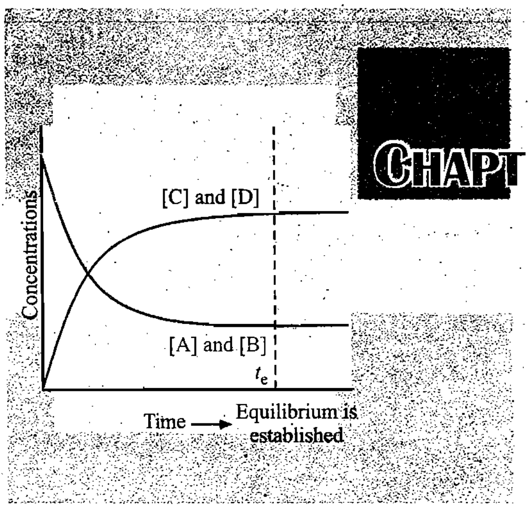


CHAPTER 9

CHEMICAL EQUILIBRIUM

9.1 INTRODUCTION

It is a well established fact that many reactions do not go to completion. They proceed to some extent leaving considerable amounts of unreacted reactants, *i.e.*, the resulting mixture contains both reactants and products. When such a stage is reached in a course of reaction that no further reaction is apparent, it is said in chemical language that the reaction has attained the state of equilibrium where the composition of the system becomes fixed. At equilibrium state both the forward and backward reactions move with equal speeds, *i.e.*, the rate of disappearance of reactants is exactly equal to rate of the appearance of reactants from the products. The study of chemical equilibrium helps in the elucidation of the optimum conditions for the greater yields of the products in the case of those reactions which attain equilibrium in the course of reaction.

Chemical reactions can be classified as **irreversible** and **reversible** reactions.

Irreversible reactions: The chemical reactions which proceed in such a way that reactants are completely converted into products, *i.e.*, the reactions which move in one direction, *i.e.*, forward direction only are called **irreversible reactions.** In such reactions, products do not react together to produce reactants again, *i.e.*, the reaction does not move in backward direction. For example, when solutions containing equimolar concentrations of barium chloride and sodium sulphate are mixed, reaction occurs and practically whole of barium is precipitated as barium sulphate.

$$BaCl_2 + Na_2SO_4 \longrightarrow \underset{\text{ppt.}}{BaSO_4} + 2NaCl$$

The reaction between $BaSO_4$ and NaCl, *i.e.*, backward reaction, is not possible under the experimental conditions. In such reactions the arrow (→) is placed between reactants and products which indicates the direction of the chemical change. Some more examples of irreversible reactions are given below:

1. (a) Thermal decomposition of potassium chlorate,

$$2KClO_3 \xrightarrow[\text{Heat}]{MnO_2} 2KCl + 3O_2$$

(b) Decomposition of ammonium nitrite,

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

2. Precipitation reactions,

(a) $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

(b) $Pb(NO_3)_2 + 2KI \longrightarrow PbI_2 + 2KNO_3$

3. Neutralisation reactions,

$$\underset{\text{Strong acid}}{H_2SO_4} + \underset{\text{Strong base}}{2NaOH} \longrightarrow Na_2SO_4 + 2H_2O$$

4. Redox and combustion reactions,

(a) $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$

(b) $2Mg + O_2 \longrightarrow 2MgO$

(c) $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

Reversible reactions: The chemical reactions which take place in both directions under similar conditions are called **reversible reactions.** In such reactions, the products also react with each other and produce reactants again. For example, when hydrogen is passed over heated magnetic oxide, metallic iron and water are produced.

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

On the other hand, if steam is passed over powdered iron at the same temperature, magnetic oxide of iron and hydrogen are formed.

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

If the reaction is carried out in a closed vessel, it is found that in no case the reaction proceeds to completion. It is, thus, clear that either of the two reactions can take place independently if steam or hydrogen is allowed to escape from system by carrying out the reaction in open vessel but if a closed vessel is used and nothing is allowed to escape both forward and backward reactions can take place in the vessel.

Reactions which thus proceed in both the directions and do not reach to completion are known as reversible reactions. The reaction proceeding from left to right is conventionally called the **forward reaction** and the opposite one proceeding from right to left is called the reverse or **backward reaction.** In such reactions the arrow (→) or sign of equality (=) is replaced by two half arrows ($\rightleftharpoons$) pointing the reaction in both the directions. This sign ($\rightleftharpoons$) represents the reversibility of the reaction.

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

Some examples of reversible reactions are given below:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$
$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$
$$2HI \rightleftharpoons H_2 + I_2$$
$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$
$$N_2 + O_2 \rightleftharpoons 2NO$$
$$NH_4HS \rightleftharpoons NH_3 + H_2S$$
$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

9.2 STATE OF 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.

$$A + B \rightleftharpoons C + D$$

In the initial state only A and B are present both react with each other, *i.e.*, rate of forward reaction is maximum as only the concentrations of A and B are involved (at the beginning, the concentrations of products C and D are nil). As soon as the products C and D are produced, the backward reaction starts functioning. By the expiry of time, the rate of forward reaction decreases as the concentrations of A and B decrease while the rate of backward reaction increases as the concentrations of products C and D increase. Ultimately, a stage comes when the rate of forward reaction becomes equal to rate of backward reaction. This state is called the **equilibrium state.**

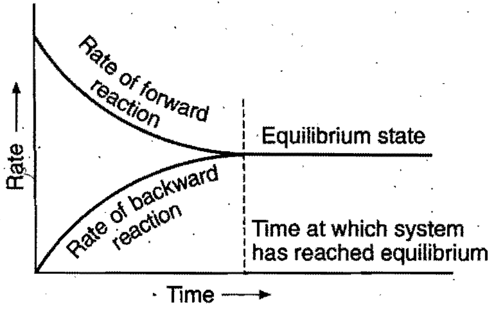


Fig. 9.1

At equilibrium state,

Rate of forward reaction = Rate of backward reaction.

It can be shown graphically as in Fig. 9.1.

Thus, chemical equilibrium in a reversible reaction is the state at which both forward and backward reactions or two opposing reactions occur at the same speed.

This state will continue indefinitely if the conditions such as temperature and concentration are not changed. At the state of equilibrium, the concentrations of reactants and products in the reaction mixture attain a constant value and the concentrations do not change with time.

When hydrogen gas and iodine vapours are heated in a closed vessel at a constant temperature 717 K, the two react to form hydrogen iodide. In the initial stage, the colour of the reaction mixture is deep violet due to the presence of large amounts of iodine. But as the reaction progresses, the intensity of the colour decreases as more and more iodine is converted into hydrogen iodide. After sometime, the intensity of the colour of the reaction mixture becomes constant. The constancy of intensity of colour indicates that concentration of both reactants and products have become constant and state of equilibrium has been attained.

The stage of the reversible reaction at which the concentrations of the reactants and products do not change with time is called the equilibrium state.

Or

The state in which the measurable properties of the system (such as pressure, density, colour or concentration) do not undergo any further noticeable change with time under given set of conditions is said to be a state of equilibrium.

The equilibrium state is **dynamic** and not static in nature. The reaction does not stop but both the opposing reactions are going on continuously with same speeds. At this stage, the 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.

Characteristics of Equilibrium State

(i) Equilibrium state can only be achieved if a reversible reaction is carried out in closed space.

No product can leave nor any reactant from outside can enter the space. If the system is not closed, some of the products may escape and thus, the backward reaction will not occur.

(ii) Chemical equilibrium, at a given temperature, is characterised by constancy of certain properties such as pressure, concentration, density or colour.

(iii) Chemical equilibrium can be attained from either side, *i.e.*, from the side of reactants or products.

$$2HI \rightleftharpoons H_2 + I_2$$

or $$H_2 + I_2 \rightleftharpoons 2HI$$

At equilibrium, each reactant and each product has a fixed concentration and this is independent of the fact whether we start the reaction with the reactants or with the products.

This reaction can be graphically represented as,

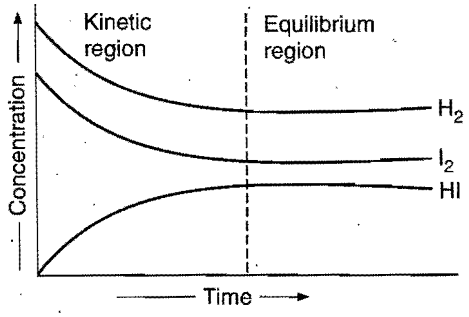


Fig. 9.2

(iv) Equilibrium state can be attained in a lesser time by the use of a positive catalyst, *i.e.*, the relative concentrations of reactants and products remain the same irrespective of the presence or absence of a catalyst. Thus, a catalyst does not change the equilibrium state but it helps in attaining it rapidly.

