ALLEN CAREER INSTITUTE KOTA (RAJASTHAN)

CHEMICAL EQUILIBRIUM

E

NEET SYLLABUS

EQUILIBRIUM : *Equilibrium in physical and chemical processes, dynamic nature of equilibrium, law of chemical equilibrium, equilibrium constant, factors affecting equilibrium-Le Chatelier's principle.*

OBJECTIVES

After studying this unit, we will be able to :

- *Identify dynamic nature of equilibrium involved in physical and chemical processes;*
- *State the law of equilibrium;*
- *Explain characteristics of equilibria involved in physical and chemical processes;*
- *Write expressions for equilibrium constants;*
- *Establish a relationship between Kp and Kc;*
- *Explain various factors that affect the equilibrium state of a reaction;*
  Understand physical equilibrium

"You cannot teach a man anything; you can only help him discover it in himself."

Galileo

CHEMICAL EQUILIBRIUM

3.0 INTRODUCTION

Chemical reaction : Symbolic representation of any chemical change in terms of reactants and products is called chemical reaction.

Types of chemical reaction :

(a) On the basis of physical state

(I) Homogeneous reactions

All reactants and products are in same phase.

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

(II) Heterogeneous reactions

Reactants and products are in two or more phases.

$Zn(s) + CO_2(g) \longrightarrow ZnO(s) + CO(g)$

(b) On the basis of speed.

(I) Fast reactions

(i) Generally these reactions are ionic reactions.

$HCl + NaOH \longrightarrow NaCl + H_2O$

Acid Base Salt Water

(ii) Rate determination is almost impossible.

(II) Slow reactions

(i) Generally these reactions are molecular reactions.

$H_2 + I_2 \longrightarrow 2HI$

(ii) Rate determination is possible.

(c) On the basis of heat

(I) Exothermic reactions

(i) Heat is evolved in these type of chemical reactions.

$R \longrightarrow P + x$ kcal

(ii) Change in enthalpy, ΔH = (–) ve

(II) Endothermic reactions

Heat is absorbed in these type of chemical reactions.

$R \longrightarrow P - x$ kcal

ΔH = (+) ve

(d) On the basis of direction

(I) Reversible reactions

(i) Chemical reaction in which products can be converted back into reactants.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$

$H_2 + I_2 \rightleftharpoons 2HI$

(ii) Proceed in forward as well as in backward direction.

(iii) Possible in closed container.

(iv) These can attain equilibrium.

(v) Reactants are never completely converted into products.

(vi) Neutralisation reactions except of strong acid and strong base.

$HCl + NH_4OH \rightleftharpoons NH_4Cl + H_2O$

(II) Irreversible reactions

(i) Chemical reaction in which products cannot be converted back into reactants.

$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$

(ii) Proceed only in one direction (forward direction).

(iii) Generally possible in open container.

(iv) These do not attain equilibrium.

(v) Reactants are nearly completely converted into products.

(vi) Neutralisation reactions of strong acid and strong base.

$HCl + NaOH \longrightarrow NaCl + H_2O$

GOLDEN KEY POINTS

- We always take forward direction if direction is not specified.
- In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice-versa.
- **Rate of Reaction**

The change in concentration of reactants or products in unit time is known as rate of the reaction.

$$\text{Rate of reaction} = (\pm)\frac{\text{change in concentration}}{\text{time taken for the change}}$$

3.1 EQUILIBRIUM AND CHEMICAL PROCESS

(A) Chemical Equilibrium

The most important characteristic property of a reversible reaction is that it always attains a state of chemical equilibrium.

Consider a general reversible reaction in a closed vessel,

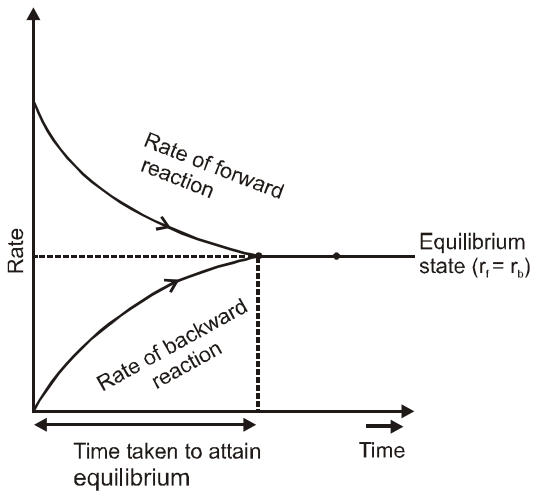
$A + B \underset{r_b}{\overset{r_f}{\rightleftharpoons}} C + D$ where, r_f = rate of forward reaction

r_b = rate of backward reaction

Initially reaction occurs in forward direction but as the concentration of products increases reaction also starts in backward direction.

At a certain stage, rate of forward reaction becomes equal to the rate of backward reaction called equilibrium state.

At equilibrium state : Rate of forward reaction (r_f) = Rate of backward reaction (r_b)



(B) Characteristics of equilibrium :

- The concentrations of the reactants and products do not change with time.
- At this stage, number of moles of substances produced per second in the forward reaction is equal to the number of moles of substances which disappear per second in the backward reaction.
- Chemical equilibrium is dynamic in nature i.e. the reaction although appears to be stopped but actually takes place in both the directions with the same speed.
- Chemical equilibrium can be approached from both sides

$$2HI \rightleftharpoons H_2 + I_2 \text{ or } H_2 + I_2 \rightleftharpoons 2HI$$

At equilibrium, each reactant and product has a constant concentration and this is independent of the fact whether the reaction starts from forward direction or backward direction with the reactant or with the product.

- Equilibrium is not affected by the presence of catalyst. The catalyst only helps in attaining equilibrium rapidly.
- The measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time at the chemical equilibrium conditions.
- Homogeneous equilibrium is the equilibrium in which the reactants and products are in the same phase.

$$CH_3COOC_2H_5(\ell) + H_2O(\ell) \overset{H^+}{\rightleftharpoons} CH_3COOH(\ell) + C_2H_5OH(\ell)$$

- Heterogeneous equilibrium is the equilibrium in which the reactants and products are in two or more phases.

$$Zn(s) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g)$$

- **ACTIVE MASS :** The term active mass means the concentration of the reactants expressed in moles per litre (molar concentration) or the pressure of the reacting gas in atmosphere. In case of gases and solutions, the molar concentration means the number of gram molecules present per litre.

  Active mass is usually expressed by enclosing the symbol of the reactant in square bracket [ ].

$$\text{Active mass} = \frac{\text{Number of gram moles of the substance}}{\text{Volume (L)}}$$

$$= \frac{\text{Weight of substance (in grams)}}{\text{Molecular weight } (M_w) \times \text{Volume (L)}} = \frac{w}{M_w \times V(L)} = \frac{w \times 1000}{M_w \times V(mL)}$$

- The active mass of solids and pure liquids is a constant quantity (unity) because it is an intensive property i.e. number of molecules present per unit volume do not change because density and molecular weight of solids and pure liquids are constant. But it does not apply for gaseous substances because for them number of molecules present per unit volume change with change in volume of vessel.

$$\text{Molar concentration} = \frac{w}{M_w \times V(L)} = \frac{\rho}{M_w} \text{ (where } \rho = \text{density (in } gL^{-1})$$

$$= \frac{\rho}{M_w} \times 1000 \qquad \text{(where } \rho = \text{density (in } gmL^{-1})$$

$$\text{Active mass} = \frac{\text{density of the substance}}{\text{molecular mass of the substance}}$$

Following other names of active mass can also be used :

(i)	mole/litre	(ii)	gram mole/litre	(iii)	gram molecules/litre
(iv)	molarity	(v)	Concentration	(vi)	Effective concentration
(vii)	active quantity	(viii)	n/v	(ix)	C
(x)	M	(xi)	[ ]		

Illustrations

Illustration 1. In any chemical reaction, equilibrium is supposed to be established when :

(1) Mutual opposite reaction undergo.

(2) concentration of reactants and resulting products are equal.

(3) Velocity of mutual reactions become equal.

(4) The temperature of mutual opposite reactions becomes equal.

Solution. **Ans. (3)**

Illustration 2. **Assertion :** The active mass of pure solids and pure liquids is taken unity.

Reason: The active mass of pure solids and pure liquids depends on density and molecular mass. The density and molecular mass of pure solids and pure liquids are constant.

Solution. **Ans. (1)**

Illustration 3. 8.5 g ammonia is present in a vessel of 0.5 litre capacity then find out the active mass of ammonia?

Solution. $\left[NH_3\right] = \frac{8.5}{17 \times 0.5} = 1\,mol\,L^{-1}$

BEGINNER'S BOX-1

1. Which of the following statement is correct regarding with chemical equilibrium :-

(1) Based on extent to which the reactions proceed to reach the equlibrium we may have negligible concentrations of reactants are left

(2) Equlibrium is not static

(3) Concentration of reactants and products becomes constant at equilibrium

(4) All of these

2. Find out the correct statement :-

(1) Equilibrium condition is a state of reversible reaction

(2) Chemical equilibrium are important in numerous biological process like transport and delivery of O_2

(3) Reversible reactions can be hemogeneous and hetrogeneous both

(4) All of these

3. Which of the following reaction is endothermic reaction :-

(1) Bond formation by two unstable atoms at certain condition

(2) Combustion reactions

(3) Conversion of more stable allotrope to less stable allotropic element

(4) Condensation of vapour to its liquid state

4. Active mass of 2 mol of NaCl kept in 4 litre vessel at NTP is :-

(1) 1 (2) 2 (3) $\frac{1}{2}$ (4) Not defined

3.2 LAW OF MASS ACTION OR LAW OF CHEMICAL EQUILIBRIUM

- The law of mass action was given by Guldberg and Waage (1864).
- It states that the rate of a chemical reaction is directly proportional to the product of active masses of the reacting substances raised to a power equal to the stoichiometric coefficient in the balanced chemical equation.

(A) Derivation of equilibrium constant :-

Consider a reversible homogeneous chemical reaction which has attained equilibrium state at a particular temperature :

$$m_1A + m_2B \rightleftharpoons n_1C + n_2D$$

Let the active masses of A, B, C and D be [A] [B] [C] and [D] respectively at equilibrium.

According to law of mass action :-

Rate of forward reaction $(r_f) \propto [A]^{m_1}[B]^{m_2}$

Rate of backward reaction $(r_b) \propto [C]^{n_1}[D]^{n_2}$

$r_f = k_f[A]^{m_1}[B]^{m_2}$ and $r_b = k_b[C]^{n_1}[D]^{n_2}$

Where K_f and K_b are forward and backward rate or velocity constants respectively.

At equilibrium state –

$$r_f = r_b$$

$$k_f[A]^{m_1}[B]^{m_2} = k_b[C]^{n_1}[D]^{n_2}$$

$$\frac{k_f}{k_b} = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$$

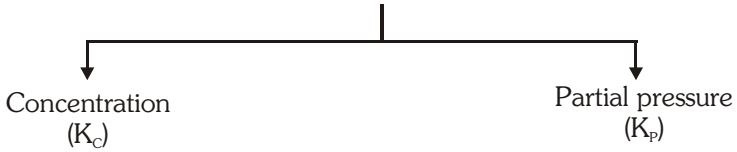
$$K = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}} \qquad \because K = \frac{k_f}{k_b}$$

K is known as equilibrium constant and has a definite value for every chemical reaction at particular temperature.

- The equilibrium constant at a given temperature is the ratio of the rate constants of forward and backward reactions,

$$K = \frac{k_f}{k_b}$$

Forms of K



For reaction $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$K_C = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$$

Unit of [ ] = mol L^{-1}

$$K_P = \frac{(P_C)^{n_1} \times (P_D)^{n_2}}{(P_A)^{m_1} \times (P_B)^{m_2}}$$

Unit of P = atm.

