

Equilibrium in Chemical Process

- **Reversible reaction:** A reaction in which not only the reactants react to form the products under certain conditions but also the products react to form reactants under the same conditions
  Examples: $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
- **Irreversible reaction:** A reaction cannot take place in the reverse direction, i.e. the products formed do not react to give back the reactants under the same condition.
  Example: $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(g)$
- Generally, a chemical equilibrium is represented as $a\,A + b\,B \rightleftharpoons c\,C + b\,D$
  Where A, B are reactants and C, D are products.

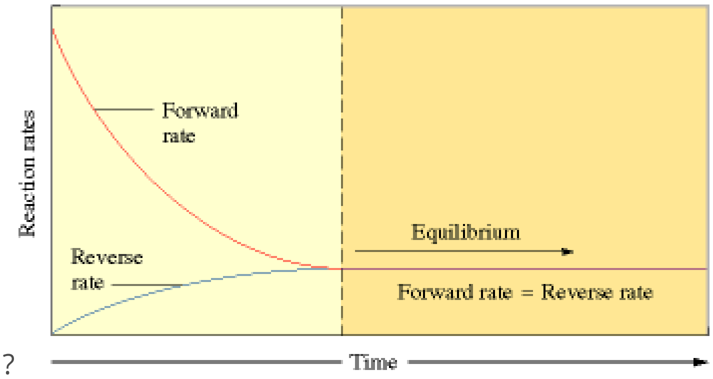
Note:

The double arrow between the left hand part and right hand part shows that changes are taking place in both the directions.

On the basis of extent of reaction, before equilibrium is attained chemical reactions may be classified into three categories.

- Those reactions which proceed to almost completion.
- Those reactions which proceed to almost only upto little extent.
- Those reactions which proceed to such an extent, that the concentrations of reactants and products at equilibrium are comparable.

- The equilibrium state is dynamic and not static in nature. A reaction is said to have attained equilibrium when the rate of forward reaction equals that of backward reaction



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- **Homogeneous equilibrium: ?A**ll the reactants and products of any reaction under equilibrium are in same physical state. Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- **Heterogeneous equilibrium?** :Physical state of one or more of the reacting species may differ i.e. all the reactants and products are not in same physical state.Example
  $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(l)$?

Characteristics of Equilibrium State

- It can be attained only if the reversible reaction is carried out in closed vessel.
- It can be attained from either side of the reaction.
- A catalyst can hasten the approach of equilibrium but does not alter the state of equilibrium.
- It is dynamic in nature i.e. reaction does not stop but both forward and backward reactions take place at equal rate.
- Change of pressure, concentration or temperature favours one of the reactions (forward or backward) resulting in shift of equilibrium point in one direction.

Law of Mass Action & Equilibrium Constant

"The rate at which a substance reacts is directly proportional to its active mass and rate of a chemical reaction is directly proportional to product of active masses of reactants each raised to a power equal to corresponding stoichiometric coefficient appearing in the balanced chemical equation".

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

Rate of reaction $\propto [A]^a.[B]^b$

or rate of reaction = $K[A]^a[B]^b$

where K is rate constant or velocity constant of the reaction at that temperature.

Unit of rate constant (K)

(where n is order of reaction.)

For unit concentration of reactants rate of the reaction is equal to rate constant or specific reaction rate.

Note:

Active mass is the molar concentration of the reacting substances actually participating in the reaction.

Hence,

Active mass = number of moles/volume in litres

Active mass of solid is taken as unity.

Also, Active mass of reactant (a) = Conc. × activity coefficient

i.e. a = Molarity × f **for dilute solution f = 1**