12

Chemical Equilibrium

Chemical Equilibrium

1. The state at which concentration of reactants or products do not change with time.

2. It is attained when rate of forward reaction becomes equal to rate of backward reaction.

3. A dynamic equilibrium, attained from either side.

Irreversible and reversible reactions

Irreversible reactions	Reversible reactions
1. Unidirectional	1. Both directional
2. Go for completion	2. Never go for completion
3. No equilibrium is attained	3. Attains equilibrium
4. A reaction is said to be irreversible when either of the product is settled down as solid or escapes out as gas, *e.g.*, $BaCl_2 + Na_2SO_4 \longrightarrow \underset{\text{(insoluble)}}{BaSO_4} + 2NaCl$	4. Otherwise the reaction is reversible, *e.g.*, $CaCO_3 \rightleftharpoons CaO + CO_2$ (in closed container)

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

Law of mass action : Guldbarg and Waage proposed that, "The rate at which a substance reacts is directly proportional to its active mass and the rate of a chemical reaction is directly proportional to product of active masses of reactants."

Active mass :

Active mass of a reactant = Concentration of reactant × activity coefficient

$$a = f \times \text{molarity} = \gamma \times \text{molality}$$

where f and γ are activity coefficients. For dilute solution f and γ are unity.

$$\therefore \quad a = \text{Molarity} = \text{Molality}$$

Formulation of law of mass action :

Consider a reversible reaction

$$m_1A + m_2B + ... \rightleftharpoons n_1Z + n_1Y + ...$$

$\therefore$ Rate of forward reaction $\propto (a_A)^{m_1}(a_B)^{m_2}$

$$= K_f(a_A)^{m_1}(a_B)^{m_2}$$

and Rate of backward reaction $\propto (a_Z)^{n_1}(a_Y)^{n_2}.......$

$$= K_b(a_Z)^{n_1}(a_Y)^{n_2}$$

where K_f and K_b are rate constants for forward and backward reactions respectively.

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$$\therefore \quad K_f(a_A)^{m_1}(a_B)^{m_2}..... = K_b(a_Z)^{n_1}(a_Y)^{n_2}....$$

$$\therefore \quad \frac{K_f}{K_b} = \frac{(a_Z)^{n_1}(a_Y)^{n_2}...}{(a_A)^{m_1}(a_B)^{m_2}...} \text{ or } K_a = \frac{(a_Z)^{n_1}(a_Y)^{n_2}...}{(a_A)^{m_1}(a_B)^{m_2}...} \quad ...(1)$$

Since, $\quad a = f \times \text{molarity}$

$$\therefore \text{ By Eq. (1).} \quad K_a = \frac{[f_z \cdot [Z]]^{n_1} \cdot [f_Y \cdot [Y]]^{n_2}...}{[f_A \cdot [A]]^{m_1} \cdot [f_B \cdot [B]]^{m_2}...}$$

$$\text{or} \quad K_a \cdot \frac{(f_A)^{m_1}(f_B)^{m_2}}{(f_z)^{n_1}(f_B)^{n_2}} = \frac{[Z]^{n_1}[Y]^{n_2}...}{[A]^{m_1}[B]^{m_2}...}$$

$$\text{or} \quad K_C = \frac{[Z]^{n_1}[Y]^{n_2}...}{[A]^{m_1}[B]^{m_2}...} \quad ...(2)$$

where $[Z]$, $[Y]$, $[A]$ and $[B]$ are concentration of respective species at equilibrium.

In case of gaseous phases, $a \propto$ Partial pressure of gas, at constant T

$$\therefore \quad K_P = \frac{(P_Z)^{n_1}(P_Y)^{n_2}...}{(P_A)^{m_1}(P_B)^{m_2}...} \quad ...(3)$$

$$\text{or} \quad K_P = \frac{[n_Z]^{n_1}[n_Y]^{n_2}...}{[n_A]^{m_1}[n_B]^{m_2}...} \times \left[\frac{P}{RT}\right]^{\Delta n}$$

where $\quad \Delta n = [m_1 + m_2 + ...] - [n_1 + n_2 + ...]$

where P_Z', P_Y', P_A' and P_B' are partial pressures of respective species 234at equilibrium.

where K_a, K_C and K_P are equilibrium constants in terms of active mass, concentration and partial pressure respectively.

NOTE: 1. Normally 'f' values are not given in numericals and thus K_C and K_P are evaluated and not K_a.

2. Reaction Quotient Q for the reaction :

$m_1A + m_2B + ... \rightleftharpoons n_1Z + n_2Y + ...$, can be written as

$$Q = \frac{[Z]^{n_1}[Y]^{n_2}.......}{[A]^{m_1}[B]^{m_2}.......}$$

or $$Q = \frac{[P'_z]^{n_1}[P'_y]^{n_2}.......}{[P'_A]^{m_1}[P'_B]^{m_2}.......} \text{ (for gaseous phase reaction)}$$

where $[Z], [Y], [A], [B]$ are concentration at $t = 0$ and P'_Z, P'_Y, P'_A and P'_B are partial pressures at $t = 0$.

The reaction Quotient helps in predicting the direction of reaction *i.e.*, is $Q > K$ backward direction
$Q < K$ forward direction
$Q = K$ At equilibrium

Relation in between K_P and K_C

$$K_P = K_C(RT)^{\Delta n} \qquad ...(4)$$

where Δn = No. of mole of product – No. of mole of reactant

For Δn, one should remember.

(1) Δn may be zero, +ve or –ve integers or fractions.

(2) Only gaseous phases are to be taken in account.

(3) If $\Delta n = 0, K_P = K_C$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta n = -2$$

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta n = 0$$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad \Delta n = +1$$

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g) \qquad \Delta n = +\frac{1}{2}$$

Units of K_P and K_C

Unit of K_P = (Unit of pressure)$^{\Delta n}$ = (atm)$^{\Delta n}$

Unit of K_C = (Unit of concentration)$^{\Delta n}$ = (mol litre^{-1})$^{\Delta n}$

if $\Delta n = 0$, no unit of K_P or K_C.

Note : Now-a-days equilibrium constant is expressed as dimensionless quantity by specifying the standard state of reactants and products. For example standard state for pure gas is 1 bar and the partial pressures are expressed with respect to this standard *e.g.*, a pressure of 2 bar in terms of standard state is $\frac{2\text{bar}}{1\text{bar}}$ *i.e.*, 2 a dimension less quantity. Similarly for solution species, the standard state is 1 *M*.

Factors influencing equilibrium constant :

(1) Temperature

The variation of K_C or K_P with temperature has been expressed in terms of :

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\frac{[T_2 - T_1]}{T_1T_2}$$

or $$2.303\log_{10}\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\frac{[T_2 - T_1]}{T_1T_2} \qquad ...(5)$$

[Integrated form of van't Hoff isochore for two temperature limits.]

or $$K = Ae^{-\Delta H^\circ/RT} \qquad ...(6)$$

[For one temperature limit]

where K is equilibrium constant; T represents temperature; ΔH° is heat of reaction; A is frequency factor; R is molar gas constant.

Case I : For endothermic reaction ΔH° = +ve and if $T_2 > T_1$

Then by Eq. (5), $\log_{10}\frac{K_2}{K_1}$ = +ve $\therefore \log_{10}K_2 > \log_{10}K_1$

or $K_2 > K_1$

i.e., **Equilibrium constant increases with increase in temperature for endothermic reaction.**

Case II : For exothermic reaction ΔH° = –ve and if $T_2 > T_1$

Then by Eq. (5),

$$\log_{10}\frac{K_2}{K_1} = -\text{ve or } \log_{10}K_2 < \log_{10}K_1 \text{ or } K_2 < K_1$$

i.e., **Equilibrium constant decreases with increase in temperature for exothermic reactions.**

NOTE : Put R in the same unit in which ΔH° is given or desired.

(2) Stoichiometry of change

The numerical values of K_C or K_P change with stoichiometry, *e.g.*,

$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$
$K_{C_1} = \frac{[NH_3]^2}{[N_2][H_2]^3}$	$K_{C_2} = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$

$$K_{C_1} = [K_{C_2}]^2 \qquad ...(7)$$

(3) The mode of representing the change

The numerical values of K_P or K_C also change with method of representing equilibrium, *e.g.*,

$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$2NH_3 \rightleftharpoons N_2 + 3H_2$
$K_{C_1} = \frac{[NH_3]^2}{[N_2][H_2]^3}$	$K_{C_3} = \frac{[N_2][H_2]^3}{[NH_3]^2}$

$$K_{C_1} = \frac{1}{K_{C_3}} \qquad ...(8)$$

By Eqs. (7) and (8), $K_{C_1} = (K_{C_2})^2 = \frac{1}{K_{C_3}}$

(4) Units in which pressures or concentrations are expressed

(a) If $\Delta n = 0$; K_P or K_C values do not change with change in units of P or C.

(b) If $\Delta n \neq 0$; K_P or K_C values change with change in units of P or C.

NOTE : When a reaction takes place in more than one step, there can be a relationship among the equilibrium constants of the overall reaction and those of the step reactions.

The reaction, $H_2O_2 + 2H^+ + 2I^- \rightleftharpoons I_2 + 2H_2O$

for which $K = \frac{[I_2][H_2O]^2}{[H_2O_2][H^+]^2[I^-]^2}$ takes place in the following steps,

$$H_2O_2 + I^- \rightleftharpoons OH^- + HOI; \quad K_1 = \frac{[OH^-][HOI]}{[H_2O_2][I^-]}$$

$$H^+ + OH^- \rightleftharpoons H_2O; \quad K_2 = \frac{[H_2O]}{[H^+][OH^-]}$$

and $$HOI + H^+ + I^- \rightleftharpoons I_2 + H_2O; \quad K_3 = \frac{[I_2][H_2O]}{[HOI][H^+][I^-]}$$

Multiplying equations for K_1, K_2 and K_3, we see that,

$$K = K_1 \cdot K_2 \cdot K_3 \qquad ...(9)$$

Thus, when a reaction takes place in more than one step, the equilibrium constant of the overall reaction is equal to the product of the equilibrium constants of each step.

Degree of dissociation and its use

$$2HI \rightleftharpoons H_2 + I_2$$

$$\text{Degree of dissociation } (\alpha) = \frac{\text{Mole dissociated}}{\text{Total mole present before dissociation}}$$

The use of 'α' should be made very cautiously.

The reaction ratio is $HI : H_2 : I_2 :: 2 : 1 : 1$

(i) *e.g.*,

	$2HI$	$\rightleftharpoons H_2$	$+ I_2$
Mole at $t = 0$	1	0	0
Mole at equilibrium	$1 - x$	$x/2$	$x/2$

$$\therefore \quad \alpha = \frac{x}{1} = x$$

(ii)

	$2HI$	$\rightleftharpoons H_2$	$+ I_2$
Mole at $t = 0$	1	0	0
Mole at equilibrium	$1 - 2x$	x	x

$$\therefore \quad \alpha = \frac{2x}{1}$$

(iii)

	$2HI$	$\rightleftharpoons H_2$	$+ I_2$
Mole at $t = 0$	a	0	0
Mole at equilibrium	$a - x$	$x/2$	$x/2$

$$\therefore \quad \alpha = \frac{x}{a}$$

(iv)

	$2HI$	$\rightleftharpoons H_2$	$+ I_2$
Mole at $t = 0$	a	0	0
Mole at equilibrium	$a - 2x$	x	x

$$\therefore \quad \alpha = \frac{2x}{a}$$

(v)

	$2HI$	$\rightleftharpoons H_2$	$+ I_2$
Mole at $t = 0$	a	0	0
Mole at equilibrium	$(a - ax)$	$\frac{ax}{2}$	$\frac{ax}{2}$
or	$a(1 - x)$		

$$\therefore \quad \alpha = \frac{ax}{a} = x$$

Select either of the case and derive K_C or K_P accordingly as reported earlier, following step by step.

Factors influencing equilibrium concentrations

(1) Temperature. (a) An increase in temperature for exothermic reactions decreases the concentration of products at equilibrium and *vice-versa*.

(b) An increase in temperature for endothermic reactions increases the concentration of products at equilibrium and *vice-versa*.

(2) Pressure. An increase in pressure to an equilibrium favours the reaction where number of mole or volume shows a decrease and *vice-versa*.

(3) Addition of inert gas. (a) Addition of inert gas to an equilibrium (if, $\Delta n = 0$) has no effect.

(b) Addition of inert gas to an equilibrium (if, $\Delta n \neq 0$) has no effect, if addition is made at constant volume but addition at constant pressure will favour the direction of reaction where total number of mole at equilibrium show an increase.

Equilibrium Constant and Standard Free Energy Change

$$\Delta G = \Delta G^\circ + 2.303\, RT \log Q$$

where Q represents the reaction quotient. At equilibrium, $\Delta G = 0$ and $Q = K_P$ or K_C as the standard state is referred in terms of partial pressure or concentration.

Thus, the equilibrium constant K_P is related to standard free energy change (ΔG°) by the relation;

$$\Delta G^\circ = -2.303\, RT \log_{10} K_P$$

Also, $$\Delta G^\circ = -2.303\, RT \log_{10} K_C$$

Since, ΔG° can be obtained from independent measurements, *e.g.*, from thermal and spectroscopic data, it is possible to calculate K_P. The ΔG° value for a spontaneous or feasible reaction is always negative. From equation, ΔG° is obtained in the same energy unit in which value of R is introduced, provided, the equilibrium constant K_P is just a pure number or it is calculated by taking partial pressure in atmosphere.

From equation we may conclude that

When $\Delta G^\circ = -\text{ve}$ or $K > 1$;

Forward reaction is feasible at unit concentration (or partial pressure)

When $\Delta G^\circ = +\text{ve}$ or $K < 1$;

Reverse reaction is feasible.

Also, is $\Delta G^\circ = 0$ then $K = 1$;

• NUMERICAL PROBLEMS •

1. State which one is homogeneous or heterogeneous ?
   - (a) $S_{Rhombus} \rightleftharpoons S_{Monoclinic}$
   - (b) $H_2O(l) \rightleftharpoons H_2O(v)$
   - (c) $H_2O(s) \rightleftharpoons H_2O(l)$
   - (d) $C_{Diamond} \rightleftharpoons C_{Amorphous}$
   - (e) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   - (f) $CuSO_4(s) + 3NH_3(l) \rightleftharpoons CuSO_4 \cdot 3NH_3(l)$
   - (g) $CaCO_3(g) \rightleftharpoons CaO(s) + CO_2(g)$
2. Write equilibrium constants for each ;
   - (a) $KClO_3(s) \rightleftharpoons KCl(s) + \frac{3}{2}O_2$
   - (b) $H_2(g) + 3Fe_2O_3(s) \rightleftharpoons H_2O(g) + 2Fe_3O_4(s)$
   - (c) $CaC_2(s) + 5O_2(g) \rightleftharpoons 2CaCO_3(s) + 2CO_2(g)$
   - (d) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
   - (e) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   - (f) $CH_3COOH(l) + CH_3OH(l) \rightleftharpoons CH_3COOCH_3(l) + H_2O(l)$
3. If a mixture of 3 mole of H_2 and one mole of N_2 is completely converted into NH_3, what would be the ratio of the initial and final volume at same temperature and pressure ?
4. Calculate the equilibrium constant for the reaction
   $$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$
   at 1395 K, if the equilibrium constants at 1395 K for the following are ;
   $$2H_2O(g) \rightleftharpoons 2H_2 + O_2(g) \qquad K_1 = 2.1 \times 10^{-13}$$
   $$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g) \qquad K_2 = 1.4 \times 10^{-12}$$
5. The equilibrium constant of the reaction,
   $$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$
   is 0.15 at 900 K. Calculate equilibrium constant for
   $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
6. Following two equilibria exist together
   $$2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} I \underset{K_4}{\overset{K_3}{\rightleftharpoons}} B + C$$
   Show that equilibrium constant for overall reaction $K_C = \frac{K_1K_3}{K_2K_4}$.
7. K_C for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is $0.5\ mol^{-2}$ $litre^{-2}$ at 400 K. Find K_P. Given $R = 0.082$ litre atm $degree^{-1}\ mol^{-1}$.
8. For the reaction $A + B \rightleftharpoons 3C$ at 25°C, a, 3 litre vessel contains 1, 2, 4 mole of A, B and C respectively. Predict the direction of reaction if :
   - (a) K_C for the reaction is 10.
   - (b) K_C for the reaction is 15.
   - (c) K_C for the reaction is 10.66.
9. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction : $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ with a degree of dissociation 'x' which is small compared to unity. Deduce the expression for 'x' in terms of the equilibrium constant K_P and the total pressure P. **(IIT 1994)**
10. In which case does the reaction go farthest to completion : $K = 1; K = 10^{10}; K = 10^{-10}$ and why?
11. The equilibrium constant K_C for $A(g) \rightleftharpoons B(g)$ is 1.1. Which gas has a molar concentration greater than 1 ?
12. The equilibrium constant for the polymerisation of HCHO to $C_6H_{12}O_6$ in aqueous solution is 6×10^{22}. If $1M$ solution of glucose was to reach the equilibrium according to :
    $$6HCHO \rightleftharpoons C_6H_{12}O_6 \qquad K_C = 6 \times 10^{22}$$
    find out the concentration of formaldehyde in solution.
13. In an equilibrium $A + B \rightleftharpoons C + D$; A and B are mixed in a vessel at temperature T. The initial concentration of A was twice the initial concentration of B. After the equilibrium has reached, concentration of C was thrice the equilibrium concentration of B. Calculate K_C.
14. The K_C for $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100°C is 50. If one litre flask containing one mole of A_2 is connected with a two litre flask containing 2 mole of B_2, how many mole of AB will be formed at 100°C?
15. For a gaseous phase reaction,
    $$A + 2B \rightleftharpoons AB_2, K_C = 0.3475\ litre^2\ mol^{-2}$$
    at 200°C. When 2 mole of B are mixed with one mole of A, what total pressure is required to convert 60% of A in AB_2?
16. For a gaseous phase reaction, $2HI \rightleftharpoons H_2 + I_2$, at equilibrium 7.8 g, 203.2 g and 1638.4 g of H_2, I_2 and HI respectively were found in 5 litre vessel. Calculate K_C. If all the reactants and products are transferred to a 2 litre *vessel*, what will be the amount of reactants and products at equilibrium?
17. 60 mL of H_2 and 42 mL of I_2 are heated in a closed vessel. At equilibrium the vessel contains 28 mL HI. Calculate degree of dissociation of HI.
18. In the dissociation of HI, 20% of HI is dissociated at equilibrium.
    Calculate K_P for $HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$.
19. The value of K_P for dissociation of $2HI \rightleftharpoons H_2 + I_2$ is 1.84×10^{-2}. If the equilibrium concentration of H_2 is 0.4789 mol $litre^{-1}$, calculate the concentration of HI at equilibrium.

20. The K_P value for the reaction ; $H_2 + I_2 \rightleftharpoons 2HI$, at 460°C is 49. If the initial pressure of H_2 and I_2 is 0.5 atm respectively, determine the partial pressure of each gas at equilibrium. **(Roorkee 1999)**

21. One mole of H_2, two mole of I_2 and three mole of HI are injected in one litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 500°C? K_C for reaction ; $H_2 + I_2 \rightleftharpoons 2HI$ is 45.9

22. 0.96 g of HI were heated to attain equilibrium $2HI \rightleftharpoons H_2 + I_2$. The reaction mixture on titration requires 15.7 mL of N/10 *hypo* solution. Calculate degree of dissociation of HI.

23. The degree of dissociation of HI at a particular temperature is 0.8. Calculate the volume of 2*M* $Na_2S_2O_3$ solution required to neutralise the iodine present in a equilibrium mixture of a reaction when 2 mole each of H_2 and I_2 are heated in a closed vessel of 2 litre capacity.

24. The activation energy of $H_2 + I_2 \rightleftharpoons 2HI$ in equilibrium for the forward reaction is 167 kJ mol^{-1} whereas for the reverse reaction is 180 kJ $mole^{-1}$. The presence of catalyst lowers the activation energy by 80 kJ mol^{-1}. Assuming that the reactions are made at 27°C and the frequency factor for forward and backward reactions are 4×10^{-4} and 2×10^{-3} respectively, calculate K_C.

25. A reversible reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ in equilibrium has $[H_2] = 0.5$, $[I_2] = 0.5$ and $[HI] = 1.23$ in one litre flask. If suddenly 0.6 mole of HI is removed, find out the new equilibrium concentrations.

26. At 700 K, hydrogen and bromine react to form hydrogen bromide. The value of equilibrium constant for this reaction is 5×10^8. Calculate the mole of H_2, Br_2 and HBr at equilibrium if a mixture of 0.6 mole of H_2 and 0.2 mole of Br_2 is heated to 700 K. **(Roorkee 1995)**

27. A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

was established with an equilibrium constant $K_C = 2.1 \times 10^{-3}$. At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fraction of N_2 and O_2. **(IIT May 1997)**

28. K_C for $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at 986°C is 0.63. A mixture of 1 mole $H_2O(g)$ and 3 mole $CO(g)$ is allowed to react to come to an equilibrium. The equilibrium pressure is 2.0 atm.

(i) How many mole of H_2 are present at equilibrium ?

(ii) Calculate partial pressure of each gas at equilibrium **(Roorkee 1992)**

29. An equilibrium mixture of

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

present in a vessel of one litre capacity at 815°C was found by analysis to contain 0.4 mole of CO, 0.3 mole of H_2O, 0.2 mole of CO_2 and 0.6 mole of H_2.

(a) Calculate K_C.

(b) If it is derived to increase the concentration of CO to 0.6 mole by adding CO_2 to the vessel, how many mole must be added into equilibrium mixture at constant temperature in order to get this change ?

30. A mixture of one mole of CO_2 and one mole of H_2 attains equilibrium at a temperature of 250°C and a total pressure of 0.1 atm for the change $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$. Calculate K_P if the analysis of final reaction mixture shows 0. 16 volume per cent of CO.

31. At 700 K, CO_2 and H_2 react to form CO and H_2O. For this purpose K_C is 0.11. If a mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated to 700 K.

(a) Find out mole of each gas at equilibrium.

(b) When equilibrium has been reached, another 0.34 mole of CO_2 and 0.34 mole of H_2 are added to the reaction mixture. Find composition of mixture at new equilibrium.

32. At a certain temperature, K_C for

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

is 16. If we take one mole of each of all the four gases in one litre container, what would be the equilibrium concentrations of NO and NO_2?

33. A mixture of SO_3, SO_2 and O_2 gases is maintained at equilibrium in 10 litre flask at a temperature at which K_C for the reaction,

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 100 mol^{-1} litre. At equilibrium.

(a) If no. of mole of SO_3 and SO_2 in flask are same, how many mole of O_2 are present ?

(b) If no. of mole of SO_3 in flask are twice the no. of mole of SO_2, how many mole of O_2 are present ?

34. At 627°C and one atmosphere pressure SO_3 is partially dissociated into SO_2 and O_2 by $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$. The density of the equilibrium mixture is 0.925 g/litre. What is the degree of dissociation ?

35. The equilibrium constant K_P of the reaction :

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

is 900 atm^{-1} at 800 K. A mixture containing SO_3 and O_2 having initial pressure of 1 atm and 2 atm respectively is heated at constant volume to equilibriate. Calculate partial pressure of each gas at 800 K at equilibrium.

36. The equilibrium mixture for

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

present in 1 litre vessel at 600°C contains 0.50, 0.12 and 5.0 mole of SO_2, O_2 and SO_3 respectively.

(a) Calculate K_C for the given change at 600°C.

(b) Also calculate K_P.

(c) How many mole of O_2 must be forced into the equilibrium vessel at 600°C in order to increase the concentration of SO_3 to 5.2 mole ?

37. At 273 K and one atm, 'a' litre of N_2O_4 decomposes to NO_2 according to equation $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. To what extent has the decomposition proceeded when the original volume is 25% less than that of existing volume ?

38. The K_P for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is 640 mm at 775 K. Calculate the percentage dissociation of N_2O_4 at equilibrium pressure of 160 mm. At what pressure, the dissociation will be 50% ? **(Roorkee 1997)**

39. 0.1 mole of $N_2O_4(g)$ was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of $NO_2(g)$ present, if the equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g), \qquad (K_P = 0.14)$$

is reached after sometime.

40. The degree of dissociation of N_2O_4 into NO_2 at one atmosphere and 40°C is 0.310. Calculate its K_P at 40°C. Also report the degree of dissociation at 10 atm pressure at same temperature.

41. At 340 K and one atmospheric pressure, N_2O_4 is 66% dissociated into NO_2. What volume of 10 g N_2O_4 occupy under these conditions ?

42. N_2O_4 dissociates as $N_2O_4 \rightleftharpoons 2NO_2$. At 55°C and one atmosphere, % decomposition of N_2O_4 is 50.3%. At what P and same temperature, the equilibrium mixture will have the ratio of $N_2O_4 : NO_2$ as 1 : 8 ?

43. An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atmosphere respectively. If the volume of container is doubled, calculate the new equilibrium pressure of two gases. **(Roorkee 1991)**

44. At 25°C and 1 atmospheric pressure, the partial pressures in equilibrium mixture of gaseous N_2O_4 and NO_2 are 0.7 and 0.3 atm respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25°C and a total pressure of 10 atm.

45. An equilibrium mixture of N_2O_4 (0.98 mole) and NO_2 (0.06 mole) in a 0.750 litre flask at 27°C is expanded through an evacuated flask of 2.250 litre at 27°C. What are the new concentrations of N_2O_4 and NO_2 in equilibrium ?

46. Prove $\alpha = \sqrt{\left(\frac{K_P}{P + K_P}\right)}$ for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; where α is degree of dissociation at temperature when equilibrium constant is K_P.

47. How much PCl_5 must be added to a one litre vessel at 250°C in order to obtain a concentration of 0.1 mole of Cl_2? K_C for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 0.0414 mol/litre.

48. At 540 K, 0.10 mole of PCl_5 are heated in a 8 litre flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_P and K_C for the reaction. **(Roorkee 1998)**

49. At some temperature and under a pressure of 4 atm. PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated, temperature remaining same. **(Roorkee 1996)**

50. The degree of dissociation of 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1.0 atmosphere. (Atomic mass of P = 31.0 and Cl = 35.5)

51. The equilibrium concentration of the reactants and products for the given equilibrium in a two litre container are shown below :

$$\underset{2M}{PCl_3(g)} + \underset{1M}{Cl_2(g)} \rightleftharpoons \underset{4M}{PCl_5(g)}$$

(i) If 2 mole of Cl_2 are added in the container, find the new equilibrium concentration of each.

(ii) If the equilibrium mixture reported initially is transferred into 4 litre vessel, what would be the new concentrations at equilibrium ?

52. At 473 K, partially dissociated vapours of PCl_5 are 62 times as heavy as H_2. Calculate degree of dissociation of PCl_5.

53. One mole of N_2 and 3 mole of PCl_5 are placed in a 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate degree of dissociation of PCl_5 and K_P of the reaction :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

54. One mole of N_2 is mixed with three mole of H_2 in a 4 litre vessel. If 0.25% N_2 is converted into NH_3 by the reaction.

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

calculate K_C. Also report K_C for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$.

55. NH_3 is heated at 15 atm from 27°C to 347°C assuming volume constant. The new pressure becomes 50 atm at equilibrium of the reaction $2NH_3 \rightleftharpoons N_2 + 3H_2$. Calculate % of mole of NH_3 actually decomposed.

56. In a mixture of N_2 and H_2 in the ratio 1 : 3 at 30 atm and 300°C, the % of NH_3 at equilibrium is 17.8. Calculate K_P for $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

57. A reaction carried out by 1 mole of N_2 and 3 mole of H_2 shows at equilibrium, the mole fraction of NH_3 as 0.012 at 500°C and 10 atm pressure. Calculate K_P. Also report the pressure at which mole % of NH_3 in equilibrium mixture is increased to 10.4.

58. At 450°C, the equilibrium constant K_P for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ was found to be 1.6×10^{-5} at a pressure of 200 atm. If N_2 and H_2 are taken in 1 : 3 ratio, what is the % of NH_3 formed at this temperature ?

59. Calculate K_C for the reaction :

$$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g)$$

If 1.58 mole of H_2S, 1.27 mole of H_2 and 2.78×10^{-6} mole of S_2 are in equilibrium in a flask of capacity 180 litre at 750°C.

60. What is the % dissociation of H_2S, if 1 mole of H_2S is introduced into a 1.10 litre vessel at 1000 K ? K_C for the reaction :

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g) \text{ is } 1 \times 10^{-6}.$$

61. At 90°C, the equilibrium, $H_2(g) + S(g) \rightleftharpoons H_2S(s)$ was established having $K = 6.8 \times 10^{-2}$. If 0.20 mole of hydrogen and 1.0 mole of sulphur are heated to 90°C in one litre vessel, what will be the partial pressure of H_2S at equilibrium ?

62. Calculate the per cent dissociation of $H_2S(g)$, if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1000 K. For the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ the value of K_C is 1.0×10^{-6}. **(Roorkee 1994)**

63. K_P for the reaction $2O_3(g) \rightleftharpoons 3O_2(g)$; is 1.3×10^{57} atm. How many O_3 molecules are present in equilibrium in 10 million cubic metres of air at 25°C and 720 mm Hg pressure ?

64. At 1000 K, the pressure of iodine gas is found to be 0.112 atm due to partial dissociation. Had there been no dissociation the pressure would have been 0.074 atm? Calculate K_P for the reaction, $I_2(g) \rightleftharpoons 2I(g)$.

65. When S in the form of S_8 is heated at 900 K, the initial pressure of 1 atmosphere falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2. Find the K_P for reaction. **(Roorkee 1990)**

66. For the reaction, $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$; H_2 is introduced into a five litre flask at 327°C, containing 0.2 mole of $CO(g)$ and a catalyst till the pressure is 4.92 atmosphere. At this point 0.1 mole of $CH_3OH(g)$ is formed. Calculate K_C and K_P. **(IIT 1990)**

67. 0.15 mole of CO taken in a 2.5 litre flask is maintained at 750 K alongwith a catalyst so that the following reaction can take place.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate :

(i) K_P and K_C

(ii) The final pressure, if the same mole of CO and H_2 as before are used but without catalyst so that the reaction does not take place. **(IIT 1993)**

68. The value of K_P is 1×10^{-3} atm^{-1} at 25°C for the reaction: $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$. A flask contains NO at 0.02 atm and at 25°C. Calculate the mol of Cl_2 that must be added, if 1% of the NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 mol of gas produce 1 atm pressure at 25°C. (Ignore probable association of NO to N_2O_2) **(Roorkee 2001)**

69. A graph plotted between $\log_{10} K_C$ and $1/T$ is straight line with intercept 10 and slope equal to 0.5. Calculate:

(i) pre-exponential factor A.

(ii) heat of reaction at 298 K.

(iii) equilibrium constant at 298 K.

(iv) equilibrium constant at 800 K assuming ΔH remains constant in between 298 K and 800 K.

70. K_P for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.6×10^{-4} atm^{-2} at 400°C. What will be K_P at 500°C? Heat of reaction in this temperature range is −25.14 kcal.

71. K_C for $\frac{3}{2}H_2 + \frac{1}{2}N_2 \rightleftharpoons NH_3$ are 0.0266 and 0.0129 atm^{-1} respectively at 350°C and 400°C. Calculate heat of formation of NH_3.

72. Equilibrium constant K_P for

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

is 0.0118 atm at 1065°C and heat of dissociation is 42.4 kcal. Find equilibrium constant at 1132°C.

73. K_P for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 400°C is 1.64×10^{-4}. Find K_C. Also find $\Delta G°$ using K_P and K_C values and interpret the difference.

74. Calculate the value of $\log K_P$ for the reactions,

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

at 25°C. The standard enthalpy of formation of $NH_3(g)$ is −46 kJ and standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 191, 130 and 192 JK^{-1} mol^{-1} respectively. ($R = 8.3$ JK^{-1}mol^{-1}) **(Roorkee 1999)**

75. $\Delta G°$ for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ is −16.5 KJ mol^{-1}. Find out K_P for the reaction. Also report K_P and $\Delta G°$ for,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \text{ at } 25°C.$$

76. The plot of $\log_{10} K_P$ against $\frac{1}{T}$ for the reaction :

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

is a straight line with slope = 4.95×10^3. Calculate K_P at 25°C if standard entropies for $SO_2(g)$, $O_2(g)$ and $SO_3(g)$ are 248.2, 205.1 and 256.8 JK^{-1} mol^{-1} at 25°C respectively.

77. Show that $2.303 \log_{10} K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$; where K is equilibrium constant and $\Delta H°$ and $\Delta S°$ are standard enthalpy and standard entropy change at temperature T.

78. The heat enthalpy and standard free energy change for the equilibrium :

$$Zn(s) + H_2O(g) \rightleftharpoons ZnO(s) + H_2(g)$$

are 224 KJ mol^{-1} and 33 KJ mol^{-1} respectively at the temperature 920 K. Calculate the temperature at which equilibrium constant becomes greater than 1. Assume ΔG° and ΔH remains constant.

79. Calculate the composition of A and B in an equilibrium mixture following the reaction :

	A	$\rightleftharpoons$ B
ΔH° (in kJ)	24.27	25.44
ΔS° (in J)	246.4	253.3

(100 mole of equilibrium mixture is present at 300 K)

80. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria :

$$B = A \quad ; \quad \Delta G_1^0 = ?$$

$$B = C \quad ; \quad \Delta G_2^0 = ?$$

From the calculated value of ΔG_1^0 and ΔG_2^0 indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

81. For the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$

$$(G^0_{N_2O_4})_{298K} = 100\,kJ\,mol^{-1} \text{and } (G^0_{NO_2})_{298} = 50\,kJ\,mol^{-1}$$

(i) When 5 mole/litre of each is taken, calculate the value of ΔG for the reaction at 298 K.

(ii) Find the direction of reaction and concentration at equilibrium **(IIT 2004)**

82. Consider the reaction $A \rightleftharpoons B$. The ΔH_f^0 for A and B are −24.27 and −25.44 kJ/mol respectively. S° for A and B are 246.4 and 252.3 JK^{-1} mol^{-1} respectively. What is the composition of equilibrium mixture at 298 K ?

83. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g/litre at 288 K and 1.84 g/litre at 348 K. Calculate the enthalpy of reaction : $N_2O_4 \rightleftharpoons 2NO_2$. Also calculate the entropy change during the reaction at 348 K.

84. Calculate the equilibrium concentration ratio of C to A, if 2.0 mol each of A and B were allowed to come to equilibrium $A + B \rightleftharpoons C + D$ at 300 K. The ΔG° for the change is 460 cal.

85. $\Delta G^\circ = 77.77$ kJ mol^{-1} at 1000 K for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$. What is the partial pressure of NO under equilibrium at 1000 K for air at 1 atm pressure containing 80% N_2 and 20% O_2 by volume ?

86. 88 g chunk of dry ice and 30 g graphite were placed in a 5 litre container and the mixture was heated to achieve the equilibrium :

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Calculate the value of K_P at 1000 K if the density of gas mixture is 18.3 g/litre. What is the value of K_p at 1100 K if density of gas mixture is 18.9 g/litre. Also calculate the enthalpy of reaction.

87. Following data are given for the reaction :

$$H_2(g) + \frac{1}{2}S_2(g) \rightleftharpoons H_2S(g)$$

T(K)	1023	1218	1362	1473	1667
$\log_{10} K_P$	2.025	1.305	0.902	0.643	0.257

Assuming ΔH° and ΔS° constant for the given range, calculate ΔH° for the reaction in the range 1000 to 1218 K. Calculate ΔG° and ΔS° at 1023 K.

88. Consider the equilibrium $A(g) \rightleftharpoons 2B(g) + 3C(g)$ at 25°C. When A is loaded into a cylinder at 10.0 atm and the system is allowed to come an equilibrium, the final pressure is found to be 15.76 atm. What is standard Gibb's energy change for the reaction ?

89. Given below are the values of ΔH° and ΔS° for the reaction at 27°C.

$$SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$$

$\Delta H^\circ = -98.32$ kJ mol^{-1} and $\Delta S^\circ = -95$ JK^{-1} mol^{-1}. Find K_P for the reaction.

90. For $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$, the observed pressure for reaction mixture in equilibrium is 1.12 atm at 106°C. What is the value of K_P for the reaction ?

91. Some solid NH_4HS is placed in flask containing 0.5 atm of NH_3. What would be pressures of NH_3 and H_2S when equilibrium is reached ?

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g); \quad K_P = 0.11$

92. The equilibrium pressure of

$NH_4CN(s) \rightleftharpoons NH_3(g) + HCN(g)$ is 0.298 atm.

Calculate K_P. If $NH_4CN(s)$ is allowed to decompose in presence of NH_3 at 0.25 atm, calculate partial pressure of HCN at equilibrium.

93. When 3.06 g of solid NH_4HS is introduced into a two-litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_C and K_P for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask ? **(IIT 1999)**

94. Ammonium carbonate dissociates as

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

In a closed vessel containing ammonium carbamate in equilibrium, ammonia is added such that partial pressure of NH_3 now equals to the original total pressure. Calculate the ratio of total pressure now to the original pressure.

95. What concentration of CO_2 be in equilibrium with 2.5×10^{-2} mol litre^{-1} of CO at 100°C for the reaction ?

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g); \quad K_C = 5.0$$

96. In the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts, calculate K_P.

97. The amount of CO_2 in a gaseous mixture of CO_2 and CO is determined by passing the mixture into an aqueous solution that contains excess of $Ba(OH)_2$. The CO_2 reacts yielding a precipitate of $BaCO_3$ but CO does not react. This method is used to analyse the equilibrium composition of gas when 1.77 g CO_2 reacted with 2.0 g graphite in a 1.0 litre container at 1100 K. The analysis yielded 3.41 g of $BaCO_3$. Use this data to calculate K_P at 1100 K for the reaction.

$$CO_2(g) + C(s) \rightleftharpoons 2CO$$

98. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm Some of the CO_2 is converted into CO on addition of graphite. Calculate the value of K, if total pressure at equilibrium is 0.8 atm. **(Roorkee 1993)**

99. At 817°C, K_P for the reaction between $CO_2(g)$ and excess hot graphite (s) is 10 atm.

(a) What are the equilibrium concentration of the gases at 817°C and a total pressure of 5 atm ?

(b) At what total pressure, the gas contains 5% CO_2 by volume ? **(Roorkee 2000)**

100. The equilibrium attained in a closed container is $H_2O(l) \rightleftharpoons H_2O(v)$ at 40°C. The aqueous tension of water in container is 23 mm at 40°C. What is its K_P?

101. When 20 g of $CaCO_3$ were put into 10 litre flask and heated to 800°C, 35% of $CaCO_3$ remained unreacted at equilibrium. Calculate K_P for decomposition of $CaCO_3$.

102. At a certain temperature, K_P for dissociation of solid $CaCO_3$ is 4×10^{-2} atm and for the reaction, $C(s) + CO_2 \rightleftharpoons 2CO$ is 2.0 atm respectively. Calculate the pressure of CO at this temperature when solid C, CaO, $CaCO_3$ are mixed and allowed to attain equilibrium.

103. Would 1% CO_2 in air be sufficient to prevent any loss in weight when M_2CO_3 is heated at 120° C?

$$M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(g)$$

$K_P = 0.0095$ atm at 120°C. How long would the partial pressure of CO_2 have to be to promote this reaction at 120°C?

104. In the preparation of quick lime from limestone, the reaction is,

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

Experiments carried out between 850°C and 950°C led to set of K_P values fitting in empirical equation $\ln K_P = 7.282 - \frac{8500}{T}$ where T is absolute temperature.