(B) Relation between K_P and K_C :

Consider a reversible homogeneous chemical equilibrium reaction

$$m_1A + m_2B \rightleftharpoons n_1C + n_2D$$

According to law of mass action (LOMA)

$$K_C = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$$

$$K_P = \frac{(P_C)^{n_1}(P_D)^{n_2}}{(P_A)^{m_1}(P_B)^{m_2}}$$

For an ideal gas **PV = nRT**

Where – P = Pressure in atm
V = Volume in litres
n = Number of gaseous moles
R = Gas constant = 0.0821 L atm $mol^{-1}k^{-1}$
T = Temperature in kelvin

$$P = \frac{n}{V}RT = \text{active mass} \times RT$$

$\frac{n}{V}$ = molar concentration or active mass

$P_A = [A]RT$, $P_B = [B]RT$, $P_C = [C]RT$ and $P_D = [D]RT$

Put all these values in K_P expression

$$\text{So } K_P = \frac{[C]^{n_1}(RT)^{n_1} \times [D]^{n_2}(RT)^{n_2}}{[A]^{m_1}(RT)^{m_1} \times [B]^{m_2}(RT)^{m_2}} = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}} \times \frac{(RT)^{n_1+n_2}}{(RT)^{m_1+m_2}}$$

$$K_P = K_C(RT)^{(n_1+n_2)-(m_1+m_2)}$$

$\Delta n_g = (n_1 + n_2) - (m_1 + m_2)$
= Sum of stoichiometric coefficient of gaseous products
– sum of stoichiometric coefficient of gaseous reactants

$$\boxed{K_P = K_C(RT)^{\Delta n_g}}$$

- The K_C is expressed by the units $(\text{mol } L^{-1})^{\Delta n_g}$ and K_P by $(\text{atm})^{\Delta n_g}$.
- Three cases may arise :-

(a) When $\Delta n_g = 0$

$K_P = K_C (RT)^0 = K_C$

For example : (i) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

(ii) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

- K_C and K_P are unit less in this case.

(b) When Δn_g = +ve

$K_P > K_C$

For example : (i) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ $\begin{pmatrix} K_C \to \text{mol L}^{-1} \\ K_P \to \text{atm} \end{pmatrix}$

(ii) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$ $\begin{pmatrix} K_C \to \text{mol}^2\text{L}^{-2} \\ K_P \to (\text{atm})^2 \end{pmatrix}$

(c) When Δn_g = –ve

$K_P < K_C$

For example :- (i) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\begin{pmatrix} K_C \rightarrow mol^{-2} L^2 \\ K_P \rightarrow atm^{-2} \end{pmatrix}$

(ii) $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$ $\begin{pmatrix} K_C \rightarrow mol^{-1} L^1 \\ K_P \rightarrow atm^{-1} \end{pmatrix}$

(d) Special point :

If $T = \frac{1}{R}$ then

$$K_P = K_C \left(R \times \frac{1}{R}\right)^{\Delta ng}$$

$$K_P = K_C\ (1)^{\Delta n_g}$$

$$K_P = K_C$$

For any value of Δn_g

(C) Application of K -

Stability of reactants and products :

Stability of reactants increases when value of K decreases

Stability of products increases when value of K increases

Ex : In the following reactions which one oxide is more stable.

$2XO\ (g) \rightleftharpoons X_2(g) + O_2(g)$; $K_1 = 1 \times 10^{24}$

$2XO_2\ (g) \rightleftharpoons X_2(g) + 2O_2(g)$; $K_2 = 2.5 \times 10^{10}$

$\because$ $K_1 > K_2$ So the stability of $XO_2 > XO$

BEGINNER'S BOX-2

1. In which of the following reaction product is more stable :-

(1) $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $K_1 = 2.3 \times 10^{-2}$ (2) $N_2 + O_2 \rightleftharpoons 2NO$; $K_2 = 2 \times 10^2$

(3) $H_2 + I_2 \rightleftharpoons 2HI$; $K_3 = 294$ (4) $XeO + \frac{1}{2}O_2 + F_2 \rightleftharpoons XeO_2F_2$; $K_4 = 1.4 \times 10^{-3}$

2. Equlibrium constant is :-

(1) $\frac{k_b}{k_f}$ (2) $\frac{k_f}{k_b}$ (3) $k_f \times k_b$ (4) $\frac{1}{k_f k_b}$

3. At 527°C, the reaction $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$ has $K_C = 4$ then what is the value of K_p for the same reaction :-

(1) $16 \times (800\ R)^2$ (2) $\left(\frac{800R}{4}\right)^{-2}$ (3) $\left(\frac{1}{4 \times 800\ R}\right)^2$ (4) None of these

4. For the equlibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$, what is the temperature at which $\frac{K_p(atm)}{K_c(M)} = 3$:-

(1) 0.027 K (2) 0.36 K (3) 36.54 K (4) 273 K

(D) Factors affecting the equilibrium constant –

(a) Temperature : The value of equilibrium constant changes with the change of temperature. If K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2 and ΔH is the change in enthalpy then

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^0}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \textbf{ or } \log K_2 - \log K_1 = \frac{\Delta H^0}{2.303R}\left[\frac{T_2 - T_1}{T_1.T_2}\right] \text{ (According to van't hoff equation)}$$

If the temperature T_2 is higher than T_1 then $\left(\frac{T_2 - T_1}{T_1.T_2}\right) > 0$.

(i) When ΔH = +ve (endothermic reaction)

$\log K_2 - \log K_1 > 0 \Rightarrow \log K_2 > \log K_1$

$\Rightarrow \quad K_2 > K_1$

$\therefore$ The value of equilibrium constant increases when temperature increases in case of endothermic reactions.

(ii) When ΔH= –ve (exothermic reaction)

$\log K_2 - \log K_1 < 0$

$\Rightarrow \quad \log K_2 < \log K_1$

$\Rightarrow \quad K_2 < K_1$

$\therefore$ The value of equilibrium constant decreases when temperature increases in the case of exothermic reactions.

(b) The mode of representation of the reaction :

Consider the reversible chemical equilibrium reaction $A + B \rightleftharpoons C + D$

Equilibrium constant $K_C = \frac{[C][D]}{[A][B]}$

If the reaction is reversed $C + D \rightleftharpoons A + B$

Equilibrium constant $K_C' = \frac{[A][B]}{[C][D]}$

The equilibrium constant K_C' is actually the reciprocal of K_C

Thus, the two equilibrium constants are related as $\rightarrow \boxed{K_C' = \frac{1}{K_C}}$

(c) Multi step reaction : If a reaction can be expressed as the sum of two or more reactions then overall K_C will be equal to the product of the individual equilibrium constants of the reactions.

Example :- $SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g) \rightarrow K_1$

$$NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2} O_2(g) \rightarrow K_2$$

then, $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g) \rightarrow K$

So, $\boxed{K = K_1 \times K_2}$

(d) Stoichiometry of the reaction :-

When a reversible reaction is multiplied or divided by a coefficient then the value of equilibrium constant will be numerically different in these cases.

For example the dissociation of NO_2 can be represented as :

$$2NO_2 \rightleftharpoons N_2 + 2O_2 \quad \text{.....(i)}$$

$$K_C = \frac{[N_2][O_2]^2}{[NO_2]^2}$$

(1) If reaction (i) is divided by 2 -

Then the reaction becomes $\Rightarrow NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2 \quad K_C' = \frac{[N_2]^{\frac{1}{2}}[O_2]}{[NO_2]}$

Thus, the two equilibrium constants are related as $K_C' = \sqrt{K_C}$

So if reaction is divided by n then $\boxed{K_C' = (K_C)^{\frac{1}{n}}}$

(2) If reaction (i) is multiplied by 2

Then the reaction becomes $\Rightarrow 4NO_2 \rightleftharpoons 2N_2 + 4O_2 \quad K_C' = \frac{[N_2]^2[O_2]^4}{[NO_2]^4}$

Thus, the two equilibrium constants are related as $K_C' = (K_C)^2$

So if reaction is multiplied by n then $\boxed{K_C' = (K_C)^n}$

GOLDEN KEY POINTS

- **Factors not affecting the equilibrium constant :**

  The value of equilibrium constant is independent of the following factors–

  (a) Concentration of reactants and products. (b) Pressure

  (c) Volume (d) The presence of a catalyst.

  (e) Presence of inert materials.

- **The value of equilibrium constant depends only on temperature.**

Illustrations

Illustration 4. $XeF_6 + H_2O \rightleftharpoons XeOF_4 + 2HF$ constant = K_1, $XeO_4 + XeF_6 \rightleftharpoons XeOF_4 + XeO_3F_2$ constant= K_2. Then equilibrium constant for the reaction $XeO_4 + 2HF \rightleftharpoons XeO_3F_2 + H_2O$ will be–

(1) $\frac{K_1}{K_2}$ (2) $K_1 + K_2$ (3) $\frac{K_2}{K_1}$ (4) $\frac{K_1}{(K_2)^2}$

Solution **Ans. (3)**

Illustration 5 ***Assertion:-*** In the presence of catalyst, the value of equilibrium constant K increases.
Reason :- Catalysts increases the rate of forward and backward reaction to same extent.
(1) A (2) B (3) C (4) D

Solution **Ans. (4)**

3.3 DEGREE OF DISSOCIATION

It is the fraction of moles of reactant dissociated $\alpha = \frac{x}{a}$

$$\% \alpha = \frac{x}{a} \times 100$$

Where α= Degree of dissociation
x= Number of dissociated moles
a= Initial number of moles (given)

Illustrations

Illustration 6 40% of PCl_5 is not dissociated at 300°C. The reaction is carried out in a flask of 1 litre capacity. The value of K_c would be :-
(1) 3.2 (2) 1.6 (3) $(3.2)^{-1}$ (4) 0.9

Solution **Ans. (4)**

Illustration 7 In the beginning of the reaction, $A \rightleftharpoons B + C$, 2 moles of A are taken, out of which 0.5 moles gets dissociated. What is the amount of dissociation of A ?
(1) 0.5 (2) 1 (3) 0.25 (4) 4.2

Solution **Ans. (3)**

	A	$\rightleftharpoons$ B	+ C	
Initially	2	0	0	x = 0.5
Moles at eq.	2 – x	x	x	
	2 – 0.5	0.5	0.5	

Since, two moles dissociated into 0.5
Therefore, one mole will dissociated into 0.25

BEGINNER'S BOX-3

1. The equilibrium constant (K_c) for the reaction $2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$ is 4×10^{-34} at 25°C. What is the equilibrium constant for the reaction :-

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$$

(1) 2×10^{-17} (2) 2.5×10^{33} (3) 5×10^{6} (4) None of these

2. Consider the following gaseous equilibrium given below
I. $N_2 + 3H_2 \rightleftharpoons 2NH_3$; eq. constant = K_1 II. $N_2 + O_2 \rightleftharpoons 2NO$; eq. constant = K_2

III. $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ eq. constant = K_3

The equilibrium constant for the reaction $2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$ in terms of K_1, K_2 and K_3 will be :-

(1) $K_1 K_2 K_3$ (2) $\frac{K_1 K_2}{K_3}$ (3) $\frac{K_1 K_3^2}{K_2}$ (4) $\frac{K_2 K_3^3}{K_1}$

3. Using molar concentrations, what is the unit of K_c for the reaction $CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$:-

(1) M^{-2} (2) M^2 (3) M^{-1} (4) M

4. If temperature is increased then equilibrium constant will be :-

(1) Increased

(2) Decreased

(3) Remains constant

(4) May increased or decreased depends on exothermic or endothermic nature

5. What will be the equilibrium constant at 127°C. If equilibrium constant at 27°C is 4 for reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = -46.06$ kJ :-

(1) 4×10^{-2} (2) 2×10^{-3} (3) 10^2 (4) 4×10^2

6. In which of the following equilibrium equation, $K_p > K_c$

(1) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ (2) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(3) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (4) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

7. If $CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g)$, $K_1 = 60$; $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$, $K_2 = 180$ then the equilibrium constant of the reaction $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ will be–

(1) 0.44 (2) 0.11 (3) 0.22 (4) 0.33

3.4 APPLICATIONS OF LAW OF MASS ACTION

[Relation of dissociation (x) with volume (V) and pressure (P)]

(A) Homogeneous Gaseous Reactions of Type-I (Δn_g=0)

Synthesis of HI :-

(i) Expression for K_C : The formation of HI from H_2 and I_2 is represented by following reaction

	1	1	2	(Stoichiometric coefficient)
	$H_2(g)$ +	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial moles	a	b	0	
Moles at equilibrium	(a – x)	(b – x)	2x	

Let us start with 'a' moles of H_2 and 'b' moles of I_2 in a closed bulb of V volume. If at equilibrium x moles of each of H_2 and I_2 have reacted, then 2x moles of HI will be formed so active masses.

$$[H_2] = \frac{(a-x)}{V} \; ; \; [I_2] = \frac{(b-x)}{V} \; ; \; [HI] = \frac{2x}{V}$$

Applying law of mass action $$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

$$\Rightarrow \quad K_C = \frac{4x^2}{(a-x)(b-x)}$$

- When a = b = 1, x becomes degree of formation of HI or degree of dissociation of H_2(or I_2). $K_C = \frac{4x^2}{(1-x)^2}$

Let if $x <<< 1$ then $1-x \simeq 1$ So $K_C = 4x^2$

$x = \sqrt{\frac{K_C}{4}}$ i.e. $\boxed{x \propto V^{\circ}}$

At equilibrium the degree of dissociation is independent to the volume.