(v) It is dynamic in nature, *i.e.*, both the reactions move with same speed. However, the reaction seems to have come to stand still because the concentrations of reactants and products do not change.

Reversible chemical reactions are classified into two types heterogeneous and homogeneous reactions.

Heterogeneous reactions: The reversible reaction in which more than one-phase is present.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$
$$2Na_2O_2(s) + 2H_2O(l) \rightleftharpoons 4NaOH(l) + O_2(g)$$
$$3Fe(s) + 4H_2O(l) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Homogeneous reactions: The reversible reaction in which only one-phase is present, *i.e.*, all the reactants and products are in the same physical state.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Homogeneous reversible reactions are further classified into three types:

First type: When there is no change in number of molecules. Examples are:

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

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

(iii) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Second type: When there is an increase in number of molecules.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Third type: When there is a decrease in number of molecules.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

9.3 THE LAW OF CHEMICAL EQUILIBRIUM (Application of Law of Mass Action)

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

$$A + B \rightleftharpoons C + D$$

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,

$$\text{Rate of forward reaction} \propto [A][B]$$

or $$\text{Rate of forward reaction} = k_f\,[A][B]$$

(where, k_f is the velocity constant for forward reaction).

Similarly,

$$\text{Rate of backward reaction} \propto [C][D]$$

or $$\text{Rate of backward reaction} = k_b[C][D]$$

(where, k_b is the velocity constant for backward reaction).

At equilibrium,

Rate of forward reaction = Rate of backward reaction,

i.e., $$k_f\,[A][B] = k_b[C][D]$$

or $$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

Since, k_f and k_b are both constants, the ratio k_f/k_b is also a new constant say K_c, *i.e.*,

$$K_c = \frac{[C][D]}{[A][B]} \quad \text{... (i)}$$

K_c is known as equilibrium constant. K_c has a definite value for every chemical reaction at a given temperature regardless of the concentration of the reactants.

Considering a more general homogeneous reversible reaction at a particular temperature which is under chemical equilibrium,

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3 + \ldots$$

$$\text{Rate of forward reaction} = k_f\,[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots$$

$$\text{Rate of backward reaction} = k_b[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots$$

At equilibrium,

$$k_f\,[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots = k_b[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots$$

or $$\frac{k_f}{k_b} = \frac{[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots}{[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots} = K_c \quad \text{... (ii)}$$

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

Or

The equilibrium constant may be defined as the ratio between the product of the molar concentrations of the products to that of the product of the molar concentrations of the reactants with each concentration term raised to a power equal to stoichiometric coefficient in the balanced chemical equation.

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

1. Initial concentrations of the reactants involved.
2. The presence of a catalyst.
3. The direction from which the equilibrium has been attained.
4. The presence of inert materials.

The value of equilibrium constant depends on the following factors:

1. The mode of representation of the reaction: Conventionally, the concentrations of the products are put in the numerator and the concentrations of the reactants in denominator in the equilibrium law equation. Consider the reversible reaction,

$$A+B \rightleftharpoons C+D$$

The equilibrium constant for the reaction,

$$K_c=\frac{[C][D]}{[A][B]} \quad \text{... (i)}$$

Now, if the products are made reactants, *i.e.*, the reaction is reversed,

$$C+D \rightleftharpoons A+B$$

The equilibrium constant for the reaction is

$$K_c'=\frac{[A][B]}{[C][D]} \quad \text{... (ii)}$$

The equilibrium constant, K_c', is actually the reciprocal of K_c, *i.e.*,

$$K_c'=\frac{1}{K_c}$$

2. Stoichiometric representation of the chemical equation: (a) When a reversible reaction can be written with the help of two or more stoichiometric equations, the value of equilibrium constant will be numerically different in these cases. For example, the dissociation of NO_2 can be represented as:

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

or

$$NO_2 \rightleftharpoons \frac{1}{2}N_2+O_2 \quad \text{... (ii)}$$

For equation (i), the value of $K_c=\dfrac{[N_2][O_2]^2}{[NO_2]^2}$ ... (iii)

For equation (ii), the value of $K_c'=\dfrac{[N_2]^{1/2}[O_2]}{[NO_2]}$ ... (iv)

Thus, the two constants are related to each other as:

$$K_c'=\sqrt{K_c} \quad \text{... (v)}$$

In general, when a balanced equation having equilibrium constant K_c, is multiplied by a certain value n, the equilibrium constant for the new equation will be equal to $(K_c)^n$.

$$A+B \rightleftharpoons C+D, \qquad K_c=\frac{[C][D]}{[A][B]}$$

$$nA+nB \rightleftharpoons nC+nD, \qquad K_c'=\frac{[C]^n[D]^n}{[A]^n[B]^n}=(K_c)^n$$

(b) Consider the following chemical equation,

$$N_2(g)+O_2(g)+Cl_2(g) \rightleftharpoons 2NOCl(g)$$

$$K_c=\frac{[NOCl]^2}{[N_2][O_2][Cl_2]} \quad \text{... (i)}$$

Suppose the above equation is split into two as:

$$N_2(g)+O_2(g) \rightleftharpoons 2NO(g); \qquad K_1=\frac{[NO]^2}{[N_2][O_2]} \quad \text{... (ii)}$$

$$2NO(g)+Cl_2(g) \rightleftharpoons 2NOCl(g); \qquad K_2=\frac{[NOCl]^2}{[NO]^2[Cl_2]} \quad \text{... (iii)}$$

Combining above two equations,

$$K_1 \times K_2=\frac{[NO]^2}{[N_2][O_2]}\times\frac{[NOCl]^2}{[NO]^2[Cl_2]}=\frac{[NOCl]^2}{[N_2][O_2][Cl_2]}=K_c$$

Thus, when an equation (having equilibrium constant, K_c) is written in two steps (having equilibrium constant K_1 and K_2), then $K_c=K_1 \times K_2$.

3. Use of partial pressures instead of concentrations: When the reactants and products are in gaseous state, the partial pressures can be used instead of concentrations at a definite temperature, as the partial pressure of a substance is proportional to its concentration in the gas phase.

Consider a general reversible homogeneous gaseous reaction

$$m_1A_1+m_2A_2+m_3A_3+\ldots \rightleftharpoons n_1B_1+n_2B_2+n_3B_3+\ldots$$

Let the partial pressures of various reactants and products be pA_1, pA_2, pA_3, ..., and $pB_1, pB_2, pB_3, \ldots$ respectively at equilibrium. The equilibrium constant for the reaction,

$$K_p=\frac{(pB_1)^{n_1}(pB_2)^{n_2}(pB_3)^{n_3}\ldots}{(pA_1)^{m_1}(pA_2)^{m_2}(pA_3)^{m_3}\ldots} \quad \text{... (i)}$$

The value of K_c for the above reaction can be given as:

$$K_c=\frac{[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots}{[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots} \quad \text{... (ii)}$$

For an ideal gas, $pV=nRT$

or $p=\dfrac{n}{V}RT$

$=$ Active mass $\times RT$

(where, n = number of moles and V = volume in litres. Thus, $\dfrac{n}{V}$ = molar concentration or active mass).

Substituting the values of partial pressures in eq. (i),

$$K_p=\frac{[B_1]^{n_1}(RT)^{n_1}\cdot[B_2]^{n_2}(RT)^{n_2}\cdot[B_3]^{n_3}(RT)^{n_3}\ldots}{[A_1]^{m_1}(RT)^{m_1}\cdot[A_2]^{m_2}(RT)^{m_2}\cdot[A_3]^{m_3}(RT)^{m_3}\ldots}$$

$$\text{or } K_p=\frac{\{[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots\}(RT)^{n_1+n_2+n_3+\ldots}}{\{[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots\}(RT)^{m_1+m_2+m_3+\ldots}}$$

$$\text{or } K_p=K_c\cdot\frac{(RT)^{\Sigma n}}{(RT)^{\Sigma m}}$$

$$= K_c (RT)^{\Sigma n - \Sigma m}$$

$$= K_c (RT)^{\Delta n} \qquad \text{... (iii)}$$

Δn = total number of molecules of gaseous products
– total number of molecules of gaseous reactants.

Three cases may arise:

First case: When, $\Delta n = 0$,

$$K_p = K_c\,(RT)^0 = K_c$$

Second case: When, $\Delta n = +\text{ve}$ or $\Delta n > 0$,

$$K_p > K_c$$

Third case: When, $\Delta n = -\text{ve}$ or $\Delta n < 0$,

$$K_p < K_c$$

4. **Temperature:** According to Arrhenius equation,

$$k = Ae^{-E/RT} \qquad \text{... (i)}$$

where, k = rate constant, E = activation energy, R = gas constant, T = absolute temperature and e = exponential constant.

$$\log \frac{k_2}{k_1} = -\frac{E}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (ii)}$$

when, $T_2 > T_1$

for forward reaction,

$$\log\left(\frac{k_{f_2}}{k_{f_1}}\right) = -\frac{E_f}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (iii)}$$

for backward reaction,

$$\log\left(\frac{k_{b_2}}{k_{b_1}}\right) = -\frac{E_b}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (iv)}$$

Subtracting eq. (iv) from eq. (iii), we get

$$\log\left(\frac{k_{f_2}/k_{b_2}}{k_{f_1}/k_{b_1}}\right) = -\frac{(E_f - E_b)}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

or

$$\log\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (v)}$$

where, ΔH is the heat of reaction at constant volume and K_1 and K_2 are the equilibrium constants of a reaction at temperatures T_1 and T_2 $(T_2 > T_1)$.