If the reaction is carried out in quiet air, what minimum temperature would be predicted from this equation for almost complete decomposition of lime ?

105. Under what pressure conditions $CuSO_4 \cdot 5H_2O$ be efflorescent at 25°C? How good a drying agent is $CuSO_4 \cdot 3H_2O$ at the same temperature ? Given

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(v)$$

$K_P = 1.086 \times 10^{-4}$ atm^2 at 25°C. Vapour pressure of water at 25°C is 23.8 mm of Hg.

106. From the data given below derive which of the following reactant is most effective drying agent at 0°C. Given $P^\circ_{H_2O} = 4.58$ mm at 0°C.

(i) $SrCl_2 \cdot 6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O(s) + 4H_2O(g)$; $K_P = 6.9 \times 10^{-12}$ atm^4

(ii) $Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$; $K_P = 4.08 \times 10^{-25}$ atm^{10}

(iii) $Na_2HPO_4 \cdot 12H_2O(s) \rightleftharpoons Na_2HPO_4 \cdot 7H_2O(s) + 5H_2O(g)$; $K_P = 5.25 \times 10^{-13}$ atm^5

107. For the reaction,

$$SnO_2(s) + 2H_2(g) \rightleftharpoons Sn(l) + 2H_2O(g)$$

the equilibrium mixture of steam and hydrogen contained 45% and 24% H_2 at 900 K and 1100 K respectively. Calculate K_P at both the temperatures. Generally should it be higher or lower temperatures for better reduction of SnO_2 ?

108. For the equilibrium :

$LiCl \cdot 3NH_3(s) \rightleftharpoons LiCl \cdot NH_3(s) + 2NH_3, K_P = 9\,\text{atm}^2$ at 40°C. A 5 litre vessel contains 0.1 mole of $LiCl \cdot NH_3$. How many mole of NH_3 should be added to the flask at this temperature to derive the backward reaction for completion ?

109. The equilibrium : $2Na(g) \rightleftharpoons Na_2(g)$ was attained at 1.013 M Pa and 1500 K. The mass % of Na(g) at equilibrium was found to be 71.0. Calculate K_P of reaction.

110. A small thermometer is broken in a closed room of dimensions $6 \times 5 \times 3\, m^3$ and the mercury shows the equilibrium : $Hg(l) \rightleftharpoons Hg(v)$ at 27°C. The atomic mass of Hg is 200.5 and vapour pressure of Hg at 27°C is 0.002 mm. Is it dangerous to enter the room if safety limit to Hg(v) is 0.05 mg/m^3 ?

111. In an experiment starting with 1 mole C_2H_5OH, 1 mole CH_3COOH and 1 mole of water, the equilibrium mixture on analysis shows that 54.3% of the acid is esterified. Calculate K_C.

112. When C_2H_5OH and CH_3COOH are mixed in equivalent proportion, equilibrium is reached when 2/3 of acid and alcohol are used. How much ester will be present when 2 g molecule of acid were to react with 2 g molecule of alcohol?

113. When $\alpha-$D glucose is dissolved in water, it undergoes a partial conversion to $\beta-$D glucose to exhibit mutarotation. This conversion stops when 63.6% of glucose is in β form. Assuming that equilibrium has been attained, calculate K_C for mutarotation.

114. Calculate K_C for the reaction, $KI + I_2 \rightleftharpoons KI_3$. Given that initial mass of KI is 1.326 g. Mass of KI_3 is 0.105 g and no. of mole of free I_2 is 0.0025 at equilibrium and the volume of solution is one litre. The solubility of I_2 in water is 0.0013 *M*.

115. Sulphide ions in alkaline solution react with solid sulphur to form polyvalent sulphide ions. The equilibrium constant for the formation of S_2^{2-} and S_3^{2-} from S and S^{2-} ions are 1.7 and 5.3 respectively. Calculate equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S.

116. To 500 mL of 0.150 *M* $AgNO_3$ solution were added 500 mL of 1.09 *M* Fe^{2+} solution and the reaction is allowed to reach an equilibrium at 25°C.

$$Ag^+(aq.) + Fe^{2+}(aq.) \rightleftharpoons Fe^{3+}(aq.) + Ag(s)$$

For 25 mL of the solution, 30 mL of 0.0832 *M* $KMnO_4$ were required for oxidation. Calculate equilibrium constant for the reaction at 25°C.

117. For the reaction,

$$2Fe^{3+}(aq.) + (Hg_2)^{2+}(aq.) \rightleftharpoons 2Fe^{2+}(aq.) + 2Hg^{2+}(aq.)$$

$K_C = 9.14 \times 10^{-6}$ at 25°C. If the initial concentration of the ions are $Fe^{3+} = 0.5\,M$, $(Hg_2)^{2+} = 0.5\,M$, $Fe^{2+} = 0.03\,M$ and $Hg^{2+} = 0.03\,M$. What will be the concentrations of ions at equilibrium?

118. 0.1 mole each of ethyl alcohol and acetic acid are allowed to react and at equilibrium, the acid was exactly neutralized by 100 mL of 0.85 *N* NaOH. If no hydrolysis of ester is supposed to have undergo, find K_C.

119. The rate of formation of the complex $[Fe(dipy)_3]^{2+}$ at 25°C following the reaction:

$$Fe^{2+} + 3\,dipy \rightleftharpoons [Fe(dipy)_3]^{2+}$$

is given as: $\text{rate} = 1.45 \times 10^{13}[Fe^{2+}][dipy]^3$

The rate of disappearance of complex is given as:

$$\text{rate} = 1.22 \times 10^{-4}\,[Fe(dipy)_3]^{2+}$$

Calculate the stability constant of complex. *dipy* is abbreviated for dipyridyl a chelating agent.

120. For the reaction $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$, the K_C at 25°C is 4×10^{-19}. Calculate $[Ag^+]$ in solution which was originally 0.1 *M* in KCN and 0.03 *M* in $AgNO_3$.

(IIT 1994)

121. The equilibrium constant for the reaction:

H_3BO_3 + glycerine $\rightleftharpoons$ (H_3BO_3 + glycerine complex)

is 0.90. How much glycerine should be added to one litre of 0.10 *M* H_3BO_3 solution, so that 60% of the H_3BO_3 is converted to boric acid-glycerine complex?

122. For gaseous reaction $A + B \rightleftharpoons C$, the equilibrium concentration of *A* and *B* at a temperature are 15 mol litre^{-1}. When volume is doubled the reaction had equilibrium concentration of *A* as 10 mol litre^{-1}. Calculate:

(a) K_C

(b) concentration of *C* in original equilibrium.

123. When NO and NO_2 are mixed, the following equilibria are readily obtained;

$$2NO_2 \rightleftharpoons N_2O_4 \qquad K_P = 6.8\ \text{atm}^{-1}$$

and $\quad NO + NO_2 \rightleftharpoons N_2O_3$

In an experiment when NO and NO_2 are mixed in the ratio of 1 : 2, the final total pressure was 5.05 atm and the partial pressure of N_2O_4 was 1.7 atm. Calculate:

(a) the equilibrium partial pressure of NO.

(b) K_P for $NO + NO_2 \rightleftharpoons N_2O_3$.

124. Following two equilibria are established on mixing two gases A_2 and *C*.

(i) $3A_2(g) \rightleftharpoons A_6(g) \qquad K_P = 1.6\ \text{atm}^{-2}$

(ii) $A_2(g) + C(g) \rightleftharpoons A_2C(g)$

If A_2 and *C* are mixed in 2 : 1 molar ratio, calculate the equilibrium partial pressure of A_2, *C*, A_2C and K_P for the reaction (ii). Given that the total pressure to be 1.4 atm and partial pressure of A_6 to be 0.2 atm at equilibrium.

125. 1 mole of *A* in 1 litre vessel maintained at constant *T* shows the equilibrium:

$$A(g) \rightleftharpoons B(g) + 2C(g) \qquad K_{C_1}$$

$$C(g) \rightleftharpoons 2D(g) + 3B(g) \qquad K_{C_2}$$

If the equilibrium pressure is $\frac{13}{6}$ times of initial pressure and $[C]_{eq.} = \frac{4}{9}[A]_{eq.}$, calculate K_{C_1} and K_{C_2}.

126. Solid NH_4I on rapid heating in a closed vessel at 357°C develops a constant pressure of 275 mm Hg owing to partial decomposition of NH_4I into NH_3 and HI, but the pressure gradually increases further (when the excess solid residue remains in the vessel) owing to dissociation of HI. Calculate the final pressure developed at equilibrium K_P for dissociation of HI is 0.015 at 357°C.

127. N_2 and O_2 combine at a given temperature to produce NO. At equilibrium the yield of NO is 'x' per cent by volume. If $x = \sqrt{K.a.b} - \frac{K(a+b)}{4}$ where K is the equilibrium constant of the given reaction at the given temperature and a and b are the volume percentage of N_2 and O_2 respectively in the initial pure mixture, what should be the initial composition of the reacting mixture in order that maximum yield of NO is ensured? Also report the maximum value of K at which 'x' is maximum.

128. The standard Gibb's energy change for the reaction :

$$2AB \rightleftharpoons A_2 + B_2$$

is 11.8 kJ at 230 K and 1 atm. Calculate degree of dissociation of AB at 230 K.

129. In a reaction at equilibrium 'X' mole of the reactant A decompose to give 1 mole each of C and D. It has been found that the fraction of A decomposed at equilibrium is independent of initial concentration of A. Calculate X.

130. The heat of reaction at constant volume for an endothermic reaction in equilibrium is 1200 cal more than at constant pressure at 300 K. Calculate the ratio of equilibrium constants K_P and K_C.

131. A vessel of 2.50 litre was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2 to attain the equilibrium at 440°C as :

$$Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$$

After equilibrium the H_2S formed was analysed by dissolving it in water and treating with excess of Pb^{2+} to give 1.029 g of PbS as precipitate. What is value of K_C of the reaction at 440°C ? (Atomic mass of Pb = 206)

132. Gas A (mol. mass 16) and gas B (mol. mass 4) are confined into a vessel at partial pressure of 2 atm each at 27°C. The gases are then allowed to effuse out at 27°C through a value till the pressure inside the vessel becomes 2 atm after which the valve is closed and the gases are heated to 127°C and allowed to react as $A + B \rightleftharpoons C \quad K_P = 0.1\ \text{atm}^{-1}$. Calculate the partial pressure of C at equilibrium assuming C is not formed till the effusing process is completed at 27°C.

133. A gas mixture of volumetric composition 45% CO, 50% CO_2 and 5% N_2 was passed at 1380 K over a briquet of ZnO, so that Zn vapours was produced according to the reaction: $ZnO(s) + CO(g) \rightleftharpoons Zn(g) + CO_2(g)$. Under steady condition, the rate of input gas flow at STP is $0.224\ \text{dm}^3\ \text{min}^{-1}$. The rate of loss of mass of ZnO is $5 \times 10^{-4}\ \text{mol min}^{-1}$. $P = 770$ torr. Find K_P at 1380 K assuming ideal gas behaviour.

134. A certain gas A polymerises to a small extent at a given temperature and pressure : $nA \rightleftharpoons (A)_n$. Show that the gas obeys the approximate equation :

$$\frac{PV}{RT} = \left[1 - \frac{(n-1)K_C}{V^{n-1}}\right].$$

where $$K_C = \frac{[A_n]}{[A]^n}$$

and V is the volume of the container. Assume initially one mole of A was taken in the container.

135. Steam is passed over hot carbon to attain the following equilibrium at 400 K.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g).$$

The equilibrium constant $K = 1.34$ (dimension less) and the total pressure of the equilibrium mixture is 200 kPa. What are the mole fractions of all substances in equilibrium mixture ?

136. If equilibrium constant K_C of the reaction :

$$2Ag(s) + 2I^- + 2H_2O \rightleftharpoons 2AgI(s) + H_2(g) + 2OH^-$$

is 1.2×10^{-23} (dimension less) at 25°. If concentrations of I^- at equilibrium is 0.10 and pressure of H_2 gas at equilibrium is 60 kPa, calculate the pH of solution at equilibrium.

137. A gaseous substance $AB_2(g)$ reacts with solid A to form $AB(g)$ and the reaction attains equilibrium :

$$AB_2(g) + A(s) \rightleftharpoons 2AB(g)$$

The initial and final pressure are 0.7 and 0.95 bar. Calculate K_P. Also if the equilibrium mixture is expanded reversibly and isothermally till the equilibrium pressure falls to 0.4 bar, calculate the volume percentage of $AB(g)$ and $AB_2(g)$ at final equilibrium.

138. For the reaction :

$$CH_3COCH_3(g) \rightleftharpoons C_2H_6(g) + CO(g)$$

initial pressure of CH_3COCH_3 is 100 mm. The mole fraction of CO(g) is 1/3 at equilibrium. What is K_C?

SOLUTIONS (Numerical Problems)

1. (1) A system is said to be homogeneous if phase (P) =1.
A system with $P \geq 2$ is heterogeneous.

(2) To determine phase follow the rules given below.

System	Phase	Explanation
$S+S$	$=2$	No. of solid in mixture give number of P, *i.e.*, $P=2$
$S+L$	$=1$	Soluble systems lead to $P=1$
$S+L$	$=2$	Insoluble system lead to $P=2$
$L+L$	$=2$	Immiscible liquids lead to $P=2$
$L+L$	$=1$	Miscible liquids lead to $P=1$
$G+G$	$=1$	All gases in a mixture give P = 1

Given Systems	a	b	c	d	e	f	g
No. of phase	2	2	2	2	1	2	3

∴ Homogeneous system is : **e**

Heterogeneous systems are : **a, b, c, d, f, g**

2. **Note :** 1. Write K_P for heterogeneous systems if gaseous phase is present.

2. Write K_C for homogeneous solution phase.

3. Write K_P or K_C for homogeneous gaseous phase.

(a) $K_P = [P'_{O_2}]^{3/2}$

(b) $K_P = [P'_{H_2O}]/P'_{H_2} = \dfrac{n_{H_2O}}{n_{H_2}} \times [P/\Sigma N]^0$

(c) $K_P = [P'_{CO_2}]^2/[P'_{O_2}]^5 = \dfrac{[n_{CO_2}]^2}{[n_{O_2}]^5} \cdot \left[\dfrac{P}{\Sigma N}\right]^{-3}$

(d) $K_P = \dfrac{[P'_{HI}]^2}{P'_{H_2} \times P'_{I_2}}$ or $K_C = \dfrac{[HI]^2}{[H_2][I_2]}$

(e) $K_P = \dfrac{[P'_{NH_3}]^2}{[P'_{N_2}][P'_{H_2}]^3}$ or $K_C = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(f) $K_C = \dfrac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$

3.

	N_2	+ $3H_2$	$\rightleftharpoons$ $2NH_3$	
Initial mole	1	3	0	
Final mole	0	0	2	(∵ complete conversion)

∴ Ratio of initial and final volumes $= \dfrac{\text{Initial mole}}{\text{Final mole}}$

(∵ $V \propto n$ if P and T are constant) $= \dfrac{4}{2} = 2$

4. For $2H_2O \rightleftharpoons 2H_2 + O_2$ $\quad K_1 = \dfrac{[H_2]^2[O_2]}{[H_2O]^2}$ ...(1)

For $2CO_2 \rightleftharpoons 2CO + O_2$ $\quad K_2 = \dfrac{[CO]^2[O_2]}{[CO_2]^2}$ ...(2)

For $CO_2 + H_2 \rightleftharpoons H_2O + CO$ $\quad K = \dfrac{[H_2O][CO]}{[CO_2][H_2]}$ ...(3)

Thus, by Eqs. $\dfrac{(2)}{(1)}$, $\dfrac{K_2}{K_1} = \dfrac{[CO]^2[O_2]}{[CO_2]^2} \times \dfrac{[H_2O]^2}{[H_2]^2[O_2]}$

$$\frac{K_2}{K_1} = \frac{[CO]^2[H_2O]^2}{[CO_2]^2[H_2]^2} = K^2 \qquad \text{By Eq. (3)}$$

or $K = \sqrt{\left(\dfrac{K_2}{K_1}\right)} = \sqrt{\left(\dfrac{1.4 \times 10^{-12}}{2.1 \times 10^{-13}}\right)} = \mathbf{2.58}$

5. For $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2$

$$K_{C_1} = \frac{[SO_2][O_2]^{1/2}}{[SO_3]} = 0.15 \qquad \text{...(1)}$$

For $\quad 2SO_2 + O_2 \rightleftharpoons 2SO_3$

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \qquad \text{...(2)}$$

By reversing Eq. (1), $\dfrac{1}{K_{C_1}} = \dfrac{[SO_3]}{[SO_2][O_2]^{1/2}}$

On making square, $\left(\dfrac{1}{K_{C_1}}\right)^2 = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]} = K_C$

By Eq. (2)

$$K_C = \left[\frac{1}{0.15}\right]^2 = \mathbf{44.44\ mol^{-1}\ litre^{1}}$$

6. For $\quad 2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} I$

$$K_{C_1} = \frac{K_1}{K_2} = \frac{[I]}{[A]^2} \qquad \text{...(1)}$$

For $\quad I \rightleftharpoons B + C$

$$K_{C_2} = \frac{K_3}{K_4} = \frac{[B][C]}{[I]} \qquad \text{...(2)}$$

For $\quad 2A \rightleftharpoons B + C$

$$K_C = \frac{[B][C]}{[A]^2}$$

By Eqs. (1) × (2), $K_C = K_{C_1} \times K_{C_2} = \dfrac{K_1}{K_2} \times \dfrac{K_3}{K_4}$

7.

$$K_P = K_C(RT)^{\Delta n}$$
$$K_P = 0.5 \times (0.082 \times 400)^{-2}$$
$$K_P = \mathbf{4.648 \times 10^{-4}\ (atm)^{-2}}$$

8. $\quad A + B \rightleftharpoons 3C$

Before reaction, $[A] = 1/3$, $\quad [B] = 2/3$, $\quad [C] = 4/3$

Thus, $\quad Q = \dfrac{[C]^3}{[A][B]} = \dfrac{4^3 \times 3 \times 3}{3^3 \times 1 \times 2} = \dfrac{64}{6} = 10.66$

(a) Since $K_C = 10$, thus Q must decrease to attain K_C value and thus, $[C]$ must decrease or $[A]$ and $[B]$ should increase. Thus, reaction will occur in backward direction.

(b) Since $K_C = 15$, thus Q must increase to attain K_C value and thus, $[C]$ must increase or $[A]$ and $[B]$ should decrease. Thus, reaction will occur in forward direction.

(c) $Q = K_C$; thus, reaction is in equilibrium.

9.

	$2AB_2(g)$	$\rightleftharpoons 2AB(g)$	$+B_2(g)$
Mole before dissociation	1	0	0
Mole after dissociation	$(1-x)$	x	$\frac{x}{2}$

Total mole at equilibrium $(\Sigma n) = 1-x+x+\frac{x}{2} = 1+\frac{x}{2}$

Now, $$K_P = \frac{{}^nB_2 \times ({}^nAB)^2}{(n_{AB_2})^2} \times \left[\frac{P}{\Sigma n}\right]^{\Delta n}$$

$$K_P = \frac{\frac{x}{2}\cdot(x)^2}{(1-x)^2} \times \left[\frac{P}{1+\frac{x}{2}}\right]^1$$

$$K_P = \frac{x^3 P}{2}\left[\because x \text{ is small}, \therefore 1-x \approx 1 \text{ and } 1+\frac{x}{2} \approx 1\right]$$

or $$x = \sqrt[3]{\frac{2K_P}{P}}$$

10. The ratio $\frac{[\text{Product}]}{[\text{Rectant}]}$ is maximum when $K = 10^{10}$ and thus, reaction goes farthest to completion when $K = 10^{10}$.

11. For $A(g) \rightleftharpoons B(g)$; $K_C = \frac{[B]}{[A]} = 1.1 \Rightarrow [B] > [A]$

If $[B] = 1$;	$[A] = 0.91$	
Case I	$0.91 < [A] \leq 1$	Only $[B] > 1$
Case II	$[A] > 1$	Both $[A]$ and $[B] > 1$

12.

	$C_6H_{12}O_6 \rightleftharpoons$	$6HCHO$
Initial conc.	1	0
Conc. at eq.	$(1-\alpha)$	6α

$$K_C = \frac{1}{6\times10^{22}}$$

$$\therefore K_C = \frac{1}{6\times10^{22}} = \frac{(6\alpha)^6}{(1-\alpha)}$$ $[1-\alpha = 1$ since K_C is very small$]$

or $(6\alpha)^6 = 1.67\times10^{-23}$ or $6 \log 6\alpha = -22.78$

or $\log 6\alpha = -3.796$

or $$\alpha = \frac{1.59\times10^{-4}}{6} = \mathbf{2.65\times10^{-5}\ M}$$

$\therefore$ $[\text{HCHO}] = 6\alpha = \mathbf{1.59\times10^{-4}\ M}$

13.

	A	$+\ B$	$\rightleftharpoons C$	$+\ D$
Initial concentration	$2a$	a	0	0
Concentration at equilibrium	$(2a-x)$	$(a-x)$	x	x

Given, initially $[A] = 2[B] = 2a$

Let concentration of B initially be a mol/litre.

$$\therefore \quad K_C = \frac{x\cdot x}{(2a-x)(a-x)} \qquad ...(1)$$

Given at equilibrium, $[C] = 3[B]$ $\therefore$ $x = 3(a-x)$

$$x = \frac{3a}{4} \qquad ...(2)$$

$\therefore$ By Eqs. (1) and (2), $$K_C = \frac{\frac{3a}{4}\times\frac{3a}{4}}{\left(2a-\frac{3a}{4}\right)\left(a-\frac{3a}{4}\right)} = \mathbf{1.8}$$

14.

	$A_2(g)$	$+\ B_2(g)$	$\rightleftharpoons 2AB(g)$
Initial mole	1	2	0
Final mole at equilibrium	$(1-x)$	$(2-x)$	$2x$

Total volume of both containers on joining becomes 3 litre.

$\therefore$ At equilibrium, $[A_2] = \frac{1-x}{3}$; $[B_2] = \frac{2-x}{3}$; $[AB] = \frac{2x}{3}$

$$\therefore K_C = \frac{[AB]^2}{[A_2][B_2]} = \frac{4x^2}{9\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)} = \frac{4x^2}{(2-3x+x^2)} = 50$$

$\therefore$ $4x^2 = 100-150x+50x^2$ or $46x^2-150x+100 = 0$

$x = 0.93$ and 2.326 which is not valid since $x \not> 2$

$\therefore$ Mole of AB $= 2x = 2(0.93) = \mathbf{1.86}$

15.

	A	$+\ 2B$	$\rightleftharpoons AB_2$
Initial mole	1	2	0
Mole at equilibrium	$(1-x)$	$(2-2x)$	x

Total mole at equilibrium $= 1-x+2-2x+x = 3-2x$

Let pressure at equilibrium be P;

$$\because \quad K_P = \frac{n_{AB_2}}{n_A \times (n_B)^2} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n}$$

$$\therefore \quad K_P = \frac{x}{(1-x)(2-2x)^2} \times \left[\frac{P}{(3-2x)}\right]^{-2}$$

$$= \frac{x(3-2x)^2}{(1-x)(2-2x)^2 \cdot P^2} \qquad ...(1)$$

Given that, $x = 0.6$ and $\Delta n = -2$

$\therefore$ $K_P = K_C(RT)^{\Delta n} = 0.3475\times(0.0821\times473)^{-2}$ ...(2)

By Eqs. (1) and (2),

$$\therefore \quad 0.3475\times(0.0821\times473)^{-2} = \frac{0.6(3-1.2)^2}{P^2(1-0.6)(2-1.2)^2}$$

$$= \frac{0.6\times(1.8)^2}{P^2(0.4)(0.8)^2}$$

$$P = \mathbf{181.5\ atm}$$

16.

	$2HI \rightleftharpoons$	H_2	$+\ I_2$
Mole at equilibrium	$\frac{1638.4}{128}$	$\frac{7.8}{2}$	$\frac{203.2}{254}$
	$= 12.8$	3.9	0.8

Let volume of container be V litre

$$[H_2] = \frac{3.9}{V}; [HI] = \frac{12.8}{V}; [I_2] = \frac{0.8}{V}$$

$$\therefore \quad K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{3.9\times0.8}{V\times V\times\left(\frac{12.8}{V}\right)^2} = 0.019$$

$\therefore$ $K_C = \mathbf{0.019}$

For the given reaction $\Delta n = 0$ and thus there will be no effect on equilibrium concentration of reactants and products if the matter is transferred to attain equilibrium in 2 litre vessel.

17. $$H_2 + I_2 \rightleftharpoons 2HI$$ Given,

	H_2	I_2	$2HI$	
Volume at $t = 0$	60	42	0	$\because 2x = 28$
Volume at equilibrium	$(60 - x)$	$(42 - x)$	$2x$	$\therefore x = 14$
	$(60 - 14)$	$(42 - 14)$	28	

Since at constant P and T, mole $\propto$ volume of gas (By $PV = nRT$). Thus, volume of gases given can be directly used as concentration. This can be done only for reactions having $\Delta n = 0$.

$$\therefore \quad K_C = \frac{28 \times 28}{46 \times 28} = \frac{28}{46}$$

Now for dissociation of HI; $2HI \rightleftharpoons H_2 + I_2$

	$2HI$	H_2	I_2
Mole at $t = 0$	1	0	0
Mole at equilibrium	$(1 - \alpha)$	$\alpha/2$	$\alpha/2$

where α is degree of dissociation

$$K_{C_1} = \frac{\alpha^2}{4(1-\alpha)^2} = \frac{1}{K_C}$$

$$\therefore \quad \frac{\alpha}{2(1-\alpha)} = \sqrt{\left(\frac{46}{28}\right)}$$

$$\therefore \quad \alpha = \mathbf{0.719} \text{ or } \mathbf{71.9\%}$$

18. $$HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$$

	HI	H_2	I_2
Initial Mole	1	0	0
Mole at equilibrium	$(1 - \alpha)$	$\alpha/2$	$\alpha/2$

Where α is degree of dissociation and volume of container is V litre.

$$K_P = K_C = \frac{\left(\frac{\alpha}{2V}\right)^{1/2}\left(\frac{\alpha}{2V}\right)^{1/2}}{\frac{(1-\alpha)}{V}} = \frac{\alpha}{2(1-\alpha)}$$

$$\therefore \quad K_P = K_C = \frac{0.2}{2(1-0.2)} \qquad (\because \alpha = 0.2)$$

$$K_P = K_C = \mathbf{0.125}$$

19. Given, $K_P = 1.84 \times 10^{-2}$

$\because \Delta n = 0 \quad \therefore K_P = K_C = 1.84 \times 10^{-2}$

	$2HI$	H_2	I_2
Concentration at equilibrium	a	0.4789	0.4789

Since, given $[H_2] = 0.4789 \quad \therefore [I_2] = 0.4789$ mole litre^{-1}

Conc. of HI at equilibrium is a mol litre^{-1}

$$\therefore \quad K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.4789 \times 0.4789}{a^2}$$

$$\therefore \quad a^2 = \frac{0.4789 \times 0.4789}{1.84 \times 10^{-2}} \qquad (\because K_C = 1.84 \times 10^{-2})$$

$$\therefore \quad a = 3.53$$

or [HI] at equilibrium = **3.53 mole litre^{-1}**

20. $$H_2 + I_2 \rightleftharpoons 2HI$$

	H_2	I_2	$2HI$
Initial pressure	0.5	0.5	0
At. eq.	$(0.5 - x)$	$(0.5 - x)$	$2x$

$$\therefore \quad K_P = \frac{(2x)^2}{(0.5-x)^2} = 49$$

$$\text{or} \quad \frac{2x}{(0.5-x)} = 7 \text{ or } 2x = 3.5 - 7x \text{ or } 9x = 3.5$$

$$x = \frac{3.5}{9} = 0.389$$

At equilibrium : $P'_{H_2} = 0.5 - 0.389 = \mathbf{0.111\ atm}$

$P'_{I_2} = 0.5 - 0.389 = \mathbf{0.111\ atm}$

$P'_{HI} = 0.389 \times 2 = \mathbf{0.778\ atm}$

21. $$H_2 + I_2 \rightleftharpoons 2HI$$

	H_2	I_2	$2HI$
Initial mole	1	2	3
Mole at equilibrium	$(1 - x)$	$(2 - x)$	$(3 + 2x)$

Let volume of container be V litre.

$$\therefore \quad K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left[\frac{3+2x}{V}\right]^2}{\left[\frac{1-x}{V}\right]\left[\frac{2-x}{V}\right]}$$

$$45.9 = \frac{(3+2x)^2}{(1-x)(2-x)} \qquad (\because K_C = 45.9)$$

$$45.9 = \frac{9 + 4x^2 + 12x}{2 - 3x + x^2}$$

$$\therefore \quad x = 0.684$$

$\therefore$ $[H_2] = 1 - 0.684 = \mathbf{0.316\ mol\ litre^{-1}}$ $\qquad (\because V = 1\text{ litre})$

$[I_2] = 2 - 0.684 = \mathbf{1.316\ mol\ litre^{-1}}$

$[HI] = 3 + 2(0.684) = \mathbf{4.368\ mol\ litre^{-1}}$

22. $$2HI \rightleftharpoons H_2 + I_2$$

	$2HI$	H_2	I_2
Mole at $t = 0$	$\frac{0.96}{128}$	0	0
or	7.5×10^{-3}	0	0
Mole at equilibrium	$(7.5 \times 10^{-3} - x)$	$\frac{x}{2}$	$\frac{x}{2}$

Meq. of I_2 formed at equilibrium = Meq. of hypo used for reaction mixture

$$\frac{w_{I_2}}{E} \times 1000 = 15.7 \times \frac{1}{10} \therefore \left(\frac{w}{E}\right) \text{of } I_2 = 1.57 \times 10^{-3}$$

$$\therefore \quad \text{Mole of } I_2 \text{ formed} = \frac{1.57 \times 10^{-3}}{2} = 0.785 \times 10^{-3}$$

$$\frac{x}{2} = 0.785 \times 10^{-3}$$

$$x = 1.57 \times 10^{-3}$$

$\therefore$ Degree of dissociation of HI

$$(\text{or } \alpha_{HI}) = \frac{\text{Mole dissociated}}{\text{Mole taken}} = \frac{1.57 \times 10^{-3}}{7.5 \times 10^{-3}}$$

$$\alpha_{HI} = \mathbf{0.209} \text{ or } \mathbf{20.9\%}$$

23. Given α for HI = 0.8

$$2HI \rightleftharpoons H_2 + I_2$$

	$2HI$	H_2	I_2
Before dissociation	1	0	0
After dissociation	$(1 - \alpha)$	$\frac{\alpha}{2}$	$\frac{\alpha}{2}$

$$\therefore \quad K_C = \frac{\alpha^2}{4(1-\alpha)^2} = \frac{(0.8)^2}{4(1-0.8)^2} = 4$$

Now,

	H_2	+ I_2	$\rightleftharpoons$ $2HI$
Initial mole	2	2	0
Mole after reaction	$(2-x)$	$(2-x)$	$2x$

$$\therefore \quad K_C' = \frac{1}{K_C} = \frac{4x^2}{(2-x)^2}$$

$$\text{or} \quad \frac{4x^2}{(2-x)^2} = \frac{1}{4} \text{ or } \frac{2x}{2-x} = \frac{1}{2} \text{ or } x = \frac{2}{5}$$

Thus, I_2 left $= 2 - \frac{2}{5} = \frac{8}{5}$ mole $= \frac{8}{5} \times 2$ equivalent

or $Na_2S_2O_3$ required can be calculated by

Meq. of $Na_2S_2O_3$ = Meq. of I_2 left

$$2 \times V = \frac{8}{5} \times 2 \times 1000$$

$$\therefore \quad V = 1600\,\text{mL} = \mathbf{1.6\ litre}$$

24. The lowering of activation energy by a catalyst occurs for forward reaction as well as for backward reaction.

Thus, in presence of catalyst,

Energy of activation for forward reaction

$$(E_{a_1}) = 167 - 80 = 87 \text{ kJ mol}^{-1}$$

Energy of activation for backward reaction

$$(E_{a_2}) = 180 - 80 = 100 \text{ kJ mol}^{-1}$$

$\therefore$ For forward reaction $\quad K_1 = A_1 e^{-E_{a_1}/RT}$

For backward reaction $\quad K_2 = A_2 e^{-E_{a_2}/RT}$

where A_1 and A_2 are frequency factors and E_{a_1} and E_{a_2} are energies of activation.

$$\therefore \quad K_C = \frac{K_1}{K_2} = \frac{A_1}{A_2} \cdot e^{[(-E_{a_1}/RT) + E_{a_2}/RT)]}$$

$$= \frac{4 \times 10^{-4}}{2 \times 10^{-3}} \times e^{[(-87+100)/(8.314 \times 10^{-3} \times 300)]}$$

$$K_C = 2 \times 10^{-1} e^{+13/(8.314 \times 300 \times 10^{-3})}$$

$$K_C = \mathbf{36.8}$$

25.

	H_2	+ I_2	$\rightleftharpoons$ $2HI$
Eq. conc.	0.5	0.5	1.23

$$\therefore \quad K_C = \frac{[1.23]^2}{0.5 \times 0.5} = 6.05$$

On removing 0.60 mole of HI the reaction will proceed in forward direction

	H_2	+ I_2	$\rightleftharpoons$ $2HI$
New conc.	0.5	0.5	0.63
Eq. conc.	$(0.5 - X)$	$(0.5 - X)$	$(0.63 + 2X)$

$$\therefore \quad 6.05 = \frac{(0.63 + 2X)^2}{(0.5 - X)(0.5 - X)} \text{ or } X = 0.134$$

$$\therefore \quad [I_2] = [H_2] = 0.5 - 0.134 = \mathbf{0.366}$$

$$[HI] = 0.63 + (2 \times 0.134) = \mathbf{0.898}$$

26. For the given reaction of H_2 and Br_2 to give HBr, the value of equilibrium constant $K_C = 5 \times 10^8$ and thus, exceptionally higher value of K_C suggests that reaction goes almost to completion, *i.e.*,

	H_2	+ Br_2	$\rightleftharpoons$ $2HBr$
Before reaction	0.6	0.2	0
At equilibrium	0.4	0	0.4

Thus, $\quad HBr = \mathbf{0.4\ mol}$

$$H_2 = \mathbf{0.4\ mol}$$

$$Br_2 = \mathbf{0.0}$$

Note : However if as all the concentrations of Br_2 is needed at equilibrium, it may be calculated as follows. Notice that $[Br_2]$ is in significant.

$2HBr$	$\rightleftharpoons$ H_2	+ Br_2
0.4	0.4	0
$(0.4 - 2x)$	$(0.4 + x)$	x

$$\therefore \quad K_C = \frac{1}{5 \times 10^8} = \frac{(0.4 + x)x}{(0.4 + 2x)^2} = \frac{0.4 \times x}{(0.4)^2}$$

$$\therefore \quad x = \mathbf{8 \times 10^{-10}\ mol}$$

27.

	N_2	+ O_2	$\rightleftharpoons$ $2NO$
Initial	a	$(100 - a)$	0
Final	$(a - x)$	$(100 - a - x)$	$2x$

Given, $\quad \frac{2x}{100} = \frac{1.8}{100} \quad \therefore x = 0.9$

Also, $\quad K_P = K_C = \frac{[NO]^2}{[N_2][O_2]}$

$$= \frac{(2x)^2}{(a - x)(100 - a - x)} = 2.1 \times 10^{-3}$$

$$\therefore \quad a = 79\%; \quad 100 - a = \mathbf{21\%}$$

Note : Two values of 'a' are obtained as $a = 79\%$ and $a = 21\%$. Note that air contains more N_2 than O_2; thus $a = 79\%$.

28. (i)

	$CO(g)$	+ $H_2O(g)$	$\rightleftharpoons$ $CO_2(g)$	+ $H_2(g)$
Initial mole	3	1	0	0
Mole at equilibrium	$(3 - x)$	$(1 - x)$	x	x

Total mole at equilibrium $= 3 - x + 1 - x + x + x = 4$

Now, $\quad K_C = \frac{x^2}{(3 - x)(1 - x)}$

$$\therefore \quad \frac{x^2}{3 + x^2 - 4x} = 0.63 \qquad (\because K_C = 0.63)$$

$$\therefore \quad x = 0.681$$

$\therefore$ Mole of H_2 formed $= \mathbf{0.681}$

(ii) Total pressure at equilibrium = 2 atm

Total mole at equilibrium = 4

$P_g' = P_M \times$ mole fraction of that gas

$$\therefore \quad P_{CO_2}' = P_{H_2} = \frac{x \cdot P}{4} = \frac{0.681 \times 2}{4} = \mathbf{0.34\ atm}$$

$$P_{CO}' = \frac{(3 - x) \cdot P}{4} = \mathbf{1.16\ atm}$$

$$P_{H_2O}' = \frac{(1 - x) \cdot P}{4} = \mathbf{0.16\ atm}$$

29.

	$CO(g)$	+ $H_2O(g)$	$\rightleftharpoons$ $CO_2(g)$	+ $H_2(g)$
Mole at equilibrium	0.4	0.3	0.2	0.6

(a) $\therefore$ $K_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{0.2 \times 0.6}{0.4 \times 0.3} = 1$

($\because \Delta n = 0$, $\therefore$ Volume terms are not needed.)

(b) Now it is desired to increase the conc. of CO by 0.2 at equilibrium by forcing CO_2 into equilibrium mixture. Suppose *a* mole of CO_2 are forced in vessel at equilibrium ; by doing so reaction proceeds in backward direction, *i.e.*,

$$\begin{array}{lcccc} & CO_2 & + \; H_2 \rightleftharpoons & CO & + \; H_2O \\ \text{Addition at initial equilibrium} & (0.2+a) & 0.6 & 0.4 & 0.3 \\ \text{Mole at} & (0.2+a-0.2) & (0.6-0.2) & (0.4+0.2) & (0.3+0.2) \\ \text{new equilibrium} & a & 0.4 & 0.6 & 0.5 \end{array}$$

$$\therefore \quad \frac{1}{K_C}=\frac{[CO][H_2O]}{[CO_2][H_2]}=\frac{0.6\times 0.5}{a\times 0.4}$$

$$\therefore \quad a=\mathbf{0.75\ mol}$$

30.

$$\begin{array}{lcccc} & CO_2(g) & +H_2(g) \rightleftharpoons & CO(g) & +H_2O(g) \\ \text{Mole at } t=0 & 1 & 1 & 0 & 0 \\ \text{Mole at equilibrium} & (1-x) & (1-x) & x & x \end{array}$$

Given that Vol. % of CO = 0.16

$\because$ Mole of CO $= x$

Total mole at equilibrium $= 1-x+1-x+x+x=2$

$$\therefore \quad \frac{x}{2}=\frac{0.16}{100} \quad \therefore \; x=0.0032$$

$$\text{Now,} \quad K_C=K_P=\frac{x^2}{(1-x^2)}$$

($\because \Delta n = 0$, volume terms are not needed)

$$K_P=\frac{(0.0032)^2}{(1-0.0032)^2}=\mathbf{1.03\times 10^{-5}}$$

31. (a)

$$\begin{array}{lcccc} & CO_2 & + \; H_2 \rightleftharpoons & CO & +H_2O \; (\because K_C=0.11) \\ \text{Mole at } t=0 & 0.45 & 0.45 & 0 & 0 \\ \text{Mole at equilibrium} & (0.45-x) & (0.45-x) & x & x \end{array}$$

$$\therefore \quad K_C=0.11=\frac{x\cdot x}{(0.45-x)^2}$$

($\because \Delta n = 0$, $\therefore$ volume terms are not needed)

$$\text{or} \quad \frac{x}{(0.45-x)}=0.3317 \;\therefore\; x=0.112$$

$\therefore$ Mole of CO_2 = Mole of $H_2 = 0.45-0.112=$ **0.338 mol**

Mole of CO = Mole of $H_2O=$ **0.112 mol**

(b)

$$\begin{array}{lcccc} & CO_2 & + \; H_2 & \rightleftharpoons CO & +H_2O \\ \text{Initial mole} & 0.45 & 0.45 & 0 & 0 \\ \text{Mole further added} & (0.45+0.34) & (0.45+0.34) & 0 & 0 \\ \text{Mole at new equilibrium} & (0.79-x) & (0.79-x) & (1+x) & (1+x) \end{array}$$

$$\therefore \quad K_C=\frac{x^2}{(0.79-x)^2}=0.11 \;\therefore\; x=0.197$$

$\therefore$ Mole of CO_2 = Mole of $H_2 = 0.79-0.197=$ **0.593 mol**

Mole of CO = Mole of $H_2O=$ **0.197 mol**

32.

$$\begin{array}{lcccc} & SO_2(g) & +NO_2(g) \rightleftharpoons & SO_3(g) & +NO(g) \\ \text{Mole at } t=0 & 1 & 1 & 1 & 1 \\ \text{Mole at equilibrium} & (1-x) & (1-x) & x & x \end{array}$$

$$\therefore \quad K_C=\frac{\left(\frac{1+x}{V}\right)\left(\frac{1+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)}=\frac{(1+x)^2}{(1-x)^2}$$

$$\therefore \quad \frac{(1+x)^2}{(1-x)^2}=16 \qquad (\because K_C=16)$$

$$\therefore \quad \frac{(1+x)}{(1-x)}=4 \text{ or } x=\frac{3}{5}=0.6$$

$\because$ Volume = 1 litre

$\therefore$ $[SO_2]=[NO_2]=1-x=1-0.6=$ **0.4 mol litre^{-1}**

$[SO_3]=[NO]=1+x=1+0.6=$ **1.6 mol litre^{-1}**

33.