(ii) Expression for K_P : The equilibrium constant K_P can also be calculated considering partial pressures of reactants and products at equilibrium.

Total number of moles at equilibrium = (a – x) + (b – x) + 2x = (a + b)

If total pressure of the system at equilibrium be P then

Partial pressure of $H_2 = \frac{(a-x)}{(a+b)}P$; Partial pressure of $I_2 = \frac{(b-x)}{(a+b)}P$; Partial pressure of HI = $\frac{2x}{(a+b)}P$

$$K_P = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} = \frac{\left(\frac{2x}{a+b}\right)^2 P^2}{\left(\frac{a-x}{a+b}\right)\left(\frac{b-x}{a+b}\right)P^2}$$

$$K_P = \frac{4x^2}{(a-x)(b-x)}$$ Thus $K_P = K_C$

Let if $x <<< 1$ then $1-x \simeq 1$ So $K_P = 4x^2$

$x = \sqrt{\frac{K_P}{4}}$ i.e. $\boxed{x \propto P^{\circ}}$

At equilibrium the degree of dissociation is independent to the pressure also.

(B) Homogeneous Gaseous reactions of Type-II ($\Delta n_g > 0$)

Dissociation of PCl_5 :-

(i) Expression for K_C : The dissociation of PCl_5 takes place according to the equation

	1	1	1 (Stoichiometric coefficient)
	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
Initial moles	a	0	0
Moles at equilibrium	(a–x)	x	x

Let a moles of PCl_5 be taken in a closed vessel of volume V. At equilibrium x moles of PCl_5 are dissociated into x moles of each PCl_3 and Cl_2.

$[PCl_5] = \frac{(a-x)}{V}$; $[PCl_3] = \frac{x}{V}$; $[Cl_2] = \frac{x}{V}$

Apply law of mass action $K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$

- When a =1, x becomes degree of dissociation(α) $K_C = \frac{\alpha^2}{(1-\alpha)V}$

If $\alpha <<< 1$ then $1-\alpha \approx 1$ $K_C \approx \frac{\alpha^2}{V}$ or $\boxed{\alpha \propto \sqrt{V}}$

The degree of dissociation of PCl_5 at equilibrium is directly proportional to the square root of the volume.

(ii) Expression for K_P :

Let the total pressure at equilibrium be P.

Total number of moles at equilibrium = (a – x) + x + x = a + x

$$p_{PCl_5} = \left(\frac{a-x}{a+x}\right)P \quad , \qquad p_{PCl_3} = \left(\frac{x}{a+x}\right)P \, , \quad p_{Cl_2} = \left(\frac{x}{a+x}\right)P$$

Apply law of mass action $$K_P = \frac{p_{PCl_3}.p_{Cl_2}}{p_{PCl_5}} = \frac{x^2p}{(a+x)(a-x)}$$

When a = 1, x becomes degree of dissociation(α) $$K_P = \frac{\alpha^2 P}{(1+\alpha)(1-\alpha)} = \frac{\alpha^2 P}{1-\alpha^2}$$

If $\alpha << 1$ then $1-\alpha^2 \approx 1$, $K_P \approx \alpha^2 P$

$$\alpha^2 \propto \frac{1}{P} \quad \Rightarrow \quad \boxed{\alpha \propto \frac{1}{\sqrt{P}}}$$

- The degree of dissociation of PCl_5 is inversely proportional to the square root of the total pressure at equilibrium.

(C) Homogeneous Gaseous reactions of Type-III($\Delta n_g < 0$)

Synthesis of Ammonia :-

(i) Expression for K_C : The formation of ammonia from nitrogen and hydrogen is represented by the equation :

	1		3		2 (Stoichiometric coefficient)
	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
Initial moles	a		b		0
Moles at equilibrium	(a–x)		(b–3x)		2x

Let us start with 'a' moles of N_2 and 'b' moles of H_2 in a closed vessel of Volume V. At equilibrium x moles of N_2 has combined with 3x moles of H_2 and produced 2x moles of NH_3.

At equilibrium $$[N_2] = \frac{(a-x)}{V}; \qquad [H_2] = \frac{(b-3x)}{V} \; ; \qquad [NH_3] = \frac{2x}{V}$$

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

If a = 1, b = 3 then $K_C = \frac{4x^2V^2}{27(1-x)^4}$

If $x << 1$ then $1-x \approx 1$

$$K_C = \frac{4x^2V^2}{27} \qquad \text{i.e.} \quad \boxed{x \propto \frac{1}{V}}$$

At equilibrium, the degree of dissociation is inversely proportional to the volume of vessel.

(ii) Expression for K_P :-

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

If total pressure is P at equilibrium then

$$p_{N_2}=\frac{(a-x)}{(a+b-2x)}P\ ,\qquad p_{H_2}=\frac{(b-3x)}{(a+b-2x)}P\ ,\qquad p_{NH_3}=\frac{2x}{(a+b-2x)}P$$

According to Law of mass action

$$K_P=\frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}=\frac{\left(\frac{2x}{a+b-2x}P\right)^2}{\left(\frac{a-x}{a+b-2x}\right)\left(\frac{b-3x}{a+b-2x}\right)^3}$$

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

If a = 1 , b = 3 then $\qquad K_P=\frac{16x^2(2-x)^2}{27(1-x)^4P^2}$

If $x<<<1$ then $2-x\approx 2$ and $1-x\approx 1$

$$K_P=\frac{64x^2}{27P^2}\ \textit{i.e.}\quad x^2\propto P^2\quad\Rightarrow\quad \boxed{x\propto P}$$

At equilibrium, the degree of dissociation is directly proportional to the pressure.

GOLDEN KEY POINTS

- If inert gas mixed at constant temperature and constant volume in an equilibrium chemical reaction then total number of moles of gases are present in a container increases i.e. total pressure of gases increases but concentration in terms of mol L^{-1} and partial pressure of reacting substances are unchanged so dissociation (x) unchanged.
- $\alpha\propto(V)^{\frac{\Delta n_g}{\text{sum of stoichiometric coefficient of gaseous products}}}$ or $\alpha\propto\left(\frac{1}{P}\right)^{\frac{\Delta n_g}{\text{sum of stoichiometric coefficient of gaseous products}}}$
-

Effect	$\Delta n_g=0$ $H_2+I_2\rightleftharpoons 2HI$ $x\propto(v)^{\circ}\propto(P)^{\circ}$	$\Delta n_g>0$ or +ve $PCl_5\rightleftharpoons PCl_3+Cl_2$ $x\propto(v)^{1/2}\propto(\frac{1}{P})^{1/2}$	$\Delta n_g<0$ or –ve $N_2+3H_2\rightleftharpoons 2NH_3$ $x\propto(\frac{1}{v})\propto(P)$
(i) Pressure (increases)	x unchanged	x decreases	x increases
(ii) Volume (increases)	x unchanged	x increases	x decreases
(iii) Mixing of inert gas at			
(a) constant pressure	x unchanged	x increases	x decreases
(b) constant volume	x unchanged	x unchanged	x unchanged

BEGINNER'S BOX-4

1. $A + B \rightleftharpoons C + D$ If initially of A and B are both are taken in equal amount but at equilibrium concentration of D will be twice of that of A then what will be the equilibrium constant of reaction :-

(1) $\frac{4}{9}$ (2) $\frac{9}{4}$ (3) $\frac{1}{9}$ (4) 4

2. At a certain temperature, only 50% HI is dissociated at equilibrium in the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ The equilibrium constant for the reaction is :-

(1) 0.25 (2) 1.0 (3) 3.0 (4) 0.5

3. The equilibrium constant K_P for the reaction $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ is 4.0 at 1660°C. Initially 0.80 mole H_2 and 0.80 mole CO_2 are injected into a 5.0 liter flask. What is the equilibrium concentration of $CO_2(g)$:-

(1) 0.533 M (2) 0.0534 M

(3) 5.34 M (4) None of these

4. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ for the reaction initially the mole ratio was 1 : 3 of N_2 : H_2. At equilibrium 50% of each has reacted. If the equilibrium pressure is p, the partial pressure of NH_3 at equilibrium is :-

(1) $\frac{p}{3}$ (2) $\frac{p}{4}$ (3) $\frac{p}{6}$ (4) $\frac{p}{8}$

5. For the reaction $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$, if the initial concentration of $[H_2] = [CO_2]$ and x moles/litre of hydrogen is consumed at equilibrium, the correct expression of K_P is :-

(1) $\frac{x^2}{(1-x)^2}$ (2) $\frac{(1+x)^2}{(1-x)^2}$ (3) $\frac{x^2}{(2+x)^2}$ (4) $\frac{x^2}{1-x^2}$

(D) Law of Mass Action as Applied to Heterogeneous Equilibrium :-

In such cases the active mass of pure solids and pure liquids is taken as unity and the value of equilibrium constant is determined by the gaseous substances only.

(i) The dissociation of $CaCO_3$ in closed vessel.

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

$$K_P = p_{CO_2}$$

(ii) $$2H_2O(\ell) \rightleftharpoons 2H_2(g) + O_2(g)$$

$$K_P = (p_{H_2})^2 (p_{O_2})$$

(iii) $$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

$$K_P = \frac{(p_{H_2})^4}{(p_{H_2O})^4}$$

Illustrations

Illustration 8 Two sample of HI each of 5 g were taken separately into vessels of volume 5 and 10 litres respectively at 27°C. The extent of dissociation of HI will be :-

(1) More in 5 litre vessel (2) More in 10 litre vessel

(3) Equal in both vessel (4) None of these

Solution **Ans. (3)**

Illustration 9 What will be the amount of dissociation, if the volume is increased 16 times of initial volume in the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$?

(1) 4 times (2) $\frac{1}{4}$ times

(3) 2 times (4) $\frac{1}{5}$ times

Solution **Ans. (1)**

$x \propto \sqrt{V}$ or $x \propto \sqrt{16}$ Thus, 4 times.

Illustration 10 ***Assertion:–*** For the reaction, $N_2 + O_2 \rightleftharpoons 2NO$, increase in pressure at equilibrium has no effect on the reaction.

Reason :– The reaction is not accompanied by any change in number of moles of gaseous species.

(1) A (2) B (3) C (4) D

Solution **Ans. (1)**

3.5 LE-CHATELIER'S PRINCIPLE

PRINCIPLE :- According to this principle, if a system at equilibrium is subjected to a change of concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

- Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

(A) CHEMICAL EQUILIBRIUM

(a) Change in concentration:-

In an equilibrium increasing the concentrations of reactants results in shifting the equilibrium in favour of products while increasing concentrations of the products results in shifting the equilibrium in favour of the reactants.

(b) Change in pressure :-

When the pressure on the system is increased, the volume decreases proportionately i.e. the total number of moles present per unit volume increases. According to Le-Chatelier's principle, the equilibrium shifts in that direction in which there is decrease in number of moles.

- If there is no change in number of moles of gases in a reaction then a pressure change does not affect the equilibrium.

(c) Change in temperature :-

If the temperature of the system at equilibrium is increased then reaction will proceed in that direction in which heat can be used. Thus increase in temperature will favour the forward reaction for endothermic reaction.

Similarly, increase in temperature will favour the backward reaction for exothermic reactions.

(B) PHYSICAL EQUILIBRIUM

Physical reaction :- Those reaction in which change in only and only physical states (solid, liquid and gas) of substance takes place without any chemical change, is called physical reaction.

Example :

(a) Ice-water system (melting of ice) :

Melting of ice is accompained by absorption of heat (endothermic) and decrease in volume

$$\underset{(H_2O)\ 1g\ (1.09\ mL)}{\text{Ice (s)}} \rightleftharpoons \underset{(H_2O)\ 1g\ (1.01\ mL)}{\text{water } (\ell)}$$

Hence both increase of temperature and pressure will favour the melting of ice into water.

(b) Water-water vapour system (Vapourisation of water) :

Vapourisation of water is an endothermic and condensation of vapour into water is an exothermic reaction:

$$\underset{(H_2O)}{\text{Water } (\ell)} \rightleftharpoons \underset{(H_2O)}{\text{Vapour (g)}}$$

- The equilibrium shifts towards right side when the temperature is increased so rise in temperature will increase the vapour.
- The equilibrium shifts towards left side when the pressure is increased (i.e. volume is decreased) so increase in pressure will favour the rate of condensation of vapour into water.
- Thus favourable conditions for conversion of water into vapour are high tempeprature and low pressure.

