

CHEMICAL EQUILIBRIUM

Topic-1

Equilibrium reactions and law of mass action, factors affecting the rate of the reaction

VERY SHORT ANSWER QUESTIONS

1. What is a reversible reaction?

Ans:

A reaction is said to be reversible, if both the forward and the backward reactions are taking place simultaneously under the given experimental conditions.

2. What is reversible reaction?

Ans:

Irreversible reactions: in these reactions reactants are converted into products and products cannot be converted into reactants

3. What is equilibrium state?

Ans:

The stage or state at which the rate of forward reaction is equal to the rate of the reverse reaction in a reversible reaction is known as the equilibrium stage or state.

4. What is law of mass action?

Ans:

The rate of a chemical reaction at a temperature at any instant is proportional to the product of the active masses of the reactants. This law is applicable to all reactions i.e. reversible and irreversible occurring in the gas phase or in the liquid phase.

5. Write expression for equilibrium constant.

Ans:

For the reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant. Is given by

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

K_f = forward reaction rate constant.

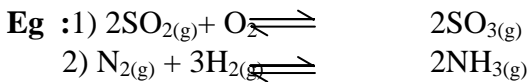
K_b = backward reaction rate constant.

The equilibrium constant

$$K_c = \frac{\text{product of the concentration of products}}{\text{product of the concentration of reactants}}$$

6. What is homogeneous equilibrium?

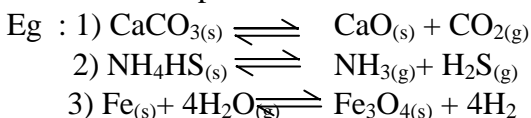
Homogeneous equilibrium: All the reactants and products are present in same physical state. i.e same phase.



7. What is heterogeneous equilibrium?

Ans:

Heterogeneous equilibrium: Reactants and products are in different physical states or different phase.



SHORT ANSWER QUESTIONS

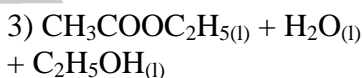
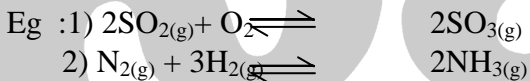
1. Explain the types of equilibrium?

Ans:

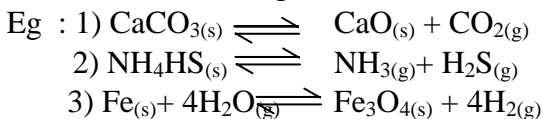
Types of chemical equilibrium:

- Based on the physical states of substances equilibrium is of two types.

1) **Homogeneous equilibrium:** All the reactants and products are present in same physical state. i.e same phase.



2) **Heterogeneous equilibrium:** Reactants and products are in different physical states or different phase.



2. Explain the relation ship between K_c and K_p ?

Ans:

Relationship between k_p and k_c :

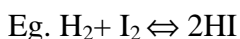
$$k_p = k_c (RT)^n$$

R = gas constant, T = absolute temperature

□ n = change in number of moles

$$= n_p - n_R \text{ (no. of moles of gaseous products – no. of moles of gaseous reactants)}$$

case (i) if $n_p = n_R$, $\Delta n = 0$, $k_p = k_c$



- (ii) if $n_P > n_R$, $\Delta n = +ve$, $k_p > k_c$
 $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
- iii) If $n_P < n_R$, $\Delta n = -ve$, $k_p < k_c$
 $N_2 + 3H_2 \rightleftharpoons 2NH_3$

3. Explain K_c and K_p ?

Ans:

$aA + bB \rightleftharpoons cC + dD$, the equilibrium constant.

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

K_f = forward reaction rate constant.

K_b = backward reaction rate constant.