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

$$K_C=100=\frac{[SO_3]^2}{[SO_2]^2[O_2]} \qquad \ldots(1)$$

(a) $\because$ $[SO_3]=[SO_2]$

By Eq. (1), $100=\dfrac{1}{[O_2]}$ or $[O_2]=\dfrac{1}{100}$

or $\dfrac{\text{mole of } O_2}{\text{volume}}=\dfrac{1}{100}$ $\qquad (\because V=10 \text{ litre})$

$\therefore$ Mole of $O_2=\dfrac{1}{100}\times 10=\mathbf{0.1}$

(b) $[SO_3]=2[SO_2]$

By Eq. (1), $100=\dfrac{4}{[O_2]}$ or $[O_2]=\dfrac{4}{100}$

$\therefore$ Mole of $O_2=\dfrac{4}{100}\times 10=\mathbf{0.4}$

34. For equilibrium mixture, $PV=\dfrac{w}{m}RT$

$$\therefore \quad \text{Molar mass}_{\text{mixture}}=\frac{wRT}{VP}$$

$\because$ $\dfrac{w}{V}=0.925\text{g/L}$, $T=900$ K, $P=1$ atm, $R=0.0821$

$$\text{Molar mass}_{\text{mixture}}=\frac{0.925\times 0.0821\times 900}{1}=68.35$$

Experimental molar mass of $SO_3 = 68.35$

Normal molar mass of $SO_3 = 80$

$$\begin{array}{lccc} \because & SO_3 \rightleftharpoons & SO_2 & +\frac{1}{2}O_2 \\ \text{Mole before equilibrium} & 1 & 0 & 0 \\ \text{Mole at equilibrium} & (1-\alpha) & \alpha & \alpha/2 \end{array}$$

where α is degree of dissociation.

$$\frac{1}{\text{Normal molar mass}} \propto$$

No. of particles before dissociation, *i.e.*, 1

$$\frac{1}{\text{Apparent molar mass}} \propto$$

No. of particles after dissociation, *i.e.*, $1+(\alpha/2)$

$$\therefore \quad \frac{\text{Normal molar mass}}{\text{Apparent molar mass}}=1+\frac{\alpha}{2} \;\therefore\; 1+\frac{\alpha}{2}=\frac{80}{68.35}$$

$$\alpha=\mathbf{0.3408} \quad \text{or} \quad \mathbf{34.08\%}$$

35. Consider the reaction,

$$\begin{array}{lccc} & 2SO_3 \rightleftharpoons & 2SO_2 & +\;O_2 ; \quad K_P=\frac{1}{900}\text{atm} \\ \text{Initial pressure} & 1 & 0 & 2 \\ \text{Pressures left at equilibrium} & (1-x) & x & 2+\frac{x}{2} \end{array}$$

$$\therefore \quad K_P=\frac{(P'_{SO_2})^2(P'_{O_2})}{(P'_{SO_3})^2}$$

$$\frac{1}{900}=\frac{x^2\left(2+\frac{x}{2}\right)}{(1-x)^2}$$

$\therefore$ Since, K_P of this reaction is small and thus, $x <<< 1$,

$\therefore$ x^3 is negligible

$$\therefore \quad \frac{1}{900}=\frac{x^2(2)}{(1-x)^2}=\frac{2x^2}{(1-x)^2} \therefore \frac{1}{30}=\frac{\sqrt{2x}}{(1-x)} \therefore x=0.0236$$

At equilibrium $\therefore$ $P'_{SO_3}=1-x=1-0.0236=\mathbf{0.9764\ atm}$

$$P'_{SO_2}=x=\mathbf{0.0236\ atm}$$

$$P'_{O_2}=2+\frac{x}{2}=\mathbf{2.0118\ atm}$$

36.

$$\begin{array}{lccccc} & 2SO_2(g) & + & O_2(g) & \rightleftharpoons & 2SO_2(g) \\ \text{Mole at equilibrium} & 0.5 & & 0.12 & & 5.0 \end{array}$$

Volume = 1 litre

(a) $$K_C=\frac{[SO_3]^2}{[SO_2]^2[O_2]}=\frac{(5)^2}{(0.5)^2(0.12)}$$

$$K_C=\mathbf{833.33\ mol\ litre^1}$$

(b) $$K_P=K_C\ (RT)^{\Delta n}=833.33\times(0.0821\times 873)^{-1}$$

$$=\mathbf{11.62\ (atm)^{-1}}$$

(c) Now O_2 is forced into the vessel in order to increase the concentration of SO_3 to 5.2 mole litre^{-1}.

Let a mole of O_2 be introduced in it to increase SO_3 to 5.2 mole. Thus, 0.2 mole of SO_2 and 0.1 mole of O_2 will be consumed to show forward reaction.

$$\begin{array}{lccccc} & 2SO_2 & + & O_2 & \rightleftharpoons & 2SO_3 \\ \text{At 1 equilibrium} & 0.5 & & 0.12 & & 5 \\ \text{New equilibrium} & (0.5-0.2) & & (0.12+a-0.1) & & 5.2 \end{array}$$

$$\therefore \quad 833.33=\frac{(5.2)^2}{(0.02+a)(0.3)^2} \quad \therefore \quad a=\mathbf{0.34\ mol}$$

37.

$$\begin{array}{lccc} & N_2O_4(g) & \rightleftharpoons & 2NO_2(g) \\ \text{Mole before equilibrium} & a & & 0 \\ \text{Mole at equilibrium} & (a-x) & & 2x \end{array}$$

Given that original volume $=\frac{75}{100}\times$ existing volume at equilibrium

Since, mole $\propto$ volume (at constant P and T)

$$\therefore \quad \text{Initial mole}=\frac{75}{100}\times\text{mole at equilibrium}$$

$$a=\frac{75}{100}(a+x)$$

$$\therefore \quad x=\frac{25}{75}a=0.33a$$

Now, % decomposition $(\alpha)=\frac{x}{a}=\frac{0.33a}{a}=\mathbf{0.33\ or\ 33\%}$

38.

$$\begin{array}{lccc} & N_2O_4 & \rightleftharpoons & 2NO_2 \\ \text{Mole before equilibrium} & 1 & & 0 \\ \text{Mole at equilibrium} & (1-x) & & 2x \end{array}$$

$$K_P=\frac{4x^2}{(1-x)}\times\left[\frac{P}{\Sigma n}\right]^{\Delta n}$$

$$640=\frac{4x^2}{(1-x)}\frac{160}{(1+x)}$$

$$4=\frac{4x^2}{1-x^2} \quad \text{or} \quad 1-x^2=x^2 \quad \text{or} \quad 2x^2=1$$

$$\therefore \quad x^2=1/2 \quad \text{or} \quad x=0.707=70.7\%$$

Also, $$640=\frac{4\times(0.5)^2}{0.5}\times\frac{P}{1.5} \qquad (\text{if } x=0.5)$$

$$P=\mathbf{480\ mm}$$

39.

$$\begin{array}{ccc} N_2O_4 & \rightleftharpoons & 2NO_2 \\ 0.1 & & 0 \\ (0.1-\alpha) & & 2\alpha \end{array} \left[\begin{array}{ll} \because P\propto 0.1 & \therefore 1\propto 0.1 \\ \left(\begin{array}{l}\text{If } V \text{ and } T\\ \text{are constant}\end{array}\right) & \begin{array}{l} P\propto 0.1+\alpha \\ P=[(0.1+\alpha)/0.1] \end{array} \end{array}\right]$$

$$K_P=\frac{(2\alpha)^2}{(0.1-\alpha)}\times\left[\frac{P}{0.1+a}\right]^1 \quad \text{or} \quad K_P=\frac{40\alpha^2}{(0.1-\alpha)}$$

or $$\frac{40\alpha^2}{(0.1-\alpha)}=0.14$$

$$\therefore \quad \alpha=0.017$$

$$\therefore \quad NO_2=0.017\times 2=\mathbf{0.034\ mol}$$

40.

$$\begin{array}{lccc} & N_2O_4 & \rightleftharpoons & 2NO_2 \\ \text{Initial mole} & 1 & & 0 \\ \text{Mole at equilibrium} & (1-0.310) & & (2\times 0.310) \\ & =0.69 & & =0.62 \end{array} \quad (\text{Given } \alpha=0.31)$$

$\therefore$ Total mole at equilibrium = 0.69 + 0.62 = 1.31

$$\because \quad K_P=\frac{(n_{NO_2})^2}{(n_{N_2O_4})}\times\left(\frac{P}{\Sigma n}\right)^{\Delta n}=\frac{(0.62)^2}{(0.69)}\times\left(\frac{1}{1.31}\right)^1$$

$$(\because \Delta n=1, P=1\ \text{atm})$$

$$=0.425\text{atm}$$

For dissociation at 10 atm pressure at 40°C

$$\begin{array}{ccc} N_2O_4 & \rightleftharpoons & 2NO_2 \\ 1 & & 0 \\ (1-\alpha) & & 2\alpha \end{array} \quad (\alpha \text{ is degree of dissociation})$$

$$K_P=\frac{(n_{NO_2})^2}{(n_{N_2O_4})}\times\left(\frac{P}{\Sigma n}\right)^{\Delta n}=\frac{4\alpha^2}{(1-\alpha)}\left(\frac{10}{1+\alpha}\right)$$

or $$0.425=\frac{4\alpha^2\times 10}{(1-\alpha^2)}$$

$$\alpha=\mathbf{10.25\%}$$

41.

$$\begin{array}{lccc} & N_2O_4 & \rightleftharpoons & 2NO_2 \\ \text{Mole before equilibrium} & 1 & & 0 \\ \text{Mole after equilibrium} & (1-\alpha) & & 2\alpha \end{array} \quad (\text{Let } \alpha \text{ be degree of dissociation})$$

$\therefore$ Total mole at equilibrium $=1+\alpha=1+0.66=1.66$

$$(\because \alpha=0.66)$$

1 mole of N_2O_4 is taken, mole at equilibrium = 1.66

$\frac{10}{92}$ mole of N_2O_4 is taken, mole at equilibrium

$$=\frac{1.66\times 10}{92}=0.18$$

$$\because \quad PV=\frac{w}{m}RT$$

$$1\times V=0.18\times 0.0821\times 340$$

$$\therefore \quad V=5.02\ \text{litre}$$

Thus, volume of 10 g N_2O_4 under above condition is **5.02 litre.**

42. $N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$2NO_2$
Mole before equilibrium	1	0
Mole at equilibrium	$1-\alpha$	2α

where α is degree of dissociation = 0.503

$$K_P = \frac{(n_{NO_2})^2}{(n_{N_2O_4})}\times\left(\frac{P}{\Sigma n}\right)^{\Delta n} = \frac{(2\alpha)^2}{(1-\alpha)}\left(\frac{P}{(1+\alpha)}\right)^1$$

$$K_P = \frac{4\alpha^2 P}{1-\alpha^2} = \frac{4\times(0.503)^2\times 1}{1-(0.503)^2} = 1.355$$

Now, $N_2O_4 \rightleftharpoons 2NO_2$ (at pressure P)

	N_2O_4	$2NO_2$
	1	0
	$(1-x)$	$2x$

Given, $\frac{N_2O_4}{NO_2} = \frac{1-x}{2x} = \frac{1}{8}$ $\left(\therefore\ x = \frac{8}{10} = 0.8\right)$

Using again at pressure P

$$\therefore \quad K_P = \frac{4x^2\times P}{1-x^2}$$

$$1.355 = \frac{4\times(0.8)^2\times P}{1-(0.8)^2}$$

$$P = \mathbf{0.19\ atm}$$

43. $N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$2NO_2$
Pressure at equilibrium	0.28	1.1

$$\therefore \quad K_P = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(1.1)^2}{0.28} = 4.32\text{atm}$$

Now if volume of container is doubled, *i.e.*, pressure decreases and will become half, the reaction will proceed in the direction where the reaction shows an increase in mole, *i.e.*, decomposition of N_2O_4 is favoured.

$N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$2NO_2$
New pressure at equilibrium	$\left(\frac{0.28}{2}-P\right)$	$\left(\frac{1.1}{2}+2P\right)$

where reactant N_2O_4 equivalent to pressure P is used up in doing so.

$$\text{Again,} \quad K_P = \frac{\left[\frac{1.1}{2}+2P\right]^2}{\left[\frac{0.28}{2}-P\right]} = \frac{[0.55+2P]^2}{[0.14-P]} = 4.32$$

$$P = \mathbf{0.045}$$

$\therefore$ Now, $P_{N_2O_4} = 0.14 - 0.045 = \mathbf{0.095\ atm}$

P_{NO_2} at new eq. $= 0.55 + 2\times 0.045$

$P_{NO_2} = \mathbf{0.64\ atm}$

44. $N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$2NO_2$
Pressure at equilibrium	0.7	0.3

$$\therefore \quad K_P = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{0.3\times 0.3}{0.7} = 0.1286\text{ atm}$$

Now assume decomposition at 10 atm pressure

$N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$2NO_2$
Initial mole	1	0
Mole at equilibrium	$(1-x)$	$2x$

$$K_P = \frac{(n_{NO_2})^2}{n_{N_2O_4}}\times\left(\frac{P}{\Sigma n}\right)^{\Delta n} = \frac{(2x)^2}{(1-x)}\times\left[\frac{10}{(1+x)}\right]^1$$

$$\text{or} \quad 0.1286 = \frac{4x^2\times 10}{(1-x^2)}$$

$$\therefore \quad x = 0.0565$$

$$\therefore \quad P'_{NO_2} = \frac{2x}{(1+x)}\times P = \frac{2\times 0.0565\times 10}{(1+0.0565)} = \mathbf{1.07\ atm}$$

$$P'_{N_2O_4} = \left[\frac{1-0.0565}{1+0.0565}\right]\times 10 = \mathbf{8.93\ atm}$$

45. $N_2O_4 \rightleftharpoons 2NO_2$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.06)^2}{0.750\times 0.98} = 4.90\times 10^{-3}$$

if $V = 0.750 + 2.250 = 3$ litre, *i.e.*, volume increases and the reaction will proceed in forward reaction, *i.e.*,

$N_2O_4 \rightleftharpoons 2NO_2$

$(0.98-x)$ $(0.06+2x)$

$$\therefore \quad 4.90\times 10^{-3} = \frac{(0.06+2x)^2}{3\times(0.98-x)} \quad \text{or} \quad x = 0.029$$

$$\therefore \quad [N_2O_4] = \frac{0.98-0.029}{3} = \mathbf{0.317\ mol\ litre^{-1}}$$

$$[NO_2] = \frac{0.06+0.029\times 2}{3} = \mathbf{0.039\ mol\ litre^{-1}}$$

46. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
Initial mole	1	0	0
Mole at equilibrium	$1-\alpha$	α	α

where α is degree of dissociation

$$\therefore \quad P'_{Cl_2} = \left[\frac{\alpha}{1+\alpha}\right]\times P; \quad P'_{PCl_3} = \left[\frac{\alpha}{1+\alpha}\right]\times P;$$

$$P'_{PCl_5} = \left[\frac{1-\alpha}{1+\alpha}\right]\times P$$

$$\therefore \quad K_P = \frac{P'_{PCl_3}\times P'_{Cl_2}}{P'_{PCl_5}} = \frac{\left[\frac{\alpha\times P}{1+\alpha}\right]\left[\frac{\alpha\times P}{1+\alpha}\right]}{\left[\frac{1-\alpha}{1+\alpha}\right]\times P}$$

$$K_P = \frac{\alpha^2 P}{1-\alpha^2}$$

$$\therefore \quad \alpha = \sqrt{\left(\frac{K_P}{P+K_P}\right)}$$

Hence proved.

47. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
Initial mole	a	0	0
Mole at equilibrium	$(a-0.1)$	0.1	0.1

$$\therefore \quad K_C = \frac{\frac{0.1}{1}\times\frac{0.1}{1}}{\frac{a-0.1}{1}} \quad (\because \text{ volume is 1 litre})$$

$$\text{or} \quad 0.0414 = \frac{0.01}{(a-0.1)}$$

$$\therefore \quad a = \mathbf{0.3415\ mol}$$

48. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
Mole before dissociation	0.1	0	0
Mole after dissociation	$(0.1-x)$	x	x

Given, volume of container = 8 litre

$$\text{Now,} \quad K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{8}\cdot\frac{x}{8}}{\frac{(0.1-x)}{8}} = \frac{x^2}{8(0.1-x)} \quad \text{...(1)}$$

Also, $PV = nRT$ for the equilibrium mixture at 540 K.

$$1 \times 8 = (0.1 + x) \times 0.082 \times 540$$

$$\therefore \quad x = 0.08$$

Thus, from Eqs. (1) and (2), ...(2)

$$K_C = \frac{0.08 \times 0.08}{8(0.1 - 0.08)} = \mathbf{4 \times 10^{-2}\ mol\ litre^{-1}}$$

Also, $K_P = K_C (RT)^{\Delta n}$; $\Delta n = +1$

$$= 4 \times 10^{-2} (0.082 \times 540) = \mathbf{1.77\ atm}$$

49.

$$\begin{array}{lccc} & PCl_5 & \rightleftharpoons PCl_3 & + \; Cl_2 \\ \text{Mole before dissociation} & 1 & 0 & 0 \\ \text{Mole after dissociation} & 1-\alpha & \alpha & \alpha \end{array}$$

Given, $\alpha = 0.1$ at 4 atm pressure

$$\therefore \quad K_P = \frac{n_{PCl_3} \times n_{Cl_2}}{n_{PCl_5}} \times \left[\frac{P}{\Sigma n}\right]^{\Delta n}$$

$$= \frac{\alpha \cdot \alpha}{(1-\alpha)}\left[\frac{P}{1+\alpha}\right]^1 = \frac{P\alpha^2}{1-\alpha^2} = \frac{4 \times (0.1)^2}{1-(0.1)^2}$$

$$K_P = 0.040 \text{ atm}$$

Again when α is desired at 0.2, K_P remains constant and thus,

$$K_P = \frac{P\alpha^2}{1-\alpha^2}$$

$$0.040 = \frac{P \times (0.2)^2}{1-(0.2)^2}$$

$$\therefore \quad P = \mathbf{0.96\ atm}$$

50.

$$\begin{array}{lccc} & PCl_5 & \rightleftharpoons PCl_3 & + Cl_2 \\ \text{Initial mole} & 1 & 0 & 0 \\ \text{Mole at equilibrium} & (1-0.4) & 0.4 & 0.4 \end{array}$$

Total mole at equilibrium $= 1 - 0.4 + 0.4 + 0.4 = 1.4$

$$\frac{\text{Normal } m_{PCl_5}}{\text{Observed } m_{PCl_5}} = 1 + \alpha = 1.4$$

$$\therefore \quad \text{Observed } m_{PCl_5} = \frac{208.5}{1.4}$$

From $PV = \frac{w}{m}RT$ at equilibrium

$$\frac{w}{V} = \frac{Pm}{RT} = \frac{1 \times 208.5}{1.4 \times 0.0821 \times 400} = \mathbf{4.53\ g / litre}$$

51.

$$\begin{array}{lccc} & PCl_3 & + \; Cl_2 & \rightleftharpoons PCl_5 \\ \text{Initially} & 2\,M & 1\,M & 4\,M \end{array}$$

$$\therefore \quad K_C = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{4}{2 \times 1} = 2$$

Now 2 mole of Cl_2 in 2 litre container are added, *i.e.*, $[Cl_2]$ is increased by 1 M, which will direct the reaction is forward. Thus,

$$\begin{array}{ccc} PCl_3 \; + & Cl_2 & \rightleftharpoons PCl_5 \\ 2\,M & 1\,M + 1\,M & 4\,M \\ (2-a) & (2-a) & (4+a) \end{array}$$

or

$$K_C = \frac{(4+a)}{(2-a)^2}$$

or

$$2 = \frac{4+a}{(2-a)^2} \quad \therefore \; a = 0.5$$

Thus, new concentrations of reactants and products at equilibrium are

$$[PCl_3] = \mathbf{1.5}\,\boldsymbol{M}; \quad [Cl_2] = \mathbf{1.5}\,\boldsymbol{M}; \quad [PCl_5] = \mathbf{4.5}\,\boldsymbol{M}$$

(ii) If the initial equilibrium mixture is transferred in 4 litre vessel then,

$$\begin{array}{lccc} & PCl_3(g) + & Cl_2(g) \longrightarrow & PCl_5(g) \\ \text{Conc. in 2 litre vessel} & 2 & 1 & 4 \\ \text{Conc. in 4 litre vessel} & \frac{2}{2} & \frac{1}{2} & \frac{4}{2} \text{ (Initial volume is doubled)} \\ & =1 & \frac{1}{2} & 2 \end{array}$$

This will cause an decrease in pressure and thus, equilibrium will shift in backward direction, *i.e.*, new equilibrium conc.

$$(1+x) \qquad \left(\frac{1}{2}+x\right) \qquad (2-x)$$

$$\therefore \quad K_C = 2 = \frac{2-x}{(1+x)\left(\frac{1}{2}+x\right)}$$

$$\text{or} \quad 2\left(\frac{1}{2} + x^2 + \frac{3}{2}x\right) = 2 - x \qquad \text{or} \quad 2x^2 + 4x - 1 = 0$$

$$\therefore \quad x = \frac{-4 \pm \sqrt{16 - 4 \times (2) \times (-1)}}{2 \times 2}$$

$$\therefore \quad x = 0.225\,M$$

$$\therefore \quad [PCl_5] = 2 - 0.225 = \mathbf{1.775}\,\boldsymbol{M}$$

$$[Cl_2] = 0.5 + 0.225 = \mathbf{0.725}\,\boldsymbol{M}$$

$$[PCl_3] = 1 + 0.225 = \mathbf{1.225}\,\boldsymbol{M}$$

52.

$$\begin{array}{lccc} & PCl_5 & \rightleftharpoons PCl_3 & + \; Cl_2 \\ \text{Mole before dissociation} & 1 & 0 & 0 \\ \text{Mole after dissociation} & 1-\alpha & \alpha & \alpha \end{array}$$

Since, $\frac{1}{\text{Normal molar mass}} \propto$ Particles before dissociation

$$\frac{1}{\text{Exp. molar mass}} \propto \text{Particles after dissociation}$$

$$\therefore \quad \frac{\text{Normal molar mass}}{\text{Exp. molar mass}} = \frac{\text{Particles after dissociation}}{\text{Particles before dissociation}}$$

$$= 1 + \alpha$$

$\because$ Exp. molar mass = 62 × molar mass of H_2 = 62 × 2

$$\frac{208.5}{62 \times 2} = 1 + \alpha \quad \therefore \; \alpha = \mathbf{0.6815} \text{ or } \mathbf{68.15\%}$$

53.

$$\begin{array}{lc|ccc|} & N_2 \; + & PCl_5 & \rightleftharpoons PCl_3 & + \; Cl_2 \\ \text{Mole at } t = 0 & 1 & 3 & 0 & 0 \\ \text{Mole at equilibrium} & 1 & (3-x) & x & x \end{array}$$

$\therefore$ Total mole present at equilibrium $= 4 + x$

Given, total pressure at equilibrium $= 2.05$

Now, $PV = nRT$ (at equilibrium)

$$2.05 \times 100 = (4 + x) \times 0.0821 \times 500$$

$$\therefore \quad x = 0.9939$$

Now degree of dissociation for $PCl_5 = \frac{\text{Mole dissociated}}{\text{Total mole}}$

$$= \frac{0.9939}{3} = \mathbf{0.3313} \text{ or } \mathbf{33.13\%}$$

$$\therefore \quad K_P = \left[\frac{n_{PCl_3} \times n_{Cl_2}}{n_{PCl_5}}\right] \times \left[\frac{P}{\Sigma n}\right]^{+1} = \frac{x^2}{(3-x)} \times \left[\frac{2.05}{4+x}\right]$$

$$= \frac{(0.9939)^2}{(3 - 0.9939)} \times \left[\frac{2.05}{4 + 0.9939}\right]$$

$$K_P = \mathbf{0.20}$$

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

	N_2	$3H_2$	$2NH_3$
Mole at $t = 0$	1	3	0
Mole at equilibrium	$(1-x)$	$(3-3x)$	$2x$

$$\therefore \quad K_C = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3} = \frac{4x^2V^2}{(1-x)(3-3x)^3} \quad ...(1)$$

Now, given $x = \frac{0.25}{100}$ and $V = 4$ litre

$\therefore$ By Eq. (1), $K_C = \mathbf{1.49 \times 10^{-5}}$ **litre^2 mol^{-2}**

Now for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$; $K_{C_1} = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$

$\therefore$ $K_{C_1} = \sqrt{(K_C)} = \mathbf{3.86 \times 10^{-3}}$ **litre mol^{-1}**

55. $$2NH_3 \rightleftharpoons N_2 + 3H_2$$

	$2NH_3$	N_2	$3H_2$
Initial Mole	a	0	0
Mole at equilibrium	$(a-2x)$	x	$3x$

Initial pressure of NH_3 of a mole = 15 atm at 27°C

The pressure of a mole of NH_3 = P atm at 347°C

$$\therefore \quad \frac{15}{300} = \frac{P}{620} \quad \therefore \quad P = 31 \text{ atm}$$

At constant volume and at 347°C mole $\propto$ pressure

$a \propto 31$ (Before equilibrium)

$a + 2x \propto 50$ (After equilibrium)

$$\therefore \quad \frac{a+2x}{a} = \frac{50}{31} \quad \therefore \quad x = \frac{19}{62}a$$

$\therefore$ % of NH_3 decomposed $= \frac{2x}{a} \times 100$

$$= \frac{2 \times 19a}{62 \times a} \times 100 = \mathbf{61.3\%}$$

56. $$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

	N_2	$3H_2$	$2NH_3$
Mole before dissociation	1	3	0
Mole at equilibrium	$(1-x)$	$(3-3x)$	$2x$

$\therefore$ Total mole at equilibrium $= 4 - 2x$

and mole of NH_3 at equilibrium $= 2x$

$\because$ % of NH_3 in mixture = 17.8

$$\therefore \quad \frac{2x}{4-2x} = \frac{17.8}{100} \quad \therefore \quad x = 0.302$$

$$\text{Now, } K_P = \frac{(n_{NH_3})^2}{n_{N_2} \times (n_{H_2})^3} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n}$$

$$= \frac{4x^2}{(1-x)(3-3x)^3} \times \left(\frac{P}{4-2x}\right)^{-2} = \frac{4x^2(4-2x)^2}{P^2(1-x)(3-3x)^3}$$

Now, $P = 30$ atm and $x = 0.302$

$\therefore$ $K_P = \mathbf{7.29 \times 10^{-4}}$ **atm^{-2}**

57. $$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

	N_2	$3H_2$	$2NH_3$
Mole before reaction	1	3	0
Mole at equilibrium	$1-x$	$(3-3x)$	$2x$

Given, mole fraction of $NH_3 = 0.012$ at $P = 10$atm

$$\therefore \quad \frac{2x}{(4-2x)} = 0.012$$

$$\therefore \quad x = 0.0237$$

$$\therefore \quad K_P = \frac{(P'_{NH_3})}{(P'_{N_2}) \times (P'_{H_2})^3} = \frac{\left[\frac{2x \cdot P}{(4-2x)}\right]^2}{\frac{(1-x) \cdot P}{(4-2x)}\left[\frac{(3-3x)P}{(4-2x)}\right]^3}$$

$$K_P = \frac{4x^2(4-2x)^2}{(1-x)(3-3x)^3 P^2} \quad ...(1)$$

$$= \frac{4(0.0237)^2[4-2(0.0237)]^2}{(1-0.0237)[3-3(0.0237)]^3 \times 100}$$

$K_P = \mathbf{1.431 \times 10^{-5}}$ **atm^{-2}**

Let mole % of NH_3 in equilibrium mixture be increased to 10.4 at pressure P.

$$\therefore \quad \frac{2x}{4-2x} = \frac{10.4}{100} \quad \text{or} \quad x = 0.1884$$

Now again using Eq. (1), $K_P = \frac{4x^2(4-2x)^2}{(1-x)(3-3x)^3 \cdot P^2}$

$$1.431 \times 10^{-5} = \frac{[4 \times (0.1884)^2][4 - 2(0.1884)]^2}{[1-0.1884][3-3(0.1884)]^3 \times P^2}$$

$P = \mathbf{105.41}$ **atm**

58. $$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

	N_2	$3H_2$	$2NH_3$
Mole before equilibrium	1	3	0
Mole after equilibrium	$(1-x)$	$3(1-x)$	$2x$

$$\therefore \quad K_P = \frac{(2x)^2(4-2x)^2}{(1-x)[3(1-x)]^3 \times P^2}$$

$$K_P = \frac{16 \times x^2 \times (2-x)^2}{27(1-x)^4 \times P^2}$$

$$\text{or} \quad 1.6 \times 10^{-5} = \frac{16x^2(2-x)^2}{27(1-x)^4 \times (200)^2}$$

$$\therefore \quad \frac{x^2(2-x)^2}{(1-x)^4} = \frac{1.6 \times 10^{-5} \times 27 \times (200)^2}{16}$$

$$= \frac{16 \times 10^{-6} \times 27 \times (200)^2}{16}$$

$$\therefore \quad \frac{x(2-x)}{(1-x)^2} = 200 \times 10^{-3} \times \sqrt{27} = 1.039$$

$$\therefore \quad x = 0.301$$

$\therefore$ Mole of NH_3 formed $= 2 \times 0.301 = 0.602$

Total mole at equilibrium $= 4 - 2 \times 0.301 = 3.398$

% of NH_3 at equilibrium $= \frac{0.602}{3.398} \times 100 = \mathbf{17.76\%}$

59. $$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g)$$

	$2H_2(g)$	$S_2(g)$	$2H_2S(g)$
Mole at equilibrium	1.27	2.78×10^{-6}	1.58

Volume of container = 180 litre

$$K_C = \frac{[H_2S]^2}{[H_2]^2[S_2]} = \frac{\left(\frac{1.58}{180}\right)^2}{\left(\frac{1.27}{180}\right)^2\left(\frac{2.78 \times 10^{-6}}{180}\right)}$$

$$= \frac{(1.58)^2 \times 180}{(1.27)^2 \times (2.78 \times 10^{-6})}$$

$$K_C = \mathbf{1.002 \times 10^8\ litre\ mol^{-1}}$$

60. $$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

Mole before dissociation	1	0	0
Mole after dissociation	$(1-\alpha)$	α	$\frac{\alpha}{2}$

Where α is degree of dissociation of H_2S

Volume of container = 1.10 litre

$$\therefore \quad K_C = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left[\frac{\alpha}{1.1}\right]^2\left[\frac{\alpha}{2\times 1.1}\right]}{\left[\frac{1-\alpha}{1.1}\right]^2} = 1\times 10^{-6}$$

Assuming $1-\alpha \approx 1$ since α is small because $K_C \approx 10^{-6}$

$$\therefore \quad \frac{\alpha^3}{2(1.1)} = 10^{-6}$$

$$\alpha = 1.3\times 10^{-2} = \mathbf{1.3\%}$$

61. $$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$

Mole before reaction	0.2	1.0	0
Mole at equilibrium	$(0.2-x)$	$(1-x)$	x

Thus, $K = \frac{[H_2S]}{[H_2]}$ or $6.8\times 10^{-2} = \frac{x}{(0.2-x)}$

$$\therefore \quad x = 0.013$$

Now, $P_{H_2S} = \frac{0.013\times 0.0821\times 363}{1}$ $\left[\text{from } P = \frac{nRT}{V}\right]$

$$P_{H_2S} = \mathbf{0.387\ atm}$$

62. **2%**

63. Volume of air $= 10\times 10^6\ m^3 = 10\times 10^6 \times 10^3$ litre $= 10^{10}$ litre

Volume of O_2 = 20% air $= \frac{20\times 10^{10}}{100} = 20\times 10^8$ litre

$$\therefore \quad n_{O_2} = \frac{PV}{RT} = \frac{720}{760}\times\frac{20\times 10^8}{0.0821\times 298} = 7.74\times 10^7$$

Now, $$K_P = \frac{(n_{O_2})^3}{(n_{O_3})^2}\times\frac{P}{\Sigma n}$$

$$\because \quad n_{O_2} >> n_{O_3} : K_P = 1.3\times 10^{57}$$

$$\therefore \quad \Sigma n = n_{O_2} = \frac{(n_{O_2})^3 \times 720}{(n_{O_3})^2 \times 760 \times n_{O_2}}$$

$$\therefore \quad (n_{O_3})^2 = \frac{(n_{O_2})^2\times 720}{760\times K_P} = \frac{(7.74\times 10^7)^2\times 720}{760\times 1.3\times 10^{57}}$$

$$\therefore \quad n_{O_3} = 2.09\times 10^{-21}$$

$\therefore$ molecules of $O_3 = 2.09\times 10^{-21}\times 6.023\times 10^{23}$

$$= \mathbf{12.58\times 10^2}$$

64. $$I_2(g) \rightleftharpoons 2I(g)$$

Initial pressure	0.074	0
Final pressure	$(0.074-P)$	$2P$

where I_2 equivalent to pressure P dissociates

$\therefore \quad 0.074 - P + 2P = 0.112$ or $P = 0.112 - 0.074 = 0.038$

Now, $$K_P = \frac{(P'_I)^2}{P'_{I_2}} = \frac{(2\times 0.038)^2}{(0.074-0.038)} = \mathbf{0.160\ atm}$$

65. $$S_8(g) \rightleftharpoons 4S_2(g)$$

Initial pressure	1	0
Pressure of equilibrium	$(1-0.29)$ 0.71	(4×0.29) 4×0.29

$\because$ Pressure of S_8 reduces by 0.29 atm

Now, $$K_P = \frac{[P'_{S_2}]^4}{[P'_{S_8}]} = \frac{[4\times 0.29]^4}{0.71} = \mathbf{2.55\ (atm)^3}$$

NOTE : It would have been better, if the physical state of S_2 have also been reported as gaseous state.