(c) Solubility of gases :

$$\underset{\text{(Solute)}}{\text{Gas (g)}} + \underset{\text{(Solvent)}}{\text{Water } (\ell)} \rightleftharpoons \underset{\text{(Solution)}}{\text{Aqueous solution } (\ell)}$$

- **Effect of pressure** $\rightarrow$ Solubility of such gases increases with increasing pressure which dissolves in a solvent with a decrease in volume.

Illustrations

Illustration 11 On applying pressure to the equilibrium ice $\rightleftharpoons$ water, which phenomenon will happen :
(1) More ice will be formed (2) More water will be formed
(3) Equilibrium will not be disturbed (4) Water will evaporate

Solution **Ans. (2)**

Illustration 12 Which of the following conditions should be more favourable for increasing the rate of forward reaction in the equilibrium $H_2 \rightleftharpoons H + H$ (ΔH = +ve) ?
(1) 2000° C temperature and 760 mm of Hg pressure.
(2) 3500° C temperature and 100 cm of Hg pressure.
(3) 3500° C temperature and 1 mm of Hg pressure.
(4) All are wrong.

Solution **Ans. (3)**

In $H_2 \rightleftharpoons H + H$, heat has to be provided to dissociate H_2 into H. Therefore, the reaction is endothermic (ΔH will positive). So, temperature should be high. Since, one mole of H_2 forms two atoms of H, so volume is increasing (Δn is positive) so pressure should be low for increasing the rate of forward reaction.

Illustration 13 **Assertion :** $SO_2(g)+\frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)+\text{heat}$; Forward reaction is favoured at low temperature and high pressure.
Reason : Reaction is endothermic.
(1) A (2) B (3) C (4) D
Solution **Ans. (3)**

Illustration 14. The reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ goes to completion in lime kiln because :
(1) of the high temperature (2) CaO is more stable than $CaCO_3$
(3) CaO is not dissociated (4) CO_2 escapes continuously
Solution **Ans. (4)**

Illustration 15. **Assertion:** For a reversible exothermic reaction, extent of reaction decreases with increase in temperature.
Reason: In reversible exothermic reaction temperature is favourable for more formation of product.
Solution **Ans. (3)**

BEGINNER'S BOX-5

1. Which of the following equilibrium remains unaffected by a change in pressure (or volume) ?
(1) $2NOCl(g) \rightleftharpoons 2NO(s)+Cl_2(g)$ (2) $H_2(g)+CO_2(g) \rightleftharpoons H_2O(g)+CO(g)$
(3) $3PbS(s)+3O_2(g) \rightleftharpoons 2PbO(s)+2SO_2(g)$ (4) $PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$

2. Consider the following equilibrium system; $2SO_{2(g)}+O_{2(g)} \rightleftharpoons 2SO_{3(g)}$; some inert gas is added to the above system at constant volume. Predict which of the following is true?
(1) More of SO_3 is produced.
(2) Less SO_2 is produced.
(3) Addition of inert gas does not affect equilibrium.
(4) system moves to new equilibrium position which cannot be predicted theoretically.

3. Which of the following is not true for the equilibrium reaction; $N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$; $\Delta H = 180\,kJ\,mol^{-1}$.
(1) the formation of NO is increased at higher temperature.
(2) The volume change at constant pressure does not affect the equilibrium.
(3) The pressure change at constant volume does not affect the equilibrium.
(4) The formation of NO is decreased at higher temperature.

4. Consider the following equilibrium system; $SO_2(g)+\frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$; set up in a cylinder fitted with a piston. Some inert gas is added and the piston is moved outwards to keep the total gaseous pressure constant. Predict which of the following is true?
(1) Addition of inert gas does not affect the equilibrium.
(2) Less $SO_3(g)$ is produced.
(3) More $SO_3(g)$ is produced.
(4) The system moves to new equilibrium position which cannot be predicted theoretically.

5. When a volatile liquid is introduced into an evacuated closed vessel at a particular temperature, both evaporation and condensation take place simultaneously. The system reaches equilibrium state when–
(1) The liquid is completely transformed into the corresponding vapour
(2) Equal amounts of liquid and vapour are present in the system
(3) The rate of evaporation becomes equal to the rate of condensation
(4) Liquid cannot be converted into vapour and vice versa.

6. Which of the following equilibrium is dynamic ?
(1) Solid $\rightleftharpoons$ Liquid (2) Liquid $\rightleftharpoons$ Vapor (3) Solid $\rightleftharpoons$ Vapor (4) All of these

7. Which of the following is not true for solid-liquid equilibrium ?

(1) It can be established at any given temperature.

(2) The mass of solid does not change with time.

(3) The mass of liquid does not change with time.

(4) There is no exchange of heat between the system and its surrounding.

8. Which of the following substances can be placed in a closed vessel to establish (solid $\rightleftharpoons$ vapour) equilibrium?

(1) Ammonium chloride (2) Camphor (3) Iodine (4) All of these

9. Which of the following solutions kept in contact with undissolved solute is an example of solid-solution equilibrium?

(1) Aqueous solution (2) Saturated solution (3) Unsaturated solution (4) Nonaqueous solution

10. Which of the following is correct regarding the gas-solution equilibrium ?

(1) The solubility of the dissolved gas increases with the increase of pressure and decreases with the increase of temperature.

(2) The solubility of the dissolved gas increases with the increase of pressure as well as temperature.

(3) The solubility of the dissolved gas decreases with the increase of pressure and increases with the increase of temperature.

(4) The solubility of the dissolved gas decreases with the increase of pressure as well as temperature.

3.6 REACTION QUOTIENT (Q)

Consider a general homogeneous reversible reaction :

$$m_1A + m_2B \rightleftharpoons n_1C + n_2D$$

Reaction Quotient (Q) $= \dfrac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$, (Applied at any stage of reaction)

Equilibrium constant K $= \dfrac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$, (Applied only at equilibrium state)

(i) When Q = K then reaction is in equilibrium state.

(ii) When Q < K then rate of forward reaction increases.

(iii) When Q > K then rate of backward reaction increases.

3.7 Calculation of degree of dissociation from vapour density :-

Ex. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$$\alpha = \frac{D_T - D_0}{D_0} = \frac{D - d}{d}$$

Where : D_T or D = Principle or theoretical vapour density or normal vapour density

D_O or d = Observed or practical vapour density or experimental vapour density or vapour density at higher temp.

α = Degree of dissociation

$$\text{Vapour density} = \frac{\text{Molecular weight}}{2}$$

Reversible reaction	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	Total moles	Volume at NTP	Vapour density
Let initial moles	1 0 0	1	V_T=22.4	$D_T \propto \frac{1}{V_T}$
Moles at equilibrium	(1–α) α α	1+α	V_0 = 22.4 (1+α)	$D_0 \propto \frac{1}{V_0}$

If α is the degree of dissociation

$$\frac{D_T}{D_0} = \frac{V_0}{V_T} = \frac{22.4(1+\alpha)}{22.4}$$

$$\frac{D_T}{D_0} = 1+\alpha \quad \text{or} \quad \alpha = \frac{D_T}{D_0} - 1 \qquad \boxed{\alpha = \frac{D_T - D_0}{D_0}}$$

So for a general reversible reaction $n_1A \rightleftharpoons n_2B + n_3C$

$$\boxed{\alpha = \frac{n_1}{\Delta n}\left(\frac{D_T - D_0}{D_0}\right)} \quad \Delta n = (n_2 + n_3) - (n_1)$$

OR

$$\boxed{\alpha = \frac{n_1}{\Delta n}\left(\frac{M_T - M_0}{M_0}\right)}$$

M_T = Theoretical molecular weight

M_0 = Observed or experiment moelcular weight

Illustrations

Illustration 16 The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2. The precentage dissociation of N_2O_4 at the final temperature is -

(1) 87 (2) 60 (3) 40 (4) 70

Solution **Ans. (1)**

Illustration 17 If PCl_5 is 80% dissociated at 250° C then its vapour density at room temperature will be

(1) 56.5 (2) 104.25 (3) 101.2 (4) 52.7

Solution **Ans. (2)**

$$\alpha = \frac{D_T - D_o}{D_o}; \; D_T = \frac{\text{Molecular weight}}{2}$$

Vapour density at room temperature (D_T) is 104.25, which is fixed.

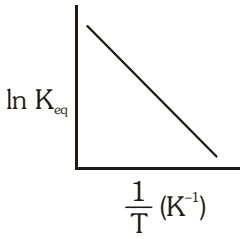
Illustration 18 ***Assertion:–*** For a reaction, reaction quotient (Q) is equal to K when the reaction is in equilibrium.

Reason:– If a catalyst is added to the reaction at equilibrium, the value of Q remains no longer equal to K.

(1) A (2) B (3) C (4) D

Solution **Ans. (3)**

BEGINNER'S BOX-6

1. 

According to this graph reaction will be :-
(1) Endothermic (2) Exothermic
(3) Spontaneous at room temperature (4) ΔH is negligible

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

If $K_p = K_c (RT)^x$, when the symbols have usual meaning the value of x is (assuming ideality) :-

(1) – 1 (2) $-\frac{1}{2}$ (3) $+\frac{1}{2}$ (4) + 1

3. For the equilibrium $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ $K_p = 63$ atm at 1000 K. If at equilibrium $P_{CO} = 10\ P_{CO_2}$ then total pressure at equilibrium is :-
(1) 6.30 atm (2) 0.693 atm (3) 6.93 atm (4) 69.3 atm

4. A(g) is 90 % converted in to B according to the reaction $A(g) \rightleftharpoons 3B(g)$ value of $\left(\frac{D}{d}\right)$ at this point is :-

(1) 1.0 (2) 2.0 (3) 2.5 (4) 2.8

5. What will be the direction of reaction if concentration of H_2, I_2 and HI are 2 mol L^{-1}, 2 mol L^{-1} and 8 mol L^{-1} respectively. K_C for reaction $H_2 + I_2 \rightleftharpoons 2HI$ is 4.
(1) forward direction (2) backward direction
(3) equilibrium condition (4) reaction will be completed

ANSWER KEY

BEGINNER'S BOX-1	**Que.**	1	2	3	4						
	Ans.	**4**	**4**	**3**	**1**						
BEGINNER'S BOX-2	**Que.**	1	2	3	4						
	Ans.	**3**	**2**	**4**	**3**						
BEGINNER'S BOX-3	**Que.**	1	2	3	4	5	6	7			
	Ans.	**4**	**4**	**2**	**4**	**1**	**1**	**4**			
BEGINNER'S BOX-4	**Que.**	1	2	3	4	5					
	Ans.	**4**	**1**	**2**	**1**	**1**					
BEGINNER'S BOX-5	**Que.**	1	2	3	4	5	6	7	8	9	10
	Ans.	**2**	**3**	**4**	**2**	**3**	**4**	**1**	**4**	**2**	**1**
BEGINNER'S BOX-6	**Que.**	1	2	3	4	5					
	Ans.	**1**	**2**	**3**	**4**	**2**					

EXERCISE-I (Conceptual Questions) — Build Up Your Understanding

FACTORS AFFECTING RATE OF REACTION

1. In an elementary reaction A + 2B → 2C + D. If the concentration of A is increased four times and B is decreased to half of its initial concentration then the rate becomes
(1) Twice
(2) Half
(3) Unchanged
(4) One fourth of the rate

2. The role of catalyst in a chemical reaction is :-
(1) To help attain equilibrium in a shorter time.
(2) To lower the activation energy.
(3) To shift the equilibrium in such a way as to increase the concentration of the product
(4) Both 1 & 2

EQUILIBRIUM AND CHEMICAL PROCESS

3. $x \rightleftharpoons y$ reaction is said to be in equilibrium, when:-
(1) Only 10% conversion x to y takes place.
(2) Complete conversion of x to y takes place
(3) Conversion of x to y is only 50% complete
(4) The rate of change of x to y is just equal to the rate of change of y to x in the system

4. In the chemical reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at equilibrium, state whether :-
(1) Equal volumes of N_2 & H_2 are reacting
(2) Equal masses of N_2 & H_2 are reacting
(3) The reaction has stopped
(4) The same amount of ammonia is formed as is decomposed into N_2 and H_2

5. Active mass of 5 g CaO :-
(1) 56 (2) 1
(3) 3.5 (4) 2

6. Ratio of active masses of 22g CO_2, 3g H_2 and 7g N_2 in a gaseous mixture :-
(1) 22 : 3 : 7
(2) 0.5: 3 : 7
(3) 1 : 3 : 1
(4) 1 : 3 : 0.5

7. Which of the following example shows effect of catalyst on reversible reaction
(1) It gives new reaction path with low activation energy.
(2) It shifts equilibrium right side.
(3) It decrease kinetic energy of activated molecules.
(4) It decrease rate of backward reaction.