The effect of temperature can be studied in the following three cases:

First case: $\Delta H = 0$, *i.e.*, neither heat is evolved, nor absorbed.

So, $\log K_2 - \log K_1 = 0$

or $\log K_2 = \log K_1$

or $K_2 = K_1$

Thus, equilibrium constant remains the same at all temperatures.

Second case: When, $\Delta H = +\text{ve}$, *i.e.*, heat is absorbed, the reaction is endothermic. The temperature T_2 is higher than T_1.

Thus, $\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ is negative.

So, $\log K_2 - \log K_1 = +\text{ve}$

or $\log K_2 > \log K_1$

or $K_2 > K_1$

The value of equilibrium constant is higher at higher temperature in the case of endothermic reactions.

Third case: When $\Delta H = -\text{ve}$, *i.e.*, heat is evolved, the reaction is exothermic. The temperature T_2 is higher than T_1.

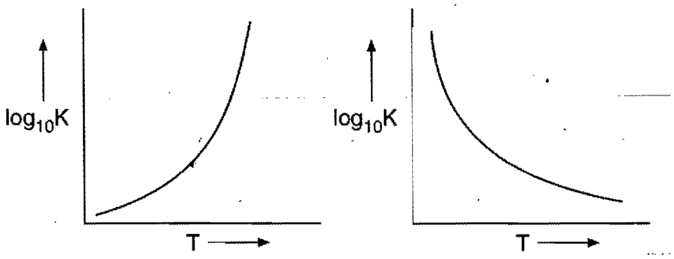
Thus, $\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ is negative.

So, $\log K_2 - \log K_1 = -\text{ve}$

or $\log K_1 > \log K_2$

or $K_1 > K_2$

The value of equilibrium constant is lower at higher temperature in the case of exothermic reactions.



(a) Endothermic reaction (b) Exothermic reaction
(Plots of log K versus T)

Fig. 9.3

Units of Equilibrium Constant

The units of equilibrium constant vary in case of different reactions. 'K' has no units for a reaction in which total number of moles of reactants and products are the same. For example, for dissociation of nitric oxide, K_c has no units.

$$2NO \rightleftharpoons N_2 + O_2$$

$$K_c = \frac{[N_2][O_2]}{[NO]^2}$$

K_c will have units for a reaction in which the total number of moles of reactants and products are different. For example, for decomposition of PCl_5, the K_c has mol/litre units.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

In the formation of ammonia,

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

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

K_c has litre^2 mol^{-2} units.

In general; unit of $K_c = [M]^{\Delta n}$

where, M = mol litre^{-1} and Δn = number of gaseous moles of product or products – number of gaseous moles of reactant or reactants.

Note: (i) The above relation can be used in homogeneous liquid system also

Δn = number of moles of product or products – number of moles of reactant or reactants

(ii) Similarly, the unit of $K_p = [\text{atm}]^{\Delta n}$

where, Δn = number of gaseous moles of product or products – number of gaseous moles of reactant or reactants.

9.4 REACTION QUOTIENT OR MASS ACTION RATIO

Let us consider a reaction:

$$A + B \rightleftharpoons C + D$$

$$Q = \frac{[C][D]}{[A][B]}$$

Q is denoted as Q_c or Q_p depending upon whether the concentration is taken in terms of moles per litre or partial pressures respectively. With the help of mass action ratio we can determine whether the reaction is at equilibrium or not.

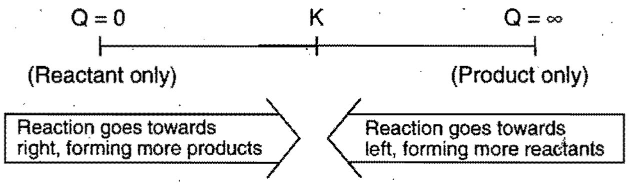
(I) When, $Q_c = K_c$ or $Q_p = K_p$ then the reversible reaction is at equilibrium, *i.e.*, the rate of forward and backward reaction becomes equal.

(II) When, $Q_c < K_c$ or $Q_p < K_p$ then the reaction is not at equilibrium. The reaction will be fast in forward direction, *i.e.*, reaction has a tendency to form product/products.

Rate of forward reaction > Rate of backward reaction.

(III) When, $Q_c > K_c$ or $Q_p > K_p$ then again the reaction is not at equilibrium. The reaction will be fast in backward direction, *i.e.*, have a tendency to form reactant/reactants.

Rate of forward reaction < Rate of backward reaction.



SOME SOLVED EXAMPLES

Example 1. *For the reactions,*

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

and $$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightleftharpoons NH_3$$

write down the expression for equilibrium constant K_c and K'_c. *How is* K_c *related to* K'_c *?*

Solution: For equation $N_2 + 3H_2 \rightleftharpoons 2NH_3$,

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \text{... (i)}$$

and for equation, $\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightleftharpoons NH_3$,

$$K'_c = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} \quad \text{... (ii)}$$

Squaring equation (ii),

$$(K'_c)^2 = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \text{... (iii)}$$

Equations (i) and (iii) are same

Thus, $$K_c = (K'_c)^2$$

or $$\sqrt{K_c} = K'_c$$

Example 2. *The equilibrium constant for the reaction,*

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

at a particular temperature is 100. *Write down the equilibrium law equations for the following reactions and determine the values of equilibrium constants:*

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

$$NO_2 \rightleftharpoons \tfrac{1}{2}N_2 + O_2 \quad \text{... (ii)}$$

Solution: The equilibrium constant for the reaction,

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

$$K_c = \frac{[NO_2]^2}{[N_2][O_2]^2} = 100 \quad \text{... (a)}$$

The equilibrium constant equation for reaction (i),

$$K_1 = \frac{[N_2][O_2]^2}{[NO_2]^2} \quad \text{... (b)}$$

This equation is reciprocal of eq. (a)

So, $$K_1 = \frac{1}{K_c} = \frac{1}{100} = 1 \times 10^{-2}$$

The equilibrium constant equation for reaction (ii),

$$K_2 = \frac{[N_2]^{1/2}[O_2]}{[NO_2]} \quad \text{... (c)}$$

Comparing eqs. (b) and (c),

$$K_2 = \sqrt{K_1} = \sqrt{10^{-2}} = 10^{-1} = 0.1$$

Example 3. *The value of* K_c *for the reaction,*

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

is 0.50 *at* 400°C. *Find the value of* K_p *at* 400°C *when concentrations are expressed in mol litre*$^{-1}$ *and pressure in atmosphere.*

Solution: Applying the relationship,

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = 0.50, \quad R = 0.082 \text{ litre-atm deg}^{-1} \text{ mol}^{-1}$$

$$T(400 + 273) = 673 \text{ K}, \quad \Delta n = (2 - 4) = -2$$

$$K_p = 0.5(0.082 \times 673)^{-2}$$

$$= 0.5(55.185)^{-2} = 1.64 \times 10^{-4}$$

Example 4. *Determine* K_c *for the reaction,*

$$\frac{1}{2}N_2(g)+\frac{1}{2}O_2(g)+\frac{1}{2}Br_2(g)\rightleftharpoons NOBr(g)$$

from the following data at 298 K;

The equilibrium constants for the following reactions,

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

and $$NO(g)+\frac{1}{2}Br_2(g)\rightleftharpoons NOBr(g)$$

are 2.4×10^{30} *and* 1.4 *respectively.*

Solution: The net reaction is,

$$\frac{1}{2}\mathrm{N_2}(g)+\frac{1}{2}\mathrm{O_2}(g)+\frac{1}{2}\mathrm{Br_2}(g)\rightleftharpoons \mathrm{NOBr}(g)$$

$$K_{c(\text{net})}=\frac{[\mathrm{NOBr}]}{[\mathrm{N_2}]^{1/2}[\mathrm{O_2}]^{1/2}[\mathrm{Br_2}]^{1/2}}$$

Considering the given equations:

$2\mathrm{NO}(g)\rightleftharpoons \mathrm{N_2}(g)+\mathrm{O_2}(g)$; equilibrium constant $=2.4\times 10^{30}$

