UNIT-8 PHYSICAL AND CHEMICAL EQUILIBRIUM

MY REVISION TIMELINE:-

SUMMARY:-

- > Types of equilibrium:
 - Physical equilibrium
 - Chemical equilibrium
- Chemical equilibrium types:
 - Homogeneous equilibrium: All reactants and products are in same phase.
 - Heterogeneous equilibrium: All reactants and products are in different phase.
- Law of mass action: At any instant, rate of a chemical reaction at a given temperature is directly proportional to the product of the active masses of the reactants at that instant. Rate α [Reactant]^x

Where x is stoichiometric coefficient.

> Relation between equilibrium constants 'k_p' and 'k_c': $k_p = k_c (RT)^{\Delta ng}$

Where Δng is the difference between the sum of number of moles of products and the sum of number of moles of reactants in the gas phase.

When $\Delta ng = 0$, $k_p = k_c$

When
$$\Delta ng = +ve$$
, $k_p > k_c$

When
$$\Delta ng = -ve$$
, $k_p < k_c$

- 'Q' is defined as the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants.
 - $Q = k_c$, the reaction is in equilibrium state.
 - $Q > k_c$, the reaction will proceed in the reverse direction i.e., formation of reactants.
 - $Q < k_c$, the reaction will proceed in the forward direction i.e., formation of products.
- Le Chatelier's principle: If a system at equilibrium is disturbed, then the system shifts itself in a direction that nullifies the effect of the disturbance.
- > Van't Hoff equation:

 $\frac{d(\ln k)}{dT} = \frac{\Delta H^{\circ}}{RT^{2}} \rightarrow \text{Differential form of Van't Hoff equation} \\ \log \frac{k_{2}}{k_{1}} = \frac{\Delta H^{\circ}}{2.303R} \left[\frac{T_{2} - T_{1}}{T_{2}T_{1}} \right] \rightarrow \text{Integral form of Van't Hoff equation}$

TEXTBOOK EVALUATION

Multiple choice questions:-

If K_b and K_f for a reversible reactions are 0.8 x 10⁻⁵ and 1.6 x 10⁻⁴ respectively, the value of the equilibrium constant is

 (a) 20
 (b) 0.2 x 10⁻¹

(d) None of these

(a) 20 (c) 0.05 Explanation:

 $k_{eq} = \frac{k_f}{k_b}$ $k_{eq} = \frac{1.6 \times 10^{-4}}{0.8 \times 10^{-5}}$

 $k_{eq} = 20$

- 2. At a given temperature and pressure, the equilibrium constant values for the equilibria $3A_2 + B_2 + 2C \stackrel{K_1}{\longrightarrow} 2A_3BC$ and $A_3BC \stackrel{K_2}{\longrightarrow} 3/2 A_2 + \frac{1}{2} B_2 + C$. The relation between K_1 and K_2 is
 - (a) $K_1 = \frac{1}{\sqrt{K_2}}$ (b) $K_2 = K_1^{-1/2}$ (c) $K_1^2 = 2K_2$ (d) $\frac{K_1}{2} = K_2$ Explanation: $K_1 = \frac{[A_3BC]^2}{[A_2]^3[B_2][C]^2} \Rightarrow (1)$ $K_2 = \frac{[A_2]^{3/2}[B_2]^{1/2}[C]}{[A_3BC]} \Rightarrow (2)$ $K_2^2 = \frac{[A_2]^3[B_2][C]^2}{[A_3BC]^2} \Rightarrow (3)$ Comparing equation (1) and (3) $K_2^2 = \frac{1}{K_1}$
- 3. The equilibrium constant for a reaction at room temperature is K_1 and that at $\overline{700 \text{ K}}$ is K_2 . If $K_1 > K_2$ then
 - (a) The forward reaction is exothermic
 - (b) The forward reaction is endothermic
 - (c) The reaction does not attain equilibrium
 - (d) The reverse reaction is exothermic

Explanation:

$$T_{1} = 298K$$

$$T_{2} = 700K$$

$$\log(\frac{k_{2}}{k_{1}}) = \frac{\Delta H^{\circ}}{2.303R} [\frac{T_{2} - T_{1}}{T_{2}T_{1}}]$$

$$T_{2} > T_{1} \text{ and } k_{1} > k_{2}$$

$$\Delta H^{\circ} = \frac{2.303R \log(\frac{k_{2}}{k_{1}})}{[\frac{T_{2} - T_{1}}{T_{2}T_{1}}]}$$

$$\Delta H^{\circ} = \frac{-ve}{+ve}$$

$$\Delta H^{\circ} \text{ is -ve}$$

Therefore forward reaction is **exothermic**.

4. The formation of ammonia from $N_2(g)$ and $H_2(g)$ is a reversible reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$