8. Select the correct statement from the following :
(1) Equilibrium constant changes with addition of catalyst
(2) Catalyst increases the rate of forward reaction.
(3) The ratio of mixture at equilibrium does not changed by catalyst
(4) Catalyst are active only in solution.

9. In reversible chemical reaction equilibrium will be establish when –
(1) Reactant completely converted into product
(2) Rate of forward and backward reaction is equal
(3) Minimum yield of product
(4) concentration of reactant and product is equal

LAW OF MASS ACTION

10. In a chemical equilibrium, the rate constant for the backward reaction is 7.5×10^{-4} and the equilibrium constant is 1.5. The rate constant for the forward reaction is:-
(1) 2×10^{-3}
(2) 5×10^{-4}
(3) 1.12×10^{-3}
(4) 9.0×10^{-4}

11. The equilibrium concentration of $[B]_e$ for the reversible reaction $A \rightleftharpoons B$ can be evaluated by the expression:-
(1) $K_C[A]_e^{-1}$ (2) $\frac{k_f}{k_b}[A]_e^{-1}$
(3) $k_f k_b^{-1}[A]_e$ (4) $k_f k_b [A]^{-1}$

12. In this reaction $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$ at 298K molar concentration of Ag^+, $Ag(NH_3)_2^+$ and NH_3 is 10^{-1}, 10^{-1} , and 10^3. The value of K_C at 298K for this equilibrium :-
(1) 10^{-6} (2) 10^6
(3) 2×10^{-3} (4) 2×10^6

13. Equilibrium constant of some reactions are given as under :

(a) $x \rightleftharpoons y$ $K = 10^{-1}$

(b) $y \rightleftharpoons z$ $K = 2 \times 10^{-2}$

(c) $P \rightleftharpoons Q$ $K = 3 \times 10^{-4}$

(d) $R \rightleftharpoons S$ $K = 2 \times 10^{-3}$

Initial concentration of the reactants for each reaction was taken to be equal :
Review the above reaction and indicate the reactions in which the reactants and products respectively were of highest concentration :-
(1) d, c (2) c, a
(3) a, d (4) b, c

14. At 1000 K, the value of K_P for the reaction :

$A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$
is 0.05 atm. The value of K_C in terms of R would be :-
(1) 20000 R (2) 0.02 R
(3) 5×10^{-5} R (4) $5 \times 10^{-5} \times R^{-1}$

15. For the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ the partial pressure of CO and CO_2 are 2.0 and 4.0 atm respectively at equilibrium. The K_P for the reaction is
(1) 0.5 (2) 4.0 (3) 8.0 (4) 1

16. For which reaction is $K_p = K_c$:-

(1) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

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

(3) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

(4) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

17. For the reaction

$CuSO_4.5H_2O_{(s)} \rightleftharpoons CuSO_4 . 3H_2O_{(s)} + 2H_2O_{(g)}$
Which one is correct representation :–

(1) $K_p = p^2_{H_2O}$ (2) $K_c = [H_2O]^2$
(3) $K_p = K_c(RT)^2$ (4) All

18. $\log \frac{K_p}{K_c} + \log RT = 0$ is true relationship for the following reaction:-

(1) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

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

(3) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(4) (2) and (3) both

19. For which reaction at 298 K, the value of $\frac{K_p}{K_c}$ is maximum and minimum respectively:-

(a) $N_2O_4 \rightleftharpoons 2NO_2$

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

(c) $X + Y \rightleftharpoons 4Z$

(d) $A + 3B \rightleftharpoons 7C$
(1) d, c (2) d, b (3) c, b (4) d, a

20. Consider the two gaseous equilibrium involving SO_2 and the corresponding equilibrium constants at 299 K

$SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$; K_1

$4SO_3(g) \rightleftharpoons 4 SO_2(g) + 2O_2(g)$; K_2
The value of the equilibrium constant are related by :-

(1) $K_2 = \frac{1}{(K_1)^4}$ (2) $K_2 = K_1^4$

(3) $K_2 = \left(\frac{1}{K_1}\right)^{\frac{1}{4}}$ (4) $K_2 = \frac{1}{K_1}$

21. For the reactions :- $A \rightleftharpoons B$; $K_C = 2$,

$B \rightleftharpoons C$; $K_C = 4$, $C \rightleftharpoons D$; $K_C = 6$

K_C for the reaction $A \rightleftharpoons D$:-
(1) 12 (2) 4/3
(3) 24 (4) 48

22. If $A \rightleftharpoons B$ ($K_c = 3$), $B \rightleftharpoons C$ ($K_c = 5$),

$C \rightleftharpoons D$ ($K_c = 2$)
The value of equilibrium constant for the above reaction are given, the value of equilibrium constant for $D \rightleftharpoons A$ will be:-
(1) 15 (2) 0.3 (3) 30 (4) 0.03

23. Which Oxide of Nitrogen is most stable :-

(1) $2NO_{2(g)} \rightleftharpoons N_{2(g)} + 2O_{2(g)}$
$K = 6.7 \times 10^{16}$ mol L^{-1}

(2) $2 NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$
$K = 2.2 \times 10^{30}$

(3) $2 N_2O_{5(g)} \rightleftharpoons 2N_{2(g)} + 5O_{2(g)}$
$K = 1.2 \times 10^{34}$ mol^5 L^{-5}

(4) $2N_2O_{(g)} \rightleftharpoons 2N_{2(g)} + O_{2(g)}$
$K = 3.5 \times 10^{33}$ mol L^{-1}

24. The equilibrium constant in a reversible reaction at a given temperature:-
(1) Depends on initial concentration of the reactants.
(2) Depends on the concentration of the products at equilibrium.
(3) Does not depend on the initial concentrations.
(4) It is not characteristic of the reaction.

25. Which one of the following statements is correct about equilibrium constant:-
(1) Equilibrium constant of a reaction changes with temperature.
(2) Equilibrium constant of a reaction depends upon the concentration of reactants with which we start.
(3) Equilibrium constant of a reaction, $3Fe(s) + 4H_2O_{(g)} \rightleftharpoons Fe_3O_4(s) + 4H_{2(g)}$ is same whether, the reaction is carried out in an open vessel or a closed vessel.
(4) Equilibrium constant of a reaction becomes double if the reaction is multiplied by 2 throughout.

26. For a reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the value of K_C does not depends upon :-
(a) Initial concentration of the reactants
(b) Pressure
(c) Temperature
(d) Catalyst
(1) Only c (2) a, b, c
(3) a, b, d (4) a, b, c, d

27. For any reversible reaction if concentration of reactants increases then effect on equilibrium constant :-
(1) Depends on amount of concentration
(2) Unchange
(3) Decrease
(4) Increase

28. Effect of increasing temperature on equilibrium constant is given by $\log K_2 - \log K_1 = \frac{-\Delta H}{2.303R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$. Then for an endothermic reaction the false statement is:-
(1) $\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$ = positive (2) $\log K_2 > \log K_1$
(3) ΔH = positive (4) $K_2 > K_1$

29. The equilibrium constant for the reaction $Br_2 \rightleftharpoons 2Br$ at 500 K and 700 K are 1×10^{-10} and 1×10^{-5} respectively. The reaction is:-
(1) Endothermic
(2) Exothermic
(3) Fast
(4) Slow

30. In an experiment the equilibrium constant for the reaction $A + B \rightleftharpoons C + D$ is K when the initial concentration of A and B each is 0.1 mol L^{-1} Under the similar conditions in an another experiment if the initial concentration of A and B are taken 2 and 3 mol L^{-1} respectively then the value of equilibrium constant will be:-
(1) $\frac{K}{2}$ (2) K
(3) K^2 (4) $\frac{1}{K}$

31. In system $A(s) \rightleftharpoons 2B(g) + 3C(g)$ at equilibrium if concentration of 'C' is doubled then concentration of B at equilibrium.
(1) Double its original concentration
(2) Half its original concentration
(3) $2\sqrt{2}$ its original concentration
(4) $\frac{1}{2\sqrt{2}}$ its original concentration

32. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ equilibrium constant, K_P changes with :-
(1) Temperature
(2) Total pressure
(3) Catalyst
(4) Amount of H_2 and I_2 present

33. The equilibrium constant (K_P) for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 16. If the volume of the container is reduced to one-half its original volume, the value of K_P for the reaction at the same temperature will be :-
(1) 32 (2) 64 (3) 16 (4) 4

34. The equilbrium constant for the reaction : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at 2000 K is 4×10^4. In presence of catalyst the equilibrium is established ten times faster at the same temperature. What is the value of equilibrium constant in presence of catalyst :-
(1) 40×10^{-4} (2) 4×10^{-4}
(3) 4×10^4 (4) None

35. The equilibrium constant of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 64. If the volume of the container is reduced to one fourth of its original volume, the value of the equilibrium constant will be
(1) 16 (2) 32
(3) 64 (4) 128

36. If some He gas is introduced into the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ at constant pressure and temperature then equilibrium constant of reaction :
(1) Increase
(2) Decrease
(3) Unchange
(4) Nothing can be said

37.

List X	**List Y**
(A) Active mass	(I) $\Delta n = 0$
(B) Dynamic nature	(II) Molar concentration
(C) A + heat $\rightleftharpoons$ B	(III) Vant hoff's equation
(D) $\log (K_{p_2}/K_{p_1}) = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$	(IV) adaptation if temperature increases
(E) $2A(g)+B(g) \rightleftharpoons 3C(g)$	(v) Chemical equilibrium

Correct match list X and Y
(1) A - (V), B - (II), C - (III), D - (I), E - (IV)
(2) A - (V), B - (IV), C - (III), D - (II), E - (I)
(3) A - (II), B - (V), C - (IV), D - (III), E - (I)
(4) None of these

DEGREE OF DISSOCIATION AND APPLICATION OF LAW OF MASS ACTION

38. For the reaction : $P \rightleftharpoons Q + R$. Initially 2 mol of P was taken. Up to equilibrium 0.5 mol of P was dissociated. What would be the degree of dissociation :-
(1) 0.5 (2) 1 (3) 0.25 (4) 4.2

39. The dissociation of CO_2 can be expressed as $2CO_2 \rightleftharpoons 2CO + O_2$. If the 2 mol of CO_2 is taken initially and 40% of the CO_2 is dissociated completely. What is the total number of moles at equilibrium:-
(1) 2.4 (2) 2.0 (3) 1.2 (4) 5

40. In $A_3(g) \rightleftharpoons 3A(g)$ reaction, the initial concentration of A_3 is "a" mol L^{-1} If x is degree of dissociation of A_3. The total number of moles at equilibrium will be:-
(1) $a - \frac{ax}{3}$ (2) $\frac{a}{3} - x$
(3) $\left(\frac{a-ax}{2}\right)$ (4) a + 2 ax

41. In the reaction $2P(g) + Q(g) \rightleftharpoons 3R(g) + S(g)$. If 2 mol each of P and Q taken initially in a 1 L flask. At equilibrium which is true:-
(1) [P] < [Q] (2) [P] = [Q]
(3) [Q] = [R] (4) None of these

42. In a 13 L vessel initially following reaction occur $C(s) + S_2(g) \rightleftharpoons CS_2(g)$ by 12 g C, 64 g S_2, 76 g CS_2 at 1027°C temperature then total pressure is.
(1) 200R (2) 158R (3) 100R (4) 79R

43. The reaction $A + B \rightleftharpoons C + D$ is studied in a one litre Vessel at 250°C. The initial concentration of A was 3n and of B was n. After equilibrium was attained then equilibrium concentration of C was found to be equal to equilibrium concentration of B. What is the concentration of D at equilibrium :-
(1) $\frac{n}{2}$ (2) $\left(3n-\frac{n}{2}\right)$
(3) $\left(n+\frac{n}{2}\right)$ (4) n

44. $X_2 + Y_2 \rightleftharpoons 2XY$ reaction was studied at a certain temperature. In the beginning 1 mole of X_2 was taken in a one litre flask and 2 moles of Y_2 was taken in another 2 litre flask. What is the equilibrium concentration of X_2 and Y_2 ? (Given equilibrium concentration of [XY] = 0.6 mol L^{-1}).
(1) $\left(\frac{1}{3}-0.3\right),\left(\frac{2}{3}-0.3\right)$
(2) $\left(\frac{1}{3}-0.6\right),\left(\frac{2}{3}-0.6\right)$
(3) (1 – 0.3), (2 – 0.3)
(4) (1 – 0.6), (2 – 0.6)