66. $$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Initial mole	0.2	a	0
Mole at equilibrium	$(0.2-0.1)$	$(a-0.2)$	0.1

Now total mole at equilibrium are $= 0.1 + a - 0.2 + 0.1 = a$

Also, mole $(n) = \frac{PV}{RT} = \frac{4.92\times 5}{0.0821\times 600} = 0.499$

$$\therefore \quad a = 0.499$$

$$\therefore \quad [CH_3OH] = \frac{0.1}{5}; [CO] = \frac{0.2-0.1}{5} = \frac{0.1}{5};$$

$$[H_2] = \frac{0.499-0.20}{5} = \frac{0.299}{5}$$

$$\because \quad K_C = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.1/5}{0.1/5\times(0.299/5)^2}$$

$$= 279.64\ litre^2\ mol^{-2}$$

$$K_C = \mathbf{279.64\ litre^2\ mol^{-2}}$$

$$K_P = K_C(RT)^{\Delta n} = 279.64\times(0.0821\times 600)^{-2}$$

$$K_P = \mathbf{0.115\ atm^{-2}}$$

67. (i) Given,

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Mole before reaction	0.15	a	0
Mole after reaction	$(0.15-x)$	$(a-2x)$	x
and			$x = 0.08$

Total mole at equilibrium $= 0.15 - x + a - 2x + x$

$= 0.15 + a - 2x$

$= 0.15 + a - 0.16 = a - 0.01$

Also total mole at equilibrium are obtained by $n = \frac{PV}{RT}$

$$n = \frac{8.5\times 2.5}{0.0821\times 750} \quad \because \left.\begin{array}{l} P = 8.5\text{atm} \\ V = 2.5\text{lit.} \\ T = 750\text{K} \end{array}\right\} \text{at equilibrium}$$

$$\therefore \quad n = 0.345$$

$$\therefore \quad a - 0.01 = 0.345$$

$$\therefore \quad a = 0.355$$

At equilibrium : Mole of CO = 0.15 – 0.08 = 0.07

Mole of H_2 = 0.355 – 0.16 = 0.195

Mole of CH_3OH = 0.08

$$\therefore \quad K_C = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{0.08/2.5}{\left(\frac{0.07}{2.5}\right)\left(\frac{0.195}{2.5}\right)^2}$$

$$= \mathbf{187.85\ mol^{-2}\ litre^2}$$

Also $K_P = K_C(RT)^{\Delta n}$

$$= 187.85 \times (0.0821 \times 750)^{-2} = \mathbf{0.05\ atm^{-2}}$$

(ii) If reaction does not take place, then

Mole of CO $= 0.15$

Mole of $H_2 = 0.355$

$\therefore$ Total mole $= 0.505$ $\therefore$ $P \times 2.5 = 0.505 \times 0.0821 \times 750$

$\therefore$ $P = \mathbf{12.438\ atm}$

68.

$$\begin{array}{llll} & 2NO(g) & + \ Cl_2(g) \rightleftharpoons & 2NOCl(g) \\ \text{Pressure at } t=0 & 0.02 & & \\ \text{Pressure at eq.} & \frac{0.02 \times 99}{100} & P & \frac{0.02 \times 1}{100} \end{array}$$

$$\because \quad K_P = \frac{[P_{NOCl}]^2}{[P_{NO}]^2[P_{Cl_2}]} = \frac{(0.02 \times 0.01)^2}{(0.99 \times 0.02)^2 \times P} = 1 \times 10^{-3}$$

$\therefore$ $P = 0.102$ atm

For Cl_2 in vessel, using $PV = nRT$

$$0.102 \times V = n \times R \times T \qquad \text{...(i)}$$

For a gas in vessel, $1 \times V = 9.2 \times R \times T$ ...(ii)

By Eqs. (i) and (ii),

$\therefore$ mole of Cl_2 (n) at equilibrium $= 0.0204$

2 atm of NO reacts with 1 atm of Cl_2 (If V, T are constant)

$\frac{0.02 \times 1\text{atm}}{100}$ NO react with $\frac{0.02 \times 1}{2 \times 100} = 0.0001$ atm Cl_2

Thus, $0.0001 \times V = n_{Cl_2 \text{ used}} \times RT$ ...(iii)

By Eqs. (ii) and (iii),

$\therefore$ n_{Cl_2} which have reacted $= 2 \times 10^{-5}$ mol

$\therefore$ Total Cl_2 added $= 0.0204 + 2 \times 10^{-5} = \mathbf{0.02042\ mol}$

69. van't Hoff isochore is :

$$\log_{10} K = \log_{10} A - \frac{\Delta H}{2.303RT}$$

(i) Thus, intercept $= \log_{10} A = 10$ $\therefore A = \mathbf{10^{10}}$

(ii) Also, slope $= \tan\theta = 0.5 = -\frac{\Delta H}{2.303R}$

$\therefore$ $\Delta H = \mathbf{-2.303\ cal\ mol^{-1}}$

(iii) Also, $\log_{10} K = 10 + \frac{2.303}{2.303 \times 2 \times 298}$

$\therefore$ $K = \mathbf{1.004 \times 10^{10}}$

(iv) Also, $\log_{10} K = 10 + \frac{2.303}{2.303 \times 2 \times 800}$

$\therefore$ $K = \mathbf{1.001 \times 10^{10}}$

70. van't Hoff equation for variation of K_P with temperature can be written as,

$$2.303 \log_{10} \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H[T_2 - T_1]}{R \times T_1 T_2}$$

$$K_{P_1} = 1.6 \times 10^{-4};\ T_1 = 673\text{K},\ K_{P_2} = ?;$$

$$T_2 = 773\text{K}, \Delta H = -25.14 \times 10^3 \text{ cal}$$

$$\therefore \quad 2.303 \log_{10} \frac{K_{P_2}}{1.6 \times 10^{-4}} = \frac{-25.14 \times 10^3}{2}\left[\frac{773 - 673}{773 \times 673}\right]$$

$$\therefore \quad K_{P_2} = \mathbf{1.462 \times 10^{-5}\ atm^{-2}}$$

71.

$$2.303 \log_{10} \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$2.303 \log_{10} \frac{0.0129}{0.0266} = \frac{\Delta H}{2}\left[\frac{673 - 623}{673 - 623}\right]$$

$$\therefore \quad \Delta H = -12140\text{cal} = \mathbf{-12.140\ kcal}$$

72.

$$2.303 \log_{10} \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\therefore \quad 2.303 \log_{10} \frac{K_{P_2}}{K_{P_1}} = \frac{42.4 \times 10^3}{2}\left[\frac{1405 - 1338}{1405 \times 1338}\right]$$

$$\therefore \quad \frac{K_{P_2}}{K_{P_1}} = 2.129$$

$$\therefore \quad K_{P_2} = 2.129 \times 0.0118 = \mathbf{0.025\ atm}$$

73.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\Delta n = \Sigma n \text{ products} - \Sigma n \text{ reactants} = 2 - 4 = -2$$

$\because$ $K_P = K_C(RT)^{\Delta n}$

$$1.64 \times 10^{-4} = K_C(0.0821 \times 673)^{-2}$$

$\therefore$ $K_C = \mathbf{0.5006\ mol^2\ litre^{-2}}$

Now since $\Delta G^\circ = -2.303RT \log_{10} K$

If $K = K_P$

Then $\Delta G^\circ = -2.303 \times 2 \times 673 \log_{10}(1.64 \times 10^{-4})$

$= \mathbf{+11.733\ kcal}$

If $K = K_C$

Then $\Delta G^\circ = -2.303 \times 2 \times 673 \log_{10}(0.5006) = \mathbf{+931\ cal}$

where ΔG° is the Gibb's energy change when all the reactants and products are in the standard state. For $\Delta G^\circ = -2.303RT \log_{10} K_P$, standard state means the partial pressure of each as 1 atm. When $\Delta G^\circ = -2.303RT \log_{10} K_C$, standard state means that concentration of each is 1 mol litre^{-1}. So the values are different.

74.

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

At equilibrium

$$-\Delta G^\circ = 2.303RT \log_{10} K_P \qquad \text{...(1)}$$

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (Given ΔH° for $NH_3 = -46$kJ)

and $\Delta S^\circ_{\text{Reaction}} = 2 \times S^\circ_{NH_3} - S^\circ_{N_2} - 3 \times S^\circ_{H_2}$

$= 2 \times 192 - 191 - 3 \times 130 = -197$ J

Also, $T = 273 + 25 = 298$ K

Thus, $\Delta G^\circ = -92 \times 10^3 - 298 \times (-197) = -92000 + 58706$

(ΔH° for reaction $= -46 \times 2$ kJ)

$\Delta G^\circ = -33294$ J

Thus, from Eq. (1)

$+33294 = 2.303 \times 298 \times 8.3 \log_{10} K_P \therefore \log_{10} K_P = \mathbf{5.845}$

75.

$$-\Delta G^\circ = 2.303RT \log_{10} K_P$$

$$-(-16.5 \times 10^3) = 2.303 \times 8.314 \times 298 \log_{10} K_P$$

$$\log_{10} K_P = \frac{16500}{2.303 \times 8.314 \times 298}$$

$$\therefore \quad K_P = \mathbf{779.41\ atm^{-1}}$$

Also, K_{P_1} for $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$K_{P_1} = (K_P)^2 = (779.41)^2$$

$$K_{P_1} = \mathbf{6.07 \times 10^5\ atm^{-2}}$$

Also, $-\Delta G_1^\circ = 2.303 \times 8.314 \times 298 \log_{10}(6.07 \times 10^5)\,\text{J}$

$= 32.998\ \text{kJ}$

$\therefore \quad \Delta G_1^\circ = \mathbf{-32.998\ kJ}$

76. $$d \ln K_P = \frac{\Delta H^\circ}{RT^2}$$

On integration $\ln K_P = -\frac{\Delta H}{RT} + C$

or $\log_{10} K_P = -\frac{\Delta H^\circ}{2.303RT} + C$

Thus, $\text{slope} = -\frac{\Delta H^\circ}{2.303R} = 4.95 \times 10^3$

$\therefore \quad \Delta H^\circ = -2.303 \times 8.314 \times 4.95 \times 10^3 = \mathbf{-9.48 \times 10^4\ J}$

Also, $\Delta S^\circ = S^\circ_{SO_3} - S^\circ_{SO_2} - \frac{1}{2} \times S^\circ_{O_2}$

$= 256.8 - 248.2 - \frac{1}{2} \times 205.1 = -93.95\ \text{JK}^{-1}\text{mol}^{-1}$

$\therefore \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= -9.48 \times 10^4 - 298 \times (-93.95) = -6.68 \times 10^4$

Now, $\Delta G^\circ = -2.303RT \log K_P$

$-6.68 \times 10^4 = -2.303 \times 8.314 \times 298 \log K_p$

$K_P = \mathbf{5.1 \times 10^{11}}$

77. $-\Delta G^\circ = 2.303RT \log_{10} K$, also $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Thus, $-(\Delta H^\circ - T\Delta S^\circ) = 2.303RT \log_{10} K$

or $2.303 \log_{10} K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

78. $$\Delta G^\circ = -2.303RT \log K$$

$\therefore \quad 33 = -2.303 \times 8.314 \times 10^{-3} \times 920 \log K$

$\therefore \quad K$ at $920\ \text{K} = 1.34 \times 10^{-2}$

Now using, $2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R} \frac{[T_2 - T_1]}{T_1 T_2}$

if $K_1 = 1.34 \times 10^{-2}$ and $K_2 = 1$; $T_1 = 920\text{K}$, then,

$$2.303 \log \frac{1}{1.34 \times 10^{-2}} = \frac{\Delta H}{R}\left[\frac{T_2 - 920}{T_2 \times 920}\right]$$

$T_2 = \mathbf{1078.5\ K}$

Thus, at any temperature above this temperature K will be greater than 1.

79. $$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ and } G^\circ = H^\circ - TS$$

$$\Delta G^\circ = \Delta G_B^\circ - \Delta G_A^\circ$$

$= [25.44 \times 10^3 - (300 \times 253.3)] - [24.27 \times 10^3 - (300 \times 246.4)]$

$= -50550 + 49650 = -900\,\text{J}$

$\Delta G^\circ = -2.303RT \log K_P$

$-900 = -2.303 \times 300 \times 8.314 \log K_P$

$K_P = 1.434$

Also, $K_P = \frac{[B]}{[A]} = 1.434$

$\therefore \quad [B] = 1.434$ and total of $[A]$ and $[B] = 1 + 1.434 = 2.434$

$\therefore \quad$ mole % of $[B]$ in mixture $= \frac{1.434}{2.434} \times 100 = \mathbf{58.92}$

mole % of A in mixture $= \mathbf{41.08}$

80. $$\text{Pentyne-1} \xrightleftharpoons{\text{KOH alc.}} \text{Pentyne-2} + \text{Pentadiene-1-2}$$

$$\begin{array}{llll} & (A) & (B) & (C) \\ \text{At eq.} & 1.3 & 95.2 & 3.5 \end{array}$$

$$K_{eq.} = \frac{[B][C]}{[A]}$$

$$= \frac{95.2 \times 3.5}{1.3} = 256.31 \qquad \text{...(i)}$$

Now, for $B \rightleftharpoons A$

$$K_1 = \frac{[A]}{[B]} \qquad \text{...(ii)}$$

Then from Eqs. (i) and (ii), $K_1 = \frac{[C]}{K_{eq.}} = \frac{3.5}{256.31} = 0.013$

$\therefore \quad \Delta G^\circ = -2.303RT \log_{10} K$

$= -2.303 \times 8.314 \times 448 \log 0.013 = 16178\,\text{J}$

$= \mathbf{16.178\ kJ}$

Stability order for A and B is $B > A$.

Similarly for $B \rightleftharpoons C$

$$K_2 = \frac{[C]}{[B]} = \frac{K_{eq.}[A]}{[B]^2} = \frac{256.31 \times 1.3}{95.2 \times 95.2} = 0.037$$

$\therefore \quad \Delta G^\circ = -2.303RT \log_{10} K$

$= 2.303 \times 8.314 \times 448 \log 0.037 = 12282\,\text{J} = \mathbf{12.282\ kJ}$

Thus, stability order for B and C is $B > C$.

The total stability order is $B > C > A$.

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot C \equiv CH \xrightarrow{\text{KOH alc.}}$$

$$[CH_3CH_2CH{=}C{=}CH_2] \longrightarrow$$

$$[CH_3CH_2C{\equiv}C{-}CH_3]$$

81. (i) $$N_2O_4 \rightleftharpoons 2NO_2; \quad G^\circ_{N_2O_4} = 100\,\text{kJ mol}^{-1}$$

conc. at $t = 0$ 5   5 $G^\circ_{NO_2} = 50\,\text{kJ mol}^{-1}$

ΔG° for reaction $= 2 \times G^\circ_{NO_2} - G^\circ_{N_2O_4} = 2 \times 50 - 100 = 0$

Now $\Delta G = \Delta G^\circ + 2.303\ RT \log Q$

$\Delta G = 0 + 2.303 \times 8.314 \times 10^{-3} \times 298 \log \frac{5^2}{5} = \mathbf{+\,3.99\ kJ}$

(ii) Since ΔG is +ve and thus reaction will not proceed in forward direction.

Also for reverse reaction :

$$2NO_2 \rightleftharpoons N_2O_4$$

$$\begin{array}{lll} \text{Mole at } t = 0 & 5 & 5 \\ \text{Mole at eq.} & (5 - 2x) & (5 + x) \end{array}$$

$\therefore \quad \Delta G^\circ = -2.303RT \log K_C$

$\therefore \quad \Delta G^\circ = 0 \quad \therefore K_C = 1$ or $1 = \frac{5 + x}{(5 - 2x)^2} \quad \therefore x = 1.25$

Thus, $[NO_2]_{\text{at eq.}} = 5 - 2.5 = 2.5\,\text{M}$

$[N_2O_4]_{\text{at eq.}} = 5 + 1.25 = \mathbf{6.25\ M}$

82. $$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \text{...(1)}$$

ΔH° for reaction $= \Delta H_B^\circ - \Delta H_A^\circ = 25.44 - (-24.27)$

$= -1.17\,\text{kJ}$

ΔS° for reaction $= S_B^\circ - S_A^\circ = 252.3 - 246.4$

$= 5.9\ \text{J} = 5.9 \times 10^{-3}\ \text{kJ}$

$$\therefore \quad \Delta G^{\circ}_{\text{reaction}} = -1.17 - (298 \times 5.9 \times 10^{-3})$$

$$= -1.17 - 1.76 = -2.93\,\text{kJ}$$

Now at equilibrium : $\Delta G^{\circ} = -2.303\,RT \log K_C$

$$\therefore \quad -2.93 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log K_C$$

$$\therefore \quad K_C = 3.26$$

Thus, $\dfrac{[B]}{[A]} = K_C = 3.26$

or the mixture contains $[B]$ and $[A]$ in the ratio **3.26 : 1**

83. **Case I :** $N_2O_4 \rightleftharpoons 2NO_2$

$$PV = \frac{w}{m} RT$$

$$\therefore \quad m_{\text{mix}} = \frac{w}{P \cdot V} \cdot RT = \frac{dRT}{P}$$

$$= 3.62 \times 0.0821 \times 288 = 85.6 \qquad \left(\frac{w}{V} = \text{g / litre}\right)$$

Let a mole of N_2O_4 and $(1-a)$ mole of NO_2 exist at equilibrium

$\therefore \quad a \times 92 + (1-a) \times 46 = 85.6 \qquad \therefore \ a = 0.86$

$\therefore \quad [n_{N_2O_4}] = 0.86$ mole and $[n_{NO_2}] = 0.14$ mole

$$\therefore \quad K_P = \frac{0.14 \times 0.14}{0.86} \times \left[\frac{1}{1}\right]^1 = 0.028\,\text{atm at } 288\,\text{K}$$

Case II: $m_{\text{mix}} = 1.8 \times 0.0821 \times 348 = 52.57$

Let a' mole of N_2O_4 and $(1-a')$ mole of NO_2 exist at equilibrium.

$\therefore \quad a' \times 92 + (1-a') \times 46 = 52.57 \qquad \therefore \quad a' = 0.14$

$$\therefore \quad [n_{N_2O_4}] = 0.14\,[n_{NO_2}] = 0.86$$

$$\therefore \quad K_P = \frac{0.86 \times 0.86}{0.14} \times \left[\frac{1}{1}\right]^1 = 5.283\,\text{atm at } 348\,\text{K}$$

Now, $2.303 \log \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H}{R} \left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$$\therefore \quad 2.303 \log \frac{5.283}{0.0228} = \frac{\Delta H}{2} \left[\frac{348 - 288}{348 \times 288}\right]$$

$$\therefore \quad \Delta H = 18196\,\text{cal} = \mathbf{18.196\ kcal}$$

Also, $-\Delta G = 2.303\,RT \log K_P$

$$\therefore \quad \Delta G = -2.303 \times 2 \times 348 \times \log 5.283 = -1158.7\ \text{cal}$$

$$\therefore \quad \Delta S = \frac{\Delta H - \Delta G}{T} = \frac{18196 + 1158.7}{348} = \mathbf{55.62\ cal}$$

84.

$$\begin{array}{lcccc} & A & + \ B & \rightleftharpoons \ C & + \ D \\ \text{At } t = 0 & 2 & 2 & 0 & 0 \\ \text{At eq.} & (2-x) & (2-x) & x & x \end{array}$$

$$K_C = \frac{[C][D]}{[A][B]} = \frac{[C]^2}{[A]^2} \quad [\because [C] = [D] \text{ and } [A] = [B]]$$

Also, $\Delta G^{\circ} = -2.303\,RT \log K_C$

or $\quad 460 = -2.303 \times 2 \times 300 \log \dfrac{[C]^2}{[A]^2}$

or $\log \dfrac{[C]^2}{[A]^2} = -0.3329$ or $\dfrac{[C]^2}{[A]^2} = 0.464$

or $\quad \dfrac{[C]}{[A]} = \mathbf{0.68}$

85. $\Delta G^{\circ} = -2.303\,RT \log_{10} K_C$

$$\therefore \quad 77.77 \times 10^3 = -2.303 \times 8.314 \times 1000 \log_{10} K_C$$

$$\therefore \quad K_C = 8.67 \times 10^{-5}$$

$$\begin{array}{lccc} & \frac{1}{2}N_2 & + \ \frac{1}{2}O_2 & \rightleftharpoons NO \\ \text{Initial pressure} & 0.8 & 0.2 & 0 \\ \text{Final pressure} & \left(0.8 - \frac{x}{2}\right) & \left(0.2 - \frac{x}{2}\right) & x \end{array}$$

$$\therefore \quad 8.67 \times 10^{-5} = \frac{x}{\left(0.8 - \frac{x}{2}\right)^{1/2} \left(0.2 - \frac{x}{2}\right)^{1/2}}$$

$$x = \mathbf{3.47 \times 10^{-5}\ atm}$$

86. **At 1000 K :**

$$\begin{array}{lccc} & CO_2(g) & + \ C(s) & \rightleftharpoons 2CO(g) \\ \text{Mole at } t = 0 & \frac{88}{44} = 2 & \frac{30}{12} = 2.5 & 0 \\ \text{Mole at equilibrium} & (2-a) & (2.5-a) & 2a \end{array}$$

mass of gaseous mixture $= [(2-a) \times 44] + (2a \times 28)$

$$= 88 - 44a + 56a = (88 + 12a)\,\text{g}$$

$\therefore$ density of mixture $= \dfrac{88 + 12a}{5} = 18.3\,\text{g / litre}$

$\therefore \quad 88 + 12a = 5 \times 18.3 \qquad \therefore \ a = 0.29$

$$\begin{array}{lccc} \therefore & CO_2(g) & + \ C(s) & \rightleftharpoons 2CO \\ \text{Mole at eq.} & (2-0.29) & (2.5-0.29) & 2 \times 0.29 \\ & = 1.71 & = 1.71 & = 0.58 \end{array}$$

$$K_c = \frac{[CO]^2}{[CO_2]} = \frac{0.58 \times 0.58}{5 \times 1.71} = 3.93 \times 10^{-2}$$

$$\therefore \quad K_P = K_c (RT)^{\Delta n} = 3.93 \times 10^{-2} \times (0.0821 \times 1000)$$

$$(\because \Delta n = 2 - 1 = 1)$$

$$= \mathbf{3.23\ atm}$$

At 1100 K : $\dfrac{88 + 12a'}{5} = 18.9 \quad \therefore \ a' = 0.54$

$$\begin{array}{lccc} \therefore & CO_2(g) & + \ C(s) & \rightleftharpoons 2CO \\ \text{Mole at eq.} & (2-0.54) & (2.5-0.54) & 1.08 \\ & = 1.46 & & 1.08 \end{array}$$

$$K_c = \frac{1.08 \times 1.08}{5 \times 1.46} = 0.16$$

$$\therefore \quad K_P = 0.16 \times 0.0821 \times 1100 = 14.43\ \text{atm}$$

Also, $2.303 \log \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H}{R} \dfrac{T_2 - T_1}{T_1 T_2}$

$$2.303 \log \frac{14.43}{3.23} = \frac{\Delta H}{2} \left[\frac{1100 - 1000}{1100 \times 1000}\right]$$

$$\therefore \quad \Delta H = 32936\,\text{cal} = \mathbf{32.936\ kcal}$$

87. $2.303 \log \dfrac{K_{p_2}}{K_{p_1}} = \dfrac{\Delta H^{\circ}}{R} \left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

or $\quad 2.303[\log K_{p_2} - \log K_{p_1}] = \dfrac{\Delta H^{\circ}}{2} \left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$$2.303[1.305 - 2.025] = \frac{\Delta H^{\circ}}{2} \left[\frac{1218 - 1023}{1218 \times 1023}\right]$$

$$\therefore \quad \Delta H^{\circ} = 21190.67\,\text{cal} = 21.19\ \text{kcal}$$

$$\Delta G^{\circ} = -2.303\,RT \log_{10} K_P$$

$$= -2.303 \times 2 \times 1023 \times 2.025$$

$$= -9541.6\ \text{cal} = -9.5416\ \text{kcal}$$

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$-9541.6 = -21190.67 - 1023 \times \Delta S^\circ$$

$$\Delta S^\circ = \frac{11649}{1023}$$

$$\Delta S^\circ = \mathbf{+11.38\ cal}$$

88.

$$\begin{array}{llll} & A(g) \rightleftharpoons & 2B(g) + & 3C(g) \\ \text{Initial pressure} & 10 & 0 & 0 \\ \text{Final pressure} & (10-P) & 2P & 3P \end{array}$$

$\because\ 10 - P + 2P + 3P = 15.76 \ \therefore\ P = 1.44$

$$\therefore\quad P'_A = 10 - 1.44 = 8.56 \text{ atm}$$

$$P'_B = 2 \times 1.44 = 2.88 \text{ atm}$$

$$P'_C = 3 \times 1.44 = 4.32 \text{ atm}$$

$$\therefore\quad K_P = \frac{(4.32)^3 \times (2.88)^2}{8.56} = 78.12$$

Also, $\Delta G^\circ = -2.303RT \log K_P$

$$= -2.303 \times 8.314 \times 298 \times \log 78.12 = -10799.8 \text{ J}$$

$$= \mathbf{-1.08 \times 10^4\ kJ}$$

89.

$$2.303 \log_{10} K_P = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\text{or } 2.303 \log_{10} K_P = \frac{98320}{8.314 \times 300} - \frac{95}{8.314}$$

(Put ΔH° and R in J)

$$\therefore\quad K_P = \mathbf{1.44 \times 10^{12}\ atm^{-1/2}}$$

90.

$$\begin{array}{llll} & NH_4HS(s) \rightleftharpoons & NH_3(g) + & H_2S(g) \\ \text{Pressure at equilibrium} & & P & P \end{array}$$

$\therefore$ Total pressure at equilibrium $= 2P = 1.12$ atm

$$\therefore\quad P = 1.12/2 \text{ atm}$$

$$\because\quad K_P = P'_{NH_3} \times P'_{H_2S}$$

$$\therefore\quad K_P = \frac{1.12}{2} \times \frac{1.12}{2} = \mathbf{0.3136\ atm^2}$$

91. For the dissociation equilibrium,

$$\begin{array}{llll} & NH_4HS(s) \rightleftharpoons & NH_3(g) + & H_2S(g) \\ \text{Pressure before dissociation} & & 0.5 & 0 \\ \text{Pressure after dissociation} & & (0.5+P) & P \end{array}$$

Let pressure equivalent to P atm is developed by NH_3 and H_2S on dissociation of NH_4HS, when 0.5 atm of NH_3 is already present.

$\therefore\ K_P = P'_{NH_3} \times P'_{H_2S} = (0.5 + P)P$ or $0.11 = (0.5 + P)P$

$$\therefore\quad P = 0.1653$$

$$\therefore\quad P'_{NH_3} = 0.5 + 0.1653 = \mathbf{0.6653\ atm}$$

$$P'_{H_2S} = \mathbf{0.1653\ atm}$$

92.

$$\begin{array}{llll} & NH_4CN(s) \rightleftharpoons & NH_3(g) + & HCN(g) \\ \text{Partial pressure at equilibrium} & 0 & P & P \end{array}$$

$\because$ Total pressure at equilibrium $= 2P = 0.298$ atm

$$\therefore\quad P = 0.149 \text{ atm}$$

Also, $K_P = P'_{NH_3} \times P'_{HCN} = 0.149 \times 0.149 = \mathbf{0.0222\ atm^2}$

Now dissociation is made when, $P_{NH_3} = 0.25$ atm

$$\begin{array}{llll} & NH_4CN(s) \rightleftharpoons & NH_3(g) + & HCN(g) \\ \text{Initial pressure} & & 0.25 & 0 \\ \text{Pressure at equilibrium} & & 0.25 + P' & P' \end{array}$$

$$\therefore\quad K_P = P'(P' + 0.25)$$

$$\therefore\quad 0.0222 = (P')^2 + 0.25P'$$

$$\therefore\quad \mathbf{P' = 0.0694\ atm}$$

93.

$$\begin{array}{llll} & NH_4HS(s) \rightleftharpoons & NH_3(g) + & H_2S(g) \\ \text{Initial mole} & \frac{3.06}{51} & 0 & 0 \\ \text{Mole at eq.} & \frac{3.06}{51} \times \frac{70}{100} & \frac{3.06}{51} \times \frac{30}{100} & \frac{3.06 \times 30}{51 \times 100} \end{array}$$

Given, $V = 2$ litre; $T = 27^\circ$C; $\Delta n = 2 - 0 = 2$

$$K_C = [NH_3][H_2S] = \frac{3.06 \times 30}{51 \times 100 \times 3} \times \frac{3.06 \times 30}{51 \times 100 \times 2}$$

$$= \mathbf{8.1 \times 10^{-5}\ mol^2\ litre^{-2}}$$

Also, $K_P = K_C(RT)^{\Delta n} = 8.1 \times 10^{-5} \times (0.082 \times 300)^2$

$$= \mathbf{4.90 \times 10^{-2}\ atm^2}$$

Addition of more NH_4HS on this equilibrium will cause no effect because concentration of NH_4HS is not involved in formulae of K_P or K_C.

94. $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

Let pressure at equilibrium of CO_2 be P, then

$P_{NH_3} = 2P$ and total pressure at equilibrium $= 3P$

$$\therefore\quad K_P = (2P)^2 \times P = 4P^3 \qquad \text{...(1)}$$

If NH_3 is added and the pressure of NH_3 after addition at equilibrium is $3P$, *i.e.*, equal to initial pressure.

$$K_P = 4P^3 = (P'_{NH_3})^2 \times P'_{CO_2} = (3P)^2 \times P'_{CO_2}$$

$$\therefore\quad P'_{CO_2} = \frac{4}{9}P$$

Thus, Total pressure in II equilibrium is $= 3P + \frac{4}{9}P = \frac{31}{9}P$

$$\frac{\text{Total pressure in II equilibrium}}{\text{Total pressure in I equilibrium}} = \frac{31P/9}{3P} = \mathbf{\frac{31}{27}}$$

95.

$$K_C = \frac{[CO_2]}{[CO]}$$

$$\therefore\quad 5 = \frac{[CO_2]}{2.5 \times 10^{-2}}$$

$\therefore\ [CO_2]$ at equilibrium $= 2.5 \times 10^{-2} \times 5$

$$= \mathbf{12.5 \times 10^{-2}\ mol\ litre^{-1}}$$

96.

$$\begin{array}{llll} & C(s) + & CO_2(g) \rightleftharpoons & 2CO(g) \\ \text{Gaseous mole before dissociation} & - & 1 & 0 \\ \text{Gaseous mole after dissociation} & - & \left(1 - \frac{50}{100}\right) & \frac{2 \times 50}{100} \\ & - & 0.5 & 1 \end{array}$$

$\therefore$ Total mole $= 1.5$ and $\Delta n = 1$

Total pressure given at equilibrium $= 12$ atm

$$K_P = \frac{(n_{CO})^2}{(n_{CO_2})} \times \left[\frac{P}{\Sigma n}\right]^{\Delta n} = \frac{(1)^2}{0.5} \times \left(\frac{12}{1.5}\right)^1$$

$$K_P = \frac{12}{1.5 \times 0.5} = \mathbf{16\ atm}$$

97.

$$\begin{array}{llll} & CO_2(g) + & C(s) \rightleftharpoons & 2CO \\ \text{Initial mole} & \frac{1.77}{44} & \frac{2}{12} & 0 \\ & = 0.040 & 0.167 & 0 \\ \text{Final mole} & 0.017 & & 0.034 \end{array}$$

$$\left[\begin{array}{l} \because \text{ Mole of } CO_2 = \text{mole of } BaCO_3 \\ \qquad (CO_2 + Ba(OH)_2 \longrightarrow BaCO_3 + H_2O) \\ \qquad \text{left} \quad n_{CO_2} = \frac{3.41}{197} = 0.017 \end{array}\right]$$

$$\therefore \quad K_C = \frac{\left[\frac{0.034}{1}\right]^2}{0.017} = 0.068$$

$$\therefore \quad K_P = 0.068 \times (0.0821 \times 1100)^1 = \mathbf{6.14\ atm}$$

98. $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

Initial pressure 0.5 0 0

Final pressure $(0.5 - P)$ 0 $2P$

$\therefore \quad 0.5 - P + 2P + = 0.8 \qquad \therefore \quad P = 0.3$ atm

Therefore, final partial pressure at equilibrium are

$$P'_{CO_2} = 0.5 - 0.3 = 0.2 \text{ atm}$$

$$P'_{CO} = 2P = 2(0.3) = 0.6 \text{ atm}$$

$$\therefore \quad K_P = \frac{(P'_{CO})^2}{P'_{CO_2}} = \frac{(0.6)^2}{(0.2)} = \mathbf{1.8\ atm}$$

99. (a) The given equilibrium is,

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Initial mole 1 0

Final mole $(1 - \alpha)$ 2α

$$K_P = \frac{(n_{CO})^2}{n_{CO_2}} \times \left[\frac{P}{\Sigma n}\right]^1 = \frac{(2\alpha)^2}{(1-\alpha)} \times \left[\frac{5}{1+\alpha}\right]$$

$$10 = \frac{20\alpha^2}{1-\alpha^2} \quad \text{or} \quad 10 - 10\alpha^2 = 2\alpha^2$$

$$\therefore \quad \alpha^2 = \frac{10}{30}$$

$$\therefore \quad \alpha = \sqrt{\frac{1}{3}} = 0.577$$

Thus, mole of CO_2 at equilibrium $= 1 - \alpha = 1 - 0.577 = 0.423$
and mole of CO at equilibrium $= 2\alpha = 2 \times 0.577 = 1.154$
Total mole present at equilibrium $= 0.423 + 1.154 = 1.577$
At equilibrium, $PV = nRT$

$$P = 5\text{atm}; \quad n = 1.577, \quad T = 817 + 273 = 1090$$

$$5 \times V = 1.577 \times 0.0821 \times 1090 \ \therefore \ V = 28.22 \text{ litre}$$

$$\therefore \quad [CO] \text{ at equilibrium} = \frac{1.154}{28.22} = \mathbf{0.041\ mol\ litre^{-1}}$$

$$[CO_2] \text{ at equilibrium} = \frac{0.423}{28.22} = \mathbf{0.015\ mol\ litre^{-1}}$$

(b) For $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

Initial mole 1 0

Final mole $(1 - \alpha)$ $2a$

Total mole at equilibrium $= 1 - a + 2a = 1 + a$

Given $\frac{1-a}{1+a} = \frac{5}{100} \quad \therefore \quad a = \frac{95}{100}$

$$K_P = \frac{(n_{CO})^2}{(n_{CO_2})} \times \left[\frac{P}{\Sigma n}\right]^1$$

$$10 = \frac{\left(\frac{2 \times 95}{100}\right)^2}{\left(\frac{5}{100}\right)} \times \left[\frac{P}{\frac{105}{100}}\right]^1$$

$$\therefore \quad P = \mathbf{0.145\ atm}$$

100. $K_P = (P_{H_2O}) = \mathbf{23\ mm}$

101. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Mole before dissociation $\frac{20}{100}$ 0 0

Mole after dissociation $\left[\frac{20}{100} \times \frac{35}{100}\right]$ $\left[\frac{20}{100} \times \frac{65}{100}\right]$ $\left[\frac{20}{100} \times \frac{65}{100}\right]$

$$\therefore \quad \text{Mole of } CO_2 \text{ formed} = \frac{20 \times 65}{10^4} = 1.3 \times 10^{-1}$$

$$\because \quad PV = nRT$$

$$P_{CO_2} = \frac{1.3 \times 10^{-1}}{10} \times 0.0821 \times 1073 = 1.145 \text{ atm}$$

Now, $K_P = P'_{CO_2} = \mathbf{1.145\ atm}$

102. Eq. I $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Given, $K_P = 4 \times 10^{-2} = P'_{CO_2}$

Eq. II Also, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

$$K_P = \frac{(P_{CO})^2}{P'_{CO_2}} = 2.0$$

Now both are at equilibrium and thus $P'_{CO_2} = 4 \times 10^{-2}$ which should remain constant, thus

$$2.0 = \frac{(P'_{CO})^2}{4 \times 10^{-2}} \quad \text{or} \quad P'_{CO} = \sqrt{4 \times 10^{-2} \times 2} = \mathbf{0.28\ atm}$$

103. For, $M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(g)$

$\because$ CO_2 is 1% in air ; $\therefore \quad P'_{CO_2} = \frac{1}{100} \times P_{air}$

$$= \frac{1}{100} \times 1\text{atm} = 0.01\text{atm}$$

Also, for equilibrium $K_P = P'_{CO_2} = 0.0095$atm

$\because$ Given, $P'_{CO_2} = 0.01$ atm

Since, decomposition is carried out in presence of P'_{CO_2} of 0.01 atm and $K_P = 0.0095$ atm, thus, practically **no decomposition of M_2CO_3. Thus, 1% CO_2 is sufficient to prevent any loss in mass.**

If at all reaction is desired the P'_{CO_2} must be lesser than 0.0095 atm as P'_{CO_2} at equilibrium cannot be more than 0.0095 atm.

Alternate solution :

For $M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(s)$

$$\left(\frac{1}{100} + P\right)$$

$\because$ $K_P = P'_{CO_2}$ and the pressure of CO_2 already present in 1/100 atm. Let the decomposition of M_2CO_3 produces the CO_2 of pressure P, then

$$\therefore \quad K_P = \frac{1}{100} + P$$

or $0.0095 = P + 0.01$ or $P = -0.0005$

The value of pressure comes negative and thus, it may be concluded that M_2CO_3 will not dissociate in pressure of CO_2 of pressure 0.01 atm.

104. $\ln K_P = 7.282 - \frac{8500}{T}$ at $T = 1123\,\text{K}$

$\ln K_P = 7.282 - 7.569$

$\ln K_P = -0.287$ $\quad\therefore\ K_P = 0.751$ at $T = 1223\,\text{K}$

$\ln K_P = 7.282 - 6.950$

$\ln K_P = 0.332;$ $\quad\therefore\ K_P = 1.394$

$\therefore\quad \text{Av. } K_P = \frac{0.751+1.394}{2} = \frac{2.145}{2} = 1.0725$

Quiet air means, the state when the decomposition of $CaCO_3$ occurs in a way that the air surrounded to it becomes saturated with a pressure of CO_2 equal to 1 atm (to pushback the air) needed to attain equilibrium.

Thus, when $K_P \geq 1$, then reaction is spontaneous is forward direction or at 950° C, the reaction occurs predominantly in forward direction. Thus, for minimum temperature, putting $K_P = 1$ in given equation.

$\therefore\ \log K_P = 7.282 - \frac{8500}{T}$ or $\log 1 = 7.282 - \frac{8500}{T}$

$\therefore\quad T = \mathbf{1167.26\ K}$ or $\mathbf{894.26°C}$

105. An efflorescent salt is one that loses H_2O to atmosphere.

For the reaction,

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(v)$$

$$K_P = (P'_{H_2O})^2 = 1.086\times10^{-4}$$

$$\therefore\ P'_{H_2O} = \mathbf{1.042\times10^{-2}\ atm = 7.92\ mm}$$

$\because$ Given P'_{H_2O} at 25°C, (*i.e.*, 23.8) > 7.92 mm and thus, reaction will proceed in backward direction, *i.e.*,

$$CuSO_4 \cdot 3H_2O + 2H_2O(v) \rightleftharpoons CuSO_4 \cdot 5H_2O(s)$$

Thus, $CuSO_4 \cdot 5H_2O$ will not act as efflorescent but on the contrary $CuSO_4 \cdot 3H_2O$ will absorb moisture from the atmosphere under given conditions. The salt $CuSO_4 \cdot 5H_2O$ will effloresce only on a dry day when the aqueous tension or partial pressure of moisture in the air is lesser than 7.92 mm or if relative humidity of air at 25° C $= \frac{7.92}{23.8} = 0.333$ or 33.3%

106. For (i) $K_P = (P_{H_2O})^4$

$\therefore\quad P_{H_2O} = \sqrt[4]{K_P} = \sqrt[4]{6.9\times10^{-12}} = 1.62\times10^{-3}$ atm

For (ii) $K_P = (P_{H_2O})^{10}$

$P_{H_2O} = \sqrt[10]{K_P} = \sqrt[10]{4.08\times10^{-25}} = 3.64\times10^{-3}$ atm

For (iii) $K_P = (P_{H_2O})^5$

$\therefore\quad P_{H_2O} = \sqrt[5]{K_P} = \sqrt[5]{5.25\times10^{-13}} = 3.50\times10^{-3}$ atm

All these reactant can be used as drying agent since their P_{H_2O} is lesser than V.P. of H_2O in atmosphere, *i.e.*, 4.58 mm or 6.02×10^{-3} atm. The efficiency order is

$SrCl_2 \cdot 6H_2O > Na_2HPO_4 \cdot 12H_2O > Na_2SO_4 \cdot 10H_2O$

107. $SnO_2(s) + 2H_2(g) \rightleftharpoons Sn(l) + 2H_2O(g)$

Case I : 900 K	45	55

$\therefore\quad K_{C_1} = \frac{(55)^2}{(45)^2} = \mathbf{1.494}$

$SnO_2(s) + 2H_2(g) \rightleftharpoons Sn(l) + 2H_2O(g)$

Case II : 1100 K	24	76

$\therefore\quad K_{C_2} = \frac{76\times76}{24\times24} = \mathbf{10.03}$

K_C increases with temperature and thus reaction should be endothermic. Thus, high temperature is preferred for reduction of SnO_2.

108. $\because\ LiCl \cdot 3NH_3(s) \rightleftharpoons LiCl \cdot NH_3(s) + 2NH_3(g)$

$[K_P = 9\,\text{atm}^2]$

$\therefore\ LiCl \cdot NH_3(s) + 2NH_3(g) \rightleftharpoons LiCl \cdot 3NH_3(s)$

$\left[K_P = \frac{1}{9}(\text{atm})^{-2}\right]$

Initial mole	0.1	a	0
Final mole at equilibrium	0	$(a-0.2)$	0.1

Let initial mole of NH_3 should be a to bring in completion of reaction.

At eq. $\quad K_{P_1} = \frac{1}{(P'_{NH_3})^2}$ or $\frac{1}{9} = \frac{1}{(P'_{NH_3})^2}$

$\therefore\quad P'_{NH_3} = 3$ atm

$\because\quad PV = nRT$

$3\times5 = n\times0.0821\times313$

$\therefore\quad n = 0.5837$

i.e., $\quad (a-0.2) = 0.5837$

$\therefore$ Initial mole of $NH_3 = a = 0.5837 + 0.2 = \mathbf{0.7837\ mol}$

109. $2Na(g) \rightleftharpoons Na_2(g)$

mass at eq.	71	29
mole at eq.	$\frac{71}{23}$ $= 3.087$	$\frac{29}{46}$ $= 0.630$

$$K_P = \frac{^{n}Na_2}{(^{n}Na)^2}\times\left[\frac{P}{\Sigma n}\right]^{-1} = \frac{0.630}{(3.087)^2}\times\left[\frac{1.013}{3.717}\right]^{-1}$$

$$= \mathbf{0.242\ M\ Pa^{-1}}$$

110. Volume of room $= 6\times5\times3 = 90\,\text{m}^3 = 90\times10^3$ litre

$Hg(l) \rightleftharpoons Hg(v)\quad K_P = P'_{Hg} = \frac{0.002}{760} = 2.63\times10^{-6}$ atm

$n_{Hg(v)} = \frac{PV}{RT} = \frac{2.63\times10^{-6}\times90\times10^3}{0.0821\times300} = 9.62\times10^{-3}$ mol

$\therefore\quad w_{Hg}(v) = 9.62\times10^{-3}\times200.5 = 1.928\,\text{g} = \frac{1.928}{90\times10^3}$

$= 2.14\times10^{-5}$ g / litre

$= \frac{2.14\times10^{-5}\times10^3}{10^{-3}}\,\text{mg/m}^3 = 21.4\,\text{mg/m}^3$

The value is higher than safety limit and thus dangerous to enter in the room.