$\mathrm{N_2}(g)+\mathrm{O_2}(g)\rightleftharpoons 2\mathrm{NO}(g)$; equilibrium constant $=\dfrac{1}{2.4\times 10^{30}}$

$$\frac{1}{2}\mathrm{N_2}(g)+\frac{1}{2}\mathrm{O_2}(g)\rightleftharpoons \mathrm{NO}(g);$$

$$\text{Equilibrium constant}=\left(\frac{1}{2.4\times 10^{30}}\right)^{1/2}$$

$$=0.6455\times 10^{-15}$$

$$\frac{[\mathrm{NO}]}{[\mathrm{N_2}]^{1/2}[\mathrm{O_2}]^{1/2}}=K_c'=0.6455\times 10^{-15}\qquad \dots\text{(i)}$$

$$\mathrm{NO}(g)+\frac{1}{2}\mathrm{Br_2}(g)\rightleftharpoons \mathrm{NOBr}(g)$$

$$\frac{[\mathrm{NOBr}]}{[\mathrm{NO}][\mathrm{Br_2}]^{1/2}}=K_c''=1.4\qquad \dots\text{(ii)}$$

Multiplying both equations

$$\frac{[\mathrm{NO}]}{[\mathrm{N_2}]^{1/2}[\mathrm{O_2}]^{1/2}}\times\frac{[\mathrm{NOBr}]}{[\mathrm{NO}][\mathrm{Br_2}]^{1/2}}=K_c'\times K_c''=0.6455\times 10^{-15}\times 1.4$$

or $$\frac{[\mathrm{NOBr}]}{[\mathrm{N_2}]^{1/2}[\mathrm{O_2}]^{1/2}[\mathrm{Br_2}]^{1/2}}=K_{c(\text{net})}=0.9037\times 10^{-15}$$

$$=9.037\times 10^{-16}$$

Example 5. *The equilibrium constant,* K_p*, for the reaction*

$N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$ *is* 1.6×10^{-4} atm^{-2} *at 400°C.*

What will be the equilibrium constant at 500°C if heat of reaction in this temperature range is − 25.14 kcal?

Solution: Using the relation,

$$\log\frac{K_{p_2}}{K_{p_1}}=\frac{\Delta H}{2.303R}\left[\frac{T_2-T_1}{T_2T_1}\right]$$

Given,

$K_{p_1}=1.6\times 10^{-4}$; $\quad\Delta H=-25.14$ kcal;

$R=2\times 10^{-3}$ kcal deg^{-1} mol^{-1}

$T_1=400+273=673\,\mathrm{K}$, $\;T_2=500+273=773\,\mathrm{K}$

$$\log\frac{K_{p_2}}{(1.6\times 10^{-4})}=\frac{-25.14}{2.303\times 2\times 10^{-3}}\left[\frac{773-673}{773\times 673}\right]$$

$$\log K_{p_2}=\log(1.6\times 10^{-4})-\frac{25.14\times 10^3\times 100}{2.303\times 2\times 773\times 673}$$

$$=-3.7960-1.049=-4.8450$$

$$K_{p_2}=1.429\times 10^{-5}\ \mathrm{atm}^{-2}$$

Example 6. *The equilibrium constant for the reaction,*

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

is 18.5 at 925 K and 9.25 at 1000 K respectively. Calculate the enthalpy of the reaction.

Solution: Using the relation,

$$\log\frac{K_2}{K_1}=\frac{\Delta H}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log\frac{9.25}{18.5}=\frac{\Delta H}{2.303\times 8.314}\times\frac{75}{925\times 1000}$$

$$-0.301=\frac{\Delta H\times 75}{2.303\times 8.314\times 925\times 1000}$$

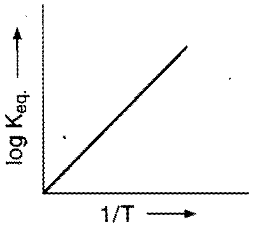
or $$\Delta H=-71080.57\ \mathrm{J\,mol^{-1}}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. For the hypothetical reactions, the equilibrium constant (K) values are given:
   $A\rightleftharpoons B$; $K_1=2$; $B\rightleftharpoons C$; $K_2=4$; $C\rightleftharpoons D$; $K_3=3$
   The equilibrium constant (K) for the reaction $A\rightleftharpoons D$ is: **[PMT (Kerala) 2005]**
   (a) 48 (b) 6 (c) 2.7 (d) 12
   (e) 24
   [**Ans.** (e)]
   [**Hint:** The reaction $A\rightleftharpoons D$ is obtained by adding the three given reactions.
   $\therefore\quad K=K_1\times K_2\times K_3=2\times 4\times 3=24$]

2. If, in the reaction $\mathrm{N_2O_4}(g)\rightleftharpoons 2\mathrm{NO_2}(g)$, x is that part of $\mathrm{N_2O_4}$ which dissociates, then the number of molecules at equilibrium will be: **(KCET 2005)**
   (a) 1 (b) 3
   (c) $(1+x)$ (d) $(1+x)^2$
   [**Ans.** (c)]
   [**Hint:**
   $$\begin{array}{ccc} & \mathrm{N_2O_4} \rightleftharpoons & 2\mathrm{NO_2}\\ t=0 & 1 & 0\\ t_{\text{eq.}} & 1-x & 2x\end{array}$$
   Total number of molecules at equilibrium $=1-x+2x=(1+x)$]

3. A schematic plot of ln $K_{eq.}$ vs inverse of temperature for a reaction is shown in the figure. The reaction must be: (AIEEE 2005)



(a) exothermic
(b) endothermic
(c) one with negligible enthalpy change
(d) highly spontaneous at ordinary temperature

[**Ans.** (a)]

[**Hint:** $K_e = Ae^{-\Delta H^\circ/RT}$

$$\log K_{eq.} = \log A - \frac{\Delta H^\circ}{2.303\,RT}$$

$$Y = C + MX$$

Slope of the line will be positive, when, $\Delta H^\circ = -$ve, *i.e.*, the reaction is exothermic.]

4. Given:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ K_1$$
$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g);\ K_2$$
$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g);\ K_3$$

The equilibrium constant for

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

will be: [CBSE (Med.) 2007]

(a) $K_1K_2K_3$ (b) $\frac{K_1K_2}{K_3}$ (c) $\frac{K_1K_3^2}{K_2}$ (d) $\frac{K_2K_3^3}{K_1}$

[**Ans.** (d)]

[**Hint:** $K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}$; $K_2 = \frac{[NO]^2}{[N_2][O_2]}$; $K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}}$

The equilibrium constant for

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

will be:

$$\frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = \frac{K_2 \times K_3^3}{K_1}]$$

5. What is the equation for the equilibrium constant (K_c) for the following reaction? (EAMCET 2006)

$$\frac{1}{2}A(g) + \frac{1}{3}B(g) \overset{T\,K}{\rightleftharpoons} \frac{2}{3}C(g)$$

(a) $K_c = \frac{[A]^{1/2}[B]^{1/3}}{[C]^{3/2}}$ (b) $K_c = \frac{[C]^{3/2}}{[A]^2[B]^3}$

(c) $K_c = \frac{[C]^{2/3}}{[A]^{1/2}[B]^{1/3}}$ (d) $K_c = \frac{[C]^{2/3}}{[A]^{1/2} + [B]^{1/3}}$

[**Ans.** (c)]

[**Hint:** Coefficient goes to the power of respective active mass.

$$\therefore \quad K_c = \frac{[C]^{2/3}}{[A]^{1/2}[B]^{1/3}}]$$

6. For the following three reactions (i), (ii) and (iii), equilibrium constants are given:

(i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g);\ K_1$

(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g);\ K_2$

(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g);\ K_3$

Which of the following relations is correct? (AIEEE 2008)

(a) $K_3K_2^3 = K_1^2$ (b) $K_1\sqrt{K_2} = K_3$

(c) $K_2K_3 = K_1$ (d) $K_3 = K_1K_2$

[**Ans.** (d)]

[**Hint :** Reaction (iii) is obtained by adding (i) and (ii) hence $K_3 = K_1 \times K_2$]

9.5 ACTIVATION ENERGIES FOR FORWARD AND BACKWARD REACTIONS

In a reversible reaction, the molecules of the reactants in the forward reaction and the molecules of the products in the backward reaction follow the same path and form the same activated complex. However, the activation energies of both forward and backward reactions are different. Fig. 9.4 (a) and (b) show the activation energies, $E_a(f)$ and $E_a(b)$ respectively, for the forward and backward reactions for exothermic and endothermic reactions. Mathematically, $E_a(f)$ and $E_a(b)$ are related to overall energy change, ΔE, in the process as:

$$\Delta E = E_a(f) - E_a(b) = \Delta H \qquad \text{(At constant volume)}$$

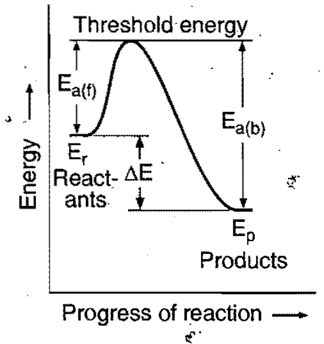


Fig. 9.4 (a) Activation energies for the forward and backward reactions where forward reaction is exothermic

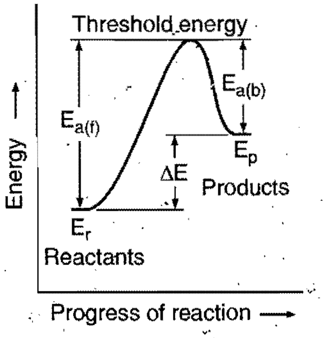


Fig. 9.4 (b) Activation energies for the forward and backward reactions where forward reaction is endothermic

For exothermic reaction,

$$E_a(f) < E_a(b)$$

Thus, ΔE is negative.