45. If the initial pressure of N_2 and H_2 mixture in a closed apparatus is 100 atm. At equilibrium 20% of the mixture reacts then total pressure at the same temperature would be -
(1) 100 (2) 90 (3) 85 (4) 80

46. In a 20 litre vessel initially 1 - 1 mole CO, H_2O, CO_2 is present, then for the equilibrium of $CO + H_2O \rightleftharpoons CO_2 + H_2$ following is true:-
(1) H_2, more then 1 mole
(2) CO, H_2O, H_2 less then 1 mole
(3) CO_2 & H_2O both more than 1 mole
(4) All of these

47. 4 mol of PCl_5 are heated at constant temperature in closed container. If degree of dissociation for PCl_5 is 0.5 then calculate total number of moles at equilibrium
(1) 4.5 (2) 6 (3) 3 (4) 4

48. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
In above reaction, at equilibrium condition mole fraction of PCl_5 is 0.4 and mole fraction of Cl_2 is 0.3. Then find out mole fraction of PCl_3
(1) 0.3 (2) 0.7 (3) 0.4 (4) 0.6

49. If 8 mol of PCl_5 heated in a closed vessel of 10 L capacity and 25% of its dissociates into PCl_3 and Cl_2 at the equilibrium then value of Kp will be equal to:-
(1) P/30 (2) P/15 (3) 2/3P (4) 3/2P

50. In the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ the partial pressure of PCl_3, Cl_2 and PCl_5 are 0.3, 0.2 and 0.6 atm respectively at equilibrium. If partial pressure of PCl_3 and Cl_2 was increased twice, what will be the partial pressure of PCl_5 is in atm at new equilibrium condition :-
(1) 0.3 (2) 1.2 (3) 2.4 (4) 0.15

51. 'a' mol of PCl_5, undergoes, thermal dissociation as: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the mole fraction of PCl_3 at equilibrium is 0.25 and the total pressure is 2.0 atm. The partial pressure of Cl_2 at equilibrium is :-
(1) 2.5 (2) 1.0 (3) 0.5 (4) None

52. In a 0.25 L tube dissociation of 4 mol of NO is take place. If its degree of dissociation is 10%. The value of K_P for reaction $2\,NO \rightleftharpoons N_2 + O_2$ is :-
(1) $\frac{1}{(18)^2}$ (2) $\frac{1}{(8)^2}$ (3) $\frac{1}{16}$ (4) $\frac{1}{32}$

53. In a chemical equilibrium $A + B \rightleftharpoons C + D$ when one mole each of the two reactants are mixed, 0.4 mol each of the products are formed. The equilibrium constant is :-
(1) 1 (2) 0.36 (3) 2.25 (4) $\frac{4}{9}$

54. K_C for the esterification reaction :
$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
is 4. If 4 mol each of acid and alcohol are taken initially, what is the equilibrium concentration of the acid :-
(1) $\frac{2}{3}$ (2) $\frac{4}{3}$ (3) $\frac{3}{4}$ (4) $\frac{3}{2}$

55. Evaluate K_P for the reaction : $H_2 + I_2 \rightleftharpoons 2HI$. If 2 moles each of H_2 and I_2 are taken initially. At equilibrium moles of HI are 2.
(1) 2.5 (2) 4 (3) 0.25 (4) 1.0

56. 4 moles of A are mixed with 4 moles of B, when 2 mol of C are formed at equilibrium, according to the reaction, $A + B \rightleftharpoons C + D$. The equilibrium constant is :-
(1) 4 (2) 1 (3) $\sqrt{2}$ (4) $\sqrt{4}$

57. Two moles of ammonia is introduced in a evacuated 500 mL vessel at high temperature. The decomposition reaction is :
$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
At the equilibrium NH_3 becomes 1 mole then the K would be :-
(1) 0.42 (2) 6.75 (3) 1.7 (4) 1.5

58. 4.5 mol each of hydrogen and iodine heated in a sealed 10 litre vessel. At equilibrium, 3 mol of HI were found. The equilibrium constant for $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is:-
(1) 1 (2) 10
(3) 5 (4) 0.33

59. 1.50 mol each of hydrogen and iodine were placed in a sealed 10 L container maintained at 717 K. At equilibrium 1.25 mol each of hydrogen and iodine were left behind. The equilibrium constant, K_c for the reaction
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 717 K is
(1) 0.4 (2) 0.16
(3) 25 (4) 50

60. AB dissociates as $2AB(g) \rightleftharpoons 2A(g) + B_2(g)$ When the initial pressure of AB is 500 mm, the total pressure becomes 625 mm when the equilibrium is attained. Calculate K_P for the reaction assuming volume remains constant.
(1) 500 (2) 125 (3) 750 (4) 375

LE-CHATLIER'S PRINCIPLE

61. Cis -2- pentene $\rightleftharpoons$ Trans -2- pentene for the above equilibrium the value of standard free energy change at 400 K is –3.67 kJ mol^{-1}. If excess of trans -2- pentene is added to the system then :-
(1) Additional trans -2- pentene will form
(2) Excess of cis -2- pentene will form
(3) Equilibrium will proceed in the forward
(4) Equilibrium will remain unaffected

62. When $NaNO_3$ is heated in a closed vessel, O_2 is liberated and $NaNO_2$ is left behind. At equilibrium –
(1) Addition of $NaNO_3$ favours forward reaction
(2) Addition of $NaNO_2$ favours reverse reaction
(3) Increasing pressure favours reverse reaction.
(4) Decreasing temperature favours forward reaction.

63. The equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ shifts forward if :-
(1) A catalyst is used.
(2) An adsorbent is used to remove SO_3 as soon as it is formed.
(3) Small amounts of reactants are used.
(4) None

64. In manufacture of NO, the reaction of N_2 and O_2 to form NO is favourable if :-
(1) Pressure is increased
(2) Pressure is decreased
(3) Temperature is increased
(4) Temperature is decreased

65. In which of the following equilibrium reactions, the equilibrium would shift to right side, if total pressure is decreased :-
(1) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (2) $H_2 + I_2 \rightleftharpoons 2HI$
(3) $N_2O_4 \rightleftharpoons 2NO_2$ (4) $H_2 + Cl_2 \rightleftharpoons 2HCl$

66. The oxidation of SO_2 by O_2 to SO_3 is exothermic reaction. The yield of SO_2 will be minimum if :-
(1) Temperature is increased and pressure is kept constant
(2) Temperature is reduced and pressure is increased
(3) Both temperature and pressure are increased
(4) Both temperature and pressure are decreased

67. For the manufacture of ammonia by the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3 + 21.9$ k Cal, the favourable conditions are :-
(1) Low temperature, low pressure & catalyst
(2) Low temperature, high pressure & catalyst
(3) High temperature, low pressure & catalyst
(4) High temperature, high pressure & catalyst

68. In the reaction $2A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + 362$ kCal. Which combination of pressure and temperature gives the highest yield of C at equilibrium:-
(1) 1000 atm and 500°C
(2) 500 atm and 500°C
(3) 1000 atm and 50°C
(4) 500 atm and 100°C

69. Does Le chatelier's principle predict a change of equilibrium concentration for the following reaction if the gas mixture is compressed

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
(1) Yes, backward reaction is favoured
(2) Yes, forward reaction is favoured
(3) No change
(4) No information

70. $aA \rightleftharpoons bB + cC$, $\Delta H = -x$ kCal.
If high pressure and low temperature are the favourable condition for the formation of the product in above reaction, hence:-
(1) $a > b + c$ (2) $a < b + c$
(3) $a = b + c$ (4) None of them

71. The reaction in which yield of production cannot be increased by the application of high pressure is :-

(1) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

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

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

(4) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

72. In a vessel containing SO_3, SO_2 and O_2 at equilibrium, some helium gas is introduced so that the total pressure increases while temperature and volume remain constant. According to Le-Chatelier principle, the dissociation of SO_3 ,
(1) Increases
(2) Decreases
(3) Remains unaltered
(4) None of these

PHYSICAL EQUILIBRIUM

73. For the equilibrium reaction, $H_2O(\ell) \rightleftharpoons H_2O_{(g)}$, What happens, if pressure is applied:-
(1) More water evaporates
(2) The boiling point of water is increased
(3) No effect on boiling point
(4) None of the above

74. On cooling of following system at equilibrium $CO_{2(s)} \rightleftharpoons CO_{2(g)}$:-
(1) There is no effect on the equilibrium state
(2) More gas is formed
(3) More gas is solidifies
(4) None of above

CALCULATION OF DEGREE OF DISSOCIATION BY V.D. METHOD

75. Vapour density of PCl_5 is 104.25 at t°C. Then degree of dissociation of PCl_5 is. (Mw = 208.5)
(1) 20% (2) 0% (3) 30% (4) 15%

76. When heating PCl_5 then it decompose PCl_3 and Cl_2 in form of gas, The vapour density of gas mixture is 70.2 and 57.9 at 200° C and 250°C. The degree of dissociation of PCl_5 at 200°C and 250°C is
(1) 48.50% & 80% (2) 60% & 70%
(3) 70% & 80% (4) 80% & 90%

77. Vapour density of PCl_5 is 104.16 but when heated to 230°C its vapour density is reduced to 62. The degree of dissociation of PCl_5 at this temperature will be :
(1) 6.8% (2) 68% (3) 46% (4) 64%

78. The equation $\alpha = \frac{D-d}{(n-1)d}$ is correctly matched for

Where D = Theoretical vapour density
d = Observed vapour density

(1) $A \rightleftharpoons \frac{nB}{2} + \frac{nC}{3}$

(2) $A \rightleftharpoons \frac{nB}{3} + \left(\frac{2n}{3}\right)C$

(3) $A \rightleftharpoons \left(\frac{n}{2}\right)B + \left(\frac{n}{4}\right)C$

(4) $A \rightleftharpoons \left(\frac{n}{2}\right)B + C$

EXERCISE-I (Conceptual Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**3**	**4**	**4**	**4**	**2**	**4**	**1**	**3**	**2**	**3**	**3**	**1**	**2**	**4**	**4**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**3**	**4**	**2**	**2**	**1**	**4**	4	**1**	**3**	**1**	**3**	**2**	**1**	**1**	**2**
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	**4**	**1**	**3**	**3**	**3**	**3**	**3**	**3**	**1**	**4**	**1**	**1**	**1**	**1**	**2**
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	**2**	**2**	**1**	**2**	**3**	**3**	**1**	**4**	**2**	**2**	**2**	**2**	**1**	**2**	**2**
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	**2**	**3**	**2**	**3**	**3**	**2**	**2**	**3**	**1**	**1**	**2**	**3**	**2**	**3**	**2**
Que.	76	77	78												
Ans.	**1**	**2**	**2**												

EXERCISE-II (Previous Year Questions) AIPMT/NEET & AIIMS (2006-2018)

AIPMT 2006

1. For the reaction :

$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

$\Delta_rH = -170.8$ kJ mol^{-1}

Which of the following statements is not true:-

(1) At equilibrium, the concentrations of $CO_2(g)$ and $H_2O(l)$ are not equal

(2) The equilibrium constant for the reaction is given by $K_P = \frac{[CO_2]}{[CH_4][O_2]}$

(3) Addition of $CH_4(g)$ or $O_2(g)$ at equilibrium will cause a shift to the right

(4) The reaction is exothermic

AIPMT 2007

2. 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 :

(1) $\frac{K_1K_2}{K_3}$ (2) $\frac{K_1K_3^2}{K_2}$

(3) $\frac{K_2K_3^3}{K_1}$ (4) $K_1K_2K_3$

AIPMT 2008

3. The dissociation equilibrium of a gas AB_2 can be represented as : $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ The degree of dissociation is 'x' and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure P is :

(1) $(2K_p/P)^{1/3}$ (2) $(2K_p/P)^{1/2}$

(3) (K_p/P) (4) $(2K_p/P)$

4. The value of equilibrium constant of the reaction

$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2$ is 8.0

The equilibrium constant of the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ will be :

(1) $\frac{1}{64}$ (2) 16 (3) $\frac{1}{8}$ (4) $\frac{1}{16}$

5. The values of K_{P_1} and K_{P_2} for the reactions

$X \rightleftharpoons Y + Z$ ---------- (1) and

$A \rightleftharpoons 2B$ ---------- (2)

are in ratio of 9:1. If degree of dissociation of X and A be equal, then total pressure at equilibrium (1) and (2) are in the ratio :

(1) 1:9 (2) 36:1 (3) 1:1 (4) 3 :1

6. If the concentration of OH^- ions in the reaction $Fe(OH)_3(s) \rightleftharpoons Fe^{+3}(aq.) + 3OH^-(aq.)$ is decreased upto $\frac{1}{4}$ times, then equilibrium concentration of Fe^{+3} will increase upto:

(1) 16 times (2) 64 times

(3) 4 times (4) 8 times

AIPMT-Pre 2010

7. The reaction :

$2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$

is start with the concentrations of A and B both at an initial value of 1.00 M. When equilibrium is reached, the concentration of D is measured and found to be 0.25 M. The value for the equilibrium constant for this reaction is given by the expression.