111. $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Mole before reaction	1	1	0	1
Mole at equilibrium	$(1-x)$	$(1-x)$	x	$1+x$

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\frac{x}{V}\cdot\frac{(1+x)}{V}}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x(1+x)}{(1-x)^2}$$

Given that, $x = 0.543$ since 54.3% of acid is used up

$\therefore \quad K_C = \mathbf{4.012}$

112. Case I:

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Mole before reaction	1	1	0	0
Mole at equilibrium	$1-x$	$1-x$	x	x

$\therefore \quad x = \frac{2}{3}$

$\therefore$ Mole at equilibrium	$\left(1-\frac{2}{3}\right)$	$\left(1-\frac{2}{3}\right)$	$\frac{2}{3}$	$\frac{2}{3}$

$$\therefore \quad K_C = \frac{\frac{2}{3}\times\frac{2}{3}}{\frac{1}{3}\times\frac{1}{3}} = 4$$

NOTE : Volume terms are eliminated as in problem 105.

Case II : $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Mole before reaction	2	2	0	0
Mole at equilibrium	$(2-x)$	$(2-x)$	x	x

$$\therefore \quad K_C = 4 = \frac{x^2}{(2-x)^2} \quad \text{or} \quad \therefore \quad \frac{x}{(2-x)} = 2$$

or $\quad x = \mathbf{1.33}$

113.

$$\alpha - \text{D glucose} \rightleftharpoons \beta - \text{D glucose}$$

At equilibrium	36.4	63.6

$$\therefore \quad K_C = \frac{63.6}{36.4} = \mathbf{1.747}$$

114.

$$KI(aq.) + I_2(aq.) \rightleftharpoons KI_3(aq.)$$

Molar mass KI = 166

Mole at $t = 0$	$\frac{1.326}{166}$		0	Molar mass $KI_3 = 420$
Mole at equilibrium	$\left[\frac{1.326}{166} - \frac{0.105}{420}\right]$	0.0013	$\frac{0.105}{420}$	
	$= 7.738\times10^{-3}$	0.0013	2.5×10^{-4}	

$$\therefore \quad K_C = \frac{[KI_3]}{[KI][I_2]} = \frac{2.5\times10^{-4}}{7.738\times10^{-3}\times0.0013}$$

($\because$ volume of solution = 1 litre)

$K_C = \mathbf{24.62}$

The free iodine should be in solid and solution state.

The I_2 in solution state, *i.e.*, $I_2(aq.) = 0.0013\,M$

Thus, I_2 in solid state $= 0.0025 - 0.0013 = 0.0012$ mol

115. Given $\quad S(s) + S^{2-} \rightleftharpoons S_2^{2-} \qquad K_{C_1} = 1.7$

$\qquad 2S(s) + S^{2-} \rightleftharpoons S_3^{2-} \qquad K_{C_2} = 5.3$

$$\therefore \quad K_{C_1} = \frac{[S_2^{2-}]}{[S^{2-}]} = 1.7 \qquad \text{...(1)}$$

$$K_{C_2} = \frac{[S_3^{2-}]}{[S^{2-}]} = 5.3 \qquad \text{...(2)}$$

Now for $\quad S_2^{2-} + S(s) \rightleftharpoons S_3^{2-}$

$$K_C = \frac{[S_3^{2-}]}{[S_2^{2-}]}$$

$\therefore$ By Eqs. (2) and (1), $\dfrac{K_{C_2}}{K_{C_1}} = \dfrac{[S_3^{2-}]}{[S_2^{2-}]} = K_C$

$\therefore \quad K_C = \mathbf{3.11}$

116.

$$Ag^+(aq.) + Fe^{2+}(aq.) \rightleftharpoons Fe^{3+}(aq.) + Ag(s)$$

Millimole before reaction	500×0.150	500×1.09		
or	$= 75$	$= 545$	0	0
Millimole after reaction	$(75-x)$	$(545-x)$	x	x

$\because$ mM = Meq. (both Ag^+/Ag and Fe^{2+}/Fe^{3+} have valency factor unity)

$$\because \quad K_C = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]}$$

$$\therefore K_C = \frac{\frac{x}{1000}}{\left(\frac{75-x}{1000}\right)\left(\frac{545-x}{1000}\right)} \quad \text{...(1)}$$

$\because$ Conc. $= \dfrac{\textbf{Millimole}}{\textbf{Total Volume}}$

$[Ag^+] = \dfrac{75-x}{1000}$

$[Fe^{2+}] = \dfrac{545-x}{1000}$

$[Fe^{3+}] = \dfrac{x}{1000}$

Now 25 mL of mixture requires 30 mL of .0832 *M* or $0.0832\times5\,N$ $KMnO_4$.

$\because \quad Fe^{2+}$ is oxidized by $KMnO_4$.

$\therefore \quad$ Milliequivalent of Fe^{2+} left at equilibrium in 1000 mL

$\qquad$ = Milliequivalent of $KMnO_4$ for 1000 mL

$$= \frac{30\times0.0832\times5\times1000}{25} = 499.2$$

$\therefore \quad 545 - x = 499.2 \qquad \therefore \; x = 545 - 499.2 = 45.8$

Thus, by Eq. (1),

$$K_C = \frac{\frac{45.8}{1000}}{\left(\frac{75-45.8}{1000}\right)\times\left(\frac{545-45.8}{1000}\right)} = \frac{45.8\times1000}{29.2\times499.2}$$

$K_C = \mathbf{3.1420}$

117.

$$2Fe^{3+}(aq.) + (Hg_2)^{2+}(aq.) \rightleftharpoons 2Fe^{2+}(aq.) + 2Hg^{2+}(aq.)$$

Conc. before reaction	0.5	0.5	0.03	0.03
Conc. after reaction at eq.	$(0.5-a)$	$(0.5-a/2)$	$(0.03+a)$	$(0.03+a)$

$$K_C = 9.14\times10^{-6} = \frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[(Hg_2)^{2+}]}$$

$$\therefore \quad 9.14\times10^{-6} = \frac{(0.03+a)^2(0.03+a)^2}{(0.5-a)^2(0.5-a/2)}$$

$\therefore \quad a = 0.0027$

$\therefore \quad [Fe^{3+}] = 0.5 - 0.0027 = \mathbf{0.4973}\,M$

$[Hg_2^{2+}] = 0.5 - \dfrac{0.0027}{2} = \mathbf{0.4987}\,M$

$[Fe^{2+}] = 0.03 + 0.0027 = \mathbf{0.0327}\,M$

$[Hg^{2+}] = 0.03 + 0.0027 = \mathbf{0.0327}\,M$

118.

$$\begin{array}{lcccc} & CH_3COOH + & C_2H_5OH \rightleftharpoons & CH_3COOC_2H_5 + & H_2O \\ \text{Before reaction} & 0.1 & 0.1 & 0 & 0 \\ \text{At equilibrium} & (0.1-x) & (0.1-x) & x & x \end{array}$$

Meq. of acetic acid left = Meq. of NaOH used

$= 100 \times 0.85 = 85$

$\therefore$ Millimole of acetic acid left $= 85$ ($\because$ mono basic)

$\therefore$ Mole of acetic acid left $= 0.085$

or $(0.1-x) = 0.085$ or $x = 0.015$

Now $K_C = \dfrac{x^2}{(0.1-x)^2} = \dfrac{(0.015)^2}{(0.085)^2} = \mathbf{0.031}$

119. For the reaction : $Fe^{2+} + 3\text{dipy} \rightleftharpoons [Fe(\text{dipy})_3]^{2+}$

$$r_{\text{forward}} = K_f \times [Fe^{2+}][3\text{dipy}]$$
$$= 1.45 \times 10^{13} [Fe^{2+}][3\text{dipy}]$$
$$r_{\text{backward}} = K_b \times [Fe(\text{dipy})_3]^{2+}$$
$$= 1.22 \times 10^{-4} [Fe(\text{dipy})_3]^{2+}$$

At equilibrium $r_f = r_b$ and $K_C = \dfrac{K_f}{K_b}$

$$= [Fe(\text{dipy})_3]^{2+} / [Fe^{2+}][\text{dipy}]^3$$

Also, stability constant of complex = Equilibrium constt. of reaction $= \dfrac{K_f}{K_b}$

$$= \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = \mathbf{1.188 \times 10^{17}}$$

120.

$$\begin{array}{ccccc} 2KCN\ + & AgNO_3 \longrightarrow & Ag(CN)_2^- \ + & KNO_3\ + & K^+ \\ 0.1 & 0.03 & 0 & 0 & 0 \\ (0.1-0.06) & 0 & 0.03 & 0.03 & 0.03 \end{array}$$

$\therefore$ $[Ag(CN)_2^-] = 0.03\,M$

Now use

$$\begin{array}{ccccc} Ag(CN)_2^- & \rightleftharpoons & Ag^+ & + & 2CN^- \\ 0.03 & & 0 & & 0.04 \\ (0.03-a) & & a & & 0.04 + 2a = 0.04 \end{array}$$

Since, K_C is too small and dissociation of $Ag(CN)_2^-$ is very less and thus,

$\therefore$ $0.04 + 2a \approx 0.04$ and $0.03 - a \approx 0.03$

$\therefore$ $[Ag(CN)_2^-] = 0.03$; $[Ag^+] = a$; $[CN^-] = 0.04$

Now $K_C = \dfrac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = \dfrac{a \times (0.04)^2}{0.03}$

$\therefore$ $a = \mathbf{7.5 \times 10^{-18}}$

121. $H_3BO_3 + \text{glycerine} \rightleftharpoons \text{complex}$; $K = \dfrac{[\text{Complex}]}{[H_3BO_3][\text{glycerine}]} = 0.9$

$$\begin{array}{cccl} 0.10 & a & 9 & \\ (0.1-x) & (a-x) & x & \text{where } x = 60 \times \frac{0.1}{100} = 0.06 \end{array}$$

If 60% of H_3BO_3 gives complex then $[H_3BO_3]$ left = 40%

Given $\dfrac{[\text{Complex}]}{[H_3BO_3]} = \dfrac{60}{40}$

Thus, $0.9 = \dfrac{60}{40[\text{glycerine}]}$

or [glycerine] or $(a-x) = \dfrac{60}{40 \times 0.9} = 1.67\,M$

$\therefore$ $a = 1.67 + x = 1.67 + 0.06 = \mathbf{1.73\,M}$

122.

$$\begin{array}{lccccl} & A & + & B & \rightleftharpoons & C \\ \text{Conc. at I equilibrium} & 15 & & 15 & & a \quad \text{(volume is } V \text{ litre)} \\ \text{Conc. when } V \text{ is doubled} & \frac{15}{2} & & \frac{15}{2} & & \frac{a}{2} \quad \text{(volume is } 2V \text{ litre)} \end{array}$$

Since, on increasing volume, pressure decreases and the reaction proceeds in the direction where it shows an increase in mole, *i.e.*, backward reaction.

$$\text{Conc. at II equilibrium} \quad \left(\frac{15}{2}+x\right) \quad \left(\frac{15}{2}+x\right) \quad \left(\frac{a}{2}-x\right)$$

$\because$ $\dfrac{15}{2} + x = 10$ $\therefore$ $x = \dfrac{5}{2}$

Now, $K_C = \dfrac{[C]}{[A][B]} = \dfrac{\left[\frac{a}{2} - \frac{5}{2}\right]}{\left[\frac{15}{2}+\frac{5}{2}\right]\left[\frac{15}{2}+\frac{5}{2}\right]}$ ...(1) for II Eq.

$K_C = \dfrac{[C]}{[A][B]} = \dfrac{a}{15 \times 15}$ ...(2) for I Eq.

$\because$ K_C are same

$\therefore$ $\dfrac{(a-5)/2}{10 \times 10} = \dfrac{a}{15 \times 15}$ $\therefore$ $a = \mathbf{45\,M}$

Now, $K_C = \dfrac{45}{15 \times 15} = \mathbf{0.2\ mol^{-1}\ litre^{1}}$

123. For I equilibrium $2NO_2 \rightleftharpoons N_2O_4$

$$K_P = \frac{P'_{N_2O_4}}{(P'_{NO_2})^2} = 6.8 \qquad \text{...(1)}$$

$\because$ $P'_{N_2O_4} = 1.7\,\text{atm}$ $\therefore$ By Eq. (1); $P'_{NO_2} = 0.5\,\text{atm}$

The equilibria are maintained using NO and NO_2 in the ratio 1 : 2

$$\begin{array}{lccccc} \text{For II equilibrium} & NO & + & NO_2 & \rightleftharpoons & N_2O_3 \\ \text{Initial pressure} & P & & 2P & & 0 \\ \text{Pressures at equi.} & (P-x) & & (2P-x-3.4) & & x \end{array}$$

$\because$ 3.4 atm of NO_2 are used for I equilibrium to have $P'_{N_2O_4} = 1.7\,\text{atm}$

$$\begin{array}{lccc} \text{At equilibrium} & (P-x) & 0.5 & x \end{array}$$

($\because$ P'_{NO_2} is same for both the equilibria since both reactions are at equilibrium at a time.)

Total pressure at equilibrium (Given 5.05 atm)

$$= P'_{NO} + P'_{NO_2} + P'_{N_2O_3} + P'_{N_2O_4}$$
$$= P - x + 0.5 + x + 1.7$$

$\therefore$ $5.05 = P + 2.20$

$\therefore$ $P = 5.05 - 2.20$ $\therefore$ $P = 2.85\,\text{atm}$

$\because$ $2P - x - 3.4 = 0.5$

$2 \times 2.85 - x - 3.4 = 0.5$

$\therefore$ $x = 5.70 - 3.90$ $\therefore$ $x = \mathbf{1.80\ atm}$

$\therefore$ $P'_{NO} = 2.85 - 1.80 = \mathbf{1.05\ atm}$

Now, K_P for $NO + NO_2 \rightleftharpoons N_2O_3$

$$K_P = \frac{P'_{N_2O_3}}{P'_{NO} \times P'_{NO_2}} = \frac{1.80}{1.05 \times 0.5} = \mathbf{3.43\ atm^{-1}}$$

124. $3A_2(g) \rightleftharpoons A_6(g) \qquad K_P = 1.6\ \text{atm}^{-2}$

$$K_P = 1.6 = \frac{P'_{A_6}}{(P_{A_2})^3}$$

$$P_{A_2} = \sqrt[3]{\frac{0.2}{1.6}} = 0.5\ \text{atm}$$

Also, pressure of A_2 used for the formation of $A_6 = 0.6\text{atm}$

$$\begin{array}{llll} \text{For} & A_2(g) & +\ C(g) \rightleftharpoons & A_2C(g) \\ t=0 & 2P & P & 0 \\ \text{At eq.} & 2P-P^1-0.6 & P-P^1 & P^1 \end{array}$$

$$\begin{array}{lll} \text{Also, for} & 3A_2(g) \rightleftharpoons & A_6(g) \\ t=0 & 2P & 0 \\ \text{At eq.} & 2P-P^1-0.6 & 0.2 \end{array}$$

$$2P-P^1-0.6 = 0.5$$

(since P_{A_2} at eq. is 0.5 for simultaneous equilibria)

Also, pressure of $A_2 + C + A_2C + A_6$

$$= (2P-P^1-0.6)+(P-P^1)+P^1+0.2 = 1.4$$

$$0.5+P+0.2 = 1.4$$

$$P = \mathbf{0.7\ atm}$$

$\therefore\quad 2P-P^1-0.6 = 0.5$

$\therefore\quad P^1 = 2\times 0.7-0.6-0.5$

$P^1 = 0.3\ \text{atm}$

$\therefore\ P_{A_2} = 0.5\ \text{atm}, P_C = 0.7-0.3 = 0.4\ \text{atm}, P_{A_2\text{C}} = 0.3\ \text{atm}$

Also, K_P for $A_2(g)+\text{C}(g) \rightleftharpoons A_2\text{C}(g)$

$$K_P = \frac{P_{A_2C}}{P_{A_2}\times P_C} = \frac{0.3}{0.5\times 0.4} = \mathbf{1.5\ atm^{-1}}$$

125.
$$\begin{array}{ccccccc} A(g) \rightleftharpoons & B(g) & +\ 2C(g) & \text{and } C \rightleftharpoons & 2D & + & 3B(g) \\ 1 & 0 & 0 & & & & \\ 1-a & (a+3b) & 2a-b & 2a-b & 2b & & (a+3b) \end{array}$$

$\therefore\ \Sigma$ mole at eq. $= 1-a+a+3b+2a-b+2b = 2a+4b+1$

Now, $P_{\text{initial}} \propto 1$

$P_{eq.} \propto 2a+4b+1$

$$\therefore\quad 2a+4b+1 = \frac{13}{6}$$

$$\text{or}\quad 2a+4b = \frac{7}{6} \qquad \text{...(1)}$$

$$\text{Also,}\quad [C]_{eq.} = \frac{4}{9}[A]_{eq.}$$

$$2a-b = \frac{4}{9}\times(1-a)$$

$$\therefore\quad 22a-9b = 4 \qquad \text{...(2)}$$

By Eqs. (1) and (2), $a = 0.25, b = 0.167$

$$\therefore\quad K_{C_1} = \frac{[B][C]^2}{[A]} = \frac{(a+3b)(2a-b)^2}{(1-a)}$$

$$= \frac{[0.25+(3\times 0.167)][0.5-0.167]^2}{(1-0.25)} = 0.11$$

$$K_{C_2} = \frac{[D]^2[B]^3}{[C]} = \frac{(2b)^2(a+3b)^3}{(2a-b)}$$

$$= \frac{[2\times 0.167]^2[0.25+(3\times 0.167)]^3}{[0.5-0.167]} = 0.142$$

126.
$$\begin{array}{lll} \text{NH}_4\text{I} \rightleftharpoons & \text{NH}_3 & +\ \text{HI} \\ & P & P \end{array} \qquad \text{...(1)}$$

For this equilibrium $2P = 275$

$\therefore\quad P = 137.5$

Thus, K_P for Eq. (1) $= P_{\text{NH}_3}\times P_{\text{HI}} = 137.5\times 137.5$ ...(2)

$$\begin{array}{llll} \text{For} & 2\text{HI} \rightleftharpoons & \text{H}_2 & +\ \text{I}_2 \\ & 1 & 0 & 0 \\ & (1-x) & \frac{x}{2} & \frac{x}{2} \end{array}$$

$$\therefore\quad K_P = K_C = \frac{x^2}{4(1-x)^2} = (0.015)^2$$

$\therefore\quad x = 0.2$

i.e., degree of dissociation of HI is 0.2. Again since HI decomposes, reaction (1) proceeds in forward direction, *i.e.*,

$$\begin{array}{lll} \text{NH}_4\text{I} \rightleftharpoons & \text{NH}_3 & +\ \text{HI} \\ & (P+A) & (P-a) \end{array} \qquad \text{...(3)}$$

$$\begin{array}{llll} 2\text{HI} \rightleftharpoons & \text{H}_2 & +\ \text{I}_2 & \\ (P-a) & \frac{a}{2} & \frac{a}{2} & [\because a = 0.2P] \end{array} \qquad \text{...(4)}$$

Also, K_P for final equilibrium Eq. (3) or Eq. (1) is

$$K_P = (P+A)(P-a) = (P+A)(P-0.2P)$$

$$= 137.5\times 137.5 = (P+A)(0.8P)$$

$\therefore\quad P+A = 171.875$

$\therefore\quad A = 34.375$

$a = 0.2P\times 0.2 = 27.5$

$$\text{Total pressure at equilibrium} = \frac{\text{NH}_3}{P+A}+\frac{\text{HI}}{P-a}+\frac{\text{H}_2}{a/2}+\frac{\text{I}_2}{a/2}$$

$$= 2P+A = 2\times 137.5+34.375$$

$$= \mathbf{309.75\ atm}$$

127.
$$\begin{array}{llll} & \text{N}_2 & +\ \text{O}_2 \rightleftharpoons & 2\text{NO} \\ \text{Initial Vol. \%} & a & b & 0 \\ \text{Final Vol. \%} & & & x \end{array}$$

$$\text{Also,}\quad x = \sqrt{K.a.b} - \frac{K(a+b)}{4} \qquad \text{...(1)}$$

The 'x' is maximum only when condition of maximum are fulfilled, *i.e.*,

$$\frac{\delta x}{\delta a} \text{ and } \frac{\delta x}{\delta b} = 0$$

By partial differentiation of 'x' w.r.t. 'b' keeping 'a' constant.

$$\text{From Eq. (1),}\quad \frac{\delta x}{\delta a} = \frac{K.b}{2\sqrt{K.a.b}} - \frac{K}{4} = \frac{\sqrt{K.b}}{2\sqrt{a}} - \frac{K}{4} = 0 \text{ ...(2)}$$

By partial differentiation of 'x' w.r.t. 'b' keeping 'a' constant.

$$\text{From Eq. (1),}\quad \frac{\delta x}{\delta b} = \frac{K.a}{2\sqrt{K.a.b}} - \frac{K}{4} = \frac{\sqrt{K.a}}{2\sqrt{b}} - \frac{K}{4} = 0 \text{ ...(3)}$$

By Eq. (2), $\quad K\cdot a\cdot b = 4b^2$

By Eq. (3), $\quad K\cdot a\cdot b = 4a^2$

$\therefore\quad a = b$

NOTE : Also, this is valid only when $K < 4$, because if $a = b$, Eq. (1) yields $x = \sqrt{Ka^2} - \frac{Ka}{2} = a\left(\sqrt{K} - \frac{K}{2}\right)$

If x is +ve $\quad \sqrt{K} > K/2 \quad$ or $\quad 4K > K^2$

or $\quad K(4-K) > 0 \quad$ or $\quad 0 < K < 4$

128. $$\Delta G^\circ = -2.303RT\log_{10}K_P \qquad \text{(at 1 atm)}$$

$$11.8\times10^3 = -2.303\times8.314\times230\log_{10}K_P$$

$$\therefore \quad K_P = 2.09\times10^{-3}$$

Also, for
$$\begin{array}{lccccc} & 2AB & \rightleftharpoons & A_2 & + & B_2 \\ & 1 & & 0 & & 0 \\ & (1-\alpha) & & \frac{\alpha}{2} & & \frac{\alpha}{2} \end{array}$$

$$\therefore \quad K_P = \frac{\alpha^2}{4(1-\alpha)^2} \quad \text{or} \quad \frac{\alpha}{2(1-\alpha)} = \sqrt{2.09\times10^{-3}}$$

$$\therefore \quad \alpha = \mathbf{0.0837} \quad \text{or} \quad \mathbf{8.37\%}$$

129.
$$\begin{array}{ccccc} XA & \rightleftharpoons & D & + & C \\ a(1-\alpha) & & \frac{a\alpha}{x} & & \frac{a\alpha}{x} \end{array}$$

$$\therefore \quad K_C = \frac{a^2\alpha^2}{V^2\cdot x^2\left[\frac{a(1-\alpha)}{V}\right]^x} = \frac{\alpha^2\cdot a^{2-x}}{x^2(1-\alpha)^x\cdot V^{2-x}}$$

Since, α is independent of a $\therefore$ $2-x=0$ $\therefore$ $x=\mathbf{2}$

130. Given that $\Delta E-\Delta H = 1200\,\text{cal}$

where ΔE is heat of reaction at constant volume and ΔH is heat of reaction at constant pressure.

Also, we have $\Delta H = \Delta E + \Delta nRT$

$$\therefore \quad \Delta nRT = -1200 \quad \text{or} \quad \Delta n = \frac{-1200}{2\times300} = -2 \qquad (R = 2\,\text{cal})$$

Now, $K_P = K_C(RT)^{\Delta n}$

$$\therefore \quad \frac{K_P}{K_C} = (0.0821\times300)^{-2} = \mathbf{1.648\times10^{-3}}$$

131. Meq. of H_2S = Meq. of PbS $= \frac{1.029\times1000}{238/2} = 8.6$

$$\therefore \quad \text{Mole of } H_2S \text{ formed} = \frac{8.6}{1000\times2} = 0.0043$$

Also,
$$\begin{array}{lccccccc} & Sb_2S_3(s) & + & 3H_2(g) & \rightleftharpoons & 2Sb(s) & + & 3H_2S(g) \\ \text{Initial mole} & 0.01 & & 0.01 & & 0 & & 0 \\ \text{Final mole} & (0.01-x) & & (0.01-3x) & & 2x & & 3x \end{array}$$

$$\because \quad 3x = 0.0043; \quad \therefore [H_2S] = \left[\frac{0.0043}{2.5}\right]M$$

and $$[H_2] = \left[\frac{0.01-0.0043}{2.5}\right]M$$

Thus, $$K_C = \frac{[H_2S]^3}{[H_2]^3}$$

Thus, $$K_C = \frac{\left[\frac{0.0043}{2.5}\right]^3}{\left[\frac{0.01-0.0043}{2.5}\right]^3} = \mathbf{0.43 = 4.3\times10^{-1}}$$

132. Let mole of A and B diffused out are n_A and n_B respectively. Initially they were present in the ratio $\frac{P'_A}{P'_B} = 1$

$$\therefore \quad \frac{n_A}{n_B} = \sqrt{\frac{m_B}{m_A}} = \sqrt{\frac{4}{16}} = \frac{1}{2}$$

Thus, mole ratio of n_A and n_B goes out in the ratio 1 : 2. Thus, mole of A and B are left after diffusion in the ratio 2 : 1. Total pressure after diffusion is 2 atm thus,

$$P'_A \text{ left} = \frac{4}{3} \text{ at } 27^\circ\text{C}$$

$$P'_B \text{ left} = \frac{2}{3} \text{ at } 27^\circ\text{C}$$

Now, vessel is heated to 127°C, thus new pressures becomes

$$P'_A = \frac{4}{3}\times\frac{4}{3} = \frac{16}{9} \qquad \left(\frac{P_1}{P_2} = \frac{T_1}{T_2}\right)$$

$$P'_B = \frac{2}{3}\times\frac{4}{3} = \frac{8}{9}$$

Now,
$$\begin{array}{lccccc} & A & + & B & \rightleftharpoons & C \\ \text{Initial P} & \frac{16}{9} & & \frac{8}{9} & & 0 \\ \text{P at eq.} & \left[\frac{16}{9}-P\right] & & \left[\frac{8}{9}-P\right] & & P \end{array}$$

$$\therefore \quad K_P = 0.1 = \frac{P}{\left[\frac{16}{9}-P\right]\left[\frac{8}{9}-P\right]} = \frac{81P}{(16-9P)(8-9P)}$$

or $81P = 12.8 - 21.6P + 8.1P^2$

or $P^2 - 12.67P + 1.58 = 0$ $\quad\therefore\quad$ $P = \mathbf{0.126\ atm}$

133. $V = 0.224\,\text{dm}^3, \quad P = 1\ \text{atm}, \quad T = 273\,\text{K}$

$\therefore$ Mole input per minute at eq.

$$= \frac{PV}{RT} = \frac{1\times0.224}{0.0821\times273} = 99.941\times10^{-4}$$

$$\begin{array}{lccc} & ZnO(s) + CO(g) & \rightleftharpoons\ Zn(g) + CO_2(g) & + N_2(g) \\ \text{Initial Mole} & 99.941\times0.45\times10^{-4} & 99.941\times10^{-4}\times0.50 & 99.941\times10^{-4}\times0.05 \\ & = 44.97\times10^{-4} & = 49.97\times10^{-4} & = 4.997\times10^{-4} \end{array}$$

$$\begin{array}{lcccc} & ZnO(s)+CO(g) & \rightleftharpoons\ Zn(g) & + CO_2(g) & + N_2(g) \\ \text{Mole at eq.} & [44.97-5]\times10^{-4} & 5\times10^{-4} & [49.97+5]\times10^{-4} & 4.997\times10^{-4} \\ & = 39.97\times10^{-4} & & = 54.97\times10^{-4} & \end{array}$$

$\therefore$ Total mole in gaseous phase at equilibrium

$$= [39.97+5+54.97+4.997]\times10^{-4} = 104.937\times10^{-4}$$

Now, $$K_P = \frac{n_{Zn}\times n_{CO_2}}{n_{CO}}\times\left[\frac{P}{\Sigma n}\right]^1$$

$$= \frac{54.97\times10^{-4}\times5\times10^{-4}}{39.97\times10^{-4}}\times\left[\frac{770}{104.937\times10^{-4}}\right]^1$$

$$= 50.45\,\text{mm} = \frac{50.45}{760} = \mathbf{0.0664\ atm.}$$

134. For the equilibrium :

$$\begin{array}{lccc} & nA & \rightleftharpoons & [A_n] \\ \text{Initially} & 1 & & 0 \\ \text{At eq.} & 1-\alpha & & \frac{\alpha}{n} \end{array}$$

$$\therefore \quad \text{Total mole at equilibrium} = 1-\alpha+\frac{\alpha}{n}$$

$$\because \quad PV = nRT$$

Thus at equilibrium

$$\therefore \quad PV = \left[1-\alpha+\frac{\alpha}{n}\right]RT \quad \text{or} \quad \frac{P}{RT} = \frac{1-\alpha+\frac{\alpha}{n}}{V} \quad \text{...(i)}$$

Given, $\frac{PV}{RT} = 1 - \frac{(n-1)K_C}{V^{n-1}}$

or $$\frac{P}{RT} = \frac{1}{V} - \frac{(n-1)K_C}{V^n} = \frac{1}{V} - \frac{(n-1)\times\frac{\alpha}{nV}}{V^n \times \frac{(1-\alpha)^n}{V^n}}$$

$$\left[\because K_C = \frac{\frac{\alpha}{nV}}{\left[\frac{1-\alpha}{V}\right]^n}\right]$$

$$= \frac{1}{V}\left[1 - \frac{(n-1)\alpha}{n(1-\alpha)^n}\right]$$

[since α is small, $\therefore (1-\alpha)^n = 1$]

$$= \frac{1}{V}\left[1 - \frac{(n-1)\alpha}{n}\right]$$

$$= \frac{1}{V}\left[1 - \alpha + \frac{\alpha}{n}\right] \qquad \text{...(ii)}$$

Eqs. (i) and (ii) are identical.

135. Equilibrium constant K is given dimension less which means that

$$K = \frac{(a_{H_2})\times(a_{CO})}{(a_{H_2O})\times(a_C)} = \frac{\left(\frac{P_{H_2}}{P^\circ}\right)\left(\frac{P_{CO}}{P^\circ}\right)}{\frac{P_{H_2O}}{P^\circ}\times 1} \quad \text{(for solid } a = 1)$$

The term a represents relative activity, *i.e.*, $a = \frac{P}{P^\circ}$ where P° standard state pressure = 100 kPa for gases and P is partial pressure of that gaseous component.

Thus for the equilibrium :

$$\begin{array}{cccc} C(s) + & H_2O(g) & \rightleftharpoons CO(g) + & H_2(g) \\ 1 & 1 & 0 & 0 \\ (1-x) & (1-x) & x & x \end{array}$$

$\therefore$ $$K = \frac{x\cdot x}{(1-x)} \times \left[\frac{P_T}{P^\circ \times (1+x)}\right]^1$$

$$1.34 = \frac{x^2}{1-x^2} \times \frac{200}{100} \qquad \therefore x = 0.633$$

$\therefore$ Mole fraction of CO = mole fraction of

$$H_2 = \frac{x}{1+x} = \frac{0.633}{1.633} = \mathbf{0.388}$$

Mole fraction of $H_2O = \frac{1-0.633}{1.633} = \mathbf{0.224}$

136. $$K_c^\circ = \frac{P_{H_2} \times [OH^-]^2}{[I^-]^2}$$

$\therefore$ $$[OH^-]^2 = \frac{K_c \times [I^-]^2}{P_{H_2}}$$

$$= \frac{1.2\times10^{-23}\times(0.1)^2}{\frac{60}{100}} \left(P_{H_2}^\circ = \frac{\text{Pressure of } H_2}{100\text{ kPa}}\right)$$

$$[OH^-] = \sqrt{2\times10^{-25}} = 4.472\times10^{-13}$$

$\therefore$ pOH = 12.35

$\therefore$ pH = **1.65**

137. $$\begin{array}{lccc} & AB_2(g) + & A(s) \rightleftharpoons & 2AB(g) \\ \text{Initial pressure} & P & 0 & 0 \\ \text{Pressure at eq.} & P - P_1 & & 2P' \end{array}$$

Given, $P = 0.7$ and $P + P' = 0.95$ bar $\therefore$ $P' = 0.25$ bar

$$K_{P_1} = \frac{(P_{AB})^2}{P_{AB_2}} = \frac{(2\times0.25)^2}{(0.7-0.25)} = 0.55$$

Let after reversible and isothermal expansion pressure of AB_2 and AB be a and b bar respectively at equilibrium

$$K_{P_1} = 0.55 = \frac{b^2}{a}z$$

Also $a + b = 0.4$

$\therefore$ $b = 0.27$ bar

$a = 0.13$ bar

Thus, mole % of $AB_2 = \frac{0.13}{0.4}\times100 = \mathbf{32.5}$

mole % of $AB = \frac{0.27}{0.4}\times100 = \mathbf{67.5}$

138. $$\begin{array}{lccc} & CH_3COCH_3(g) \rightleftharpoons & CO(g) + & C_2H_6(g) \\ \text{Initial mole} & a & 0 & 0 \\ \text{at eq.} & (a-x) & x & x \end{array}$$

$\because$ $P \propto a$

$\therefore$ $100 \propto a$ (Initial prressue is 100 mm)

Also given mole fraction of CO $= \frac{x}{a+x} = \frac{1}{3}$

$\therefore$ $3x = a + x$

or $x = \frac{a}{2}$

Let pressure at equilibrium be P', $P' \propto a + x$

$\therefore$ $P' \propto a + \frac{a}{2} = \frac{3a}{2}$

Then $P' = \frac{3\times100}{2} = 150$ mm

and pressure of $x = 50$ mm

$\therefore$ $$K_p = \frac{P_{CO}\times P_{C_2H_6}}{P_{CH_3COCH_3}} = \frac{50\times50}{50} = \mathbf{50\ mm}$$

• SINGLE INTEGER ANSWER PROBLEMS •

1. Maximum number of phases in which sulphur exists are......
2. For $2A+2B \rightleftharpoons 2C+2D$ $K_c = 1/16$ then K_c for $C+D \rightleftharpoons A+B$ is ....
3. For the reaction $2P \underset{K_2}{\overset{K_1}{\rightleftharpoons}} Q \underset{K_4}{\overset{K_3}{\rightleftharpoons}} R+S; K_1, K_2, K_3$ and K_4 are $4\times10^3, 2\times10^4, 16\times10^2$ and 40 respectively. The overall equilibrium constant is ......
4. In the reaction : $C(s)+CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 6 atm. If 50% of CO_2 reacts then K_P of the reaction is ......
5. The mole at equilibrium obtained during experiment for the given reaction in 1 litre vessel are shown below the reactants and products.

$$\begin{array}{lcccc} & 2A(g) & +\,B(g) \rightleftharpoons & 3C(g) & +\,3D \\ \text{Mole at equilibrium} & 8 & 16 & 4 & 4 \end{array}$$

If reaction in forward direction is to be made, the initial conc. of reactants and products should be such that reaction Quotient should be less than.........

6. The rate of disappearance of A in the reaction at equilibrium $A \rightleftharpoons B$ is given by

$$-\frac{d[A]}{dt} = 2\times10^{-2}[A] - 4\times10^{-3}[B] \text{ at } 300\text{ K.}$$

The equilibrium constant K_c is ......

7. If $K_p = K_c \times [RT]^{\Delta n}$, for the reaction

$$2CO_2(g)+2CaCO_3(s) \rightleftharpoons 2CaC_2(s)+5O_2(g); \quad \Delta n$$

is equal to ......

8. Negative slope of the line drawn as In K_c vs. $\frac{1}{T}$ for a given reaction is -1. The heat of reaction is ...... cal.
9. If $\Delta G°$ for a reaction is -8290.8 cal. The K_c for the reaction 300 K is 10^n. The value of n is :
10. The plot of ln K vs. $\frac{1}{T}$ shows an intercept of ln $a = 4$. The change in standard entropy for the reaction at equilibrium is ...... cal.
11. What is the % dissociation of H_2S, if one mole of H_2S is introduced in 1 litre vessel at 1000 K, if K_c for the reaction :

$$2H_2S(g) \rightleftharpoons 2H_2(g)+S_2(g) \text{ is } 4\times10^{-6}$$

12. In a reaction at equilibrium, 'x' mole of the reactant, A decompose to give 1 mole each of B and C. The experimental studies suggest that the decomposition of A at equilibrium is independent of initial concentration of A. Calculate 'x'.
13. Given below are two reversible reactions:

$$A+B \rightleftharpoons Z; \; K_{c_1} = 24$$

$$2B+C \rightleftharpoons 2Y; \; K_{c_2} = 16$$

The equilibrium constant K_c for the reaction

$$A+Y \rightleftharpoons Z+\frac{C}{2} \text{ is ....}$$

14. For a reversible reaction $A \rightleftharpoons B, \log_{10} K = 1.737 - \frac{2500}{T}$ (in litre atm unit). The standard entropy, change to the closest value in cal K^{-1} is......
15. For a reversible reaction $\frac{K_p}{K_c} = (RT)^{\Delta n}$ at 300 K. If $K_p / K_c = 14941.5$ (in litre atm unit) for a given reaction then Δn for the reaction is...... (given log $K_p / K_c = 4.17$ and log 24.93 = 1.39).
16. If pK_a of HCN is 10 and of HCO_3^- is 9, the $pK_{eq.}$ for the given reaction is......

$$CO_3^{2-} + HCN \longrightarrow CN^- + HCO_3^-$$

17. Δn for the reaction :

$$NH_4Cl(s) \rightleftharpoons NH_3(v)+HCl(g) \text{ is......}$$

18. The variation of ln K_C vs. $\frac{1}{T}$ gives a straight line having an angle of 45°. The value of heat of reaction in cal is......
19. Vapour density of N_2O_4 at temperature T K is 43.80. The % dissociation of N_2O_4 to NO_2 is......
20. For the reaction : $AB(g) \rightleftharpoons A(g)+B(g)$, the total pressure P at which AB is 50% dissociated is given by $P = a \times K_p$. The value of a is......
21. Total number of present of equilibrium in the given reaction are......

$$CuSO_4(s)3NH_3(l) \rightleftharpoons CuSO_4 \cdot 3NH_3(l)$$

22. 5 mole of PCl_5 are heated to attain the equilibrium at constant volume V and temperature T as :

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$; the degree of dissociation of PCl_5 is 0.2 at these conditions. Now 2 mole of N_2 are added to maintain V and T. The total mole of gases present at new equilibrium are.....

23. A one litre container was used to study the following equilibria occuring simultaneously

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If 10 mole of each CH_4 and H_2O, were used and if 2 mole of H_2O reacts with CH_4 and CO separately, to attain equilibria, then mole of H_2 formed are.....

24. For the reaction : $2CO(g)+O_2(g) \rightleftharpoons 2CO_2(g)$ $K_c = 0.75$

$$\begin{array}{lccc} \text{Conc at eq.} & 4 & 3 & a \end{array}$$

What is the value of a?