The equilibrium constant

$$k_c = \frac{\text{product of the concentration of products}}{\text{product of the concentration of reactants}}$$

Partial pressure of the gas = mole fraction of gas \times total pressure.

$$K_p = \frac{k_f}{k_b} = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

$$K_p = \frac{\text{product of partial pressures of products}}{\text{product of partial pressures of reactants}}$$

k_c = equilibrium constant in terms of molar concentration.

k_p = equilibrium constant in terms of partial pressure.

$$\text{Active mass} = \frac{\text{no. of moles}}{\text{volume in litres}}$$

Active mass is considered for gas or liquid.

The active mass of a solid is unity whatever may be its mass.

4. What are the characteristics of equilibrium constant?

Ans:

Characteristics of equilibrium constant: (k_p or k_c)

- The value of k depends on the nature of the reaction.
- The value of k will be a constant for a given reaction at a given temperature.
- The value of k depends on temperature of reaction.
- The value of k is independent of concentration and pressure.

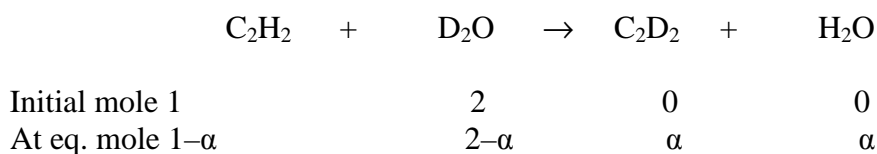
LONG ANSWER QUESTIONS

1. For the gaseous reaction: $C_2H_2 + D_2O \rightarrow C_2D_2 + H_2O$, ΔH is 530 cal. At $25^\circ C$, $K_p = 0.82$. Calculate how much C_2D_2 will be formed if 1 mole of C_2H_2 and 2 moles of D_2O are put together at a total pressure of 1 atm at $100^\circ C$?

Sol. Firstly calculate K_p at $100^\circ C$ by using equation

$$\log (K_p)_{100^\circ C} / (K_p)_{25^\circ C} = \Delta H / 2.303R (T_2 - T_1 / T_1 T_2)$$

On solving we get, $(K_p)_{100^\circ C} = 0.98$

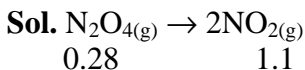


$$\Delta 0.98 = \alpha^2 / (1-\alpha)(2-\alpha)$$

$$0.02\alpha + 2.94\alpha - 1.96 = 0$$

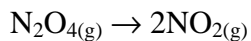
On solving we get, $\alpha = 0.75$

2. An equilibrium mixture at 300K contains N_2O_4 and NO_2 at 0.28 and 1.1 atm respectively. If the volume of container is doubled, calculate the new equilibrium pressure of two gases.



$$K_p = (1.1)^2 / 0.28 = 4.32 \text{ atm}$$

When volume is doubled pressure will reduced to half



$$(0.28/2 - p) \quad (1.1/2 + 2p)$$

$$\square K_p = (1.1/2 + 2p)^2 / (0.28/2 - p) = 4.32 \text{ @ } p = 0.045$$

$$\square p(N_2O_4) = 0.14 - 0.045 = 0.095$$

$$p(NO_2) = 0.55 - 0.045 = 0.64 \text{ atm}$$

3. At 540K, 0.10 mole of PCl_5 are heated in a 8 litre flask. The pressure of the equilibrium mixture is found to be 1 atm. Calculate the K_p for the reaction?

Sol. $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$

$$0.1 - \alpha \quad \alpha \quad \alpha$$

$$\text{Total no. of moles} = 0.1 - \alpha + \alpha + \alpha = 0.1 + \alpha$$

$$\text{Now, } P = nRT/V \quad \square \alpha 1 = (0.1 + \alpha) \times 0.082 \times 540/8$$

$$\square (0.1 + \alpha) = 0.180$$

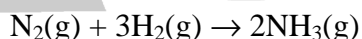
$$\alpha = 0.08$$

$$\text{So, } K_p = (p_{\text{PCl}_3} \times p_{\text{Cl}_2}) / (p_{\text{PCl}_5})$$

$$= (\alpha p / 0.1 + \alpha) (\alpha p / 0.1 + \alpha) / (0.1 - \alpha) / (0.1 + \alpha) p = \alpha^2 p / (0.1 + \alpha) (0.1 - \alpha)$$