(1) $[(0.75)^3\ (0.25)] \div [(0.50)^2\ (0.75)]$

(2) $[(0.75)^3\ (0.25)] \div [(0.50)^2\ (0.25)]$

(3) $[(0.75)^3\ (0.25)] \div [(0.75)^2\ (0.25)]$

(4) $[(0.75)^3\ (0.25)] \div [(1.00)^2\ (1.00)]$

AIPMT-Mains 2010

8. In which of the following equilibrium K_c and K_p are not equal ?

(1) $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

(2) $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$

(3) $SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$

(4) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

AIIMS 2010

9. Two moles of gas A_2 are mixed with two moles of gas B_2 in a flask of volume 1 lit. If at equilibrium 0.5 moles of A_2 are obtained. Then find out K_p for reaction

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

(1) 12 (2) 9
(3) 4 (4) 36

AIPMT-Pre 2011

10. For the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the equilibrium constant is K_1. The equilibrium constant is K_2 for the reaction $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$.

What is K for the reaction $NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$?

(1) $1/(2K_1K_2)$ (2) $1/(4K_1K_2)$
(3) $[1/K_1K_2]^{1/2}$ (4) $1/(K_1K_2)$

AIIMS 2011

11. Which of the following is not a characteristics of equilibrium:
(1) Rate is equal in both direction
(2) Measurable quantities are constant at equilibrium
(3) Equilibrium occurs in reversible condition
(4) Equilibrium occurs only in open vessel at constant temperature

AIPMT-Mains 2012

12. Given that the equilibrium constant for the reaction

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

has a value of 278 at a particular temperature. What is the value of the equilibrium constant for the following reaction at the same temperature ?

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$$

(1) 6.0×10^{-2} (2) 1.3×10^{-5}
(3) 1.8×10^{-3} (4) 3.6×10^{-3}

13. Given the reaction between 2 gases represented by A_2 and B_2 to give the compound AB(g).
$A_{2(g)} + B_{2(g)} = 2AB_{(g)}$.
At equilibrium, the concentration
of $A_2 = 3.0 \times 10^{-3}$ M
of $B_2 = 4.2 \times 10^{-3}$ M
of AB = 2.8×10^{-3} M
If the reaction takes place in a sealed vessel at 527°C, then the value of K_C will be :-
(1) 0.62 (2) 4.5
(3) 2.0 (4) 1.9

AIIMS 2012

14. $\frac{K_P}{K_C}$ for following reaction will be :-

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$

(1) RT (2) $\frac{1}{RT}$ (3) $\frac{1}{\sqrt{RT}}$ (4) $\frac{RT}{2}$

15. At 60° C initial pressure 1 atm of N_2O_4 is 50% dissociated into NO_2 then Kp is :-
(1) 1.33 atm (2) 2 atm
(3) 2.67 atm (4) 3 atm

AIPMT 2014

16. For the reversible reaction :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$$

The equilibrium shifts in forward direction :
(1) By increasing the concentration of $NH_3(g)$
(2) By decreasing the pressure
(3) By decreasing the concentrations of $N_2(g)$ and $H_2(g)$
(4) By increasing pressure and decreasing temperature

17. For a given exothermic reaction, K_p and K'_P are the equilibrium constants at temperatures T_1 and T_2, respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2, it is readily observed that :-
(1) $K_p > K'_P$ (2) $K_p < K'_P$
(3) $K_p = K'_P$ (4) $K_p = \frac{1}{K'_P}$

AIIMS 2014

18. For a reaction $\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI$;
Equilibrium constant is K.
Then what will be equilibrium constant for $2HI \rightleftharpoons H_2 + I_2$ will be :-

(1) $\frac{1}{K^2}$ (2) $\frac{1}{\sqrt{K}}$ (3) K (4) 2K

AIPMT-2015

19. If the value of an equilibrium constant for a particular reaction is 1.6×10^{12}, then at equilibrium the system will contain :-
(1) mostly reactants
(2) mostly products
(3) similar amounts of reactants and products
(4) all reactants

Re-AIPMT-2015

20. If the equilibrium constant for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is K, the equilibrium constant for $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$ will be:-

(1) K (2) K^2 (3) $K^{1/2}$ (4) $\frac{1}{2}K$

AIIMS-2016

21. For a reaction $A_{(g)} \rightleftharpoons B_{(g)}$ if initial pressure at 300°C is 1 atm and its K_p is 4, Then calculate P_B at equilibrium state.

(1) $\frac{1}{5}$atm (2) $\frac{2}{5}$atm (3) $\frac{4}{5}$atm (4) $\frac{3}{5}$atm

NEET(UG) 2017

22. The equilibrium constant of the following are :

$N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1

$N_2 + O_2 \rightleftharpoons 2NO$; K_2

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$; K_3

The equilibrium constant (K) of the reaction :

$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$, will be :

(1) $K_2 K_3^3 / K_1$ (2) K_2K_3/K_1

(3) $K_2^3K_3 / K_1$ (4) $K_1K_3^3 / K_2$

23. 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 : $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$, Kp = 1.6atm)
(1) 10 litre (2) 4 litre
(3) 2 litre (4) 5 litre

AIIMS-2017

24. At a certain temperature and total pressure of 1 atm., Equilibrium mixture contains 20% by volume of A atoms $A_2(g) \rightleftharpoons 2A(g)$. The K_P of reaction is-
(1) 5×10^{-2} (2) 2×10^{-3}
(3) 5×10^{-3} (4) 4×10^{-4}

25. In a reversible reaction $A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$. Initially 1 mol of each reactant is taken in 2L container if at equilibrium 20% of A reacts with B. Then what will be equilibrium constant K_C for reaction :-
(1) 0.225 (2) 0.412
(3) 0.625 (4) 0.925

NEET(UG) 2018

26. Which one of the following conditions will favour maximum formation of the product in the reaction, $A_2(g) + B_2(g) \rightleftharpoons X_2(g)$ $\Delta_rH = -X$ kJ ?
(1) Low temperature and high pressure
(2) Low temperature and low pressure
(3) High temperature and high pressure
(4) High temperature and low pressure

AIIMS-2018

27. $2ICl_{(g)} \rightleftharpoons I_{2(g)} + Cl_{2(g)}$

Equilibrium constant K_C for given reaction is 0.14 If initally 0.6M ICl was taken then what will equilibrium concentration of I_2 is :-
(1) 0.1275 M (2) 0.3250 M
(3) 0.35 M (4) 0.2550 M

28. At constant temprature on increasing pressure which is correct :-
(1) Solid $\rightleftharpoons$ Liquid more liquid formed
(2) Formation of ammonia from N_2 and H_2 decreases
(3) $CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)}$
reaction will shifted in forward direction
(4) Solubility of gas in liquid increases

29. For reaction

$A + 2B \rightleftharpoons 2C$

Initially 2 mole of A and B are taken in 10 lit flask at equilibrium 1 mole of C is formed then calculate K_C for given reaction :-

(1) 6.66 (2) 3.33 (3) 2.22 (4) 1.11

30. At constant temprature in a closed container $CaCO_3$ was decomposed as per following reaction

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

Which of the following will give change in pressure?

(1) Size of container

(2) Temprature

(3) Addition of $CaO_{(s)}$

(4) Amount of $CaCO_{3(s)}$

EXERCISE-II (Previous Year Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**2**	**3**	**1**	**1**	**2**	**2**	**1**	**1**	**4**	**3**	**4**	**1**	**1**	**3**	**2**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**4**	**1**	**1**	**2**	**3**	**3**	**1**	**4**	**1**	**3**	**1**	**1**	**4**	**1**	**2**

EXERCISE-III (Analytical Questions) — Check Your Understanding

1. For which of the following reaction the degree of dissociation (α) and equilibrium constant (K_p) are related as $K_p = \frac{4\alpha^2 P}{(1-\alpha^2)}$:-

(1) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

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

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

(4) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

2. Pure ammonia is placed in a vessel at a temperature where its dissociation constant is appreciable. At equilibrium:-

(1) K_p does not change significantly with pressure
(2) Degree of dissociation does not change with pressure
(3) concentration of NH_3 does not change with pressure
(4) concentration of H_2 is less than that of N_2

3. For the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the degree of dissociation varies inversely as the square root of pressure of the system. Supposing at constant temperature If the volume is increased 16 times the intial volume, the degree of dissociation for this reaction will becomes

(1) 4 times (2) $\frac{1}{4}$ times

(3) 2 times (4) $\frac{1}{2}$ times

4. A reaction in equilibrium is represented by the following equation –

$2A_{(s)} + 3B_{(g)} \rightleftharpoons 3C_{(g)} + D(g) + Q$ if the pressure on the system is reduced to half of its original value:-
(1) The amounts of C and D decreases
(2) The amounts of C and D increases
(3) The amount of D decreases
(4) All the amounts remain constant

5. Two systems $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ and $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ are simultaneously in equilibrium in a vessel at constant volume. If some CO(g) is introduced in the vessel at constant volume, then at new equilibrium the concentration of :
(1) PCl_5 is increases
(2) PCl_3 remains unchanged
(3) PCl_5 is decreases
(4) Cl_2 is increases

6. The effect of adding krypton (Kr) gas on position of equilibrium, keeping the volume of the system constant is :-
(1) If $\Delta n = 0$, backward reaction is favoured.
(2) If Δn = +ve, forward reaction is favoured
(3) If Δn = -ve , forward reaction is favoured
(4) No effect whatever be the value of Δn

7. Match list –I (equilibrium) with List –II (conditions for reaction) and select the correct answer using the codes given below the lists :-

List–I (Equilibrium)	List–II (Conditions)
P. $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ Endothermic	1.High temperature
Q. $2AB_2(g)+B_2(g) \rightleftharpoons 2AB_3(g)$ Exothermic	2. Low temperature
R. $2AB_3(g) \rightleftharpoons A_2(g) + 3B_2(g)$ Endothermic	3. High pressure 4. Low pressure 5. Independent of pressure

CODE :

	P	Q	R
(1)	1 & 3	2 & 3	2 & 4
(2)	2 &3	1 & 4	1 & 3
(3)	1 & 5	2 & 3	1 & 4
(4)	2 & 4	1 & 5	1 & 3

8. $aA + bB \rightleftharpoons cC + dD$

in above reaction low pressure and high temperature, conditions shift equilibrium in backward direction so correct set is :–
(1) $(a + b) > (c + d)$, $\Delta H > 0$
(2) $(a + b) < (c + d)$, $\Delta H > 0$
(3) $(a + b) < (c + d)$, $\Delta H < 0$
(4) $(a + b) > (c + d)$, $\Delta H < 0$

9. For reaction $aA \rightleftharpoons \ell L + mM$. In condition of suddenly volume increase, degree of dissociation decreases it represents that.
(1) $a < (\ell + m)$
(2) $a = (\ell + m)$
(3) $a = (\ell - m)$
(4) $a > (\ell + m)$

10. For the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ 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 volume of the container
(e) Introducing PCl_5 at constant volume
(1) a, b, c (2) b, c, d
(3) c, d, e (4) a, c, d, e

11. Following equilibrium is present in a closed container at the temperature of 25° C.

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

When Cl_2 is added to the equlibrium mixture, the following statements will be correct for the system.
(a) Concentrations of SO_2, Cl_2 and SO_2Cl_2 change.
(b) Cl_2 is formed in more amount.
(c) Concentration of SO_2 decreases and that of SO_2Cl_2 increases.
(1) a, c (2) a, b
(3) b, c (4) a, b, c

12. A reaction mixture containing H_2, N_2 and NH_3 has partial pressures 2 atm, 1 atm and 3 atm respectively at 725K. If the value of K_P for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 4.28×10^{-5} atm^{-2} at 725K, in which direction the net reaction will go
(1) Forward
(2) Backward
(3) No net reaction
(4) Direction of reaction cannot be predicted

13. For reaction $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, K_C at 427°C is 3×10^{-6} L^{-1} mol. The value of K_P is nearly :–
(1) 7.50×10^{-5} (2) 2.50×10^{-5}
(3) 2.50×10^{-4} (4) 1.75×10^{-4}