25. The variation of ln K_c vs. $\frac{1}{T}$ gives a straight line having an angle of 45°. The value of heat of reaction in cal is.....
26. For the equilibrium at temperature T :

$$Na_2HPO_4 \cdot 12H_2O(s) \rightleftharpoons Na_2 \cdot HPO_4 \cdot XH_2O(s) + YH_2O(g);$$

$K_p = 25\times10^{-3Y}$. If vapour pressure of H_2O at T K is 5×10^{-3} atm, how many molecule of H_2O are lost by $Na_2HPO_4 \cdot 12H_2O$ at equilibrium ?

27. For an equilibrium reaction : $A + 2B \rightleftharpoons 2C + D$; A and B are mixed in a reaction vessel at 300 K. The initial concentration of B was 1.5 times the initial concentration of A. After the equilibrium, the equilibrium concentrations of A and D are same. What is K_c ?

28. Vapour density of N_2O_4 at temperature T K is 43.80. What is % dissociation of N_2O_4 to NO_2 ?

29. Hot copper turnings are used to absorb O_2 in order to produce inert gas atmosphere. At 500 K,

$$2Cu(s) + \frac{1}{2}O_2(g) \rightleftharpoons Cu_2O(s),$$

the value of $(K_p)^2$ is $2.5\times10^{+21}$ atm^{-1}. If $R = 0.08$ and Av.no. is 6×10^{23}, how many molecules of O_2 are left at equilibrium in 1 litre container ?

30. For the reaction $AB(g) \rightleftharpoons A(g) + B(g)$, the total pressure P at which AB is 50% dissociated is given by $P = a \times K_p$. The value of a is.....

31. A certain gas A polymerises as $nA \rightleftharpoons (A)_n$. If $n = 2$ and degree of polymerisation is 20% then if reaction is carried out by taking 10 mole of A, then total mole at equilibrium are.....

32. Total number of phases present at equilibrium in the reaction

$$CuSO_4(s) + 3\ NH_3(l) \rightleftharpoons CuSO_4{\cdot}3NH_3(l)$$

33. For the reaction at 300 K, $A(g) \rightleftharpoons B(g) + C(g)$, $\Delta_r H° = -30\ kJ\ mol^{-1}$ and $\Delta_r S° = -100\ JK^{-1}\ mol^{-1}$, then equilibrium constant K for the reaction is ....

34. The value of $\Delta G°$, when $K_C = 1$ for a reaction in equilibrium is ....

35. A vessel of 250 litre containing 0.01 mole of Sb_2S_3 was filled with 0.01 mole of H_2 and reaction at 440°C,

$$Sb_2S_3(s) + 3H_2(g) \longrightarrow 2Sb(s) + 3H_2S(g)$$

was allowed to attain equilibrium. The H_2S formed was just sufficient to react with $Pb(NO_3)_2$ to give 1.19 g of PbS. The value of K_C at 440°C is ....

36. The value of $\dfrac{K_P\ \text{(in atm)}}{K_C\ \text{(in M)}}$ for the reaction, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ at temperature 365.4 K is 3×10^a. The value of a is ....

37. The values of K_{p_1} and K_{p_2} for the reaction given below are in the ratio 2 : 1. If degree of dissociation of X and A are equal, then total pressure at eq. (1) and eq. (2) are in the ratio.

$$X \rightleftharpoons Y + Z; \qquad K_{p_1}$$
$$A \rightleftharpoons 2B; \qquad K_{p_2}$$

38. For the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$; $G^o_{N_2O_4}$ and $G^o_{NO_2}$ are 100 kJ mol^{-1} and 50 kJ mol^{-1} at 298 K when 5 mole of each are taken initially than the approximate value of Gibbs energy change for the above reaction in kJ is ....

39. The degree of dissociation of PCl_5 at 1 atm and 400 K is 60%. Assuming ideal behaviour the density of equilibrium mixture is approximately in g/litre is ....

40. K_p for $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ is 9 $(atm)^2$ at T K. The total pressure at equilibrium at T K is ....

41. For the decomposition of $NH_4HS \rightleftharpoons NH_3 + H_2S$, if $K_p = n_{NH_3} \times n_{H_2S} \times \left(\frac{P}{\Sigma n}\right)^a$, then a is equal to ....

42. If K_p for $LiCl{\cdot}3NH_3(s) \rightleftharpoons LiCl{\cdot}NH_3(s) + 2NH_3(g)$, is 9 atm^2. If 0.1 mole of $LiCl \cdot NH_3$ at equilibrium, the pressure of NH_3 at equilibrium is ....

43. 2 mol SO_2 and 1 mol O_2 are heated in closed vessel to attain equilibrium : $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ The equilibrium mixture shows a pressure of 5 atm and requires $\frac{1}{3}$ mol of $K_2Cr_2O_7$ in acidic medium for oxidation. What is K_p in atm^{-1}.

44. Consider a reaction : $AB_2(g) \rightleftharpoons AB(g) + B(g)$ in equilibrium. The initial pressure and equilibrium pressure are 100 and 120 torr respectively. The equilibrium constant in torr is .... .

ANSWERS

1. Four 2. Four 3. Eight 4. Eight 5. Four 6. Five 7. Three 8. Two 9. Six 10. Eight 11. Two 12. Two
13. Six 14. Eight 15. Three 16. One 17. Two 18. Two 19. Five 20. Three 21. Two 22. Eight 23. Eight 24. Six
25. Two 26. Two 27. Four 28. Five 29. Six 30. Three 31. Nine 32. Two 33. One 34. Zero 35. One 36. One
37. Eight 38. Four 39. Four 40. Six 41. Two 42. Three 43. One 44. Five

OBJECTIVE PROBLEMS (One Answer Correct)

1. The rate for the $A_2 + C \longrightarrow$ Product for which mechanism is given below is 5.0 mol $\text{litre}^{-1}\,\text{s}^{-1}$ when the concentration of reactant A_2 and C are 10 mol/litre and 4 mol/litre respectively :

Step I. $A_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2A \; K_1 = 10^{10}\,\text{s}^{-1}$

and $K_2 = 10^9$ litre $\text{mol}^{-1}\,\text{sec}^{-1}$

Step II. $A + C \longrightarrow AC$

The rate constant for the change $A + C \longrightarrow AC$ is :

(a) 1.25×10^{-1} (b) 1.25×10^{-3}

(c) 1.25×10^{-2} (d) 1.25

2. The equilibrium constant K_c for $A_{(g)} \longrightarrow B_{(g)}$ is 1 : 1. The gas having its concentration at equilibrium greater than 1 is :

(a) only A

(b) only B

(c) both A and B

(d) both $[A]$ and $[B]$ if $[A] \geq 1$ and only $[B]$ if $0.91 < A \leq 1$

3. For the reaction in equilibrium : $2\text{NOCl}_{(g)} \rightleftharpoons 2\text{NO}_{(g)} + \text{Cl}_{2(g)}$ if $P_{\text{Cl}_2} = \frac{P}{4}$, when P is initial pressure of NOCl, then total pressure at equilibrium is :

(a) $\frac{5P}{4}$ (b) $2P$

(c) $\frac{P}{4}$ (d) $\frac{3P}{4}$

4. The standard internal energy change during the course of reaction at equilibrium at 300 K : $2A_g + B_g \rightleftharpoons A_2B_g$ is :

(Given, $K_p = 10^{-10}\,\text{atm}^{-2}$ and $\Delta S^\circ = 5\,\text{JK}^{-1}$)

(a) −63.93 kJ (b) +63.93 kJ

(c) +58.94 kJ (d) −58.94 kJ

5. An aquatic species needs atleast 4 mg/litre O_2 for their survival. The solubility of O_2 in water at 273 K and 1 atm pressure is 2.21×10^{-3} mol litre^{-1}. The partial pressure of O_2 above water (in atmosphere at 273 K) needed for survival of species is :

(a) 0.56 atm (b) 5.525×10^{-3} atm

(c) 5.525 atm (d) 0.056 atm

6. The equilibrium constants for the reactions are :

$\text{NO}_{2(g)} \rightleftharpoons \text{NO}_{(g)} + \text{O}_{(g)}$ $K_{P_1} = 6.0 \times 10^{-50}$

$\text{O}_3 + \text{NO}_{(g)} \rightleftharpoons \text{NO}_{2(g)} + \text{O}_{2(g)}$ $K_{P_2} = 5.0 \times 10^{-35}$

The equilibrium constant for $\text{O}_{2(g)} + \text{O}_{(g)} \rightleftharpoons \text{O}_{3(g)}$ is :

(a) 8.3×10^{14} (b) 1.2×10^{-15}

(c) 3.0×10^{-84} (d) 3.3×10^{83}

7. If K_{a_2} for $\text{H}_2\text{S} = 1.0 \times 10^{-15}$ and K_{sp} of $\text{Ba}_3(\text{AsO}_4)_2$, Ag_2S and Ag_3AsO_4 are 7.70×10^{-51}, 2.0×10^{-49} and 1.0×10^{-22} respectively. The equilibrium constant for the reaction :

$$3\text{Ag}_2\text{S}_{(s)} + \text{Ba}_3(\text{AsO}_4)_{2(s)} + 3\text{H}^+ \rightleftharpoons 2\text{Ag}_3\text{AsO}_{4(s)} + 3\text{HS}^- + 3\text{Ba}^{2+}$$ is :

(a) 5.6×10^{-124} (b) 3.0×10^{-109}

(c) 5.6×10^{-108} (d) 4.63×10^{-108}

8. Vapour density of N_2O_4 at 60°C is found to be 30.6. The degree of dissociation of N_2O_4 is :

(a) 10 % (b) 20 %

(c) 40 % (d) 50 %

9. The dissociation equilibrium pressure of $\text{NH}_4\text{HS}_{(s)}$ is 60 cm at 27°C. The total pressure at equilibrium when the NH_4HS is dissociated in presence of 45 cm of NH_3 is :

(a) 85 cm (b) 100 cm

(c) 105 cm (d) 75 cm

10. The rate of disappearance of A at two temperatures is given by : $A \rightleftharpoons B$

I. $-\frac{d[A]}{dt} = 2 \times 10^{-2}[A] - 4 \times 10^{-3}[B]$ at 300 K

II. $-\frac{d[A]}{dt} = 4 \times 10^{-2}[A] - 16 \times 10^{-4}[B]$ at 400 K

The heat of reaction for the change is :

(a) 3.863 kcal (b) 6.93 kcal

(c) 1.68 kcal (d) 1.68×10^2 kcal

11. The decomposition of HNO_3 represented below attains equilibrium at a given $P_{eq.}$ and T. If we start

$4\text{HNO}_{3(g)} \rightleftharpoons 4\text{NO}_{2(g)} + 2\text{H}_2\text{O}_{(g)} + \text{O}_{2(g)}$

with pure HNO_3 having initial pressure P_i, then at equilibrium which one is not correct ?

(a) $K_p = \frac{1024(P_{\text{O}_2})^7}{(P_{eq.} - 7P_{\text{O}_2})^4}$ (b) $K_P = \frac{1024(P_{\text{O}_2})^7}{(P_i - 4P_{\text{O}_2})^4}$

(c) $K_p^\circ = \frac{1024(P_{\text{O}_2})^7}{(P_{eq.} - 7P_{\text{O}_2})^4} \times \left(\frac{1}{P^\circ}\right)^3$

(d) All of these

12. Hot copper turnings can be used as oxygen getter for inert gas supplies by slowly passing the gas over the turnings at 600 K.

$2\text{Cu}_{(s)} + \frac{1}{2}\text{O}_{2(g)} \rightleftharpoons \text{Cu}_2\text{O}_{(s)}; K_p = 7.5 \times 10^{10}\,\text{atm}^{-1/2}$

The number of molecules per litre left after equilibrium has reached are :

(a) 2.17 (b) 2.17×10^{23}
(c) 3.61×10^{24} (d) 1.78×10^{22}

13. 0.2 mole of NH_4Cl are introduced into an empty container of 10 litre and heated to 327 to attain equilibrium as : $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$; $K_p = 0.36$ atm^2. The quantity of solid NH_4Cl left is :
(a) 0.02 mol (b) 0.078 mol
(c) 0.095 mol (d) 0.035 mol

14. For the reaction :

$$2CaSO_{4(s)} \rightleftharpoons 2CaO_{(s)} + 2SO_{2(g)} + O_{2(g)};$$

$K_p^\circ = 0.143$ dimension less. If mole fraction of SO_2 is 0.4 at equilibrium, the dissociation pressure at equilibrium (in mm) is :
(a) 868 mm (b) 40.3 mm
(c) 76 mm (d) 86.8 mm

15. The dissociation of N_2O_4 is carried out at constant volume and temperature *T*. The degree of dissociation α of N_2O_4 is : ($P_{eq.}$ and P_{ini} are pressure at equilibrium and initial pressure at equilibrium and initial pressure before dissociation and assume ideal gas nature)
(a) $\dfrac{P_{eq.} - P_{ini}}{P_{ini}}$
(b) $\left[\dfrac{K_P}{4P + K_p}\right]^{1/2}$
(c) dependent of initial mass of N_2O_4
(d) all of the above

16. NO and NO_2 are mixed in a container at constant volume to attain for the equilibrium :

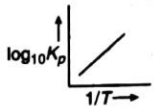
$$2NO_2 \rightleftharpoons N_2O_4 \quad NO + NO_2 \rightleftharpoons N_2O_3$$

If partial pressures of P'_{NO_2} and $P'_{N_2O_4}$ are 0.5 and 1.7 atm respectively and equilibrium pressure is 5.05 atm, the initial pressure (atm) of NO would be :
(a) 2.20 (b) 2.85
(c) 3.20 (d) 3.85

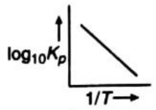
17. The equilibrium constant K_p for the reaction has the following characteristics :
(a) $K_p = K_p^\circ$ if pressure are expressed in bar or in standard state
(b) K_p° values rises exponentially with the constant, if reaction is multiplied by the constant
(c) on increasing the temperature equilibrium is shifted towards high enthalpy side whereas on decreasing temperature, it is shifted towards low enthalpy side :
(d) all of the above

18. Which graph correctly represents for $\log_{10} K_p$ *vs.* $\dfrac{1}{T}$ plots ?

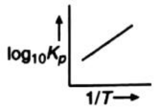
(a) Exothermic reaction :



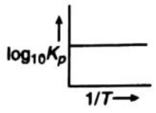
(b) Exothermic reaction :



(c) Endothermic reaction :



(d) Endothermic reaction :



19. The intercepts and plots of graph of $\log_{10} K_p^\circ$ *vs.* $\dfrac{1}{T}$ are :
(a) $\Delta G^\circ, \Delta H^\circ$ (b) $\dfrac{\Delta G^\circ}{2.303R}, \dfrac{\Delta H^\circ}{2.303R}$
(c) $\dfrac{\Delta S^\circ}{2.303\,R}, -\dfrac{\Delta H^\circ}{2.303\,R}$ (d) $\dfrac{\Delta H^\circ}{2.303R}, \Delta S^\circ$

20. If S° for N_2, O_2, N_2O, NO, NO_2 and N_2O_4 are 45.7, 49.0, 48.2, 50.24, 57.24 and 72.77 cal respectively and
$N_2 + \frac{1}{2}O_2 \rightleftharpoons N_2O$; $\Delta H^\circ = 19.49$ kcal at 300 K
$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$; $\Delta H^\circ = 21.60$ kcal at 300 K
$\frac{1}{2}N_2 + O_2 \rightleftharpoons NO_2$; $\Delta H^\circ = 8.09$ kcal at 300 K
$N_2 + 2O_2 \rightleftharpoons N_2O_4$; $\Delta H^\circ = 2.19$ kcal at 300 K
For which ΔG° is more +ve :
(a) N_2O (b) NO
(c) NO_2 (d) N_2O_4

21. For the reaction : $AB_{2(g)} \rightleftharpoons AB_{(g)} + B_{(g)}$, the degree of dissociation of AB_2 is negligible compared to unity, then which one is not correct ?
(a) $K_{eq.} = \dfrac{C\alpha^2}{4}$ (b) $\alpha = \sqrt{\dfrac{K_{eq.}}{C}}$
(c) $\alpha = \sqrt{\dfrac{K_P}{P}}$ (d) $K_{eq.} = \dfrac{\alpha^2 \times P}{(1+\alpha)}$

22. In a reaction at equilibrium '*x*' mole of the reactant *A* decompose to give 1 mole of *C* and *D*. It has been found that the fraction of *A* decomposed at equilibrium is independent of initial concentration of *A*. The value of '*x*' is :
(a) 1 (b) 2
(c) 3 (d) 4

23. A certain reaction has equilibrium constant 10 and 100 at 300 K and 400 K respectively. The ratio of ΔG° at 300 K and 400 K respectively is :

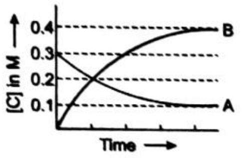
(a) $\frac{1}{10}$ (b) $\frac{3}{8}$

(c) $\frac{1}{2}$ (d) $\frac{3}{4}$

24. The equilibrium constant K_c for the reaction,

$$A(g) \rightleftharpoons 2B(g),$$

obeying the graph is :

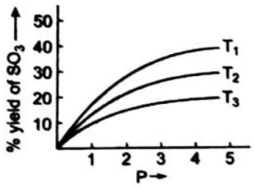


(a) 1.6 (b) 1.0

(c) 1.3 (d) 4

25. The preparation of $SO_3(g)$ by the reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

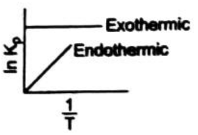


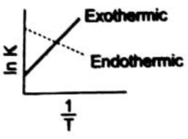
shows the following figure in % yield against pressure at different temperature then :

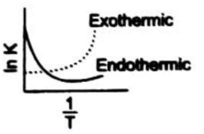
(a) $T_3 > T_2 > T_1$ (b) $T_1 > T_2 > T_3$

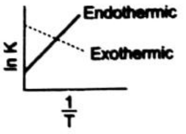
(c) $T_1 = T_2 = T_3$ (d) $T_2 > T_1 > T_3$

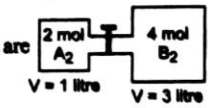
26. Which of the following is correct for the equilibrium constant involving exothermic and endothermic change :

(a)


(b)


(c)


(d)


27. Gases are  present in two containers at 300 K separated by a narrow tube of negligible volume having valve in between. On opening the valve the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ attains equilibrium at 300 K. If $K_c = 4$ at 300 K, the concentration of AB at equilibrium is :

(a) 1.33 *M* (b) 2.66 *M*

(c) 1.66 *M* (d) 0.66 *M*

28. Two solid compounds A_1 and A_2 in a container dissociates at temperature T to show the equilibrium :

$$A_1(s) \rightleftharpoons A(g) + 2B(g); \quad K_{p_1} = 9 \times 10^{-3}$$

$$A_2(s) \rightleftharpoons C(g) + 2B(g); \quad K_{p_2} = 4.5 \times 10^{-3}$$

The total pressure of gases at equilibria will be :

(a) 1.5 atm (b) 0.45 atm

(c) 0.6 atm (d) 2 atm

29. 10% of a mixture of 0.2 mole of N_2 and 0.6 mole of H_2 react to give NH_3 according to the equation to give NH_3 following the reaction equilibrium :

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

at constant temperature. The ratio between the initial moles and final mole is:

(a) 1.05 (b) 2.20

(c) 0.8 (d) 0.6

30. At a definite temperature, the equilibrium constant for a reaction, $A + B \rightleftharpoons 2C$, was found to be 81. Starting with 1 mole A and 1 mole of B, the mole fraction of C at equilibrium is :

(a) $\frac{9}{11}$ (b) $\frac{1}{11}$

(c) $\frac{2}{11}$ (d) $\frac{7}{11}$

31. Addition of 1 mole of N_2 is made to an equilibrium mixture of PCl_5 in a piston fitted cylinder. Which of the following is correct :

(a) No effect on equilibrium constant K_c or K_p

(b) The degree of dissociation of PCl_5 decreases

(c) The volume of container does not change

(d) No effect on equilibrium concentration

32. Which of the following represent chemical equilibria on mixing?

(a) 20 mL of 0.1 *M* HCl + 20 mL of 0.1 *M* NaOH

(b) 20 mL of 0.1 *M* NH_4OH + 20 mL of 0.1 *M* HCl

(c) 20 mL of 0.1 *M* $AgNO_3$ + 20 mL of 0.1 *M* KCl

(d) 20 mL of 0.1 *M* K_2CrO_4 + 20 mL of 0.1 *M* $Pb(NO_3)_2$

33. Which of the following relation correctly represents the equilibrium constant in terms of standard state for the dissociation of :

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

Partial pressure at eq. P_1 P_2 P_3
(in kPa)

(a) $K_{P_{ss}} = \frac{(P_3)^2}{(P_1)^2 \times (P_2)}$

(b) $K_{P_{ss}} = \frac{(P_3)^2}{(P_1)^2 \times (P_2)} \times 100$

(c) $K_{p_{ss}} = \dfrac{(P_3)^2}{(P_1)^2 \times (P_2)} \times 1000$

(d) $K_{p_{ss}} = \dfrac{(P_3)^2}{(P_1)^2 \times (P_2)} \times 10$

34. Select the incorrect statement :

(a) Solubility of hydrated salts usually increases with temperature

(b) $P_W \longrightarrow P_R; \Delta H = +\text{ve}$

(c) Dissolution of water soluble gas is always exothermic

(d) Le chatelier principle is not valid for solid-solid systems

35. Select the incorrect statement :

(a) m.pt. of ice is lowered at higher altitute

(b) m.pt. of solid is raised at higher altitude

(c) Ice melts slowly at higher altitude

(d) Melting of ice takes place slowly on spraying NaCl at same pressure

36. Select the incorrect statement :

(a) On dissolution 0.1 mole of CH_3COONa in 10 mL water in a beaker shows equilibrium

(b) Chemical equilibrium is attained only at constant *P* or at constant *V*

(c) On dissolving $CuSO_4$ in water a turbid solution is formed which forms a transparent solution on addition of little CH_3COOH

(d) $SbCl_3$ in aqueous solution gives a transparent solution

37. For the reaction,

$$X + Y \rightleftharpoons 3Z,$$

if α mole of each *X* and *Y* per litre are taken initially in the container, which are correct at equilibrium :

(a) $[X]+[Y]=0$ (b) $3[X]+[Z]=3\alpha$

(c) $[X]-\frac{1}{3}[Y]=\alpha$ (d) $[X]+[Z]=3\alpha$

38. The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if :

(a) temperature is increased and pressure is kept constant

(b) temperature is reduced and pressure is increased

(c) both temperature and pressure are increased

(d) both temperature and pressure are reduced

39. For the reaction,

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

the equilibrium constant K_p changes with :

(a) total pressure

(b) catalyst

(c) the amounts of H_2 and I_2 present

(d) temperature

40. Pure ammonia is placed in a vessel at a temperature where its dissociation constant *a* is appreciable. At equilibrium :

(a) K_p does not change significantly with pressure

(b) *a* does not change with pressure

(c) concentration of NH_3 does not change with pressure

(d) concentration of hydrogen is less than that of nitrogen

41. An example of a reversible reaction is :

(a) $Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$

(b) $AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

(c) $2Na(s) + H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

(d) $KNO_3(aq) + NaCl(aq) \rightarrow KCl(aq) + NaNO_3(aq)$

42. The reaction which proceeds in the forward direction is :

(a) $Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$

(b) $NH_3 + H_2O + NaCl = NH_4Cl + NaOH$

(c) $SnCl_4 + Hg_2Cl_2 = SnCl_2 + 2HgCl_2$

(d) $2CuI + I_2 + 4K^+ = 2Cu^{2+} + 4KI$

43. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under 1 atm. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is :

(a) 1.2 atm (b) 2.4 atm

(c) 2.0 atm (d) 1.0 atm

44. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by :

(a) temperature and pressure

(b) temperature only

(c) pressure only

(d) temperature, pressure and catalyst

45. Consider a hypothetical equilibrium :

$$A(aq.) \rightleftharpoons 2B(aq.) + C(aq.)$$

Before the reaction, *A* and *B* were present such that mole fraction of *B* is 1/3 as well as molar concentration of *B* is *M*. At equilibrium the reaction mixture has mole fraction of *A* equal to 1/2. The equilibrium constant of the reaction can be given by :

(a) $\dfrac{27M^3}{28}$ (b) $\dfrac{28M^3}{27}$

(c) $\dfrac{M^2}{7}$ (d) $\dfrac{9M^2}{28}$

46. One mole of *A* at pressure *P* in a closed container of 1 litre shows the following equilibria :

$$A(g) \rightleftharpoons B(g) + C(g) \quad ; \quad K_1$$
$$C(g) \rightleftharpoons D(g) + B(g) \quad ; \quad K_2$$

The pressure at equilibrium is 2*P* and $\dfrac{[C]_{eq.}}{[A]_{eq.}} = 2.1$. The ratio of $\dfrac{K_1}{K_2}$ can be given by :

(a) 3 : 1 (b) 4 : 1

(c) 2 : 1 (d) 1 : 2

47. Consider a hypothetical reaction : $A + B \rightleftharpoons C$; $K_C = 0.9$. The mole of *A* added to 1 litre of 0.1 *M B* so that 60% of *B* is converted to *C* are :

(a) 1.83 (b) 1.93
(c) 1.73 (d) 1.63

48. For the given endothermic equilibrium, the heat of reaction at constant volume is 1200 cal more than that of heat of reaction at constant pressure at 300 K. The ratio of equilibrium constants K_p and K_C for the above equilibrium is :

(a) 3.6×10^5 (b) 6.2×10^6
(c) 3.6×10^{-5} (d) 1.64×10^{-3}

49. The concentrations of A and B are $3M$ and $4M$ respectively in the state of equilibrium of $A(g) + 2B(g) \rightleftharpoons C(g)$. After the equilibrium is attained, the volume of container is doubled so that equilibrium is restablished and at this state $[B]_{eq.}$ is $3M$. The equilibrium constant K_C for the reaction is :

(a) 0.083 (b) 12
(c) 4 (d) 0.25

50. Equal volumes of 0.06 M $AgNO_3$ and 0.2 M KCN solutions are mixed. K_C for the reaction $Ag(CN)_2^-(aq.) \rightleftharpoons Ag^+(aq.) + 2CN^-(aq.)$ is 1.6×10^{-19} at 25°C. The concentration of $Ag^+(aq.)$ in solution is :

(a) $3 \times 10^{-18}\,M$ (b) $1.5 \times 10^{-19}\,M$
(c) $1.5 \times 10^{-18}\,M$ (d) $3 \times 10^{-20}\,M$

51. Two solids A and C shows the following dissociation equilibria :

$A(s) \rightleftharpoons B(g) + D(g)$
$C(s) \rightleftharpoons E(g) + D(g)$

The pressure over excess solid A is 40 atm and over excess C is 80 atm. The total pressure of the gaseous mixture over the solid mixture is :

(a) 67.0 atm (b) 89.4 atm
(c) 134 atm (d) 178.8 atm

52. For the equilibrium : $A(s) \rightleftharpoons 2B(g) + 3C(g)$, the concentration of B and C are x and y mole litre^{-1} respectively at equilibrium. If concentration of C is two times of y at equilibrium then what would be the value of $[B]$ at equilibrium?

(a) $2x$ (b) $3x$
(c) $8x$ (d) $\frac{x}{2\sqrt{2}}$

53. The colour of given reaction mixture is blue at room temperature. On

$$\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}(aq.)} + 4Cl^- \rightleftharpoons \underset{\text{Blue}}{[CoCl_4^{2-}](aq.)} + 6H_2O$$

cooling it becames pink, this indicates that :
(a) reaction is exothermic
(b) reaction is endothermic
(c) reaction shifts in forward direction on cooling
(d) none of the above

54. The activation energy for the forward and backward reactions are 10.303 and 8.0 k cal respectively at 500 K. Assuming pre exponential factor same for both forward and reverse reaction are same and $R = 2$cal, the equilibrium constant for the reaction $A \rightleftharpoons B$ is :

(a) 10 (b) 100
(c) 1000 (d) 0.1

55. N_2O_4 is dissociated to 33% and 40% at total pressure P_1 and P_2 respectively at equilibrium. The ratio of $\frac{P_1}{P_2}$ is :

(a) 2.0 (b) 1.55
(c) 2.5 (d) 3.0

56. For the reaction at equilibrium :

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

if $P_{Br_2} = \frac{P}{9}$ at equilibrium and total pressure is P, then ratio of $\frac{K_p}{P}$ is equal to :

(a) $\frac{1}{9}$ (b) $\frac{1}{81}$
(c) $\frac{1}{27}$ (d) $\frac{1}{3}$

57. 500 mL vessel contains 1.5 M each of A, B, C and D at equilibrium. If 0.5 M each of C and D are taken out, the value of K_C for $A + B \rightleftharpoons C + D$ is :

(a) 1.0 (b) $\frac{1}{9}$
(c) $\frac{4}{9}$ (d) $\frac{8}{9}$

58. For the reaction at 500 K, $2A + B \rightleftharpoons 2C$; $\Delta G^\circ = 2$ kJ mol^{-1}. What is the value of K for the reaction $A + \frac{1}{2}B \longrightarrow C$ at 500 K.

(a) 0.786 (b) 0.527
(c) 0.22 (d) 0.46

59. N_2O_4 dissociates to NO_2 for which equilibrium constant (K_p) is 0.2 at 300 K. Find out the fraction of N_2O_4 dissociated at total pressure of 4 atm pressure having 1 mole of Argon at equilibrium. Assume α being small for solving the problem.

(a) 0.158 (b) 0.058
(c) 0.250 (d) 0.015

60. 4 mole of SO_3 shows dissociation equilibrium in 2 litre flask as :

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

The equilibrium mixture requires 6.4 mL of 0.1 M acidified $KMnO_4$ for the redox change. K_c for the reaction equilibrium is mol litre^{-1} is :

(a) 0.178 (b) 0.356
(c) 0.702 (d) 0.0178

61. The ΔU° and ΔS° for the change :

$$2A(g) \rightleftharpoons 2B(g) + C(g)$$

are 30 kcal and 100 cal/° at 300 K. The equilibrium constant for the reaction is :

(a) e^{-2} (b) e^{-1}

(c) e (d) e^{-3}

62. The equilibrium pressure of the reaction mixture :

$$NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g)$$

is P atm at temperature T K. The standard Gibbs energy change for the reaction is :

(a) $-2RT[\ln P - \ln 2]$ (b) $-RT[\ln P - \ln 2]$

(c) $-RT[\ln 2 - \ln P]$ (d) $-2RT \ln P$

63. Variation of equilibrium constant 'K' with temperature is given by :

$$\ln K = 4 - \frac{100}{T}$$

The value of ΔS_r (in cal) for the reaction : $A \rightleftharpoons B$ at 300 K is :

(a) 2 (b) 4

(c) 6 (d) 8

64. 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 : $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$ $K_p = 1.6$ atm)

(a) 5 litre (b) 10 litre

(c) 4 litre (d) 2 litre

65. The equilibrium constants of the following are :

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ K_1

$N_2 + O_2 \rightleftharpoons 2NO$ K_2

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ K_3

The equilibrium constant (K) of the reaction :

$$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$$; will be :

(a) $\frac{K_1K_3^3}{K_2}$ (b) $\frac{K_2K_3^3}{K_1}$

(c) $\frac{K_2K_3}{K_1}$ (d) $\frac{K_2^3K_3}{K_1}$

SOLUTIONS (One Answer Correct)

1. (a) The step II is slow since I K_1 and K_2 are very high

$$\therefore \quad K_C = \frac{[A]^2}{[A_2]} = \frac{K_1}{K_2} = \frac{10^{10}}{10^9} = 10^1$$

$$\therefore \quad [A] = \sqrt{[A_2] \times 10}$$

$$r = K[A][C]$$

$$= K \times \sqrt{[A_2] \times 10} \times [C]$$

$$\text{or} \quad 5 = K\sqrt{10 \times 10} \times 4$$

$$\therefore \quad K = \frac{5}{4 \times 10} = 0.125$$

2. (d) Mathematical observation.

3. (a) $2NOCl \rightleftharpoons 2NO + Cl_2$

$$\underset{P-\frac{P}{2}}{} \qquad \underset{P/2}{} \qquad \underset{P/4}{}$$

$$\therefore \quad P_r = \frac{P}{2} + \frac{P}{2} + \frac{P}{4} = \frac{5P}{4}$$

4. (b)

$$\Delta G^\circ = -2.303\, RT \log K_p$$

$$\therefore \quad = -2.303 \times 8.314 \times 10^{-3} \times 300 \log 10^{-10}$$

$$= +57.44 \text{ kJ}$$

$$\text{Now,} \quad \Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

$$+57.44 = \Delta H^\circ - 300 \times 5 \times 10^{-3}$$

$$\Delta H^\circ = +58.94 \text{ kJ}$$

$$\text{Also,} \quad \Delta H^\circ = \Delta U^\circ + \Delta nRT \text{ kJ}$$

$$58.94 = \Delta U^\circ + (-2) \times 8.314 \times 10^{-3} \times 300, \ \Delta U^\circ = 63.93 \text{kJ}$$

5. (d) Acc. to Henry's law $K_p = \frac{a}{p} = \frac{2.21 \times 10^{-3}}{1}$

$$= 2.21 \times 10^{-3} \text{ mol atm}^{-1}$$

Now, O_2 required for survival $= 4 \times 10^{-3}$ g/litre

$$= \frac{4 \times 10^{-3}}{32} \text{ mol litre}^{-1}$$

$$\text{Now,} \quad 2.21 \times 10^{-3} = \frac{4 \times 10^{-3}}{P \times 32}$$

$$\therefore \quad P = 0.056 \text{ atm}$$

6. (d)

$$K_{P_1} = \frac{[NO][O]}{[NO_2]} \text{ and } K_{P_2} = \frac{[NO_2][O_2]}{[O_3][NO]}$$

$$\therefore \quad \frac{1}{K_{P_1}} \times \frac{1}{K_{P_2}} = \frac{[NO_2]}{[NO][O]} \times \frac{[O_3][NO]}{[NO_2][O_2]}$$

$$= \frac{[O_3]}{[O][O_2]} = K$$

$$\therefore \quad K = \frac{1}{6 \times 10^{-50} \times 5 \times 10^{-35}} = 3.3 \times 10^{83}$$

7. (d)

$$K_{2_{H_2S}} = \frac{[H^+][S^{2-}]}{[HS]} \qquad \text{...(i)}$$

$$K_{sp_{Ag_2S}} = [Ag^+]^2[S^{2-}] \qquad \text{...(ii)}$$

$$K_{sp_{Ba_3(AsO_4)_2}} = [Ba^{2+}]^3[AsO_4^{3-}]^2 \qquad \text{...(iii)}$$

$$K_{sp_{Ag_3AsO_4}} = [Ag^+]^3[AsO_4^-] \qquad \text{...(iv)}$$

$$K_{eq.} = \frac{[HS^-]^3[Ba^{2+}]^3}{[H^+]^3} \qquad \text{...(v)}$$

By Eqs. (i), (ii), (iii) and (iv)

$$K = K_{sp_{Ba_3AsO_4}} \times \left(\frac{1}{K_{2_{H_2S}}}\right)^3 \times (K_{sp_{Ag_2S}})^3 \times \left(\frac{1}{K_{sp_{Ag_3AsO_4}}}\right)^2$$

$$= \frac{7.70 \times 10^{-51} \times (2.0 \times 10^{-49})^3}{(1.10 \times 10^{-15})^3 \times (1.0 \times 10^{-22})^2} = 4.63 \times 10^{-108}$$

8. (d)

$$\underset{1-\alpha}{N_2O_4} \rightleftharpoons \underset{2\alpha}{2NO_2}$$

$$2 \times 30.6 = \frac{(1-\alpha) \times 92 + 2\alpha \times 46}{(1+\alpha)} \quad \therefore \alpha = 0.5$$

9. (d)

$$NH_4HS_{(s)} \rightleftharpoons NH_3 + H_2S$$

K_p for NH_4HS $= P \times P = P^2$ Also given $2P = 60$ cm

$\therefore$ $P = 30$ cm

$$K_p = 30 \times 30 = 900 \text{cm}^2$$

$$NH_4HS_{(s)} \rightleftharpoons \underset{P'+45}{NH_3} + \underset{P'}{H_2S}$$

$$(P' + 45) \times P' = 900$$

$$\therefore \quad P' = 15 \text{ cm}$$

$$\therefore \quad P_r = 15 + 45 + 15 = 75 \text{cm}$$

10. (a)

$$K_1 = \frac{K_f}{K_b} = \frac{2 \times 10^{-2}}{4 \times 10^{-3}} = 5 \text{ at } 300 \text{ K}$$

$$K_2 = \frac{K_f}{K_b} = \frac{4 \times 10^{-2}}{16 \times 10^{-4}} = 25 \text{ at } 400 \text{ K}$$

$$\therefore \quad 2.303 \log \frac{25}{5} = \frac{\Delta H}{2} \times \left[\frac{400 - 300}{400 \times 300}\right]$$

$$\text{or} \quad \Delta H = 3863.3 \text{ cal} = 3.86 \text{ kcal}$$

11. (d) $4HNO_{3(g)} \rightleftharpoons 4NO_{2(g)} + 2H_2O_{(g)} + O_2$;

Pressure at equilibrium is $P_{eq.}$

$$\begin{array}{cccc} P_i & 0 & 0 & 0 \\ P_i - 4P & 4P & 2P & P \end{array}$$

$$P_{eq.} = P_i - 4P + 4P + 2P + P$$

$$\therefore \quad P_i - 4P = P_{eq.} - 7P = P_{eq.} - 7P_{O_2}; \qquad P = P_{O_2}$$

$$K_P = \frac{(P_{NO_2})^4 (P_{H_2O})^2 P_{O_2}}{(P_{HNO_3})^4}$$

$$= \frac{1024(P_{O_2})^7}{(P_{eq.} - 7P_{O_2})^4} = \frac{1024(P_{O_2})^7}{(P_i - 4P_{O_2})^4}$$

$$\text{and} \quad K_P^\circ = \frac{(P_{NO_2})^4 \times (P_{H_2O})^2 P_{O_2}}{(P_{HNO_3})^4} \times \frac{1}{(P^0)^3}$$

$$= \frac{(4P)^{21} \times (2P)^2 \times P}{(P_{eq.} - 7P_{O_2})^4} \times \frac{1}{(P^0)^3}$$

$$= \frac{1024(P_{O_2})^7}{(P_{eq.} - 7P_{O_2})^4} \times \frac{1}{(P^\circ)^3}$$

12. (a) $K_P = (P_{O_2})^{-1/2}$

$\therefore \quad 7.5 \times 10^{10} = (P_{O_2})^{-1/2}$

$\therefore \quad P_{O_2} = 1.78 \times 10^{-22}$

Now, $PV = nRT$

$\therefore \quad n = \dfrac{1.78 \times 10^{-22} \times 1}{600 \times 0.0821} = 3.61 \times 10^{-24}$

$\therefore$ Number of molecules of O_2 left

$= 3.61 \times 10^{-24} \times 6.023 \times 10^{23} = 2.17$

13. (b) $NH_4Cl \rightleftharpoons NH_3 + HCl$

mole at t = 0 $\quad 0.20 \quad 0 \quad 0$

mole at eq. $\quad (0.20-a) \quad a \quad a$

Also, $K_p = P_{NH_3} \times P_{HCl} = P^2$

$P = \sqrt{K_P} = \sqrt{0.36} = 0.6$ atm

Now, NH_3 formed $n = \dfrac{PV}{RT} = \dfrac{0.6 \times 10}{0.0821 \times 600}$

$= 0.122$ mol

= mole of NH_4Cl decomposed

$\therefore$ NH_4Cl left $= 0.2 - 0.122 = 0.078$ mol

14. (a) $2CaSO_{4(s)} \rightleftharpoons 2CaO_{(s)} + 2SO_{2(g)} + O_{2(g)}$

$K_P = (P_{SO_2})^2 \cdot P_{O_2}$ and $K_P^\circ = \dfrac{(P'_{SO_2})^2 \cdot P'_{O_2}}{(P^\circ)^3}$

($P^\circ = 1$ atm)

$\therefore \quad (P_{SO_2})^2 \cdot P_{O_2} = K_P^\circ \times (P^\circ)^3 = 0.143 = 0.143$ atm

Let dissociation pressure be P atm, then $P'_{SO_2} = P \times 0.4$ and $P'_{O_2} = P \times 0.6$

$\therefore \quad 0.143 = (P \times 0.4)^2 \times P \times 0.6$

$\therefore \quad P = 1.14$ atm $= 1.14 \times 760$ mm $= 867.96$ mm

15. (d) $N_2O_4 \rightleftharpoons 2NO_2$

mole at t = 0 $\quad a \quad 0$

mole at eq. $\quad (a - a\alpha) \quad 2a\alpha$ where, α is degree of dissociation.

