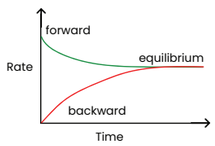
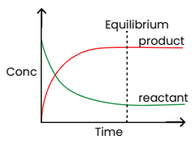
CHEMICAL EQUILIBRIUM

EQUILIBRIUM

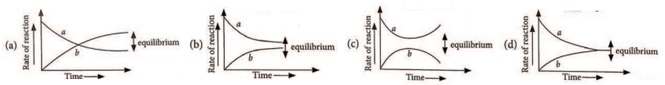
- The chemical reactions which takes place in both directions are called reversible reactions
- Equilibrium is the end state of a reversible reaction.
- Gaseous Equilibrium is established only in a closed container.
- At equilibrium, the rate of forward and backward reactions are equal.
- At equilibrium, the concentration of reactants & products becomes constant.

GRAPHICAL REPRESENTATIONS





Q. For the equilibrium A ⇌ B, the variation of the rate of the forward (a) & reverse (b) reaction with time is given by



PHYSICAL EQUILIBRIUM

- Such equilibrium is established in physical reactions.
- It is dynamic in nature.

LIQUID ⇌ VAPOUR EQUILIBRIUM

- Here vapour pressure is constant at a constant temp for given.

SOLID ⇌ LIQUID EQUILIBRIUM

- Established only at a constant temparature
- Ice-water equilibrium established at 0°C (at1 atm)

SOLID IN LIQUID EQUILIBRIUM

- Established only in a Saturated solution
- eg: Saturated sugar solution.
  Sugar (dissolved) ⇌ Sugar (undissolved)

GAS IN LIQUID EQUILIBRIUM

- Here solubility depends upon pressure (Henry's law)
- eg: Soda water

CO_2 (dissolved) ⇌ CO_2 (undissolved)

Q. Which of the given statements does not elucidate the equilibrium state precisely?
(A) The equilibrium can be approached from either direction.
(B) The equilibrium can be attained only if the system is an isolated system.
(C) The free energy change at constant pressure and temperature is zero.
(D) It is dynamic in nature.

CHEMICAL EQUILIBRIUM

- Chemical equilibrium approaches from both forward & backward direction
- Chemical equilibrium is dynamic in nature.

EQUILIBRIUM CONSTANT [K_c]

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

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

REACTION QUOTIENT [Q]

- At any time during the reaction $aA+bB \rightleftharpoons cc+dD$ the ratio $\frac{[C]^c [D]^d}{[A]^a [B]^b}$ is known as concentration quotient, Q_c.
- At equilibrium $Q_c = K_c$

CHARACTERISTICS OF K [eqb. const]

1. Value of K does not depends upon initial concentration of reactants and products.
2. Value of K does not depends upon the direction from which equilibrium is attained.

Q In the given reaction: $A+2B \rightleftharpoons 2C$, 2 moles each of A & B present in 10 L of solution combine to form 1 mole of C. Calculate K_c for the reaction.

(A) 1.5 (B) 6.67 (C) 0.15 (D) 2.3

Applications of K & Q

- Value of K depends only on temperature.
- If K for the reaction aA + bB ⇌ cC+dD is K, then K for the reaction cC+dD ⇌ aA+ bB will be $\frac{1}{K}$
- If K for the reaction aA + bB ⇌ cC+dD is K, then K for the reaction naA+ nbB ⇌ ncC + ndD will be $(K)^n$
- During the addition of two reactions having equilibrium constants K_1 & K_2, then the net Constant $K = K_1 \times K_2$
- During the subtraction of a reaction having constant K_2 from a reaction having constant K_1, then the net constant $K = K_1/K_2$
- If Q<K, the reaction will proceed in forward direction
- If Q>K, the reaction will proceed in backward direction
- If Q=K, the system is in equilibrium.
- If $K > 10^3$, the reaction is almost complete in forward direction.
- If $K < 10^{-3}$, the reaction is in backward direction.
- If K is in b/w 10^3 & 10^{-3}, almost same reaction takes place in both forward and backward direction

Q At a given temperature, the equilibrium constants for the reactions,
$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$ & $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$
are K_1 and K_2 respectively. If K_1 is 4×10^{-3} . then K_2 will be
(A) 8×10^{-3} (B) 16×10^{-3} (C) 6.25×10^{4} (D) 6.25×10^{6}

HOMOGENEOUS EQUILIBRIUM

- If they are in solid or liquid phase(or aqueous), K can be represented as Kc.
- If they are in gaseous phase, K can be represented as Kp
- For a general reaction
  $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \& \quad K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

- $K_p = K_c (RT)^{\Delta n_g}$ $\Delta n_g = n_p - n_R$

UNIT OF EQUILIBRIUM CONSTANT

- Unit of K_c = $(mol/L)^{\Delta n_g}$
- Unit of K_p = $(atm)^{\Delta n_g}$
- If $\Delta n_g = 0$, equilibrium constant has no unit

HETEROGENEOUS EQUILIBRIUM

- In heterogeneous equilibrium, concentration of pure solid & pure liquid is taken as one
- eg : $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
  $K_p = P_{CO_2}$

Q For the reaction,
$Fe_2N_{(s)} + \frac{3}{2}H_{2(g)} \rightleftharpoons 2Fe_{(s)} + NH_{3(g)}$
(a) $K_c = K_p(RT)$ (b) $K_c = K_P(RT)^{-1/2}$
(c) $K_c = K_P(RT)^{1/2}$ (d) $K_c = K_P(RT)^{3/2}$

LE CHATELIER'S PRINCIPLE

According to Le-chatelier's principle, if a system at equilibrium is subjected to a change in concentration, temperature or pressure, the equilibrium will shifts automatically in one direction which will nullify the effect of the change.

1. Conc. of reactant increases → shift towards forward reaction.
2. Conc. of product decreases → shift towards forward reaction.
3. Conc. of reactant decreases → shift towards backward reaction.
4. Conc. of product increases → shift towards backward reaction.
5. Pressure increases → shift towards lesser number of gaseous moles
6. Pressure decreases → shift towards higher number of gaseous moles
7. No. of gaseous moles of reactants & products are equal, pressure has no effect.
8. If temperature increases → shift towards endothermic
9. If temperature decreases → shift towards exothermic
10. Catalyst helps to attain eqm state easily. After the establishment of eqm, catalyst has no effect.
11. Addition of inert gas at constant volume, no effect.
12. Addition of inert gas at constant pressure → shift towards higher number of gaseous moles

Q Which one of the following conditions will favour maximum formation of the product in the reaction $A_2(g) + B_2(g) \rightleftharpoons X_2(g)$. ΔrH = -XkJ/mol?

(A) Low temperature and high pressure (B) High temperature and high pressure
(C) Low temperature and low pressure (D) High temperature and low pressure