What is the effect of increase of temperature on this equilibrium reaction

 $K_2 = K$

(a) equilibrium is unaltered (b) formation of ammonia is favoured (c) equilibrium is shifted to the left (d) reaction rate does not change **Explanation:** Formation of NH₃ is exothermic, so reverse is endothermic. With increase in temperature, equilibrium shifts to left. 5. Solubility of carbon dioxide gas in cold water can be increased by (a) increase in pressure (b) decrease in pressure (c) increase in volume (d) none of these **Explanation:** $H_2O_{(1)}$ (2 mole) + $CO_{2(g)} \rightleftharpoons H_2CO_{3(1)}$ (1 mole) With increase in pressure forward reaction is favoured. 6. Which one of the following is incorrect statement? (a) for a system at equilibrium, Q is always less than the equilibrium constant (b) equilibrium can be attained from either side of the reaction (c) presence of catalyst affects both the forward reaction and reverse reaction to the same extent (d) Equilibrium constant varied with temperature 7. K₁ and K₂ are the equilibrium constants for the reactions respectively. $N_2(g) + O_2 \stackrel{K_1}{\longleftarrow}$ 2NO(g) and 2NO(g) + O₂(g) $\stackrel{\kappa_2}{\longrightarrow}$ 2NO₂ (g). What is the equilibrium constant for the reaction NO₂(g) \rightleftharpoons $\frac{1}{2}N_2(g) + O_2(g)$? (a) $\frac{1}{\sqrt{K_1K_2}}$ (b) $(K_1 = K_2)^{1/2}$ (d) $\left(\frac{1}{K_1 K_2}\right)^{3/2}$ (c) $\frac{1}{2K_1K_2}$ **Explanation:** $K_{1} = \frac{[NO]^{2}}{[N_{2}][O_{2}]}; K_{2} = \frac{[NO_{2}]^{2}}{[NO]^{2}[O_{2}]}; K = \frac{[N_{2}]^{2}[O_{2}]}{[NO_{2}]}$ $\sqrt{K_1} = \frac{[NO]}{[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}}; \sqrt{K_2} = \frac{[NO_2]}{[NO][O_2]^{\frac{1}{2}}}$

 $K = \frac{1}{\sqrt{K_1 K_2}}$

8. In the equilibrium, $2A(g) \rightleftharpoons 2B(g) + C_2(g)$ the equilibrium concentrations of \overline{A} , \overline{B} and \overline{C} , at 400 K are 1 x 10⁴ M, 2.0 x 10⁻³ M, 1.5 x 10⁻⁴ M respectively. The value of K_c. for the equilibrium at 400 K is

(b) 0.09 (d) 3 x 10⁻²

(a) 0.06 (c) 0.62 Explanation: $2A_{(g)} \rightleftharpoons 2B_{(g)} +$

$$2A_{(g)} \rightleftharpoons 2B_{(g)} + C_{2(g)}$$

$$k = \frac{[B]^2[C_2]}{[A]^2}$$

$$k = \frac{(2 \times 10^{-3})^2 (1.5 \times 10)^{-4}}{(1 \times 10^{-4})^2}$$

 $\sqrt{K_1 \cdot K_2} = \frac{[NO_2]}{[N_2]^{\frac{1}{2}}[O_2]}$

k = 0.06

9. An equilibrium constant of 3.2 x 10⁻⁶ for a reaction means, the equilibrium is
(a) largely towards forward direction
(b) largely towards reverse direction
(c) never established
(d) none of these

Explanation: $k_{c} = \frac{[products]}{[reactants]}$ $3.2 \ge 10^{-6} = \frac{[products]}{[reactants]}$ $k_{c} = 10^{-3} \text{ indicates } [reactants] >> [products]$ $10. \frac{K_{c}}{K_{p}} \text{ for the reaction, } N_{2}(g) + 3H_{2}(g) \rightleftharpoons 2NH_{3}(g) \text{ is}$ (a) $\frac{1}{RT}$ (b) $g\sqrt{RT}$ (c) RT
(d) $(RT)^{2}$ Explanation: $N_{2}(g) + 3H_{2}(g) \rightleftharpoons 2NH_{3}(g)$ $\Delta n_{g} = 2 - 4 = -2$ $K_{p} = K_{c} (RT)^{-2}$

 $\frac{K_c}{K_p} = (RT)^2$

11. For the reaction, $AB(g) \rightleftharpoons A(g) + B(g)$, at equilibrium, AB is 20% dissociated at a total pressure of R The equilibrium constant K is related to the total pressure by the expression

(a) $P = 24 K_p$				(b) $P = 8 K_p$
(c) $24 p = K_p$				(d) none of these
Explanation:				
	AB	A	В	
Initial no. of moles	100	-	-	\frown X
No. of moles	20	20	20	
dissociated and				
formed				$\lambda \times$
No. of moles at	80	20	20	
equilibrium				
Total no of males		1:1	. 00	20 20 120

Total no. of moles at equilibrium = 80 + 20 + 20 = 120

$$K_{p} = \frac{\frac{P_{A}P_{B}}{P_{AB}}}{K_{p}} = \frac{\left[\frac{20 P}{120}\right]\left[\frac{20 P}{120}\right]}{\left[\frac{80 P}{120}\right]} = \frac{P}{24}$$

 $24K_p = P$

12. In which of the following equilibrium, K and K are not equal?

(a) 2NO(g) ≓ N₂(g) + O₂(g)
(b) SO₂(g) + NO₂(g) ≓ SO₃(g) + NO(g)
(c) H₂(g) + I₂(g) ≅ 2HI(g)
(d) PCI₅(g) ≅ PCI₃(g) + CI₂(g)
Explanation:
For reactions given in options (a), (b) and (c) Δn_g = 0
For option (d) Δn_g = 2 - 1 = 1
∴ K_p = K_c (RT)
13. If x is the fraction of PCI₅ dissociated at equilibrium in the reaction,
PCI₅ ≅ PCI₃ + CI₂
then starting with 0.5 mole of PCI₅ the total number of moles of reactants and products at equilibrium is
(a) 0.5 - x
(b) x + 0.5

(a) 0.5 - x(b) x + 0.5(c) 2x + 0.5(d) $x \pm 1$

Explanation:

	PCl ₅	PCl ₃	Cl ₂
Initial no. of moles	0.5	_	-
No. of moles dissociated	х	—	-
No. of moles at equilibrium	0.5 – x	х	х

Total no. of moles at equilibrium =0.5-x + x + x

= 0.5 + x

14. The values of K_{p1} and K_{p2} for the reactions X ≓ Y + Z and A ≓ 2B are in the ratio 9 : 1 if degree of dissociation and initial concentration of X and A be equal then total pressure at equilibrium P₁, and P₂ are in the ratio
(a) 36 • 1