$\therefore \quad P_{ini} = \dfrac{aRT}{V}, \quad P_{eq.} = \dfrac{(a + a\alpha) \cdot RT}{V}$

$\therefore \quad \dfrac{P_{ini}}{P_{eq.}} = \dfrac{1}{(1+\alpha)}$ or $\alpha = \dfrac{P_{eq.} - P_{ini}}{P_{ini}}$

Also, $K_p = \dfrac{(2a\alpha)^2}{(a - a\alpha)} \times \left[\dfrac{P}{a + a\alpha}\right]^1 = \dfrac{4\alpha^2 P}{1 - \alpha^2}$

$\therefore \quad \alpha = \sqrt{\dfrac{K_p}{4P + K_p}}$

16. (b) $2NO_2 \rightleftharpoons N_2O_4$

At eq. $\quad 0.5 \quad 1.7$

$NO + NO_2 \rightleftharpoons N_2O_3$

At eq. $\quad P - x \quad 0.5 \quad x$ (where, P is initial pressure)

$\therefore$ Eq. pressure $= P - x + 0.5 + x + 1.7$

or $\quad 5.05 = P + 2.20$

$\therefore \quad P = 2.85$ atm

17. (d) $A + B \rightleftharpoons C + D: \quad K_{P_1} = \dfrac{P'_C \times P'_D}{P'_A \times P'_B}$

$nA + nB \rightleftharpoons nC + nD; \quad K_{P_2} = \dfrac{(P'_C)^n \times (P'_D)^n}{(P'_A)^n \times (P'_B)^n}$

$\therefore \quad K_{P_2} = (K_{P_1})^n$

18. (a) $-\dfrac{\Delta H}{2.303\,R} = +\text{ve}$

$\therefore \quad \Delta H = -\text{ve}$

19. (c) $-\Delta G^\circ = 2.303\,RT \log K_p$

$-(\Delta H^\circ - T\Delta S) = 2.303\,RT \log K_P$

$\therefore \quad \log K_p = -\dfrac{\Delta H^\circ}{2.303\,RT} + \dfrac{\Delta S^\circ}{2.303\,R}$

20. (a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ_{f_{N_2O}} = 19.49 - \left[48.2 - 45.7 - \dfrac{49.0}{2}\right] \times 300 \times 10^{-3}$

$= 26.09$ kcal

$\Delta G^\circ_{f_{NO}} = 21.60 - \left[50.24 - \dfrac{45.7}{2} - \dfrac{49.0}{2}\right] \times 300 \times 10^{-3}$

$= 20.73$ kcal

$\Delta G^\circ_{f_{NO_2}} = 8.09 - \left[57.24 - \dfrac{45.7}{2} - 49.0\right] \times 300 \times 10^{-3}$

$= 12.47$ kcal

$\Delta G^\circ_{f_{N_2O_4}} = 2.19 - [72.77 - 45.7 - 98.0] \times 300 \times 10^{-3}$

$= 23.47$ kcal

21. (a) $AB_2 \rightleftharpoons A + B$

$1 \quad 0 \quad 0$

$1 - \alpha \quad \alpha \quad \alpha$

$\therefore \quad K_{eq.} = \dfrac{C\alpha^2}{1 - \alpha}$ and $K_p = \alpha^2 \left[\dfrac{P}{1+\alpha}\right]^1$

22. (b) $XA \rightleftharpoons D + C$

$a(1-\alpha) \dfrac{a\alpha}{x} \cdot \dfrac{a\alpha}{x}$

$\therefore \quad K_c = \dfrac{a^2\alpha^2}{V^2 \cdot X^2 \left[\dfrac{a(1-\alpha)}{v}\right]^x} = \dfrac{\alpha^2 a^{2-x}}{X^2 (1-\alpha)^x \cdot V^{2-x}}$

Since, α is independent of a

$\therefore \quad 2 - x = 0$

$x = 2$

23. (b) $\Delta G^\circ = -RT \ln K$

$\dfrac{\Delta G_1^0}{\Delta G_2^0} = \dfrac{300 \ln 10}{400 \ln 100} = \dfrac{300}{400} \times \dfrac{1}{2} = \dfrac{3}{8}$

24. (a) At. eq. $[B] = 0.4\,M$; $[A] = 0.1\,M$

$\therefore \quad K_c = \dfrac{0.4 \times 0.4}{0.1} = 1.6$

25. (a) The formation of SO_3 is exothermic and thus at high temperature backward reaction will proceed to give lower percentage yield.

26. (b) $\ln K = \dfrac{-\Delta H^\circ}{RT} + \dfrac{\Delta S^\circ}{R}$

For endothermic change $\Delta H^\circ = +$ ve

$\therefore$ slope of $\ln K$ vs $\dfrac{1}{T}$ is negative.

For exothermic change $\Delta H^\circ = -$ ve

$\therefore$ slope of $\ln K$ vs $\dfrac{1}{T}$ is positive.

27. (d)

$$\begin{array}{llll} & A_2 + & B_2 \rightleftharpoons & 2AB \\ \text{mole at } t=0 & 2 & 4 & 0 \\ \text{at eq.} & (2-x) & (4-x) & 2x \end{array}$$

Total volume at equilibrium is $1+3=4$ litre

$$\therefore \quad K_c = 4 = \frac{\left[\frac{2x}{4}\right]^2}{\left[\frac{2-x}{4}\right]\left[\frac{4-x}{4}\right]} = \frac{4x^2}{8-6x+x^2} = 4$$

$$\therefore \quad 4x^2 = 32-24x+4x^2$$

$$\therefore \quad x = \frac{32}{24} = \frac{4}{3} = 1.33$$

$$\therefore \quad [AB] = \frac{2\times 1.33}{4} = 0.66$$

28. (b)

$$\begin{array}{l} A_{1(s)} \rightleftharpoons A_{(g)} + 2B_{(g)} \\ \qquad\quad\; {}^{*}P_1 \quad 2P_1+2P_2 \end{array}$$

$$\begin{array}{l} A_2 \rightleftharpoons C + 2B_{(g)} \\ \qquad\; {}^{*}P_2 \quad 2P_1+2P_2 \end{array}$$

$$\therefore \quad \frac{K_{P_1}}{K_{P_2}} = \frac{(2P_1+2P_2)^2 \times P_1}{(2P_1+2P_2)^2 \times P_2}$$

$$\frac{P_1}{P_2} = 2$$

$$P_1 = 2P_2$$

Also, from $K_{P_1} = P_1(2P_1+2P_2)^2$;

$P_1 = 0.1\,\text{atm}$ and $P_2 = 0.05\,\text{atm}$

$$\begin{aligned} \text{Total pressure} &= P_1+P_2+2P_1+2P_2 \\ &= 3(P_1+P_2) = 3(0.1+0.05) \\ &= 0.45\,\text{atm} \end{aligned}$$

29. (a)

$$\begin{array}{lllll} & N_2(g) + & 3H_2 \rightleftharpoons & 2NH_3 & \\ \text{Initial mole} & 0.2 & 0.6 & & \text{Total mole present} = 0.8 \\ \text{Mole at eq.} & (0.2-0.02) & (0.6-0.06) & & \\ & 0.18 & 0.54 & 0.04 & \end{array}$$

10% of the react *i.e.*, 0.08 mole react. Let x mole of N_2 and $3x$ mole of H_2 react, then

$$\therefore \quad 4x = 0.08$$

$$x = 0.02$$

Total mole at eq. $= 0.18+0.54+0.04 = 0.76$

$$\therefore \quad \frac{\text{Mole at } t=0}{\text{Mole at } eq.} = \frac{0.80}{0.76} = 1.05$$

under similar conditions of P & T, this is also volume ratio.

30. (b)

$$\begin{array}{ccccc} A & + & B & \rightleftharpoons & 2C \\ 1 & & 1 & & 0 \\ 1-x & & 1-x & & 2x \end{array}$$

$$\therefore \quad 81 = \frac{4x^2}{(1-x)^2}$$

$$\text{or} \quad \frac{2x}{(1-x)} = 9$$

$$\therefore \quad x = \frac{1}{11}$$

$$\text{Thus,} \quad \begin{array}{ccccc} A & + & B & \rightleftharpoons & 2C \\ \frac{10}{11} & & \frac{10}{11} & & \frac{2}{11} \end{array}$$

$$\left(\text{Total mole} = \frac{10}{11}+\frac{10}{11}+\frac{2}{11} = \frac{22}{11}\right)$$

$$\therefore \text{ Mole fraction of } C = \frac{\frac{2}{11}}{\frac{22}{11}} = \frac{1}{11}$$

31. (a) Addition of inert gas either at constt. P or V does not bring any effect on K_c or K_p values. Volume increases and thus degree of dissociation of PCl_5 increases.

32. (b) $PbCrO_4$ and AgCl are precipitated out. Salt of strong acid + weak base shows hydrolysis equilibrium.

33. (b) In standard state,

$$K_{p_{ss}} = \frac{\left(\frac{P_{SO_3}}{P^\circ}\right)^2}{\left(\frac{P_{SO_2}}{P^\circ}\right)\times\left(\frac{P_{O_2}}{P^\circ}\right)} = K_p \times P^\circ$$

Also $P^\circ = 100\,\text{kPa}$ or 1 bar in standard state.

34. (b) White phosphorus is more reactive than red P and possess more enthalpy.

35. (d) Melting of ice takes place fastly on spraying salt at same pressure.

36. (d) $SbCl_3 + H_2O \rightleftharpoons \underset{\text{turbid}}{SbOCl} + 2HCl$

37. (b)

$$\begin{array}{ccccc} X & + & Y & \rightleftharpoons & 3Z \\ \alpha & & \alpha & & 0 \\ (\alpha-a) & & (\alpha-a) & & 3a \end{array}$$

$$\therefore (\alpha-a)-(\alpha-a) = 0 = [X]-[Y]$$

$$\text{Also,} \quad 3[X]+[Z] = 3\alpha$$

$$3(\alpha-a)+3a = 3\alpha$$

38. (b) $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3; \Delta H = -\text{ve};$

Follow Le Chatelier principle.

39. (d) K_p depends only on temperature.

40. (a) Follow solution 39.

41. (d) An irreversible reaction is one in which either of the product is precipitated or separated out as solid or escaped out as gas.

42. (a) Acid-base reactions occur spontaneously.

43. (b)

$$\begin{array}{ccc} N_2O_4 & \rightleftharpoons & 2NO_2 \\ 1 & & 0 \\ 1-0.20 & & 2\times 0.20 \end{array}$$

Mole of $N_2O_4 = 1\,\text{mol}$

Dissociated $N_2O_4 = \frac{1\times 20}{100} = 0.2\,\text{mol}$

$P_{N_2O_4}$ at 300 K = 1 atm. $\therefore$ $P_{N_2O_4}$ at 600 K = 2 atm

$\therefore$ Total mole present at eq. $= 1-0.20+0.40 = 1.20$

$$\because \frac{P_1}{P_2} = \frac{n_1}{n_2} \qquad \text{(at constant } T, V\text{)}$$

$$\therefore \frac{2}{P_2} = \frac{1}{1.2} \qquad \therefore \quad P_1 = 2.4\,\text{atm}$$

44. (a) The formation of product is favoured by increase in P for this reaction and change in temperature.

45. (d)

	$A(aq.) \rightleftharpoons$	$2B(aq.)+$	$C(aq.)$
mole fraction at $t = 0$	$\frac{2}{3}$	$\frac{1}{3}$	0
molarity $t = 0$	$2M$	$1M$	0
At eq.	$(2M - x)$	$(M + 2x)$	x

(Since mole fraction are in the ratio 2 : 1 for A and B thus their molarity will also show same ratio)

Thus total mole at equilibrium

$$= 2M - x + M + 2x + x = 3M + 2x$$

Given mole fraction of A at eq. $= \frac{1}{2} = \frac{2M - x}{3M + 2x}$

$\therefore \quad x = \frac{M}{4}$;

Thus $\quad [B] = M + \frac{2M}{4} = \frac{3M}{2}$

and $\quad [A] = 2M - \frac{M}{4} = \frac{7M}{4}$

Now, $\quad K_C = \frac{[B]^2[C]}{[A]} = \frac{\left[\frac{3M}{2}\right]^2\left[\frac{M}{4}\right]}{\frac{7M}{4}} = \frac{9M^2}{28}$

46. (b)

	$A(g) \rightleftharpoons$	$B(g)\ +$	$C(g)$
Initial mole	1	0	0
final mole at eq.	$1-x$	$x+y$	$x-y$

$C(g) \rightleftharpoons$	$D(g)\ +$	$B(g)$
x	0	0
$(x-y)$	y	$x+y$

Given $\quad \frac{[C]}{[A]} = \frac{x-y}{1-x} = 2$

$\therefore \quad 3x - y - 2 = 0 \quad \ldots$ (i)

Also $\quad$ pressure $\propto$ mole (V and T are constant)

Thus, $\quad P \propto 1$

$$2P \propto 1 - x + (x+y) + (x-y) + y = 1 + x + y$$

$\therefore \quad 1 + x + y = 2 \quad \ldots$ (ii)

From (i) and (ii)

$\therefore \quad x = \frac{3}{4}$ and $y = \frac{1}{4}$

Therefore $\quad K_1 = \frac{(x+y)(x-y)}{(1-x)}$

$$K_2 = \frac{(x+y)y}{(x-y)}$$

$\therefore \quad \frac{K_1}{K_2} = \frac{(x-y)^2}{(1-x)y} = \frac{\left(\frac{3}{4}-\frac{1}{4}\right)^2}{\frac{1}{4}\left(1-\frac{3}{4}\right)} = 4$

47. (c)

	$A\ +$	$B \rightleftharpoons$	C	$K_C = 0.9$
at $t = 0$	a	0.1	0	x = 60% of 0.1 or 0.06
at equilibrium	$(a-0.06)$	$(0.1-0.06)$	0.06	
	$(a-0.06)$	0.04	0.06	

$\therefore \quad K_C = \frac{[C]}{[A][B]}$

$$0.9 = \frac{0.06}{(a-0.06)\times 0.04}$$

$$0.9 = \frac{3}{2a - 0.12}$$

or $\quad 1.8a - 0.108 = 3$

$\therefore \quad a = \frac{3.108}{1.8} = 1.73$

48. (d) $\quad \Delta H = \Delta U + \Delta nRT$

$\therefore \quad \Delta n = \frac{\Delta H - \Delta U}{RT} = -\frac{1200}{2\times 300} = -2$

Now $\quad \frac{K_P}{K_C} = (RT)^{\Delta n} = (0.0821\times 300)^{-2}$

$$= 1.64\times 10^{-3}$$

49. (a)

	$A(g)\ +$	$2B(g) \rightleftharpoons$	C
Concentration at I eq.	3	4	a

$\therefore \quad K_C = \frac{a}{3\times 4^2} = \frac{a}{48}$

Also if volume is doubled *i.e.*, pressure decreases the reaction will proceed in the direction where mole increases, thus

	$A\ +$	$2B \rightleftharpoons$	C
when $V = V$	3	4	a
when $V = 2V$	1.5	2	$\frac{a}{2}$
Re-establishment of eq.	2	3	$\frac{a}{2} - 0.5$

$\therefore \quad K_C = \frac{\left(\frac{a}{2} - 0.5\right)}{2\times 3^2} = \frac{(a-1)}{36}$

or $\quad \frac{a-1}{36} = \frac{a}{48}$

$$48a - 48 = 36a$$

$\therefore \quad 12a = 48$

$$a = 4\text{ M}$$

or $\quad K_C = \frac{a-1}{36} = \frac{(4-1)}{36} = \frac{1}{12} = 0.083$

50. (a)

	$AgNO_3\ +$	$2KCN \longrightarrow$	$Ag(CN)_2^-\ +$	$2K^+\ +$	NO_3^-
Initially	$0.06\times V$	$0.2\times V$	0	0	0
After mixing	--	$0.08\times V$	$0.06\ V$	$0.12\ V$	$0.06\ V$

Thus, $\quad [Ag(CN)_2]^- = \frac{0.06V}{2V} = 0.03\text{ M}$

$$[CN^-] = \frac{0.08\times V}{2V} = 0.04$$

Now	$Ag(CN)_2^-(aq.) \rightleftharpoons$	$Ag^+\ +$	$2CN^-$
	0.03	—	0.04
	$(0.03-a)$	a	0.04

$$K_C = 1.6\times 10^{-19} = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-}$$

or $\quad 1.6\times 10^{-19} = \frac{a\times (0.04)^2}{(0.03-a)}$

a is very small as K_C is very low $0.03 - a \simeq 0.03$

Thus, $a = \frac{1.6 \times 10^{-19} \times 0.03}{(0.04)^2} = 3 \times 10^{-18}$

51. (b) $A(s) \rightleftharpoons B + D$

$P_B + P_D = 40$

$\therefore$ $2P = 40$

or $P = 20\,\text{atm}$

$\therefore$ $K_p = (P)^2 = 20 \times 20 = 400$

Similarly, $C(s) \rightleftharpoons E(g) + D(g)$

$P_E + P_D = 80$

$\therefore$ $2P = 80$

or $P = 40\,\text{atm}$

$\therefore$ $K_p = 40 \times 40 = 1600$

For simultaneous equilibrium $A(s) \rightleftharpoons \underset{P_1}{B} + \underset{P_1+P_2}{D}$

$$C(s) \rightleftharpoons \underset{P_2}{E} + \underset{P_2+P_1}{D}$$

$\therefore$ $400 = P_1 \times (P_1 + P_2)$

$1600 = P_2(P_1 + P_2)$

or $\frac{P_1}{P_2} = \frac{1}{4}$ or $P_2 = 4P_1$

Also, $P_1(P_1 + P_2) = 400$

$P_1(P_1 + 4P_1) = 400$

$5P_1^2 = 400$

$P_1 = 8.94\,\text{atm}$

Total pressure at eq. $= P_1 + (P_1 + P_2) + P_2$

$= 2(P_1 + P_2) = 2(P_1 + 4P_1)$

$= 10P_1 = 10 \times 8.94 = 89.4$

52. (d) $A(s) \rightleftharpoons 2B(g) + 3C(g)$

$\therefore$ $K_C = [B]^2[C]^3 = x^2(y)^3 = x^2y^3$

If concentration of C is two times to that of y at equilibrium *i.e.*, $2y$ then if concentration of B is B_2

$K_C = [B_2]^2[2y]^3$

or $[x]^2[y]^3 = 8[B_2]^2[y]^3$

$\therefore$ $[B_2] = \frac{x}{\sqrt{8}} = \frac{x}{2\sqrt{2}}$

53. (b) Follow Le-Chatelier principle

54. (d) $K_c = \frac{K_f}{K_b} = \frac{Ae^{-10.303\times10^3/RT}}{Ae^{-8\times10^3/RT}}$

$= e^{-2.303\times10^3/RT} = e^{-2.303\times10^3/2\times500}$

$K_C = e^{-2.303} = 0.1$

55. (b)

$$\underset{\substack{1\\1-0.33}}{N_2O_4} \rightleftharpoons \underset{\substack{0\\2\times0.33}}{2NO_2}$$

$\therefore$ $K_p = \frac{(2\times0.33)^2}{0.67} \times \frac{P_1}{1.33}$

$$\left[\because K_p = \frac{(n_{NO_2})^2}{n_{N_2O_4}} \times \left(\frac{P}{\Sigma n}\right)\right]^1$$

Similarly for 40%

$K_p = \frac{(2\times0.4)^2}{0.6} \times \frac{P_2}{1.40}$

$\therefore$ $\frac{P_1}{P_2} = 1.55$

56. (b) $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$

At eq. P' $\quad \frac{2P}{9} \quad \frac{P}{9}$

$\therefore$ $P' + \frac{2P}{9} + \frac{P}{9} = P$

or $P' = \frac{2}{3}P$

$\therefore$ $K_p = \frac{\left(\frac{2P}{9}\right)^2\left(\frac{P}{9}\right)}{\left(\frac{2P}{3}\right)^2} = \frac{P}{81}$

57. (a) K_C does not depend on concentration of reactants or products.

$K_C = \frac{[D][C]}{[A][B]} = \frac{1.5\times1.5}{1.5\times1.5} = 1$

58. (a) $2A + B \rightleftharpoons 2C \quad \Delta G^\circ = 2\,\text{kJ mole}^{-1}$

$A + \frac{1}{2}B \rightleftharpoons C \quad \Delta G^\circ = 1\,\text{kJ mole}^{-1}$

Now, $-\Delta G^\circ = 2.303RT\log K$

$-1000 = 2.303 \times 8.314 \times 500 \log K$

$K = 0.786$

59. (a)

$$\underset{\substack{1\\1-\alpha}}{N_2O_4} \rightleftharpoons \underset{\substack{0\\2\alpha}}{2NO_2}$$

$\Sigma\,\text{mole} = 1 - \alpha + 2\alpha + 1$ (for Ar)

$= 2 + \alpha$

$K_p = \frac{(2\alpha)^2}{(1-\alpha)}\left[\frac{P}{2+\alpha}\right]^1 = \frac{4\alpha^2P}{2-\alpha^2-\alpha}$

$\alpha <<< 2$

$\therefore$ $K_p = \frac{4\alpha^2P}{2} = \frac{4\times\alpha^2\times4}{2} = 0.2$

$\therefore$ $\alpha = 0.158$

60. (a)

$$\begin{array}{llll} & 2SO_3 & \rightleftharpoons 2SO_2 & + O_2 \\ \text{Initial mole} & 4 & 0 & 0 \\ \text{At eq.} & 4-x & x & \frac{x}{2} \end{array}$$

SO_2 will show redox change with $KMnO_4$

$Mn^{7+} + 5e \longrightarrow Mn^{2+}$

$2e + \overset{+6}{S} \longrightarrow S^{4+}$

meq. of SO_2 = meq. of $KMnO_4$

$= 6.4 \times 0.1 \times 5 = 3.2$

$\therefore$ mole of SO_2 at eq. $= \frac{3.2}{2} = 1.6$

(n-factor of $SO_2 = 2$)

$\therefore$ $x = 1.6$

$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$

$$K_c = \frac{\left(\frac{x}{2}\right)^2\left(\frac{x}{2\times 2}\right)}{\left[\frac{(4-x)}{2}\right]^2} = \frac{\left(\frac{1.6}{2}\right)^2\left(\frac{1.6}{4}\right)}{\left[\frac{4-1.6}{2}\right]^2} \quad (V = 2 \text{ litre})$$

$$= 0.178 \text{ mole litre}^{-1}$$

61. (b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Also, $\Delta H^\circ = \Delta U^\circ + \Delta nRT$

$\therefore$ $\Delta H^\circ = 30\times 10^3 + 1\times 2\times 300$

$= 30600$ cal

$\therefore$ $\Delta G^\circ = 30600 - 300\times 100$

$= 600$ cal

$-\Delta G^\circ = RT \ln K_p$

$$K_p = e^{-\Delta G^\circ/RT} = -e^{-\frac{600}{2\times 300}} = e^{-1}$$

62. (a) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$$K_p = P'_{NH_3} \times P'_{H_2S} = \frac{P}{2}\times\frac{P}{2} = \frac{P^2}{4}$$

$$\Delta G^\circ = -RT\ln K_p = -RT\ln\frac{P^2}{4} = -RT\ln\frac{P^2}{2^2}$$

$$= -2RT[\ln P - \ln 2]$$

63. (d) $\Delta G^\circ = -RT\ln K_p$

and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K_p$

$\therefore$ $\ln K_p = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$

On comparing $\ln K_p = 4 - \frac{100}{T}$

$\therefore$ $\frac{\Delta S^\circ}{R} = 4$

$\Delta S^\circ = 4\times 2 = 8$ cal

64. (a) $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$;

$$K_p = P_{CO_2} = 1.6 \text{ atm}$$

The reaction should favour forward direction as $Q < K_p$, but since $SrCO_3$ is not taken initially, reaction cannot take place in forward direction.

$SrO(s) + CO_2(g) \rightleftharpoons SrCO_3$;

$$K_p = \frac{1}{1.6} = 0.625 \text{ atm}$$

Thus on increasing pressure, volume of container will decrease till P_{CO_2} becomes 1.6 atm having same mole of CO_2.

The reaction will attain equilibrium till $P = 0.625$

$\therefore$ Initial mole of $CO_2 = \frac{PV}{RT} = \frac{0.4\times 20}{RT} = \frac{8}{RT}$

At eq. $V = \frac{nRT}{P}$

$$= \frac{8}{RT}\times\frac{RT}{1.6} = 5 \text{ litre}$$

65. (b) $2NH_3 \rightleftharpoons N_2 + 3H_2$; $\frac{1}{K_1} = \frac{[N_2][H_2]^3}{[NH_3]^2}$ ...(i)

$N_2 + O_2 \rightleftharpoons 2NO$; $K_2 = \frac{[NO]^2}{[N_2][O_2]}$ ...(ii)

$3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O$; $K_3^3 = \frac{[H_2O]^3}{[H_2]^3[O_2]^{3/2}}$ ...(iii)

$$\overline{2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O}$$

$$K = \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}}$$

By multiplying (i), (ii) and (iii),

$$\frac{1}{K_1}\times K_2\times K_3^3 = \frac{[N_2][H_2]^3}{[NH_3]^2}\times\frac{[NO]^2}{[N_2][O_2]}\times\frac{[H_2O]^3}{[H_2]^3[O_2]^{3/2}}$$

$$= \frac{[NO]^2\times[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = K$$

$$\therefore \quad K = \frac{K_2\times K_3^2}{K_1}$$

• PREVIOUS YEARS PROBLEMS •

1. For the reversible reaction :
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ at 500°C. The value of K_p is 1.44×10^{-5}, when partial pressure is measured in atmosphere. The corresponding value of K_c with concentration in mol L^{-1} is : **(IIT 2000)**
(a) $1.44 \times 10^{-5} / (0.082 \times 500)^2$
(b) $1.44 \times 10^{-5} / (8.314 \times 773)^2$
(c) $1.44 \times 10^{-5} / (0.082 \times 500)^2$
(d) $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$

2. When two reactants A and B are mixed to give products C and D, the reaction quotient Q, at the initial stages of the reaction : **(IIT 2000)**
(a) is zero (b) decrease with time
(c) independent of time (d) increase with time

3. At constant temperature, the equilibrium constant (K_P) for the decomposition reaction. $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = 4x^2 p / (1 - x^2)$ where, P is pressure, x is extent of decomposition. Which of the following statement is true ? **(IIT 2001)**
(a) K_p increases with increase of P
(b) K_p increases with increase of x
(c) K_p increases with decrease of x
(d) K_p remains constant with change in P or x

4. Consider the following equilibrium in a closed container : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$. At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α) : **(IIT 2002)**
(a) neither K_p nor α changes
(b) both K_p and α change
(c) K_p changes, but α does not change
(d) K_p does not change, but α changes

5. The following equilibrium are given :
$$N_2 + 3H_2 \rightleftharpoons 2NH_3;\ K_1$$
$$N_2 + O_2 \rightleftharpoons 2NO;\ K_2$$
$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O;\ K_3$$
The equilibrium constant of the reaction :
$$2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$$
in terms of K_1, K_2 and K_3 is : **(IIT 2003)**
(a) $\dfrac{K_1K_2}{K_3}$ (b) $\dfrac{K_1K_3^2}{K_2}$
(c) $\dfrac{K_2K_3^3}{K_1}$ (d) $K_1K_2K_3$

6 For the reaction : $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; $\Delta H = -$ve, the correct statement is : **(IIT 2006)**
(a) Addition of catalyst does not change K_p but changes ΔH.
(b) At equilibrium, $2G_{NH_3} = G_{N_2} + 3G_{H_2}$. ($G$ is Gibbs energy)
(c) At higher temperature, the rate of forward and backward reaction increases by a factor 2.
(d) At 400 K, addition of catalyst increase rate of forward reaction by 2 times and backward by 1.7 times

7. If $Ag^+ + NH_3\ [Ag(NH_3)]^+$; $K_1 = 3.5 \times 10^{-3}$ and $[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ ; K_2 = 1.74 \times 10^{-3}$ the formation constant of $[Ag(NH_3)_2]^+$ is : **(IIT 2006)**
(a) 6.08×10^{-6} (b) 6.08×10^{6}
(c) 6.08×10^{-9} (d) none of these

8. The value of $\log_{10} K$ for the reaction : $A \rightleftharpoons B$, if $\Delta H° = -54.07$ kJ mol^{-1} at 298 K, $\Delta S° = 10 JK^{-1}\ mol^{-1}$ at 298 K, R = 8.314 $JK^{-1}\ mol^{-1}$ and 2.303×8.314×298 = 5705, is : **(IIT 2007)**
(a) 5 (b) 10
(c) 95 (d) 100

9. For the reaction $SO_2(g) + 1/2O_2(g) \rightleftharpoons SO_3(g)$ if $K_P = K_C(RT)^x$ where the symbols have usual meaning then the value of x is : (assuming ideality) **[JEE (Main) 2014]**
(a) -1 (b) $-\frac{1}{2}$
(c) $\frac{1}{2}$ (d) 1

10. The following reaction is performed at 298 K.
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$
The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K ? $(K_p = 1.6 \times 10^{12})$ **[JEE (Main) 2015]**
(a) $R(298)\ln(1.6 \times 10^{12}) - 86600$
(b) $86600 + R(298)\ln(1.6 \times 10^{12})$
(c) $86600 - \dfrac{\ln(1.6 \times 10^{12})}{R(298)}$
(d) $0.5[2 \times 86600 - R(298)\ln(1.6 \times 10^{12})]$

11. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, $[B] = 2$

and $[C]=\frac{1}{2}$. The reaction proceeds in the :

$[R = 8.314\ J/K/mol, e = 2.718]$ **[JEE (Main) 2015]**

(a) forward direction because $Q > K_c$

(b) reverse direction because $Q > K_c$

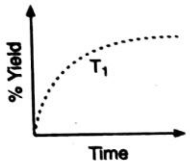
(c) forward direction because $Q < K_c$

(d) reverse direction because $Q < K_c$

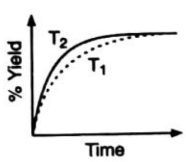
12. The % yield of ammonia as a function of time in the reaction **[JEE (Advanced I) 2015]**

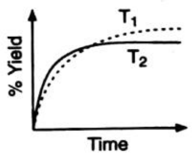
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \Delta H < 0$$

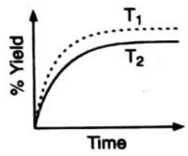
at (P, T_1) is given below :

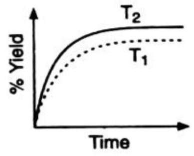


If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by :

(a)


(b)


(c)


(d)


13. The equilibrium constant at 298 K for a reaction $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be : **[JEE (Main) 2016]**

(a) 0.818 (b) 1.818

(c) 1.182 (d) 0.182

SOLUTIONS (Previous Year Problems)

1. (d) $K_p = K_c \times (RT)^{\Delta n}$;

Δn for the change $= 2-(1+3) = -2$

Thus, $K_p = K_c \times (RT)^{-2}$

or $$K_c = \frac{K_p}{(RT)^{-2}} = \frac{1.44\times10^{-5}}{(0.082\times773)^{-2}}$$

2. (d) At the initial state if only reactants are used $Q = 0$, but from initial stage to attain equilibrium is continuously increase with time till it because equal to K_c.

3. (d) K_p is a characteristic constant for a given reaction and changes only with temperature.

4. (d) For the reaction ; $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$$K_c = \frac{4\alpha^2 a^2}{(a-a\alpha)V} \qquad ...(1)$$

where, a is initial mole on N_2O_4 in V litre vessel and α is degree of dissociation of N_2O_4.

If volume is reduced to $V/2$, the initial concentration of N_2O_4 becomes $\frac{a}{\frac{V}{2}} = \frac{2a}{V}$.

An increase in concentration of reactants leads to forward reaction, *i.e.*, the decomposition of N_2O_4 to have constant value of K_p.

5. (c) $$K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad ...(i)$$

$$K_2 = \frac{[NO]^2}{[N_2][O_2]} \qquad ...(ii)$$

$$K_3 = \frac{[H_2O]}{[H_2]^2[O_2]^{1/2}} \qquad ...(iii)$$

$$K = \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}}$$

By inspection of (i), (ii) and (iii)

$$\frac{K_2\times K_3^3}{K_1} = \frac{[NO]^2}{[N_2][O_2]}\times\frac{[N_2][H_2]^3}{[NH_3]^2}\times\frac{[H_2O]^3}{[H_2]^3[O_2]^{3/2}}$$
$$= \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = K$$

6. (b) $\Delta G = 2G_{NH_3} - G_{N_2} - 3\times G_{H_2}$

and $\Delta G = 0$ at equilibrium.

7. (a) $$K_1 = 3.5\times10^{-3} = \frac{[Ag(NH_3)]^+}{[Ag^+][NH_3]}$$

$$K_2 = 1.74\times10^{-3} = \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)^+][NH_3]}$$

$$K_3 = K_1\times K_2 = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$$

$\therefore$ Formation constant K_3 for

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$
$$K_3 = 3.5\times10^{-3}\times1.74\times10^{-3}$$
$$= 6.08\times10^{-6}$$

8. (b) $$\Delta G^\circ = -2.303\,RT\log K$$
$$\Delta H^\circ - T\Delta S^\circ = -2.303\,RT\log K$$
$$[-54.07\times10^3 - 298\times10] = -2.303\times8.314\times298\log K$$
$$\therefore \quad \log K = \frac{57050}{5705} = 10$$

9. (b) $\Delta n_{(g)}$ = (Number of product molecules − Number of reactant molecules) in gaseous state $= 1-\left(1+\frac{1}{2}\right) = -\frac{1}{2}$

10. (d) $$\Delta G_f^\circ = 2\times G^\circ NO_2 - [2\times G_{NO}^\circ + G_{O_2}^\circ]$$
$$= 2G_{NO_2}^\circ - 2G_{NO}^\circ \qquad [G_{O_2}^\circ = 0]$$
$$\therefore \quad G_{NO_2}^\circ = \frac{1}{2}\Delta G_f^\circ + G_{NO}^\circ$$
$$= \frac{1}{2}[-RT\ln K_p] + G_{NO}^\circ$$
$$= \frac{1}{2}[-R\times298\ln(1.6\times10^{12})] + 86600$$
$$= 0.5[-R\times298\ln1.6\times10^{12} + 2\times86600]$$

11. (b) $$Q = \frac{[B][C]}{[A]^2} = \frac{2\times\frac{1}{2}}{\left(\frac{1}{2}\right)^2} = 4$$

$$\Delta G^\circ = -2.303\,RT\log K_C$$
$$2494.2 = -2.303\times8.314\times300\log K_C$$

$\therefore$ $K_C = 0.36$

$\because$ $Q > K_C$ thus backward reaction.

12. (c) The combination of N_2 and H_2 to give NH_3 takes place at slower rate if temperature is reduced to 473 K (200°C) because fewer energetic collisions occurs between molecules, however yield of NH_3 is 88%. On the other hand the combination occurs at faster rate at 723 K (450°C) but the yield of NH_3 is 15%. Actually it is the number of energetic collisions which really matters to lead a chemical reaction and the rate of reaction is reduced at low temperature (473 K). The 15% yield of NH_3 is better at 723 K because equilibrium is achieved earlier. The NH_3 formed is dissolved in water and is drained off as $NH_3(aq)$ from the system so that unreacted N_2 and H_2 recombines again to produce NH_3 in order to maintain constant value of K_c. Thus, all the N_2 and H_2 are converted to NH_3 with a faster rate.

---

13. (b)

	A +	B $\rightleftharpoons$	C +	D
Concentration at $t = 0$	1	1	1	1
Concentration at eq.	$1-x$	$1-x$	$1+x$	$1+x$

$\because$ $$K_c = \frac{[C][D]}{[A][B]} = \frac{(1+x)^2}{(1-x)^2} = 100$$

or $$\frac{1+x}{1-x} = 10$$

or $$1+x = 10-10x$$

$\therefore$ $$x = \frac{9}{11}$$

Now $$[D] = 1+x = 1+\frac{9}{11} = 1.818$$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Select the correct statements :

(a) An increase in pressure increases the boiling point of liquid.

(b) An increase in pressure increases the melting point of water.

(c) On spraying NaCl on ice, the melting point of ice is lowered and it does not melt.

(d) The three phases of a substance exists at triple point only.

2. Which are heterogeneous systems ?

(a) Ice $\rightleftharpoons$ Water (b) Water $\rightleftharpoons$ Liquid

(c) $S_{Rhombic} \rightleftharpoons S_{Monoclinic}$ (d) $C_{Daimond} \rightleftharpoons C_{Amorphous}$

3. Select the incorrect statements :

(a) K_P or K_c are dimensionless if pressure or concentrations are expressed in standard state.

(b) The numerical value of K_P changes with experimental conditions, *i.e.* P, T and C at which equilibrium is attained.

(c) Active mass of a reactant = concentration of reactant.

(d) Dissolution of NH_3 in water obeys Henry's law.

4. Select the correct statements :

(a) Volume of gas dissolved per unit volume of solvent $\propto (P)^\circ$ at constant T.

(b) Amount of gas dissolved per unit volume of solvent $\propto P$ at constant T.

(c) Mole fraction of gas dissolved per unit of solvent $\propto P$ at constant T.

(d) Henry law is a special case of Nernst distribution law

5. A reaction $S_{8(g)} \rightleftharpoons 4S_{2(g)}$ is carried out by taking 2 mole of $S_{8(g)}$ and 0.2 mole of $S_{2(g)}$ in a reaction vessel of 1 litre. Which are correct if $K_c = 6.30 \times 10^{-6}$:

(a) reaction quotient is 8×10^{-4}

(b) reaction proceeds in backward direction

(c) $K_p = 2.55 \text{ atm}^3$

(d) reaction proceeds in forward direction

6. The equilibrium is attained in a reaction as :

$$N_2 + 3H_2 \underset{Fe}{\overset{500\,K}{\rightleftharpoons}} 2NH_3; \Delta H = -ve.$$

The yield of NH_3 can be predicted as :

(a) the yield of NH_3 is lesser (15%) at 500 K than at 200 K (88%)

(b) the reaction equilibrium at 500 K attains equilibrium earlier at 500 K than at 200 K

(c) the yield of NH_3 can be increased by forcing a jet of water in vessel

(d) the rate of forward reaction is faster at 500 K

7. Which are true for the reaction : $A_2 \rightleftharpoons 2C + D$?

(a) If $\Delta H = 0$; K_p and dissociation of A_2 are independent of temperature

(b) If $\Delta H = +ve$; K_p increases with temperature and dissociation of A_2 increases

(c) If $\Delta H = -ve$; K_p decreases with temperature and dissociation of A_2 decreases

(d) $K_p = 4\alpha^3 \left[\frac{P}{1+2\alpha}\right]^2$

8. For given two equilibria attained in a container which are correct if degree of dissociation of A and A' are α and α'.