14. Equilibrium constants K_1 and K_2 for the following equilibrium :

$NO(g) + \frac{1}{2}O_2(g) \overset{K_1}{\rightleftharpoons} NO_2(g)$ and

$2NO_2(g) \overset{K_2}{\rightleftharpoons} 2NO(g) + O_2(g)$

are related as :-
(1) $K_2 = \frac{1}{K_1}$ (2) $K_2 = \frac{K_1}{2}$
(3) $K_2 = \frac{1}{K_1^2}$ (4) $K_2 = K_1^2$

15. 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 atmospheres. The corresponding value of K_C, with concentration in mol L^{-1} is:-
(1) $1.44 \times 10^{-5} / (0.082 \times 500)^{-2}$
(2) $1.44 \times 10^{-5} / (8.314 \times 773)^{-2}$
(3) $1.44 \times 10^{-5} / (0.082 \times 773)^{2}$
(4) $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$

16. For the reaction, $A + B \rightleftharpoons C + D$, $K_c = 9$. If A and B are taken 1 mole each, then amount of C at equilibrium is :-
(1) 1
(2) 0.25
(3) 0.75
(4) None of these

17. In which reaction equilibrium moves in left hand side when pressure is increased :-

(1) $H_2 + Cl_2 \rightleftharpoons 2HCl$

(2) $2Mg(s) + O_2(g) \rightleftharpoons 2MgO(s)$

(3) $2H_2O \rightleftharpoons 2H_2 + O_2$

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

18. $K_p \rightarrow 10^{-2}$ 10^{-3}
Temperature $\rightarrow$ 400K 450K
What would you consider by above information :-
(1) Equilibrium constant increases with increase in concentration
(2) more molecules form on left hand side
(3) Energy is released
(4) None

19. For the reaction $N_2 + O_2 \rightleftharpoons 2NO$, K_C is 100

then K_C for reaction $2NO \rightleftharpoons N_2 + O_2$ will be :-
(1) 0.01 (2) 0.1
(3) 10 (4) 100

20. 3.1 mol of $FeCl_3$ and 3.2 mol of NH_4SCN are added to one litre of water. At equilibrium 3.0 mol of $FeSCN^{2+}$ are formed. The equilibrium constant K_C of the reacion $Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$ will be
(1) 6.66×10^{-3} (2) 0.30
(3) 3.30 (4) 150

21. One mole of N_2O_4 in a 1 L flask decomposes to attain the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
At the equilibrium the mole fraction of NO_2 is 1/2. Hence K_C will be :
(1) 1/3 (2) 1/2
(3) 2/3 (4) 1

22. In reversible chemical reaction equilibrium will be establish when –
(1) Reactant completely converted into product
(2) Rate of forward and backward reaction is equal
(3) Minimum yield of product
(4) concentration of reactant and product is equal

23. In the manufacture of NH_3 by Haber's process which condition give maximum yield–
(1) High temperature, High pressure and high concentration of reactants
(2) High temperature, low pressure and low concentration of reactants
(3) Low temperature, high pressure and high concentration of reactants
(4) Low temperature, low pressure and low concentration of reactants

24. Increase in temperature in a reversible equilibrium reaction favours –
(1) Forward reaction only
(2) Backward reaction only
(3) Either forward or backward reaction
(4) Neither forward nor backward reaction

25. For which of the following reaction $K_P=K_C$ –
(1) $H_2 + I_2 \rightleftharpoons 2HI$
(2) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(3) $2NH_3 \rightleftharpoons 3H_2 + N_2$
(4) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

26. K for the synthesis of HI is 50. What is K for its dissociation
(1) 50 (2) 5
(3) 0.2 (4) 0.02

27. Which of the following is in favour of forward reaction
(1) Q = Kc (2) Q > Kc
(3) Q < Kc (4) None

28. At equilibrium 500mL vessel contains 1·5 M of each A, B, C, D. If 0·5M of C and D expelled out than what would be the K_C :–
$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$
(1) 1 (2) $\frac{1}{9}$
(3) $\frac{4}{9}$ (4) $\frac{5}{9}$

29. If K_C is 41 for, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ then for $NH_3 \rightleftharpoons \frac{1}{2} N_2 + \frac{3}{2} H_2$ K_C will be :–
(1) 41 (2) $\sqrt{41}$
(3) 20·5 (4) $\sqrt{\frac{1}{41}}$

30. For which of the following reaction value of K_P and K_C is equal :–
(1) $2NOCl \rightleftharpoons 2NO + Cl_2$
(2) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(3) $H_2 + Cl_2 \rightleftharpoons 2HCl$
(4) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

31. In a reaction, equilibrium proceeds towards reactants then K will be :-
(1) K > > 1 (2) K < < 1
(3) K = 0 (4) K = 1

32. For following reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ value of K_C depends on
(1) Initial concentration of reactant
(2) Pressure
(3) Temperature
(4) All of these

33. $N_2 + O_2 \rightleftharpoons 2NO$ – Heat
reaction shift in right hand direction on :-
(1) On decreasing pressure
(2) On increasing pressure
(3) On decreasing temperature
(4) On increasing temperature

34. If K_p for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is 0.66 then what is the equilibrium pressure of N_2O_4. (Total pressure at equilibrium is 0.5 atm)
(1) 0.168 (2) 0.322 (3) 0.1 (4) 0.5

35. For the reaction $2HBr \rightleftharpoons H_2 + Br_2$ which relation is true :-

(1) $2K_p = K_C$ (2) $\frac{1}{K_p} = K_C$

(3) $K_p = K_C$ (4) None of these

36. For the process $A(g) \rightleftharpoons 2B(g)$. If pressure is doubled then which is true information about A:-
(1) Increase in A
(2) Decrease in A
(3) No effect
(4) can't say because data is insufficient

37. For the reaction $2A + 3B \rightleftharpoons 2C$ the expression for K_C is :

(1) $\frac{[A]^2[B]^3}{[C]^2}$ (2) $\frac{[C]}{[A][B]}$

(3) $\frac{[C]^2}{[A]^2[B]^3}$ (4) $\frac{[C]^2}{[A]^3[B]^2}$

38. For the equation $2A + B \rightleftharpoons BA_2$, the equilibrium concentration of A, B, BA_2 is 4, 2 and 2 respectively. The value of K_c will be :-
(1) 0.0625 (2) 0.625 (3) 6.280 (4) 6.250

39. 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 the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :-
(1) 0.3 atm (2) 0.18 atm
(3) 1.8 atm (4) 3 atm

40. The equilibrium constant (K_C) for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_C for the reaction. $NO(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g)$ at the same temperature is :-
(1) 50.0 (2) 0.02
(3) 2.5×10^2 (4) 4×10^{-4}

41. For the reaction $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$, if $K_p = K_C(RT)^x$ where the symbols have usual meaning then the value of x is (assuming ideality)

(1) $\frac{1}{2}$ (2) 1

(3) –1 (4) $-\frac{1}{2}$

42. If the amount of dissociation is $\sqrt{0.5}$, the value of K_p for the reaction $N_2O_3 \rightleftharpoons NO + NO_2$ will be
(1) equal to the pressure of the system.

(2) $\frac{2}{8}$ of the pressure of the system.

(3) $\frac{8}{3}$ of the pressure of the system.

(4) 5 times of the pressure of the system.

43. How many moles per litre of PCl_5 has to be taken to obtain 0.1 mol of Cl_2, if the value of equilibrium constant K_c is 0.04 ?
(1) 0.15 (2) 0.25
(3) 0.35 (4) 0.05

44. For the reaction, $N_2O_3 \rightleftharpoons NO + NO_2$, the value of equilibrium constant K_p at fixed temperature is 4. What will be the amount of dissociation at same temperature and 5 atmospheric pressure ?

(1) $\frac{1}{3}$ (2) $\frac{2}{3}$

(3) $\frac{7}{9}$ (4) $\frac{2}{4}$

45. One mole of PCl_5 is heated in a closed container of one litre capacity. At equilibrium, 20% PCl_5 is not dissociated. What should be the value of K_c ?
(1) $(3.2)^{-1}$ (2) 3.2
(3) 2.4 (4) 42

46. For $N_2O_3 \rightleftharpoons NO + NO_2$, if total pressure is P atm and amount of dissociation is 50%, the value of K_p will be

(1) 3 P (2) 2 P

(3) $\frac{P}{3}$ (4) $\frac{P}{2}$

47. If 2/9 of 1 mol of HI is dissociates, the equlibrium constant of disintegration of acid at same temperature will be

(1) 64 (2) $\frac{1}{64}$

(3) 49 (4) $\frac{1}{49}$

48. 1.1 mol of A mixed with 2.2 mol of B and the mixture is kept in a 1 L flask and the equilibrium,

$A + 2B \rightleftharpoons 2C + D$ is reached. If at equilibrium 0.2 mol of C is formed then the value of K_C will be.

(1) 0.1 (2) 0.01
(3) 0.001 (4) 0.0001

49. If 0.5 mol of H_2 is reacted with 0.5 mol of I_2 in a 10 L container at 444 °C and at same temperature value of equilibrium constant K_c is 49, the ratio of [HI] and [I_2] will be :-

(1) 7 (2) $\frac{1}{7}$

(3) $\sqrt{\frac{1}{7}}$ (4) 49

EXERCISE-III (Analytical Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**1**	**1**	**1**	**2**	**3**	**4**	**3**	**4**	**4**	**3**	**1**	**2**	**4**	**3**	**4**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**3**	**3**	**3**	**1**	**4**	**3**	**2**	**3**	**3**	**1**	**4**	**3**	**1**	**4**	**3**
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	**2**	**3**	**4**	**1**	**3**	**1**	**3**	**1**	**3**	**1**	**4**	**1**	**3**	**2**	**2**
Que.	46	47	48	49											
Ans.	**3**	**4**	**3**	**1**											

EXERCISE-IV (Assertion & Reason) — Target AIIMS

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.

(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.

(C) If Assertion is True but the Reason is False.

(D) If both Assertion & Reason are false.

1. **Assertion :-** There is no effect on equilibrium constant if inert gas is added to the reaction

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

Reason :- Equilibrium constant changes only with temperature.

(1) A (2) B (3) C (4) D

2. ***Assertion :–*** For the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $K_p = K_c$.

Reason :– K_p of all gaseous reactions is equal to K_c.

(1) A (2) B (3) C (4) D

3. ***Assertion :–*** $K_P = K_C$ for all reactions.

Reason :– At constant temperature, the pressure of the gas is proportional to the concentration.

(1) A (2) B (3) C (4) D

4. ***Assertion :–*** The value of K increases when concentration of the reactants are increased.

Reason :– With increases of concentration of reactants the equilibrium shifts in forward direction.

(1) A (2) B (3) C (4) D

5. ***Assertion :–*** The effect of temperature on equilibrium constant is given by vant Hoff's equation.

Reason :– vant Hoff's equation is

$$\log\frac{K_1}{K_2} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

(1) A (2) B (3) C (4) D

6. ***Assertion :–*** Effect of temperature on K_C or K_P depends on enthalpy change.

Reason :– Increase in temperature shifts the equilibrium in exothermic direction and decrease in temperature shifts the equilibrium position in endothermic direction.

(1) A (2) B (3) C (4) D

7. ***Assertion :–*** On opening a sealed soda bottle dissolved carbon dioxide gas escapes.

Reason :– Gas escapes to reach the new equilibrium condition of lower pressure.

(1) A (2) B (3) C (4) D

8. ***Assertion :–*** Solubility of a gas in liquids increases with increase in pressure of the gas in equilibrium with solution.

Reason :– The dissolution of a gas in liquids is an exothermic process.

(1) A (2) B (3) C (4) D

9. ***Assertion :–*** Solubility of a gas in water decreases with increase in temperature.

Reason :– Dissolution of a gas in water is an exothermic process.

(1) A (2) B (3) C (4) D

10. ***Assertion :-*** Catalyst affects the final state of the equilibrium.

Reason :- It enables the system to attain a new equilibrium state by complexing with the reagents.

(1) A (2) B (3) C (4) D

11. ***Assertion :-*** For the reaction $A \rightleftharpoons B + C + x\,kCal$ at equilibrium state [A] = [B] = [C] = 3×10^{-4} M and equilibrium constant is 3×10^{-4}.

Reason :- Given reaction is exothermic.

(1) A (2) B (3) C (4) D

12. ***Assertion :-*** For a reaction $A_{(g)} + B_{(g)} \rightleftarrows AB_{(g)}$ if inert gas is added in a container at constant volume. The equilibrium shifts to left side.

Reason :- Because partial pressure of A, B and AB decreases.

(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason) — ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12
Ans.	1	3	4	4	3	3	1	2	1	4	2	4