(a) 36 : 1					(b)	1:1
(c) 3 : 1					(d)	1:9
Explanation:						
	X	È y+	Z		È 2B	
	x	у	z	A	В	
Initial no. of moles	a	-	_	a	-	
Number of moles dissociated	X	_	_	x	-	O_{λ}
No. of moles at equilibrium	a – x	Х	x	a – x	2x	\searrow
Total no.	a – x	+ x +	x +	a – x	+2x	
of moles at		a + x		a +	- x	
equilibriant				, u		
$\frac{K_{P_1}}{K_{P_2}} = \frac{P_y F}{P_x}$	$\frac{P_{a}}{P_{B}^{2}}$	() x)	[(a)	-r)	1
$\frac{\mathbf{K}_{\mathbf{P}_{1}}}{\mathbf{K}_{\mathbf{P}_{2}}} = \boxed{\frac{1}{2}}$	$\frac{\left(\frac{a}{a+x}\right)P_1}{\frac{(a-x)}{(a+x)}}$	$\frac{a+x}{a+x}$	P_1	$\times \left[\frac{\frac{(a)}{(a)}}{\frac{4}{(a)}} \right]$	$\frac{x^{\prime}}{x^{2}P_{2}^{2}}$ $\frac{x^{\prime}}{x^{2}P_{2}^{2}}$ $+x)^{2}$	2
$=\left(\frac{1}{(a)}\right)$	$\frac{x^2 \mathbf{P}_1}{(a-1)(a-1)}$	$\overline{(x)}$	$\left(\frac{(a-b)}{a}\right)$	$\frac{(x)(a+1)}{4x^2P_2}$	$\left(\frac{+x}{x}\right)$	*
	$\frac{\mathbf{K}_{\mathbf{P}_1}}{\mathbf{K}_{\mathbf{P}_2}} =$	$\frac{P_1}{4P_2}$				
Given that	$\frac{K_{P_1}}{K_{P_2}} =$	$\frac{9}{1}$				
	$\frac{9}{1} =$	$\frac{P_1}{4P_2}$	$\Rightarrow \frac{P_1}{P_2}$	$=\frac{36}{1}$		

$P_1:P_2 = 36:1$

15. In the reaction, $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^{-}(aq)$, if the concentration of OH⁻ ions is decreased by ¹/₄ times, then the equilibrium concentration of Fe³⁺ will

(a) not changed(c) increase by 4 times

(b) also decreased by ¼ times(d) increase by 64 times

Explanation:

$$K_{\rm C} = [{\rm Fe}^{3+}] \times \frac{1}{64} [{\rm OH}^{-}]^{3}$$

To maintain K_C as constant, concentration of Fe^{3+} will **increase by 64 times**. **16.** Consider the reaction where $K_p = 0.5$ at a particular temperature

 $PCI_5(g) \rightleftharpoons PCI_3(g) + Cl_2(g)$ if the three gases are mixed in a container so that the partial pressure of each gas is initially 1 atm, then which one of the following is true?

(a) more PCI₃ will be produced
(c) more PCI₅ will be produced
Explanation:

(b) more Cl₂ will be produced (d) none of these

 $Q = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_3}}$

 $K_{p} = 0.5$

$$Q = \frac{1 \times 1}{1}$$

 $Q > k_{p}$. Therefore **more PCl**₅ will be produced.

17. Equimolar concentrations of H_2 and I_2 are heated to equilibrium in a 1 litre flask. What percentage of initial concentration of H_2 has reacted at equilibrium if rate constant for both forward and reverse reactions are equal

(a) 33%
(b) 66%
(c)
$$(33)^2$$
%
Explanation:
V = 1L
H₂ + I₂ \rightleftharpoons 2HI
[H₂]_{initial} = [I₂]_{initial} = a
[H₂]_{eq} = [I₂]_{eq} = (a - x)

and
$$[HI]_{eq} = 2x$$

 $K_{C} = \frac{[HI]^{2}}{[H_{2}][I_{2}]}$
 $\therefore K_{C} = \frac{4x^{2}}{(a-x)^{2}}$

Given that $K_{c} = \frac{K_{f}}{K_{r}} = 1$

$$\therefore 4x^{2} = (a - x)^{2}$$

$$4x^{2} = a^{2} + x^{2} - 2ax$$

$$3x^{2} + 2ax - a^{2} = 0$$

$$x = -a \& x = \frac{a}{3}$$

Degree of dissociation = $\frac{a}{3} \times 100$

Degree of dissociation = 33.33%

18. In a chemical equilibrium, the rate constant for the forward reaction is 2.5 x 10² and the equilibrium constant is 50. The rate constant for the reverse reaction is
(a) 11.5
(b) 5

(d) 2×10^3

(a) 11.5 (c) 2 x 10² **Explanation:** $K_f = 2.5 \times 10^2$ $K_C = 50$ $K_f = ?$ $K_C = \frac{K_f}{K_r}$ $50 = \frac{2.5 \times 10^2}{K_r}$

 $K_r = 5$

19. Which of the following is not a general characteristic of equilibrium involving physical process

(a) Equilibrium is possible only in a closed system at a given temperature

(b) The opposing processes occur at the same rate and there is a dynamic but stable condition

(c) All the physical processes stop at equilibrium /

(d) All measurable properties of the system remains constant

20. For the fórmation of two moles of $SO_3(g)$ from SO_2 and O_2 , the equilibrium constant is K_1 . The equilibrium constant for the dissociation of one mole of SO_3 into SO_2 and O_2 is

(a)
$$\frac{1}{K_1}$$

(c) $\left(\frac{1}{K_1}\right)^{1/2}$
Explanation:

 $2SO_{2} + O_{2} \rightleftharpoons 2SO_{3}$ $K_{1} = \frac{[SO_{3}]^{2}}{[SO_{2}]^{2}[O_{2}]}$ Dissociation of one mole of SO₃ $SO_{3} \rightleftharpoons SO_{2} + \frac{1}{2}O_{2}$ $K_{2} = \frac{[SO_{2}][O_{2}]^{1/2}}{[SO_{3}]}$



21. Match the equilibria with the corresponding conditions

- (i) Liquid ⇒ Vapour
 (ii) Solid ⇒ Liquid
 (iii) Solid ⇒ Vapour
 (iii) Solid ⇒ Liquid
 (iv) Solute (s) ⇒ Solute (Solution)
 1. Melting point
 2. Saturated solution
 3. Boiling point
 4. Sublimation point
- 5. Unsaturated solution

(i)	(ii)	(iii)	(iv)
(a) 1	2	3	4
(b) 3	1	4	2
(c) 2	1	3	4
(d) 3	2	4	5

- **22.** Consider the following reversible reaction at equilibrium, $A + B \rightleftharpoons C$, if the concentration of the reactants A and B are doubled, then the equilibrium constant will
 - (a) be doubled

(b) become one fourth(d) remain the same

(c) be halved

Explanation:

- $A + B \rightleftharpoons C$
- $\mathbf{K}_{\mathbf{C}} = \frac{[C]}{[A][B]}$

If [A] and [B] are doubled, [C] increases 4 times to maintain K_C as constant.

: Equilibrium constant will remain the same.

23. $[CO(H_2O)_6]^{2+}$ (aq) (pink) + 4C⁻ (aq) \rightleftharpoons $[COCI_4]^{2-}$ (aq) (blue) + 6H₂O (1) In the above reaction at equilibrium, the reaction mixture is blue in colour at room temperature. On cooling this mixture, it becomes pink in colour. On the basis of this information, which one

of the following is true?

(a) $\Delta H > 0$ for the forward reaction

- (b) $\Delta H = 0$ for the reverse reaction
- (c) $\Delta H < 0$ for the forward reaction
- (d) Sign of the ΔH cannot be predicted based on this information.

Explanation:

Decrease in temperature, favours the reverse reaction (i.e.) reverse reaction is exothermic and forward reaction is endothermic ($\Delta H > 0$)

- **24.** The equilibrium constants of the following reactions are:
 - $N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1 $N_2 + O_2 \rightleftharpoons 2NO$; K_2 $H_2 + 12O_2 \rightleftharpoons H_2O$; K_3

The equilibrium constant (K) for the reaction; $2NH_3 + 5/2 O_2 \rightleftharpoons 2NO + 3H_2O$ will be (a) $K_2^3 \frac{K_3}{K_1}$ (b) $K_1 \frac{K_3^3}{K_2}$

(a)
$$K_2^3 \frac{K_3}{K_1}$$
 (b) $K_1 \frac{K_3^3}{K_2}$
(c) $K_2 \frac{K_3^3}{K_1}$ (d) $K_2 \frac{K_3}{K_1}$
Explanation:
 $k = \frac{[k_2][k_3]^3}{[k_1]}$
 $k = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[H_2O]^3}{[H_2]^3[O_2]^{3/2}} \times \frac{[N_2][H_2]^3}{[NH_3]^2}$
 $k = \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{3/2}}$

25. A 20 litre container at 400 K contains $CO_2(g)$ at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value will be

Given that: SrCO₃(s) \rightleftharpoons SrO(s) + CO₂(g) (a) 2 litre (b) 5 litre (c) 10 Litr

 $V_2 = 5L$

Write brief answers to the following questions:-

26. If there is no change in concentration, why is the equilibrium state considered dynamic?

Because both **forward** and **reverse reaction** are still occurring with the **same rate**. No **macroscopic change** is observed.

- 27. For a given reaction at a particular temperature, the equilibrium constant has constant value. Is the value of Q also constant? Explain.
 - > The equilibrium constant is a constant and it is for **equilibrium condition**.
 - > But 'Q', the reaction quotient is not a constant as it is for **non-equilibrium condition**.
 - 'Q' is the ratio of the product of active masses of a reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that fo reactants, under non-equilibrium conditions.
 - $\mathbf{Q} = \mathbf{k}_{\mathbf{c}}$, the reaction is in **equilibrium** state.
 - **Q** > **k**_c, the reaction will proceed in the **reverse** direction i.e., formation of reactants.
 - $Q < k_c$, the reaction will proceed in the **forward** direction i.e., formation of products.
- 28. What is the relation between K_p and K_c . Give one example for which K_p is equal to Kc.
 - > Relation between K_p and K_c : $k_p = k_c (RT)^{\Delta ng}$
 - > When $\Delta ng = 0$, $k_p = k_c$. Example: $\mathbf{H}_{2(g)} + \mathbf{I}_{2(g)} \rightleftharpoons 2\mathbf{HI}$ (g)
- 29. For a gaseous homogeneous reaction at equilibrium, number of moles of products are greater than the number of moles of reactants. Is K_c is larger or smaller than K_p .

 $\Delta n_{g} = \Sigma n_{p(g)} - \Sigma n_{r(g)}$ $\Delta n_{p(g)} \text{ is greater, } \Delta n_{(g)} = +ve$ $K_{p} = K_{C}. (RT)^{+ve}$ $K_{p} > K_{C}$ So K is smaller than K_p

30. When the numerical value of the reaction quotient (Q) is greater than the equilibrium constant (K), in which direction does the reaction proceed to reach equilibrium?

The reaction will proceed in the **reverse direction** (i.e.) formation of reactants to proceed to reach the **equilibrium**.