On the other hand, for the endothermic reaction,

$$E_a(f) > E_a(b).$$

Thus, ΔE is positive

Heat of reaction ΔH = Activation energy of forward reaction −Activation energy of backward reaction.

Example 7. *For the dissociation of gaseous HI, the energy of activation is 44.3 kcal. Calculate the energy of activation for the reverse reaction. Given, ΔH for the formation of 1 mole of HI from H_2 and I_2 is −1.35 kcal.*

Solution:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g);\quad E_a = 44.3\ \text{kcal}$$

$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$; $\Delta H = -1.35\,\text{kcal}$

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g);\ \Delta H = 2 \times 1.35 = 2.70\,\text{kcal}$$

$$\Delta H = E_a(f) - E_a(b)$$

$$2.70 = 44.3 - E_a(b)$$

$$E_a(b) = (44.3 - 2.70)$$

or $$= 41.60\,\text{kcal}$$

Example 8. *For a reaction $X \rightarrow Y$, heat of reaction is $+83.68$ kJ, energy of reactant X is 167.36 kJ and energy of activation is 209.20 kJ. Calculate (i) threshold energy (ii) energy of product Y and (iii) energy of activation for the reverse reaction ($Y \rightarrow X$).*

Solution: (i) Given, $E_a(f) = 209.20\,\text{kJ}$

$$\Delta E = +83.68\,\text{kJ}$$

Energy of reactant, $X = 167.36\,\text{kJ}$

Threshold energy = Energy of reactant X + Activation energy for forward reaction

$$= 167.36 + 209.20 = 376.56\,\text{kJ}$$

(ii) Energy of reaction, ΔE = Energy of product − Energy of reactant

Energy of product = $83.68 + 167.36 = 251.04\,\text{kJ}$

(iii) Activation energy for backward reaction

= Threshold energy − Energy of product

$= 376.56 - 251.04 = 125.52\,\text{kJ}$

9.6 STANDARD FREE ENERGY CHANGE OF A REACTION AND ITS EQUILIBRIUM CONSTANT

Let ΔG° be the difference in free energy of the reaction when all the reactants and products are in the standard state (1 atmospheric pressure and 298 K) and K_c or K_p be the thermodynamic equilibrium constant of the reaction. Both are related to each other at temperature T by the following relation:

$$\Delta G^\circ = -2.303\,RT \log K_c$$

and $$\Delta G^\circ = -2.303\,RT \log K_p \quad \text{(in case of ideal gases)}$$

This equation represents one of the most important results of thermodynamics and relates to the equilibrium constant of a reaction to a thermochemical property. It is sometimes easier to calculate the free energy in a reaction rather than to measure the equilibrium constant.

Standard free energy change can be thermodynamically calculated as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Here, ΔH° = standard enthalpy change,

ΔS° = standard entropy change.

$$-RT \log_e K_p = \Delta H^\circ - T\Delta S^\circ$$

$$\log_e K_p = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\log_{10} K_p = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT}$$

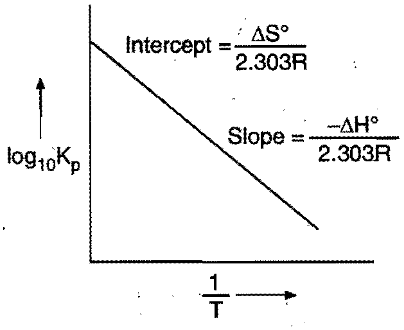


Fig. 9.5

(i) When, $\Delta G^\circ = 0$, then $K_c = 1$.

(ii) When, $\Delta G^\circ > 0$, *i.e.*, +ve, then $K_c < 1$. In this case reverse reaction is feasible, *i.e.*, less concentration of products at equilibrium state.

(iii) When, $\Delta G^\circ < 0$, *i.e.*, −ve, then $K_c > 1$. In this case forward reaction is feasible showing thereby a large concentrations of products till the equilibrium is reached.

Example 9. *For the reaction,*

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

calculate the standard equilibrium constant at 298 K. Given that the values of ΔH° and ΔS° of the reaction at 298 K are 77.2 kJ mol^{-1} and 122 JK^{-1} mol^{-1}.

Solution: Using the relation,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= 77200 - 298 \times 122$$

$$= 40844\ \text{J mol}^{-1}$$

Let the equilibrium constant be K_c°. We know that,

$$\Delta G^\circ = -2.303RT \log K_c^\circ$$

or $$\log K_c^\circ = -\frac{\Delta G^\circ}{2.303 \times 8.314 \times 298} = -\frac{40844}{2.303 \times 8.314 \times 298}$$

$$= -7.158$$

$$K_c^\circ = 6.95 \times 10^{-8}$$

Example 10. ΔG° *for* $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ *is* -16.5 *kJ mol^{-1}. Find out K_p for the reaction at 25°C. Also report K_p and ΔG° for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 25°C.*

Solution:

$$\log K_p = -\frac{\Delta G^\circ}{2.303RT} = -\frac{(-16.5 \times 10^3)}{2.303 \times 8.314 \times 298} = 2.8917$$

$$K_p = 779.41$$

K_p for reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is equal to $(779.41)^2 = 6.07 \times 10^5$

$$\Delta G^\circ = -2.303 \times 8.314 \times 298 \log 6.07 \times 10^5\ \text{joule}$$

$$= -32.998\ \text{kJ mol}^{-1}$$

9.7 EQUILIBRIUM CONSTANT EXPRESSIONS FOR SOME REACTIONS

Case I: Homogeneous gaseous equilibria when, $\Delta n = 0$.

Synthesis of hydrogen iodide: The formation of hydrogen iodide from hydrogen and iodine is represented by the equation:

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

Let a start be made with 'a' moles of hydrogen and 'b' moles of I_2. These are heated in a sealed bulb having a volume V litre by keeping the bulb in a thermostat till equilibrium is established. If at equilibrium, x moles of each of H_2 and I_2 have reacted, $2x$ moles of HI will be formed.

Thus, the active masses of various reactants and products present at equilibrium are:

$$[H_2] = \frac{(a-x)}{V} \text{ mol L}^{-1}$$

$$[I_2] = \frac{(b-x)}{V} \text{ mol L}^{-1}$$

$$[HI] = \frac{2x}{V} \text{ mol L}^{-1}$$

Applying law of mass action,

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

When, $a = b = 1$, x becomes degree of formation of HI and

$$K_c = \frac{4x^2}{(1-x)^2}$$

The equilibrium constant, K_p, can also be calculated considering partial pressures of reactants and products at equilibrium.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial no. of moles	a	b	0
No. of moles at equilibrium	$(a-x)$	$(b-x)$	$2x$

Total number of moles at equilibrium

$$= (a-x) + (b-x) + 2x = (a+b)$$

Let the total pressure of the system at equilibrium be P atmosphere.

Partial pressure of H_2, $p_{H_2} = \frac{(a-x)}{(a+b)} \cdot P$

Partial pressure of I_2, $p_{I_2} = \frac{(b-x)}{(a+b)} \cdot P$

Partial pressure of HI, $p_{HI} = \frac{2x}{(a+b)} \cdot P$

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} = \frac{\left(\frac{2x}{a+b}\right)^2 P^2}{\left(\frac{a-x}{a+b}\right)P \times \left(\frac{b-x}{a+b}\right)P} = \frac{4x^2}{(a-x)(b-x)}$$

Thus, $K_p = K_c$

This also follows from the relationship, $K_p = K_c(RT)^{\Delta n}$.

$$\Delta n = 0, \text{ So } K_p = K_c,$$

i.e., for all gaseous reactions of first type, K_p and K_c are identical. Both K_p and K_c have no units.