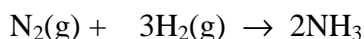
$$= 0.0064 \times 1 / 0.18 \times 0.02 = 1.78 \text{ atm}$$

4. In a mixture of N_2 and H_2 initially in a mole ratio of 1:3 at 30 atm and 300°C , the percentage of ammonia by volume under the equilibrium is 17.8. Calculate the equilibrium constant (K_p) of the mixture, for the reaction?



Sol. Let the initial moles of N_2 and H_2 be 1 and 3 respectively (this assumption is valid as K_p will not depend on the exact no. of moles of N_2 and H_2 . One can even start with x and $3x$).

Alternatively



$$\text{Initial} \quad 1 \quad 3 \quad 0$$

$$\text{At eqb.} \quad 1-x \quad 3-3x \quad 2x$$

Since % by volume of a NH_3 gas is same as % by mole,

$$\square 2x/4 - 2x = 0.178$$

$$\square x = 4 \times 0.178 / (2 + 2 \times 0.178) = 0.302$$

$$\square \text{ Mole fraction of H}_2 \text{ at equilibrium} = 3 - 3x/4 - 2x = 0.6165$$

$$\text{Mole fraction of N}_2 \text{ at equilibrium} = 1 - 0.6165 - 0.178$$

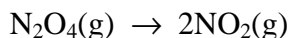
$$= 0.2055$$

$$\square K_P = (X_{\text{NH}_3} \times P_T)^2 / (X_{\text{N}_2} \times P_T)(X_{\text{H}_2} \times P_T)^3 = (0.178 \times 30)^2 / (0.2055 \times 30)(0.6165 \times 30)^3$$

$$= 7.31 \times 10^{-4} \text{ atm}^{-2}$$

5. The density of an equilibrium mixture of N₂O₄ and NO₂ at 1 atm. and 348 K is 1.84 g dm⁻³. Calculate the equilibrium constant of the reaction, N₂O₄(g) ⇌ 2NO₂(g).?

Sol. Let us assume that we start with C moles of N₂O₄(g) initially.



Initial	C	0
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At equilibrium	C(1-α)	2Cα
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Where α is the degree of dissociation of N₂O₄(g)

Since $\frac{\text{Total moles at equilibrium}}{\text{Total moles initially}} = \frac{\text{Vapour density initial}}{\text{Vapour density at equilibrium}}$

$$\text{Initial vapour density} = 92/2 = 46$$

$$C(1+\alpha)/C = 46/d$$

Since vapour density and actual density are related by the equation,

$$\text{V.D.} = \rho RT/2P = 1.84 \times 0.082 \times 348/2$$

$$= 26.25$$

$$\square 1 + \alpha = 46/26.25 = 1.752$$

$$\square \alpha = 0.752$$

$$\square K_p = (2C\alpha/C(1+\alpha) \times P_T)^2 / C(1-\alpha)/C(1+\alpha) \times P_T = (2 \times 0.75/1.752 \times 1)^2 / 0.248/1.752 \times$$

1

$$= 5.2 \text{ atm}$$

6. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction?

$2AB_2(g) \rightarrow 2AB(g) + B_2(g)$ with a degree of dissociation x , which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant, K_p and the total pressure P .

Sol. Let the initial pressure of $AB_2(g)$ be P_1



$$P_1(1-x) \quad P_1x \quad P_1x/2$$

The total pressure is $= P_1(1+x/2) \approx P_1$ ($\because x \ll 1$) $\square P_1 = P$

$$\text{So, } K_p = \frac{(Px)^2 \times Px/2}{[P(1-x)]^2} \approx \frac{Px^3}{2}$$

$$\square x = \sqrt[3]{2K_p/P}$$

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