31. For the reaction, A₂(g) + B₂(g) **⇒** 2AB(g) ; ΔH is –ve. The following molecular scenes represent different reaction mixture (A – green, B – blue)



i) Calculate the equilibrium constant \mathbf{K}_p and \mathbf{K}_c

ii) For the reaction mixture represented by scene (x), (y) the reaction proceed in which directions?

iii) What is the effect of increase in pressure for the mixture at equilibrium?

$$K_{C} = \frac{[AB]^{2}}{[A_{2}][B_{2}]}$$
At equilibrium,

$$K_{C} = \frac{(\frac{4}{V})^{2}}{(\frac{2}{V})(\frac{2}{V})}$$

$$K_{C} = 4$$

$$K_{p} = k_{c} (RT)^{\Delta ng}$$

$$K_{p} = 4(RT)^{0}$$

$$K_{p} = 4$$

→ At state 'x' $Q = \frac{(\frac{b}{V})^2}{(\frac{c}{V})(\frac{1}{V})} = 18$

 $Q > K_C$ i.e., **reverse** reaction is favoured.

At state 'y' Q =
$$\frac{(\frac{2}{V})^2}{(\frac{3}{V})(\frac{3}{V})} = \frac{4}{9}$$

 $K_C > Q$ i.e., **forward** reaction is favoured.

Since $\Delta n_g = 2 - 2 = 0$, thus, pressure has no effect. So by increasing the pressure, equilibrium will not be affected.

32. State Le-Chatelier principle.

If a system at equilibrium is disturbed, then the system shifts itself in a direction that nullifies the effect of the disturbance.

33. Consider the following reactions,

a) $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$

b)
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

c) $S(s) + 3F_2(g) \rightleftharpoons SF_6(g)$

In each of the above reaction find out whether you have to increase (or) decrease the volume to increase the yield of the product.

- Volume of gaseous molecules is equal on both sides. So increase or decrease the volume will not affect the equilibrium and there will be **no change** in the yield of product.
- Volume is greater in product side. By decreasing the pressure, volume will increase thus, to get more of product CO₂, the **pressure should be decreased or volume should be increased.**
- Volume is lesser in product side. So by increasing the pressure, volume will decrease and the equilibrium shifts to the product side.

34. State law of mass action.

At any instant, **rate of a chemical reaction** at a given temperature is directly proportional to the **product of the active masses** of the **reactants** at that instant.

Rate α [Reactant]^x

Where x is **stoichiometric coefficient**.

35. Explain how will you predict the direction of a equilibrium reaction.

By knowing the values of K_c and Q, the direction of reaction is predicted.

- \rightarrow **Q** = **k**_c, the reaction is in **equilibrium** state.
- > Q > k_c, the reaction will proceed in the **reverse** direction i.e., formation of reactants.

 \geq Q < k_c, the reaction will proceed in the **forward** direction i.e., formation of products.

36. Derive a general expression for the equilibrium constant K_p and K_c for the reaction $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$.

In the formation of ammonia, 'a' moles of Nitrogen and 'b' moles of hydrogen gas are allowed to react in a container of volume of 'V'. Let 'x' moles of nitrogen react with 3x moles of hydrogen to give 2x moles of ammonia.

	, ,(8)				
	N ₂	H ₂	NH ₃		
Initial number of moles	а	b	0		
number of moles reacted	x	3x	0		
Number of moles at equilibrium	a-x	b-3x	2x		
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{b-3x}{V}$	$\frac{2x}{V}$		

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

Applying law of mass action,

$$K_{\rm C} = \frac{[{\rm NH}_3]^2}{[{\rm N}_2] \, [{\rm H}_2]^3}$$
$$K_{\rm C} = \frac{(\frac{2x}{V})^2}{(\frac{a-x}{V})(\frac{b-3x}{V})^3}$$
$$K_{\rm C} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

The equilibrium constant K_p can be calculated as follows:

$$\begin{split} K_{p} &= K_{c} \; (RT)^{\Delta ng} \\ \Delta n_{g} &= n_{p} - n_{r} = 2 - 4 = -2 \\ K_{p} &= \frac{4x^{2}V^{2}}{(a - x)(b - 3x)^{3}} \; (RT)^{-2} \end{split}$$

Total number of moles at equilibrium, n = a-x + b-3x + 2x = a+b-2x

$$K_{p} = \frac{4x^{2}V^{2}}{(a-x)(b-3x)^{3}} \left[\frac{PV}{n}\right]^{-2}$$

$$K_{p} = \frac{4x^{2}V^{2}}{(a-x)(b-3x)^{3}} \left[\frac{n}{PV}\right]^{2}$$

$$K_{p} = \frac{4x^{2}V^{2}}{(a-x)(b-3x)^{3}} \left[\frac{a+b-2x}{PV}\right]^{2}$$

$$K_{p} = \frac{4x^{2}(a+b-2x)^{2}}{P^{2}(a-x)(b-3x)^{3}}$$

37. Write a balanced chemical equation for the equilibrium reaction for which the equilibrium constant is given by expression

$$\mathbf{K}_{c} = \frac{[\mathbf{0}_{2}]^{5}[\mathbf{NH}_{3}]^{4}}{[\mathbf{N0}]^{4}[\mathbf{H}_{2}\mathbf{0}]^{6}}$$
$$4\mathbf{NO}_{(g)} + 6\mathbf{H}_{2}\mathbf{O} \rightleftharpoons 4\mathbf{NH}_{3(g)} + 5\mathbf{O}_{2(g)}$$

38. What is the effect of added inert gas on the reaction at equilibrium at constant volume.

Addition of an inert gas to a reaction at equilibrium at constant volume has no effect.

39. Derive the relation between \mathbf{K}_{p} and $\mathbf{K}_{c}.$

Consider a general reaction in which all reactants and products are ideal gases.