(a) Effect of pressure: The equation, $K_c = \frac{4x^2}{(a-x)(b-x)}$, does not include the volume term; hence K_c is independent of pressure. **Thus, change of pressure will not alter the final state of equilibrium.**

(b) Effect of adding substances (Reactants or products): On adding H_2 to the equilibrium mixture, the value of denominator of equation $K_c = 4x^2/[(a-x)(b-x)]$ will increase. To maintain the constant value of K_c, the value of numerator must also increase. This can happen if more of HI is formed, *i.e.*, hydrogen combines with iodine to form more of HI. Thus, the reaction moves in a direction in which the added hydrogen is used up. A similar effect is observed when iodine is added to the equilibrium mixture.

The reverse effect is observed when HI is added to the equilibrium mixture, *i.e.*, HI decomposes into H_2 and I_2.

(c) Effect of temperature: The formation of HI from H_2 and I_2 is an exothermic reaction, *i.e.*, by increasing temperature, the value of equilibrium constant, K_c, decreases. Thus, the yield of HI decreases, *i.e.*, high temperature is not favourable for greater yield of HI.

(d) Effect of adding an inert gas: Addition of an inert gas to equilibrium mixture will make no effect on equilibrium state as in the first type of reactions, volume and pressure changes have no effect on equilibrium state.

Case II: Homogeneous gaseous reaction when, $\Delta n > 0$.

Dissociation of PCl_5: The dissociation of PCl_5 takes place according to the equation:

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

Let a moles of PCl_5 be taken in a closed vessel of volume V litre. It is heated and by the time equilibrium is established, x moles are dissociated into PCl_3 and Cl_2. One molecule of PCl_5 on dissociation gives one molecule of PCl_3 and one molecule of Cl_2. Thus, x moles of PCl_5 will give x moles of PCl_3 and x moles of Cl_2.

At equilibrium,

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

Applying law of mass action,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(a-x)}{V}} = \frac{x^2}{(a-x)V}$$

When, $a = 1$, x becomes degree of dissociation and

$$K_c = \frac{x^2}{(1-x)V} \qquad (\text{units} = \text{mol L}^{-1})$$

Calculation of K_p: Let the total pressure at equilibrium be P. Total number of moles at equilibrium

$$= (a-x)+x+x=(a+x)$$

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

$$K_p = \frac{p_{PCl_3}\times p_{Cl_2}}{p_{PCl_5}} = \frac{\dfrac{x}{(a+x)}\cdot P\times\dfrac{x}{(a+x)}\cdot P}{\left(\dfrac{a-x}{a+x}\right)\cdot P} = \frac{x^2P}{(a-x)(a+x)};$$

(units = atm)

(a) Effect of pressure: In this case, $K_c = x^2/(a-x)V$. If pressure is increased, the value of 'V' decreases, *i.e.*, the value of denominator decreases. To maintain constant value of K_c, x must also decrease. In other words, the dissociation of PCl_5 decreases. Thus, the increase of pressure would suppress the dissociation of PCl_5.

(b) Effect of concentration: If PCl_5 is added to the equilibrium mixture, the rate of forward reaction increases, *i.e.*, dissociation of PCl_5 increases. In case PCl_3 or Cl_2 is added, the rate of backward reaction increases. This shall decrease the dissociation of PCl_5.

(c) Effect of temperature: The dissociation of PCl_5 is an endothermic reaction. Thus, the value of equilibrium constant increases with increase of temperature. It is thus concluded that dissociation increases with the increase of temperature.

(d) Effect of adding an inert gas: When an inert gas is added at constant volume the equilibrium state is not disturbed. In case an inert gas is added at constant pressure, the volume increases. To maintain the constant value of K_c, x must also increase. Thus, the addition of an inert gas at constant pressure increases the degree of dissociation of PCl_5.

Case III: Homogeneous gaseous reaction when, $\Delta n < 0$.

Synthesis of ammonia: The formation of ammonia from nitrogen and hydrogen is represented by the equation:

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

Let a start be made by mixing 'a' moles of N_2 and 'b' moles of hydrogen in a closed vessel of V litre capacity. By the time equilibrium is established 'x' moles of nitrogen have combined with $3x$ moles of hydrogen and produced $2x$ moles of ammonia.

At equilibrium, $$[N_2] = \frac{(a-x)}{V}$$

$$[H_2] = \frac{(b-3x)}{V}$$

$$[NH_3] = \frac{2x}{V}$$

Applying law of mass action,

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\dfrac{2x}{V}\right)^2}{\left(\dfrac{a-x}{V}\right)\left(\dfrac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

If $a = 1$ and $b = 3$, then,

$$K_c = \frac{4x^2V^2}{27(1-x)^4};\qquad \text{(units} = \text{mol}^{-2}\ \text{L}^2)$$

The effect of various factors at equilibrium is discussed here.

(a) Effect of pressure: By increasing pressure, the volume term decreases. The value of x must increase to maintain the constant value of K_c. In other words, the formation of ammonia increases with increase of pressure.

(b) Effect of concentration: By increasing the concentration of either nitrogen or hydrogen in the reaction mixture, the rate of forward reaction increases, *i.e.*, the formation of ammonia increases.

(c) Effect of temperature: The synthesis of ammonia is an exothermic reaction. The value of equilibrium constant decreases with increase of temperature. Thus, high temperature is not favourable for the synthesis of ammonia.

Calculation of K_p: Let the total pressure at equilibrium be P.

Total number of moles at equilibrium

$$= (a-x)+(b-3x)+2x = (a+b-2x)$$

$$p_{NH_3} = \frac{2x}{(a+b-2x)}\times P;\qquad p_{N_2} = \frac{(a-x)}{(a+b-2x)}\times P;$$

$$p_{H_2} = \frac{(b-3x)}{(a+b-2x)}\times P$$

$$K_p = \frac{[p_{NH_3}]^2}{[p_{N_2}][p_{H_2}]^3} = \frac{\left[\dfrac{2x}{(a+b-2x)}P\right]^2}{\left[\dfrac{(a-x)}{(a+b-2x)}P\right]\left[\dfrac{(b-3x)}{(a+b-2x)}P\right]^3}$$

$$= \frac{4x^2\,(a+b-2x)^2}{(a-x)(b-3x)^3\,P^2}\qquad \text{(units} = \text{atm}^{-2})$$

Case IV: Homogeneous liquid system: Formation of ethyl acetate:

The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.

$$CH_3COOH(l)+C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l)+H_2O(l)$$

Let a start be made by mixing 'a' moles of an acid and 'b' moles of an alcohol. By the time equilibrium is established, x moles of ester and 'x' moles of water are formed, *i.e.*, x moles of acid and x moles of alcohol have been consumed. Let V be the total volume. At equilibrium, the active masses of reactants and products are:

$$[CH_3COOH] = \frac{(a-x)}{V},\ [C_2H_5OH] = \frac{(b-x)}{V},$$

$$[CH_3COOC_2H_5] = \frac{x}{V} \text{ and } [H_2O] = \frac{x}{V}$$

Applying law of mass action,

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{\dfrac{x}{V}\times\dfrac{x}{V}}{\left(\dfrac{a-x}{V}\right)\times\left(\dfrac{b-x}{V}\right)}$$

$$= \frac{x^2}{(a-x)(b-x)}$$

If $a = b = 1$, then $K_c = \frac{x^2}{(1-x)^2}$, ($K_c$ has no units)

This does not involve the volume term. Thus, K_c is not affected by the change of volume.

Case V: Heterogeneous equilibria:

Law of mass action can also be applied to the study of equilibria in which the substances are not in the same phase. Considering the decomposition of solid $NaHCO_3$ to produce solid Na_2CO_3, gaseous CO_2 and H_2O.

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Applying the law of mass action,

$$K_c' = \frac{[Na_2CO_3][CO_2][H_2O]}{[NaHCO_3]^2}$$

It involves two pure solids, Na_2CO_3 and $NaHCO_3$. It is customary not to include the concentrations of pure solids in equilibrium expressions.

$$\frac{K_c'[NaHCO_3]^2}{[Na_2CO_3]} = [CO_2][H_2O]$$

or $$K_c = [CO_2][H_2O]$$

In terms of partial pressures we have $K_p = p_{CO_2} \times p_{H_2O}$. Similarly, in reactions in which a reactant or product occurs as a pure liquid phase, the concentration of that substance in the pure liquid is also constant. **As a result, the concentrations of pure solid and pure liquid phases do not appear in the equilibrium constant expression.**

Many other examples of heterogeneous equilibria are available. Such as:

1. Decomposition of $CaCO_3$,

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

$$K_c = [CO_2] \quad \text{or} \quad K_p = p_{CO_2}$$

When $CaCO_3$ is heated in a closed vessel at a definite temperature, the pressure or concentration of CO_2 produced becomes constant irrespective of the amount of $CaCO_3$ taken.