$A_{(s)} \rightleftharpoons 2B_{(g)} + C_{(g)}$; $K_{p_1} = 8 \times 10^{-2}$

$A'_{(s)} \rightleftharpoons 2B_{(g)} + D_{(g)}$; $K_{p_2} = 2 \times 10^{-2}$

(a) $\frac{K_{p_1}}{K_{p_2}} = \left[\frac{(3\alpha' + 2\alpha)}{(3\alpha + 2\alpha')}\right]^3 \times \frac{\alpha}{\alpha'}$

(b) $P'_C / P'_D = 4$

(c) $P'_B = 2P'_C + 2P'_D$

(d) $\alpha > \alpha'$

9. For the equilibrium at 298 K : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$; $G^\circ_{N_2O_4} = 100 \text{ kJ mol}^{-1}$ and $G^\circ_{NO_2} = 50 \text{ kJ mol}^{-1}$. If 5 mole of N_2O_4 and 2 moles of NO_2 are taken initially in one litre container then which statements are correct :

(a) Reaction proceeds in forward direction

(b) $K_C = 1$

(c) $\Delta G = -0.55$ kJ, $\Delta G^\circ = 0$

(d) At equilibrium $[N_2O_4] = 4.894\,M$ and $[NO_2] = 0.212\,M$

10. Plots of log K *vs.* $\frac{1}{T}$ plots shows an intercept of 2 on Y-axis with a slope of 45° for the studied reaction. Which of the following are correct assuming ΔH° and ΔS° as temperature independent :

(a) $\Delta S^\circ = 4.606$ cal (b) $\Delta H^\circ = -4.606$ cal

(c) $\Delta G^\circ = -2.75$ kcal (d) $K = 100.8$

11. The rate of effusion of an equilibrium mixture in one litre vessel of at 300 K $A_2 \rightleftharpoons 2A$ through a pin hole is 0.707 times of rate of diffusion of O_2 under identical conditions of P and T. Which of the following are correct if at. wt. of A is 46 :

(a) mole ratio of $A / A_2 = 0.643$

(b) $K_c = 25.16$ mol / litre

(c) $\Delta G^\circ = -8.01 \times 10^3$ J

(d) molar mass of mixture = 64

12. For the gas phase reaction :

$C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ($\Delta H = -32.7$ kcal) carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by :

(a) Increasing the temperature
(b) Decreasing the pressure
(c) Removing some H_2
(d) Adding some C_2H_6

13. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium :
(a) addition of $NaNO_2$ favours reverse reaction
(b) addition of $NaNO_3$ favours forward reaction
(c) increasing temperature favours forward reaction
(d) increasing pressure favours reverse reaction

14. The equilibrium, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$, is attained at 25°C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct?
(a) Concentration of SO_2, Cl_2 and SO_2Cl_2 do not change
(b) More chlorine is formed
(c) Concentration of SO_2 is reduced
(d) More SO_2Cl_2 is formed

15. For the reaction, $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$. The forward reaction at constant temperature is favoured by :
(a) introducing an inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) increasing the volume of the container
(e) introducing PCl_5 at constant volume

16. For the reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g),$$

at a given temperature the equilibrium amount of $CO_2(g)$ can be increased by :
(a) adding a suitable catalyst
(b) adding an inert gas
(c) decreasing the volume of the container
(d) increasing the amount of $CO(g)$

17. Which of the following are correct :
(a) A plot of $\log K_p$ *vs* $\frac{1}{T}$ is linear
(b) A plot of $\log[x]$ *vs* time is linear for a I order reaction
(c) A plot of $\log P$ *vs* $\frac{1}{T}$ is linear at constant volume
(d) A plot of P *vs* $\frac{1}{V}$ is linear at constant temperature

18. In a flask, colourless N_2O_4 is in equilibrium with NO_2. At equilibrium when the flask is heated at 100°C, the brown colour deepens and on cooling it fades. Which statements are correct :
(a) $\Delta H = +$ ve
(b) $\Delta H = -$ ve
(c) $\Delta S = +$ ve
(d) $\Delta S = -$ ve

19. For the reaction : $X(g) \rightleftharpoons nY(g)$,
the degree of dissociation is α, then which one is not correct.
(a) $K_c = \frac{n^n\alpha^n}{(1-\alpha)} \text{mol}^{n-1}\text{litre}^{1-n}$
(b) $K_p = \left[\frac{n\alpha}{1-\alpha}\right]\left[\frac{P}{1-\alpha+n\alpha}\right]^{n-1} \text{atm}^{n-1}$
(c) $K_c = \frac{n\alpha^n}{(1-\alpha)n} \text{mol}^{n-1}\text{litre}^{1-n}$
(d) $K_p = \frac{(n\alpha)^n}{(1-\alpha)}\left[\frac{P}{1-\alpha+n\alpha}\right]^{n-1} \text{atm}^{n-1}$

20. The thermal dissociation equilibrium of $CaCO_3(s)$ is studied under different conditions.

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

For this equilibrium, the correct statement(s) is (are) :
[JEE (Advanced) II 2013]
(a) ΔH is dependent on T
(b) K is independent of the initial amount of $CaCO_3$
(c) K is dependent on the pressure of CO_2 at a given T
(d) ΔH is independent of the catalyst, if any

SOLUTIONS (More Than One Answer Correct)

1. (a,b,d,) On spraying NaCl on ice, m.pt. of ice is lowered and at melts earlier.
2. (a,b,c,d) Heterogeneous have $P > 1$; two solids have two phases.
3. (b,c,d) NH_3 show H-bonding with H_2O.
4. (a,b,c,d) Distribution of gas occurs between gaseous and solution phase.

$$\begin{array}{ccc} \text{Gas} + H_2O & \rightleftharpoons & \text{Solution} \\ \text{Phase I} & & \text{Phase II} \end{array}$$

5. (a,c,d) $Q = \frac{[S_2]^4}{[S_8]} = \frac{(0.2)^4}{[2]} = 8\times10^{-4}, K_c = 6.3\times10^{-6}$

$$K_p = K_c \times (RT)^{\Delta n}$$
$$= 6.3\times10^{-6} \times (0.0821\times900)^3 = 2.55$$

Thus, reaction proceeds in backward direction since $Q > K_c$.

6. (a,b,c,d) All are facts about Haber's process. For concept of this reaction follow concepts of physical chemistry by P.Bahadur, Prakash publications, Muzaffarnagar.
7. (a,b,c,d)

$$\begin{array}{ccccc} A_2 & \rightleftharpoons & 2C & + & D \\ 1 & & 0 & & 0 \\ 1-\alpha & & 2\alpha & & \alpha \end{array}$$

$$\therefore \quad K_p = (2\alpha)^2 \cdot \alpha \times \left[\frac{P}{\Delta n}\right]^2 = \frac{4\alpha^3 \cdot P^2}{(1+2\alpha)^2}$$

Use $2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$ for effect of temperature on K.

8. (a,b,c,d)

$$\begin{array}{ccccc} A_{(s)} & \rightleftharpoons & 2B_{(g)} & + & C_{(g)} \\ & & 2\alpha + 2\alpha' & & \alpha \\ A'_s & \rightleftharpoons & 2B & + & D \\ & & 2\alpha'+2\alpha & & \alpha' \end{array}$$

$$\therefore \quad K_{p_1} = (2\alpha + 2\alpha')^2 \alpha' \times \alpha \times \left[\frac{P}{(3\alpha + 2\alpha')}\right]^3$$

$$K_{p_2} = (2\alpha + 2\alpha')^2 \alpha' \times \left[\frac{P}{(3\alpha' + 2\alpha)}\right]^3$$

$$\therefore \quad \frac{K_{p_1}}{K_{p_2}} = \frac{[3\alpha' + 2\alpha]^3}{[3\alpha + 2\alpha']^3} \times \frac{\alpha}{\alpha'}$$

Also, $K_{p_1} = (P'_B)^2 \times P'_C$

$$K_{p_2} = (P'_B)^2 \times P'_D ; \frac{P'_C}{P'_D} = \frac{K_{p_1}}{K_{p_2}} = \frac{8\times10^{-2}}{2\times10^{-2}} = 4$$

Also, $P'_B = 2\times(P'_C + P'_D)$

$$K_{p_1} > K_{p_2} \quad \therefore \alpha > \alpha_1$$

9. (a,b,c,d) $\Delta G = \Delta G^\circ + 2.303\,RT \log Q$

$$\Delta G^\circ = 2\times G^\circ_{NO_2} - G^\circ_{N_2O_4} = 2\times50 - 100 = 0$$

$$\therefore \Delta G = 0 + 2.303\times8.314\times10^{-3}\times298 \log\frac{2^2}{5} = 0 - 0.55\,\text{kJ}$$

$\therefore \Delta G = -0.55\,\text{kJ}$ *i.e.*, reaction proceeds in forward direction.

Also, $\Delta G^\circ = 0 = 2.303\,RT \log K \qquad \therefore K = 1$

Now,

$$\begin{array}{ccc} N_2O_4 & \rightleftharpoons & 2NO_2 \\ 5 & & 2 \\ (5-x) & & (2+2x) \end{array}$$

$$\therefore \quad 1 = \frac{(2+2x)^2}{(5-x)} \text{ or } x = 0.106$$

10. (b,c,d) $\Delta G^\circ = -2.303\,RT \log K$,

$$\Delta H^\circ - T\Delta S^\circ = -2.303\,RT \log K$$

$$2.303 \log K = -\frac{\Delta H^\circ}{R} + \frac{\Delta S^\circ}{R}, \text{Slope} = -\frac{\Delta H^\circ}{2.303\,R} = \tan 45^\circ$$

$$\therefore \quad \Delta H^\circ = -2.303\times2\times1\,\text{cal}$$
$$= -4.606\,\text{cal}, \text{ Intercept} = \frac{\Delta S^\circ}{2.303R} = 2$$

$$\therefore \quad \Delta S^\circ = 2.303\times2\times2 = 9.212\,\text{cal}$$

$$\therefore \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -4.606 - 298\times9.212$$
$$= -2.75\,\text{kcal}$$

11. (a,b,c,d) $\frac{r_m}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{\text{mix}}}} = \sqrt{\frac{32}{M}} = 0.707 \text{ or } M = 64$

Let a mole of A_2 be present in mixture, then

$$\therefore \quad 64 = \frac{a\times92 + (100-a)\times46}{100}$$

$$A = a = 39.13\,\text{mole and } A_2 = 60.87\,\text{mole}$$

$$\therefore \quad K_C = \frac{[A]^2}{[A_2]} = \frac{(39.13)^2}{60.87} = 25.16;$$

$$\Delta G^\circ = -2.303\,RT \log K$$

$$\therefore \Delta G^\circ = -2.303\times300\times8.314 \log 25.16 = -8.01\times10^3\,\text{J}$$

12. (a,b,c,d) Increase in C_2H_4 means backward reaction predominates. This can be done by increasing T, decreasing P, lowering $[H_2]$, increasing $[C_2H_6]$ according to Le-Chatelier principle.
13. (c, d) $NaNO_3(s) \rightleftharpoons NaNO_2(s) + \frac{1}{2}O_2$;

    $\Delta H = +\text{ve}$ for dissociation.
14. (a) No effect of addition of inert gas at constant volume. However, if addition is made at constant pressure answer will be (b). Both types are possible in closed container.
15. (c,d,e) Follow effect of addition of inert gas at constant P and Le-Chateliers principle.
16. (c) Forward reaction predominates if [reactants] is increased.
17. (a,c,d) Plots of $\log(a-x)$ *vs* time is linear for I order reaction.

18. (a,c) $N_2O_4 \rightleftharpoons 2NO_2$; $\Delta H = +\text{ve}$

The reaction absorbs heat and N_2O_4 shows decomposition. Also entropy increases due to the formation of 2 mole of NO_2 by 1 mole of N_2O_4.

19. (a,b)

$$\begin{array}{ccc} X(g) & \rightleftharpoons & nY(g) \\ 1 & & 0 \\ 1-\alpha & & n\alpha \end{array}$$

$$\therefore \quad K_C = \frac{(n\alpha)^n}{(1-\alpha)} \text{mol}^{n-1} \text{ litre}^{1-n}$$

$$\text{and } K_p = \frac{n\alpha}{(1-\alpha)} \times \left[\frac{P}{1-\alpha+n\alpha}\right]^{n-1} \text{atm}^{n-1}$$

20. (a,b,d)

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

$\Delta H_{T_2} - \Delta H_{T_1} = \Delta(nC_P)dT$

$\Delta(nC_P) \neq 1$

$\therefore$ ΔH is temperature dependent.

Equilibrium constant is not dependent on amount of $CaCO_3$ K remains constant with temperature since $K_p = P^1_{CO_2}$. Catalyst does not alter the heat of reaction.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : For the equilibrium :

$NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2}O_2(g)$, one mole of NO_2 is placed in a vessel and allowed to attain the equilibrium at pressure 1 atm. Given that P_{NO} / P_{NO_2} at 700 K and 800 K are 0.872 and 2.5 respectively.

[1] K_p at 700 K and 800 K in atm$^{1/2}$ for the given reaction are respectively
(a) 13.632 (b) 0.585, 0.385 g
(c) 0.385, 1.30 (d) 1.30, 0.385

[2] Heat of reaction for the change is :
(a) 1.3632×10^3 J (b) 13.632 cal
(c) 13.632×10^3 cal (d) 13.632 J

[3] K_c for the given reaction at 700 K is :
(a) 0.02 (b) 0.01
(c) 0.03 (d) 0.04

Comprehension 2: Two solid compounds A and B dissociate into gaseous products at 20° C as

(i) $A(s) \rightleftharpoons A'(g) + H_2S(g)$
(ii) $B(s) \rightleftharpoons B'(g) + H_2S(g)$

At 20°C pressure over excess solid A is 50 mm and that over excess solid B is 68 mm.

[1] The dissociation constants of A and B in mm^2 are :
(a) 1156, 625 (b) 625, 1156
(c) 578, 312 (d) 312, 578

[2] Relative numbers of mole of A' and B' in the vapour phase over a mixture of the solids A and B are :
(a) 0.54 (b) 0.64
(c) 0.44 (d) 0.74

[3] The total pressure of gas over the solid mixture in mm is :
(a) 86.21 (b) 84.38
(c) 73.69 (d) 74.38

Comprehension 3 : 10 mole of NH_3 is heated at 15 atm from 27°C to 347°C assuming volume constant. The pressure at equilibrium is found to be 50 atm. The equilibrium constant for dissociation of NH_3 :

$$2NH_3 \rightleftharpoons N_2 + 3H_2; \ \Delta H = 91.94 \text{ kJ}$$

can be written as $K_p = \dfrac{P_{N_2} \times (P_{H_2})^3}{(P_{NH_3})^2} (\text{atm})^2$

[1] The degree of dissociation of NH_3 is :
(a) 61.3% (b) 20%
(c) 48% (d) none of these

[2] The equilibrium constant K_p for the reaction is :
(a) 7.08×10^2 (b) 3.06×10^2
(c) 7.6×10^2 (d) 1.53×10^3

[3] The volume of container in which gas is heated is :
(a) 16.42 litre (b) 8.21 litre
(c) 20 litre (d) 15 litre

[4] The increase in pressure and temperature on the reaction in equilibrium favours :
(a) forward reaction in both cases
(b) less dissociation of NH_3
(c) backward reaction and forward reaction respectively
(d) more formation of N_2 but less formation of H_2

[5] The vapour density of mixture at equilibrium is :
(a) 6.97 (b) 28.42
(c) 14.14 (d) 5.27

[6] The change in internal energy (in kJ) during the reaction is :
(a) 91.94 kJ (b) 81.63 kJ
(c) 102.25 kJ (d) 86.20 kJ

[7] The equilibrium constant for NH_3 at 247°C would be :
(a) 49.58 atm^2 (b) 45.28 atm^2
(c) 54.98 atm^2 (d) 40.18 atm^2

Comprehension 4 : For a reversible reaction at a certain temperature when it is at equilibrium or equilibrium has been attained whether physical or chemical, a change in certain variables might change the state of equilibrium. These variables include pressure, volume, concentration and temperature. Due to these changes, a system under equilibrium changes its state in such manner, *i.e.*, the equilibrium moves in forward direction or backward direction, so that the effect of change is annuled. For a gaseous phase endothermic decomposition of phosphorus pentachloride, can be made spontaneous by increasing concentration of PCl_5, lowering the pressure and increasing temperature of the system.

[1] Which of the following reactions proceeds in forward direction with increase in temperature are :
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + 3000 \text{ cal}$
(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43200 \text{ cal}$
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22400 \text{ cal}$
(d) $C(s) + O_2(g) \longrightarrow CO_2(g) + 94300 \text{ cal}$

[2] The equilibrium, solid $\rightleftharpoons$ liquid $\rightleftharpoons$ gas, will shift in forward direction when :
(a) temperature is raised (b) no effect of temperature
(c) temperature is lowered (d) pressure is increased

[3] The change in free energy for a reaction at equilibrium, *e.g.*, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, on addition of an inert gas at constant pressure and then at constant volume respectively are :
(a) decreases, no change (b) increases, no change
(c) no change, no change (d) no change, decreases

Comprehension 5 : Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation :

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $\beta_{\text{equilibrium}}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given : $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$)

[1] The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{\text{equilibrium}}$, is : **[JEE (Advanced) II 2016]**

(a) $\dfrac{8\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ (b) $\dfrac{8\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

(c) $\dfrac{4\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ (d) $\dfrac{4\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

[2] The **INCORRECT** statement among the following, for this reaction, is : **[JEE (Advanced) II 2016]**

(a) Decrease in the total pressure will result in formation of more moles of gaseous X

(b) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously

(c) $\beta_{\text{equilibrium}} = 0.7$

(d) $K_C < 1$

SOLUTIONS

Comprehension 1

$$\begin{array}{ccc} NO_2(g) \rightleftharpoons & NO(g) + & \frac{1}{2}O_2 \\ P & 0 & 0 \\ P-P' & P' & \frac{P'}{2} \end{array}$$

[1] (c) **At 700 K**

Given, $\frac{P'}{P-P'} = 0.872$ at 700 K

$$P' = \frac{0.872P}{1.872} = 0.47P$$

Also, $P - P' + P' + \frac{P'}{2} = 1$

$$P + \frac{0.47P}{2} = 1$$

$\therefore$ $P = 0.81$ atm

$\therefore$ $P' = 0.47 \times 0.81 = 0.38$ atm

$\therefore$ $$K_p = \frac{(P_{O_2})^{1/2} \times (P_{NO})}{(P_{NO_2})}$$

$$= \frac{\left[\frac{0.38}{2}\right]^{1/2} \times 0.38}{(0.81 - 0.38)} = \mathbf{0.385\ atm^{1/2}}$$

Similarly, at 800 K $\frac{P'}{P-P'} = 2.5 \quad \therefore \quad P' = 0.71P$

Also, $P + \frac{0.71P}{2} = 1$

$P = 0.74$ atm $\therefore P' = 0.74 \times 0.71 = 0.53$ atm

$\therefore$ $$K_P = \frac{\left[\frac{0.53}{2}\right]^{1/2} \times 0.53}{[0.74 - 0.53]} = \mathbf{1.30\ atm^{1/2}}$$

[2] (c) Now, $$2.303 \log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$2.303 \log \frac{1.30}{0.385} = \frac{\Delta H}{2}\left[\frac{100}{800 \times 700}\right]$$

$\therefore$ $\Delta H = \mathbf{13.632 \times 10^3\ cal}$

[3] (b) $$K_p = K_c(RT)^{\Delta n}$$

$$0.385 = K_c \times (2 \times 700)^{1/2}$$

$\therefore$ $K_c = 0.0102\ \text{mol}^{1/2}\ \text{litre}^{-1/2}$

Comprehension 2

[1] (b) For dissociation of $A(s) \rightleftharpoons A'(g) + H_2S(g)$

$\because$ $P'_{A'} + P'_{H_2S} = 50$

$\therefore$ $P'_{A'} = 25\,\text{mm}$ and $P'_{H_2S} = 25$ mm $\quad$ ($\because$ 1:1 ratio)

$$K_{P_1} = P'_{A'} \times P'_{H_2S} = 25 \times 25 = \mathbf{625\ (mm)^2}$$

Similarly, for $B(s) \rightleftharpoons B'(g) + H_2S(g)$

$$K_{P_2} = P'_{B'} \times P'_{H_2S} = 34 \times 34 = \mathbf{1156\ (mm)^2}$$

[2] (a) For mixture showing an equilibrium simultaneously,

$$\begin{array}{lcccc} & A(s) \rightleftharpoons A'(g) + & H_2S; & B(s) \rightleftharpoons B'(g) + & H_2S \\ \text{Pressure after dissociation} & x & x & y & y \end{array}$$

$\therefore$ $K_{P_1} = x(x+y)$ and $K_{P_2} = y(x+y)$

$\therefore$ $\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y} \quad \therefore \quad \frac{x}{y} = \frac{625}{1156}$

$\because$ V and T are same and thus, ratio of pressure is ratio of mole, *i.e.*,

$$\frac{n_{A'}}{n_{B'}} = \frac{625}{1156} = \mathbf{0.5407}$$

[3] (b) $\because$ $\frac{x}{y} = \frac{625}{1156}$ and $x(x+y) = 625$

$\therefore$ $x = 14.81\,\text{mm}$ and $y = 27.38\,\text{mm}$

$\therefore$ $P_T = P'_{A'} + P'_{B'} + P'_{H_2S} = x + y + (x + y)$

$= 2(x+y) = 2(14.81 + 27.38)$

$= \mathbf{84.38\ mm}$

Comprehension 3

[1] (a)

$$\begin{array}{cccl} 2NH_3 \rightleftharpoons & N_2 + & 3H_2 & \\ 10 & 0 & 0 & \text{at } 300\text{ K} \\ (10-2x) & x & 3x & \text{at } 620\text{ K} \end{array}$$

Pressure increase due to increases in temperature as well as due to increase in mole.

Initially $P \propto T$

$\therefore$ $15 \propto 300$

$P \propto 620$

$\therefore$ $P = \frac{620}{300} \times 15 = 31$ atm of 10 mole of NH_3 at 620 K

Now, NH_3 is dissociated to attain 50 atm at 620 K.

Thus, $P \propto n$ or $10 \propto 31$

$10 + 2x \propto 50$

$\therefore$ $2x = 6.13$

$\therefore$ $\alpha = \frac{2x}{10} \times 100 = \frac{6.13 \times 100}{10} = \mathbf{61.3\%}$

[2] (d) $$K_p = \frac{n_{N_2} \times (n_{H_2})^3}{(n_{NH_3})^2} \times \left[\frac{P}{\Sigma n}\right]^2$$

$$= \frac{\frac{6.13}{2} \times \left[\frac{6.13 \times 3}{2}\right]^3}{[10 - 6.13]^2} \times \left[\frac{50}{10 + 6.13}\right]^2$$

$= \mathbf{1.528 \times 10^3\ atm^2}$

[3] (a) $PV = nRT$

$15 \times V = 10 \times 0.0821 \times 300$

$\therefore V =$ **16.42 litre**

[4] (c) Increase in pressure favours the reaction showing decrease in volume, *i.e.*, backward reaction and increase in temperature favours endothermic reaction, *i.e.*, forward one.

[5] (d) $\text{V.D.} = \frac{\text{Molar mass}}{2}$

$$= \frac{3.87 \times 17 + \frac{6.13}{2} \times 28 + \frac{6.13}{2} \times 3 \times 2}{2 \times \left[3.87 + \frac{6.13}{2} + \frac{6.13}{2} \times 3\right]} = 5.27$$

[6] (b) $\Delta H = \Delta U + \Delta n RT$

$\therefore \Delta U = 91940 - 2 \times 8.314 \times 620 =$ **81630.6 J**

[7] (a) $2.303 \log \frac{K_{P_2}}{1.53 \times 10^3} = \frac{91940}{8.314}\left[\frac{-100}{620 \times 520}\right]$

$\therefore K_{p_2} =$ **49.58 atm^2**

Comprehension 4

[1] (b) Endothermic reactions are favoured with increase in temperature.

$N_2 + O_2 \longrightarrow 2NO; \Delta H = +ve$ (Endothermic)

[2] (a) Increase in temperature will favour the change showing absorption of heat.

[3] (a) At equilibrium, addition of inert gas at constant V does not change pressure, the condition. However addition at constant pressure, the equilibrium get shifted to right. No doubt ΔG° remains constant but ΔG decrease as the reaction goes spontaneously in forward direction to attain new equilibrium conditions.

Comprehension 5

[1] (b) Given,

$$X_2(g) \rightleftharpoons 2X(g)$$

	$X_2(g)$	$2X(g)$
Initial mole	1	0
At. eq.	$(1-a)$	$2a$

Where a mole of X_2 are decomposed at equilibrium

Given $2a = \beta_{\text{equilibrium}}$

So $\quad a = \frac{\beta_{\text{equilibrium}}}{2}$

Total mole at equilibrium $= (1+a) = \left[1 + \left(\frac{\beta_{eq}}{2}\right)\right]$

Let P_T be total pressure at equilibrium

$$K_p = \frac{(n_x)^2}{n_{x_2}} \times \left[\frac{P}{\Sigma n}\right]^1$$

So $\quad K_p = \frac{\left[\frac{2\beta_{eq}}{2}\right]^2}{\left[1 - \frac{\beta_{eq}}{2}\right]} \times \left[\frac{P}{1 + \frac{\beta_{eq}}{2}}\right]^1$

$$K_p = \frac{4\beta_{eq}^2}{4 - \beta_{eq}^2} \times P_T = \left(\frac{8\beta_{eq}^2}{4 - \beta_{eq}^2}\right) \qquad (\because P_T = 2\,\text{bar})$$

[2] (c)

(a) is correct as on decreasing pressure reaction proceeds in the direction where no. of gaseous molecules increase *i.e.*, forward reaction.

(b) is correct. No doubt ΔG is positive but since given dissociation takes place at 298 K and equilibrium is attained. At the start of reaction $Q_P < K_P$ so dissociation of X_2 take place spontaneously.

$$Q_P = \left[\frac{(P_X)^2}{P_{X_2}}\right] = 0$$

(c) is incorrect, $K_P = \frac{8\beta_{eq}^2}{4 - \beta_{eq}^2} = \frac{8 \times (0.7)^2}{4 - (0.7)^2} > 1$

(d) is correct.

As ΔG° positive and $\Delta G^\circ = -RT \ln K_P$

So K_P should be less than 1.

So $K_p < 1$

$K_P = K_C(RT)^{\Delta n_{(g)}} \qquad [\Delta n_{(g)} = 1]$

$K_C = \frac{K_P}{RT}$

$K_C < K_P \quad$ So $\quad K_C < 1$

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E). Choose the correct answers from the codes (a), (b), (c) and (d) given for each question :

(a) S is correct but E is wrong

(b) S is wrong but E is correct

(c) Both S and E are correct and E is correct explanation of S

(d) Both S and E are correct but E is not correct explanation of S

1. S : Recent convention to represent K_p is dimensionless.

E : The standard state of pure gas is 1 bar and the partial pressure of reactants and products measured with respect to this standard are used to determine K_p for the equilibrium.

$$A(g) + 2B(g) \longrightarrow C(g)$$

2. S : A reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$; has K_p at 298 K and 500 K as 4.0×10^{24} and 8.5×10^{10} respectively.

E : The E_a for the forward reaction is lesser than E_b for the backward reaction.

3. S : K_c, K_p and K_x are the equilibrium constant of a reaction in terms of concentration, pressure and mole fraction respectively.

E : The values of K_c or K_p or K_x change with temperature.

4. S : Vapour pressure of H_2O is constant at given temperature.

E : The equilibrium $H_2O(l) \rightleftharpoons H_2O(v)$ at a temperature has $K_p = P_{H_2O}$ and K_p is constant at the given temperature.

5. S : A dynamic equilibrium means a balance between the tendency towards minimum and maximum enthalpies.

E : The reaction having $\Delta H = -$ ve; occurs from high enthalpy side to low enthalpy side and the reaction $\Delta H = +$ ve; occurs from low enthalpy side to high enthalpy side.

6. S : Melting of ice at 10°C is a reversible process.

E : Evaporation of water at 100°C and 1 atm pressure is a reversible process.

7. S : The equilibrium in physical system is also dynamic in nature.

E : The equilibrium ice $\rightleftharpoons$ water is static in nature.

8. S : An increase in temperature disturbs, Gas + Solvent $\rightleftharpoons$ Solution, in backward direction.

E : Gaseous molecules escape out of solution due to increase in kinetic energy.

9. S : The m.pt. of ice is lowered on increasing the pressure, whereas m.pt. of solids other than ice is raised upon increasing pressure.

E : Ice show H-bonding and leads to the three dimensional solid of more volume.

10. S : The red colour shown by $[Fe(SCN)]^{2+}$ (*aq*) in a reversible reaction between Fe^{3+} and SCN^- $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$ deepens if few more drops KCNS are added in equilibrium mixture.

E : Addition of KCNS favours backward reaction.

11. S : Water boils at higher temperature in pressure cooker.

E : Increase in pressure leads an increase in boiling temperature.

12. S : Snow does not melt easily at mountains.

E : A decrease in pressure leads to an increase in freezing point.

13. S : The solubility of gases always increases with increase in pressure.

E : High pressure favours the change where volume decreases.

14. S : The melting point of solid (except ice) increases with increase in pressure

E : An increase in pressure favours the change where volume decreases.

15. S : Addition of an inert gas at constant pressure to dissociation equilibrium of $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ favours forward reaction.

E : $K_c = \dfrac{\alpha^2}{V(1-\alpha)}$ for the dissociation equilibrium of PCl_5 where α is degree of dissociation of PCl_5.

16. S : $\Delta G = \Delta G° + 2303RT \log Q$, where Q is reaction quotient.

E : Q may be greater or lesser than K_c but equal to K_c, if $\Delta G = 0$.

17. S : The equilibrium constant K_c or K_p has the unit (mol $\text{litre}^{-1})^{\Delta n}$ or $(\text{atm})^{\Delta n}$ respectively.

E : The numerical value of $K_c = K_p$ at $\Delta n = 0$.

18. S : A catalyst does not influence equilibrium constant of reaction but it simply helps in attaining the equilibrium earlier.

E : A catalyst increases both the rate of forward reaction and backward reaction.

19. S : The synthesis of NH_3 in Haber's process needs 500°C and 200 atm pressure inspite of the fact that reaction is favoured at high P and low T according to Le Chatelier's principle.

E : The high temperature is required to attain higher energy of activation for the reaction because bond energy of N_2 and H_2 are high.

20. S : The equilibrium constant may show higher or lower values with increase in temperature.

E : The change depends on the heat of reaction at equilibrium.

21. S : The dissociation of PCl_5 decreases on increasing pressure.

E : An increase in pressure favours the forward reaction.

22. S : When a soda water bottle is opened, the gas fizzes out.

E : Sealed soda water bottle contains CO_2 gas dissolved at high pressure. On releasing seal, the pressure decreases and CO_2 comes out.

23. S : The solubility of a gas in water decreases with rise in temperature.

E : Rise in temperature increases the kinetic energy of gaseous molecules dissolved in water.

24. S : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

E : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. **[IIT 2008]**

25. S : The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at high temperature.

E : When a system in equilibrium is disturbed by changing the temperature. It will tend to adjust itself so as to overcome of the effect of change.

[IIT 2008]

ANSWERS (Statement Explanation Problems)

1. (c) Let partial of reactants and products are a, b, c bar respectively with respect to standard state, then

For $$A(g)+2B(g) \longrightarrow C(g)$$

$$P'_A = \frac{a \text{ bar}}{1 \text{ bar}} = a; \text{ Similarly, } P'_B = b \text{ and } P'_C = c.$$

Thus, $$K_c = \frac{a \times b^2}{c} \text{ is dimensionless.}$$

2. (c) K_p decreases with temperature and thus, $\Delta H = -\text{ve}$. Also, $\Delta H = E_a(f) - E_a(b)$. The negative value of ΔH is possible only when $E_a(b) > E_a(f)$.

3. (d) Consider a reaction : $aA \rightleftharpoons bB$

$$K_c = \frac{[B]^b}{[A]^a}; \quad K_p = \frac{(P'_B)^b}{(P'_A)^a}$$

$$\because \quad K_p = \frac{(P'_B)^b}{(P'_A)^a} = \frac{(P_T \cdot X_B)^b}{(P_T \cdot X_A)^a} = \frac{(X_B)^b}{(X_A)^a} \times (P_T)^{b-a}$$

$$K_p = K_x \times (P_T)^{b-a}$$

or $$K_x = K_p \times (P_T)^{a-b} = K_P(P_T)^{-\Delta n}$$

Thus, eq. constant K_c, K_p or K_x varies with temperature.

4. (c) Explanation is correct reason for statement.

5. (c) $A + B \rightleftharpoons C + D; \Delta H = +\text{ ve}$, then

$C + D \rightleftharpoons A + B; \Delta H = -\text{ ve}$, *i.e.*, a balance in enthalpies is noticed at equilibrium.

6. (b) Water $\rightleftharpoons$ Vapour at b.pt. V.P. = 760 mm.

7. (a) Ice $\rightleftharpoons$ Water shows dynamic equilibrium.

8. (c) Explanation is correct reason for statement.

9. (c) $$\text{Ice} \rightleftharpoons \text{Water}$$
$$V_S > V_W$$

Thus, forward reaction occurs on increasing pressure, *i.e.*, more ice will melt or m.pt. is lowered.

$$\text{Solid} \rightleftharpoons \text{Liquid}$$
$$V_S < V_L$$

Thus, more solid will be formed on increasing pressure.

10. (a) Addition of KCNS favours forward reaction.

11. (c) Boiling of a liquid occurs when its vapour pressure becomes equal to atmospheric pressure.

12. (c) Ice $\rightleftharpoons$ water, increase in pressure leads to melting of ice as it favours the change showing decrease in volume.

13. (c) Gas + solvent $\rightleftharpoons$ solution; Increase in pressure leads to the change showing decrease in volume.

14. (c) Solid $\rightleftharpoons$ Liquid $V_L > V_S$; follow answer 12.

15. (c) Inert gas addition at constant pressure leads to an increase in volume. To have K_c constant 'α' must increase.

16. (d) $Q < K_c$ forward reaction

$Q > K_c$ backward reaction

$Q = K_c$ if $\Delta G = 0$

17. (d) $\Delta n = 0$

$$\therefore \quad K_p = K_c$$

18. (c) Explanation is correct reason for statement.

19. (c) Explanation is correct reason for statement.

20. (c) $2.303 \log \frac{K_{c_2}}{K_{c_1}} = \frac{\Delta H}{R} \frac{[T_2 - T_1]}{T_1 T_2}$; if $\Delta H = -\text{ ve}, K_{c_2} < K_{c_1}$

if $\Delta H = +\text{ve}, K_{c_2} > K_{c_1}$

21. (a) $$\underset{\substack{1 \\ 1-\alpha}}{PCl_5} \rightleftharpoons \underset{\substack{0 \\ \alpha}}{PCl_3} + \underset{\substack{0 \\ \alpha}}{Cl_2}$$

$$K_p = \left[\frac{\alpha^2}{1-\alpha}\right] \cdot \left[\frac{P}{1+\alpha}\right]^1$$

An increase in pressure will decrease α, to have K_p constant and thus backward reaction occurs.

22. (c) Explanation is correct reason for statement.

23. (c) Explanation is correct reason for statement.

24. (b) $\Delta G° \neq 0$ at equilibrium .

$\Delta G = 0$ at equilibrium

25. (b) Follow Le Chatelier's principle.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

List-I Reaction	List-II Degree of dissociation 'α' (Assume $\alpha << 1$)
A. $2X_{(g)} \rightleftharpoons 3Y_{(g)} + Z_{(g)}$	a. $\alpha = \sqrt{\frac{K_c}{V}} \times 3$
B. $4X_{(g)} \rightleftharpoons Y_{(g)} + Z_{(g)}$	b. $\alpha = [2K_cV]^{1/3}$
C. $2X_{(g)} \rightleftharpoons Y_{(g)} + 2Z_{(g)}$	c. $\alpha = \frac{4}{V}\sqrt{K_c}$
D. $3X_{(g)} \rightleftharpoons Y_{(g)} + Z_{(g)}$	d. $\alpha = \left[\frac{16V^2K_c}{27}\right]^{1/4}$

2.

List-I	List-II $\Delta_o S$ in cal and $\Delta_r H$ in kcal respectively
A. $\ln K = 2 - \frac{1000}{T}$	a. 8, 2
B. $\ln K = \frac{1}{2} - \frac{500}{T}$	b. 4, 2
C. $\ln K = 4 - \frac{1000}{T}$	c. 1, 1
D. $\ln K = 3 - \frac{4000}{T}$	d. 6, 8

3.

List-A	List-B
(A) $A(g)+B(g) \rightleftharpoons AB(g)$	1. Addition of inert gas at constant P shows forward shift
(B) $A_2(g)+B_2(g) \rightleftharpoons 2AB(g)$	2. Addition of inert gas at constant P shows backward shift
(C) $A(s) \rightleftharpoons B(g)+C(g)$	3. No effect on addition of inert gas at constant P or V
(D) $AB_3(g) \rightleftharpoons \frac{1}{2}A_2(g)+\frac{3}{2}B_2(g)$	4. No effect on addition of small amount of reactant

Type II : More Than One Match Are Possible

4.

List-A	List-B
(A) $\log_e K$ vs. $\frac{1}{T}$ plots	1. Slope $= -\frac{\Delta H^\circ}{R}$
(B) Exothermic reaction	2. Intercept $= \frac{\Delta S^\circ}{R}$
(C) Endothermic reaction	3. $K > 1$ if ΔH° is large and negative
	4. $K < 1$ if ΔH° is large and positive
	5. $K > 1$ if ΔS° is large and positive and $\Delta S^\circ > \Delta H^\circ$
	6. $K < 1$ if ΔH° is small and negative and ΔS° is large and negative

5.

List A	List B
(A) $N_2 + 3H_2 \rightleftharpoons 2NH_3$	1. High P
(B) $2SO_3 \rightleftharpoons 2SO_2 + O_2$	2. Low T
(C) Melting of ice	3. 88% yield at 200°C
(D) $N_2 + O_2 \rightleftharpoons 2NO$	4. 15% yield at 500°C
	5. High T
	6. Low P

6.

List-A	List-B
(A) $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3$; $\Delta H = -\text{ve}$	1. K increases with increase in T
(B) $N_2(g)+O_2(g) \rightleftharpoons 2NO_2$; $\Delta H = +\text{ve}$	2. K decreases with increase in T
(C) $PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$; $\Delta H = +\text{ve}$	3. No effect of P on equilibrium
(D) $A(g)+B(g) \rightleftharpoons 2C(g)+D(g)$; $\Delta H = +\text{ve}$	4. Addition of inert gas at constant P give more products

ANSWERS

1. A–d; B–c; C–b; D–a
2. A–b; B–c; C–a; D–d
3. A–2; B–3; C–4; D–1
4. A–1,2; B–3,6; C–4,5;
5. A–1,2,3,4; B–5,6; C–1,5; D–5
6. A–2; B–1,3; C–1,4; D–1,4