 $x A + y B \rightleftharpoons IC + mD$

The equilibrium constant K_C is

$$K_{C} = \frac{[C]^{l}[D]^{m}}{[A]^{x}[B]^{y}} \rightarrow (1)$$

The equilibrium constant K_p is

$$\mathbf{K}_{\mathrm{p}} = \frac{p_{C}^{l} \times p_{D}^{m}}{p_{A}^{x} \times p_{B}^{y}} \rightarrow (2)$$

The ideal gas equation is PV = nRTSince Active mass = molar concentration = n/V

$P = active mass \times (RT)$

Based on the above expression the partial pressure of the reactants and products can be expressed as,

$$p_{A}^{x} = [A]^{x} (RT)^{x}$$

$$p_{B}^{y} = [B]^{y} (RT)^{y}$$

$$p_{C}^{l} = [C]^{l} (RT)^{1}$$

$$p_{D}^{m} = [D]^{m} (RT)^{m}$$
On substituting in equation (2),
$$K_{p} = \frac{[C]^{l} (RT)^{l} [D]^{m} (RT)^{m}}{[A]^{x} (RT)^{x} [B]^{y} (RT)^{y}} \rightarrow (3)$$

$$K_{p} = \frac{[C]^{l} [D]^{m}}{[A]^{x} [B]^{y}} (RT)^{(l+m)-(x+y)} \rightarrow (4)$$

By comparing equation (1) and (4), we get

$\mathbf{K}_{\mathbf{p}} = \mathbf{K}_{\mathbf{C}} \ (\mathbf{R}\mathbf{T})^{\Delta \mathbf{n}\mathbf{g}}$

where Δn_g is the difference between the sum of number of moles of products and the sum of number of moles of reactants in the gas phase.

- If Δng = 0, K_b = K_C(RT)⁰ K_p = K_C Example: H₂(g) + I₂ ≈ 2HI(g)
 When Δng = +ve
 - $K_p = K_C (RT)^{+ve}$
 - $K_p = K_C$

Example: $2NH_3(g) N_2(g) + 3H_2(g)$

When $\Delta \mathbf{n}_{g} = -\mathbf{v}\mathbf{e}$ $K_{p} = K_{C} (RT)^{-ve}$

 $\mathbf{K}_p = \mathbf{K}_c$

 $K_p < K_C$

Example: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

40. One mole of PCl₅ is heated in one litre closed container. If 0.6 mole of chlorine is found at equilibrium, calculate the value of equilibrium constant. Given:

 $[PCl_{5}]_{initial} = \frac{1 \text{ mole}}{1 \text{ dm}^{3}}$ $[CL_{2}]_{eq} = 0.6 \text{ mole dm}^{-3}$ $PCl_{5} \rightleftharpoons PCl_{3} + Cl_{2}$

Formula used:

$$\begin{split} K_{\rm C} &= \frac{[C]^{\rm I}[D]^{\rm m}}{[A]^{\rm x}[B]^{\rm y}} \\ \textbf{Solution:} \\ [PCl_3]_{\rm eq} &= 0.6 \text{ mole } dm^{-3} \\ [PCl_5]_{\rm eq} &= 0.4 \text{ mole } dm^{-3} \\ K_{\rm C} &= \frac{[PCl_3][Cl_2]}{[PCl_5]} \\ K_{\rm C} &= \frac{0.6 \times 0.6}{0.4} \end{split}$$

 $K_C = 0.9$

41. For the reaction SrCO₃ (s) \Rightarrow SrO (s) + CO₂ (g), the value of equilibrium constant K_p = 2.2×10^{-4} at 1002 K. Calculate K_c for the reaction.

Given: $K_p = 2.2 \times 10^{-4}$ T = 1002 KFormula used: $K_p = K_C (RT)^{\Delta ng}$ Solution: For the reaction, $SrCO_2(s) \rightleftharpoons SrO(s) + CO_2(g)$ $\Delta n_g = 1 - 0 = 1$ $K_p = K_C (RT)$ $2.2 \times 10^{-4} = K_C (0.0821)(1002)$ $K_C = \frac{2.2 \times 10^{-4}}{0.0821 \times 1002}$

 $K_C = 2.674 \times 10^{-6}$

42. To study the decomposition of hydrogen iodide, a student fills an evacuated 3 litre flask with 0.3 mol of HI gas and allows the reaction to proceed at 500°C. At equilibrium he found the concentration of HI which is equal to 0.05 M. Calculate K_c and K_p for this reaction.

Given: V = 3 LFormula used: $K_C = \frac{[C]^1[D]^m}{[A]^x[B]^y}$ $K_p = K_C (RT)^{\Delta ng}$ Solution:

 $[HI]_{initial} = \frac{0.3 \text{ mol}}{3L} = 0.1 \text{M}$ $[HI]_{eq} = 0.05 \text{M}$

```
2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)
```

	HI(g)	$H_2(g)$	$I_2(g)$
Initial Con-	0.1	_	—
centration			
Reacted	0.05	_	—
Equilibri-	0.05	0.025	0.025
um concen-			
tration			
$K_{C} = \frac{[H_{2}][I_{2}]}{[I_{2}]}$			
$[HI]^2$			

$$K_{\rm C} = \frac{0.025 \times 0.025}{0.05 \times 0.05}$$

$$K_{\rm p} = K_{\rm C} (RT)^{\Delta ng}$$

$$\Delta n_{\rm g} = 2 - 2 = 0$$

$$K_{\rm p} = K_{\rm C}$$

$$K_{\rm p} = 0.25$$

43. 1 mol of CH₄, 1 mole of CS₂ and 2 mol of H₂S ard 2 mol of H₂ are mixed in a 500 ml flask. The equilibrium constant for the reaction $K_c = 4 \times 10^{-2} \text{ mol}^2 \text{ lit}^{-2}$. In which direction will the reaction proceed to reach equilibrium?