2. Reaction of steam on heated iron,

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

$$K_c = \frac{[H_2]^4}{[H_2O]^4} \text{ or } K_p' = \frac{p_{H_2}}{p_{H_2O}} = \sqrt[4]{K_p}$$

3. Reaction of steam on heated carbon,

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

$$K_c = \frac{[CO][H_2]}{[H_2O]} \quad \text{or} \quad K_p = \frac{p_{CO} \times p_{H_2}}{p_{H_2O}}$$

4. Dissociation of ammonium carbamate,

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

$$K_c = [NH_3]^2[CO_2]; \quad K_p = [p_{NH_3}]^2 \times [p_{CO_2}]$$

SOME SOLVED EXAMPLES

Example 11. *For the following reaction,*

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

If initially 25 mL of H_2 and 20 mL of I_2 are present in a container and at equilibrium 30 mL of HI is formed then calculate equilibrium constant. **[AIPMT (Mains) 2009]**

Solution: The given reaction is :

$$\begin{array}{llll} & H_2(g) + & I_2(g) \rightleftharpoons & 2HI(g), \\ t_0 & 25\text{ mL} & 20\text{ mL} & 0 \\ t_{eq.} & 25-x & 20-x & 2x \end{array}$$

Give, $2x = 30\text{ mL} \quad \therefore \quad x = 15\text{ mL}$

Equilibrium constant may be calculated as,

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{[30]^2}{[10][5]} = \frac{900}{15} = 60$$

Example 12. *In the reaction,*

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

the amounts of H_2, I_2 and HI are 0.2 g, 9.2525 g and 44.8 g respectively at equilibrium at a certain temperature. Calculate the equilibrium constant of the reaction.

Solution: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$,

Applying law of mass action,

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Let the total volume be V litre, then

$$[H_2] = \frac{0.2}{2V} = \frac{0.1}{V}; [I_2] = \frac{9.2525}{254V} = \frac{0.0364}{V}$$

$$[HI] = \frac{44.8}{128V} = \frac{0.35}{V} \text{ mol L}^{-1} \text{ respectively}$$

So, $$K_c = \frac{\left(\frac{0.35}{V}\right)^2}{\frac{0.1}{V} \times \frac{0.0364}{V}} = \frac{0.35 \times 0.35}{0.1 \times 0.0364} = 33.65$$

Example 13. 0.5 *mole of hydrogen and* 0.5 *mole of iodine react in a* 10 *litre evacuated vessel at* 448°C; *hydrogen iodide is formed. The equilibrium constant, K_c for the reaction is* 50.

(*a*) *Calculate the number of moles of iodine which remain unreacted at equilibrium.*

(*b*) *What is the value of K_p?*

Solution: (a)

$$\begin{array}{lccc} & H_2(g) & + \ I_2(g) & \rightleftharpoons \ 2HI(g) \\ \text{Initial moles} & 0.5 & 0.5 & 0 \\ \text{No. of moles at equilibrium} & (0.5-x) & (0.5-x) & 2x \end{array}$$

$$K_c = \frac{4x^2}{(0.5-x)(0.5-x)} = 50$$

$$\frac{2x}{(0.5-x)} = \sqrt{50} = 7.07$$

$$2x = 0.5 \times 7.07 - 7.07x$$

or $$2x + 7.07x = 0.5 \times 7.07$$

$$x = \frac{0.5 \times 7.07}{9.07} = 0.39 \text{ mole}$$

(b) No. of moles of I_2 at equilibrium $= (0.5 - 0.39) = 0.11$ mole

$$K_p = K_c (RT)^{\Delta n}$$

As $\Delta n = 0$, $K_p = K_c = 50$

Example 14. *25 mL of H_2 and 18 mL of I_2 vapours were heated in a sealed glass tube at 465°C and at equilibrium 30.8 mL of HI was formed. Calculate the percentage degree of dissociation of HI at 465°C.*

Solution: Since, the number of moles in a gas under the same conditions of temperature and pressure are proportional to volumes (Avogadro's Law), the volumes in mL of gases may be used instead of concentrations in the case of reversible reactions in which there is no change in the number of molecules of reactants and products.

Given, $2x = 30.8$ mL

So, $x = 15.4$ mL

Vol. of H_2 at equilibrium $= (25 - 15.4) = 9.6$ mL

Vol. of I_2 at equilibrium $= (18 - 15.4) = 2.6$ mL

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(30.8)^2}{9.6 \times 2.6} = 38.0$$

Consider the equation,

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

Let the degree of dissociation be x

$$K'_c = \frac{x^2}{4(1-x)^2} \qquad \left(K'_c = \frac{1}{K_c} = \frac{1}{38}\right)$$

$$\frac{1}{38} = \frac{x^2}{4(1-x)^2} \quad \text{or} \quad \frac{1}{6.1644} = \frac{x}{2(1-x)}$$

or $x = 0.245$, *i.e.*, 24.5% dissociated

Example 15. *3.2 mole of HI were heated in a sealed bulb at 444°C till the equilibrium state was reached. Its degree of dissociation was found to be 20%. Calculate the number of moles of hydrogen iodide, hydrogen and iodine present at the equilibrium point and determine the equilibrium constant.*

Solution: The dissociation of HI is represented by the equation,

$$\begin{array}{ccc} 2HI(g) \rightleftharpoons & H_2(g) & + I_2(g) \\ (1-x) & x/2 & x/2 \end{array}$$

Degree of dissociation, $x = 0.20$ and initial concentration of HI, $a = 3.2$ mole.

At equilibrium,

No. of moles of HI $= a(1-x) = 3.2 \times 0.8 = 2.56$

No. of moles of $H_2 = \frac{a \cdot x}{2} = 3.2 \times 0.1 = 0.32$

No. of moles of $I_2 = \frac{a \cdot x}{2} = 3.2 \times 0.1 = 0.32$

$$K_c = \frac{x^2}{4(1-x)^2} = \frac{0.2 \times 0.2}{4 \times 0.8 \times 0.8} = 0.0156$$

Also, $$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.32 \times 0.32}{2.56 \times 2.56} = 0.0156$$

Example 16. *The equilibrium constant of the reaction,*

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

at 100°C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2, how many moles of AB will be formed at 373 K?

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

	A_2	B_2	$2AB$
Initial no. of moles	1	2	0
No. of moles at equilibrium	$(1-x)$	$(2-x)$	$2x$
(Total volume = 3 litre)			
Active masses	$\frac{(1-x)}{3}$	$\frac{(2-x)}{3}$	$\frac{2x}{3}$

Applying law of mass action,

$$K_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2x}{3}\right)^2}{\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)} = \frac{4x^2}{(1-x)(2-x)}$$

But, $$\frac{4x^2}{(1-x)(2-x)} = 50$$

or $$4x^2 = (2 - 3x + x^2)50$$

or $$2x^2 = (2 - 3x + x^2)25$$

or $$23x^2 - 75x + 50 = 0$$

$$x = \frac{75 \pm \sqrt{(75)^2 - 4 \times 23 \times 50}}{2 \times 23}$$

$x = 2.317$ or 0.934

The value of x cannot be more than 1, *i.e.*, greater than the number of moles of A_2 and hence $x = 0.943$.

No. of moles of $AB = 2x = (2 \times 0.934)$

$= 1.868$

Example 17. *The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.*

Solution: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Mol. mass of $N_2O_4 = (28 + 64) = 92$

Vapour density, $D = \frac{92}{2} = 46$

Let the degree of dissociation be x

Given, $d = 30$

Applying the relationship,

$$x = \frac{D-d}{d} = \frac{(46-30)}{30} = \frac{16}{30} = 0.533$$

Degree of dissociation = 53.3%

Example 18. *3 g mole of phosphorus pentachloride is heated in a flask of 4 litre volume. At equilibrium it dissociates to give 40% of phosphorus trichloride and chlorine. Calculate the equilibrium constant.*

Solution: Degree of dissociation = 0.4

$$\begin{array}{llll} PCl_5(g) \rightleftharpoons & PCl_3(g) + & Cl_2(g) & \\ a(1-x) & ax & ax & \text{(at equilibrium)} \end{array}$$

Given, $a = 3, x = 0.4$ and $V = 4$.