Given: $K_C = 4 \times 10^{-2} \text{ mol lit}^{-2}$ Volume = 500 ml = $\frac{1}{2}$ L Solution: $[CH_4]_{in} = \frac{1mol}{\frac{1}{2}L} = 2 \text{ mol } L^{-1}$ $[CS_2]_{in} = \frac{1mol}{\frac{1}{2}L} = 2 \text{ mol } L^{-1}$ $[H_2S]_{in} = \frac{2mol}{\frac{1}{2}L} = 4 \text{ mol } L^{-1}$ $[H_2]_{in} = \frac{2mol}{\frac{1}{2}L} = 4 \text{ mol } L^{-1}$ $Q = \frac{[CS_2][H_2]^4}{[CH_2] [H_2S]^2}$ $Q = \frac{2 \times (4)^2}{2 \times (4)^2}$ $Q > K_C$

The reaction will proceed in the reverse direction to reach the equilibrium.

44. At particular temperature $K_c = 4 \times 10^{-2}$ for the reaction $H_2S(g) \rightleftharpoons H_2(g) + \frac{1}{2}S_2(g)$. Calculate K_c for each of the following reaction

i) $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ ii) $3H_2S(g) \rightleftharpoons 3H_2(g) + 3/2 S_2(g)$ Given: $K_C = 4 \times 10^{-2}$ Formula: $K_C = \frac{[C]^1[D]^m}{[A]^x[B]^y}$ Solution: $H_2S(g) \rightleftharpoons H_2(g) + \frac{1}{2} S_2(g)$ $K_c = \frac{[H_2][S_2]^{\frac{1}{2}}}{[H_2S]}$ $4 \times 10^{-2} = \frac{[H_2][S_2]^{\frac{1}{2}}}{[H_2S]}$ For the reaction, $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ $K_C = \frac{[S_2][H_2]^2}{[H_2S]^2} = (4 \times 10^{-2})^2$

 $K_C = 16 \times 10^{-4}$

For the reaction, $3H_2S(g) \rightleftharpoons 3H_2(g) + 3/2 S_2(g)$ $K_C = \frac{[S_2]^{\frac{3}{2}}[H_2]^3}{[H_2S]^3} = (4 \times 10^{-2})^2$

 $K_C = 16 \times 10^{-4}$

45. 28 g of Nitrogen and 6 g of hydrogen were mixed in a 1 litre closed container. At equilibrium 17 g NH₃ was produced. Calculate the weight of nitrogen, hydrogen at equilibrium.

Given:

 $m_{N_2} = 28g$ $m_{H_2} = 6g$ V = 1L

Solution: $(m_{N_2})_{\text{initial}} = \frac{28}{28} = 1 \mod (m_{H_2})_{\text{initial}} = \frac{6}{2} = 3 \mod (m_{H_2}) \mod (m_{H_2})$

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

	$N_2(g)$	$H_2(g)$	$NH_3(g)$	
Initial concentra-	1	3	_	
tion				
Reacted	0.5	1.5	—	
Equilibrium con-	0.5	1.5	1	
centration				1
17				1

 $[NH_3] = \frac{17}{17} = 1 \text{ mol} = 2x$ x = 0.5 mol

At equilibrium, $[N_2] = 1 - x = 0.5 \text{ mol}$

 $[H_2] = 3 - 3x = 3 - 3 (0.5) = 1.5 mol$

Weight of $N_2 = (no. of moles of N_2) x molar mass of N_2 = 0.5 x 28$

Weight of $H_2 = (no. of moles of H_2) x molar mass of H_2= 1.5 x 2$

Weight of
$$N_2 = 14g$$

Weight of $H_2 = 3g$

46. The equilibrium for the dissociation of XY₂ is given as, 2XY₂ (g) ≠ 2XY (g) + Y₂ (g) if the degree of dissociation x is so small compared to one. Show that 2 K_p = PX³ where P is the total pressure and K_p is the dissociation equilibrium constant of XY₂. 2XY₂ (g) ≠ 2XY (g) + Y₂(g)

	XY ₂	XY	Y ₂
Intial no. of moles	1	-	-
No. of moles dissociated	Х	-	-
No. of moles at equilibrium	$(1-x) \cong 1$	х	x/2

Total number of moles = $1-x+x+(x/2) = 1 + (x/2) \approx 1$ [Given that x<<1 and $1-x \approx 1$ and $1 + (x/2) \approx 1$]

$$K_{p} = \frac{\left(P_{XY}\right)^{2} \left(P_{Y_{2}}\right)}{\left(P_{XY_{2}}\right)^{2}} = \frac{\left(\frac{x}{1} \times P\right)^{2} \left(\frac{x}{2} \times P\right)}{\left(\frac{1}{1} \times P\right)^{2}}$$
$$K_{p} = \frac{x^{2} P^{2} \times P}{2P^{2}}$$

 $2K_p = x^3 P$

47. A sealed container was filled with 1 mol of A_2 (g), 1 mol B_2 (g) at 800 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that K = 1 for the reaction A_2 (g) + B_2 (g) \rightleftharpoons 2AB (g). Solution:

$A_2(g) + B_2(g) \rightleftharpoons 2AB$	6 (g)			
	A ₂	B ₂	AB	
Initial Concentration	1	1	-	
No. of moles reacted	X	X	-	
No. of moles at equi-	1 – x	1 – x	2x	
librium				
Total number of moles	s = 1 - x +	-1-x+2	$\mathbf{x} = 2$	\sim
$K_{p} = \frac{(P_{AB})^{2}}{(P_{A_{2}})(P_{B_{2}})} = \frac{(1-x)^{2}}{(1-x)^{2}}$	$\left(\frac{2\mathbf{x}}{2} \times \mathbf{P}\right)$	$\frac{1-x}{2} \times P$)	0
$\mathbf{K}_{\mathbf{p}} = \frac{4\mathbf{x}^2}{\left(1 - \mathbf{x}\right)^2}$		\wedge	C)
Given that $K_p = 1; -\frac{1}{2}; -1$	$\frac{4x^2}{1-x)^2} =$	5	\geq	
$\Rightarrow 4x^2 = (1-x)^2$)		
$\Rightarrow 4x^2 = 1 + x^2 - 2x$	\searrow			
$3x^2 + 2x - 1 = 0$				
$x = \frac{-2 \pm \sqrt{4 - 4 \times 3 \times -1}}{2(3)}$	-)			
$x = \frac{-2 \pm \sqrt{4 + 12}}{6}$				
$=\frac{-2\pm\sqrt{16}}{6}$				
$x = \frac{2}{6}; \frac{-6}{6}$				
$x = 0.33^\circ$, -1(not possil	ole)			
-				

48. Deduce the Vant Hoff equation.

This equation gives the quantitative temperature dependence of equilibrium constant K. The relation between standard **free energy change** ΔG° and **equilibrium constant** is $\Delta G^{\circ} = - RT \ln K \rightarrow (1)$

 $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \rightarrow (2)$

Substituting (1) in equation (2)

 $- RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ}$

Rearranging,

$$\ln K = \frac{-\Delta H^{\circ}}{RT} \frac{\Delta S^{\circ}}{R} \rightarrow (3)$$

Differentiating equation (3) with respect to temperature

$$\frac{d(\ln k)}{dT} = \frac{\Delta H^{\circ}}{RT^2} \rightarrow (4)$$

Equation (4) is known as **differential form of Van't Hoff equation**.

On integrating the equation 4, between T_1 and T_2 with their respective equilibrium constants K_1 and K_2 .

$$\int_{K_{1}}^{K_{2}} d(\ln k) = \frac{\Delta H^{\circ}}{R} \int_{T_{1}}^{T_{2}} \frac{dT}{T^{2}}$$

$$[\ln K]_{K_{1}}^{K_{2}} = \frac{\Delta H^{\circ}}{R} \left[\frac{-1}{T}\right]_{T_{1}}^{T_{2}}$$

$$\ln K_{2} - \ln K_{1} = \frac{\Delta H^{\circ}}{R} \left[-\frac{1}{T_{2}} + \frac{1}{T_{1}}\right]$$

$$\ln \frac{k_{2}}{k_{1}} = \frac{\Delta H^{\circ}}{R} \left[\frac{T_{2} - T_{1}}{T_{2} T_{1}}\right]$$

$$\log \frac{k_{2}}{k_{1}} = \frac{\Delta H^{\circ}}{2.303R} \left[\frac{T_{2} - T_{1}}{T_{2} T_{1}}\right] \Rightarrow (5)$$

Equation (5) is known as integral form of Van't Hoff equation.

49. The equilibrium constant K_p for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 8.19×10^2 at 298 K and 4.6×10^{-1} at 498 K. Calculate ΔH^0 for the reaction.

Given:

$$K_{P1} = 8.19 \times 10^{2} \quad T_{1} = 298 \text{ K}$$

$$K_{P2} = 4.6 \times 10^{-1} \quad T_{2} = 498 \text{ K}$$
Formula used:

$$log \frac{k_{2}}{k_{1}} = \frac{\Delta H^{\circ}}{2.303R} \left[\frac{T_{2} - T_{1}}{T_{2}T_{1}}\right]$$
Solution:

$$log \frac{k_{2}}{k_{1}} = \frac{\Delta H^{\circ}}{2.303R} \left[\frac{T_{2} - T_{1}}{T_{2}T_{1}}\right]$$

$$log \frac{4.6 \times 10^{-1}}{8.19 \times 10^{2}} = \frac{\Delta H^{\circ}}{2.303 \times 8.314} \left[\frac{498 - 298}{498 \times 298}\right]$$

$$\Delta H^{\circ} = \frac{-3.2505 \times 2.303 \times 8.314 \times 498 \times 298}{200}$$

 $\Delta \mathbf{H}^{\circ} = -46.18 \text{ kJmol}^{-1}$

50. The partial pressure of carbon dioxide in the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is 1.017×10^{-3} atm at 500°C. Calculate K_p at 600°C for the reaction. ΔH for the reaction is 181 KJ mol⁻¹ and does not change in the given range of temperature.

Given: $P_{\rm CO2} = 1.017 \times 10^{\text{-3}}$ atm $T = 500^{\circ}C$ $K_p = P_{\rm CO2}$ $K_{p1} = 1.017 \times 10^{-3}$ T = 500 + 273 = 773 K $K_{p2} = ?$ T = 600 + 273 = 873 K $\Delta H^{\circ} = 181 \text{ kJmol}^{-1}$ Formula used: $\log \frac{k_2}{k_1} = \frac{\Delta H^{\circ}}{2.303R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$ Solution: $log \frac{k_{p2}}{k_{p1}} = \frac{\Delta H^{\circ}}{2.303R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$ $log \frac{k_{p2}}{1.017 \times 10^{-3}} = \frac{181 \times 10^3}{2.303(8.314)} \left[\frac{873 - 773}{873 \times 773} \right]$ $\frac{k_{p2}}{1.017 \times 10^{-3}} = \text{antilog (1.40)}$ $\frac{\frac{k_{p2}}{1.017 \times 10^{-3}} = 25.12$ $K_{p2} = 25.54 \times 10^{-3}$