So, at equilibrium,

$$[PCl_5] = \frac{3(1-0.4)}{4} = \frac{3 \times 0.6}{4} \text{ mol L}^{-1}$$

$$[PCl_3] = \frac{3 \times 0.4}{4} \text{ mol L}^{-1}$$

$$[Cl_2] = \frac{3 \times 0.4}{4} \text{ mol L}^{-1}$$

Applying law of mass action,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{3 \times 0.4 \times 3 \times 0.4}{4 \times 3 \times 0.6} = 0.2 \text{ mol L}^{-1}$$

Example 19. *N_2O_4 is 25% dissociated at 37°C and one atmospheric pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C.*

Solution: (i)

$$\begin{array}{lcc} & N_2O_4(g) \rightleftharpoons & 2NO_2(g) \\ \text{Initial} & 1 & 0 \\ \text{At equilibrium} & (1-x) & 2x \end{array}$$

$$\text{Total moles} = (1-x) + 2x = (1+x)$$

$$p_{N_2O_4} = \left(\frac{1-x}{1+x}\right)P, \quad p_{NO_2} = \frac{2x}{(1+x)} \cdot P$$

Given, $x = 0.25$ and $P = 1$ atm

$$p_{N_2O_4} = \left(\frac{1-0.25}{1+0.25}\right) \times 1 = 0.6 \text{ atm}$$

$$p_{NO_2} = \left(\frac{2 \times 0.25}{1+0.25}\right) \times 1 = 0.4 \text{ atm}$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{0.4 \times 0.4}{0.6} = 0.267 \text{ atm}$$

(ii) Let the degree of dissociation of N_2O_4 at 0.1 atm be 'α', then,

$$p_{N_2O_4} = \left(\frac{1-\alpha}{1+\alpha}\right) \times 0.1 \text{ and } p_{NO_2} = \frac{2\alpha}{(1+\alpha)} \times 0.1$$

$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 \times (0.1)^2}{\left(\frac{1-\alpha}{1+\alpha}\right) \times 0.1} = \frac{4\alpha^2 \times 0.1}{(1-\alpha)(1+\alpha)} = \frac{0.4\alpha^2}{(1-\alpha^2)}$$

or $$0.267 = \frac{0.4\alpha^2}{(1-\alpha^2)} \text{ or } 0.267 = 0.667\alpha^2$$

$$\alpha = 0.632$$

Hence, dissociation of $N_2O_4 = 63.2\%$

Example 20. *1.0 mole of nitrogen and 3.0 moles of PCl_5 are placed in 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction,*

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

Solution:

$$\begin{array}{lccc} & PCl_5(g) \rightleftharpoons & PCl_3(g) + & Cl_2(g) \\ \text{Initial} & 3 & 0 & 0 \\ \text{At equilibrium} & 3(1-x) & 3x & 3x \end{array}$$

(x = degree of dissociation)

$$\text{Total moles} = 3(1-x) + 3x + 3x = 3(1+x)$$

1 mole of nitrogen is present, hence actual total number of moles at equilibrium $= 3(1+x) + 1$.

According to gas equation,

$$PV = nRT$$

Given, $P = 2.05$ atm, $V = 100$ litres, $R = 0.082$

and $$T = (273 + 227) = 500 \text{ K}$$

So, $$n = \frac{2.05 \times 100}{0.082 \times 500} = 5$$

or $$3(1+x) + 1 = 5$$

$$3x = 1 \text{ or } x = 0.333$$

Thus, $3(1+x) + 1 = 3 + 3 \times 0.333 + 1 = 4 + 0.999$

At equilibrium, $$p_{PCl_5} = \frac{3(1-x)}{(3x+4)} \times 2.05$$

$$p_{PCl_3} = p_{Cl_2} = \frac{3x}{(3x+4)} \times 2.05$$

$$K_p = \frac{\frac{3x}{(3x+4)} \times 2.05 \times \frac{3x}{(3x+4)} \times 2.05}{\frac{3(1-x)}{(3x+4)} \times 2.05}$$

$$= \frac{9x^2 \times 2.05}{3(3x+4)(1-x)} = \frac{3 \times (0.333)^2 \times 2.05}{(4 + 0.999)(0.667)}$$

$$= 0.204 \text{ atm}$$

Example 21. *For a gas reaction, $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, the partial pressures of H_2 and N_2 are 0.4 and 0.8 atmosphere, respectively. The total pressure of the entire system is 2.8 atmosphere. What will be the value of K_p if all the concentrations are given in atmospheres?*

Solution:

$$\begin{array}{lccc} & N_2(g) + & 3H_2(g) \rightleftharpoons & 2NH_3(g) \\ \text{Partial pressures at equilibrium} & 0.8 & 0.4 & [2.8 - (0.8 + 0.4) = 1.6] \end{array}$$

Applying law of mass action,

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} = \frac{1.6 \times 1.6}{0.8 \times 0.4 \times 0.4 \times 0.4}$$

$$= 50 \text{ atm}^{-2}$$

Example 22. *One mole of nitrogen and three moles of hydrogen are mixed in a 4 litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction:*

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

calculate the equilibrium constant (K_c) in concentration units. What will be the value of K for the following equilibrium?

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightleftharpoons NH_3(g)$$

Solution:

	$N_2(g)$ +	$3H_2(g)$ $\rightleftharpoons$	$2NH_3(g)$
At equilibrium	$(1-x)$	$(3-3x)$	$2x (x=0.0025)$
Active masses	$\frac{(1-0.0025)}{4}$	$\frac{(3-0.0075)}{4}$	$\frac{(0.0050)}{4}$

Applying law of mass action,

$$K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}=\frac{\left(\frac{0.0050}{4}\right)^2}{\left(\frac{0.9975}{4}\right)\left(\frac{2.9925}{4}\right)^3}$$

$$=1.49\times10^{-5}\ \text{litre}^2\ \text{mol}^{-2}$$

K for the reaction,

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightleftharpoons NH_3(g)$$

is equal to $\sqrt{K_c}$.

$$K=\sqrt{K_c}=\sqrt{1.49\times10^{-5}}$$

$$=3.86\times10^{-3}\ \text{litre mol}^{-1}$$

Example 23. *In an experiment one mole of acetic acid and one mole of alcohol were allowed to react until equilibrium was established. The equilibrium mixture was found to contain 2/3 mole of ester. Calculate the equilibrium constant of the reaction.*

Solution:

	$CH_3COOH(l)$ +	$C_2H_5OH(l)$ $\rightleftharpoons$	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
Initial no. of moles	1	1	0	0
No. of moles at equilibrium	$\left(1-\frac{2}{3}\right)$	$\left(1-\frac{2}{3}\right)$	$\frac{2}{3}$	$\frac{2}{3}$
Active masses	$\frac{1}{3V}$	$\frac{1}{3V}$	$\frac{2}{3V}$	$\frac{2}{3V}$

V is the total volume in litres.

Applying law of mass action,

$$K_c=\frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]}$$

$$=\frac{\frac{2}{3V}\times\frac{2}{3V}}{\frac{1}{3V}\times\frac{1}{3V}}=4$$

Example 24. *Ammonium hydrogen sulphide dissociates according to the equation:*

$$NH_4HS(s)\rightleftharpoons NH_3(g)+H_2S(g)$$

If the observed pressure at equilibrium is 1.12 atm at 380 K, what is the equilibrium constant K_p of the reaction?

Solution: $NH_4HS(s)\rightleftharpoons NH_3(g)+H_2S(g)$

$$p_{NH_3}=p_{H_2S}=\frac{1}{2}\times1.12=0.56\ \text{atm}$$

$$K_p=p_{NH_3}\times p_{H_2S}=0.56\times0.56=0.3136$$

Example 25. *A vessel at 1000 K contains carbon dioxide with a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K_p if total pressure at equilibrium is 0.8 atm.*

(IIT 1993)

Solution:

	$CO_2(g)+C(s)\rightleftharpoons$	$2CO(g)$
Initial	0.5 atm	0 atm
At equilibrium	$(0.5-x)$ atm	$2x$ atm

At equilibrium, the total pressure is 0.8 atm.

$$p_{\text{total}}=p_{CO_2}+p_{CO}$$

$$0.8=(0.5-x)+2x=0.5+x$$

or $x=0.3$ atm

Applying law of mass action,

$$K_p=\frac{(p_{CO})^2}{p_{CO_2}}=\frac{(2\times0.3)^2}{0.2}=\frac{0.36}{0.2}=1.8\ \text{atm}$$

Example 26. *A sample of $CaCO_3(s)$ is introduced into a sealed container of volume 0.654 litre and heated to 1000 K until equilibrium is reached. The equilibrium constant for the reaction,*

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

is 3.9×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.

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

$$K_p=p_{CO_2}$$

Let the number of moles of CO_2 be formed $=n$

$$n=\frac{p_{CO_2}\times V}{RT}=\frac{3.9\times10^{-2}\times0.654}{0.082\times1000}$$

$$=3.11\times10^{-4}\ \text{mol}$$

The amount of CaO(s) formed will also be $=3.11\times10^{-4}$ mol

Hence, mass of CaO formed $=3.11\times10^{-4}\times56=0.0174$ g

Example 27. *The decomposition of ammonium carbamate at 30°C is represented as:*

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

The equilibrium constant K_p is 2.9×10^{-5} atm^3.

What is the total pressure of gases in equilibrium with $NH_2COONH_4(s)$ at 30°C?

Solution:

	$NH_2COONH_4(s)\rightleftharpoons$	$2NH_3(g)$ +	$CO_2(g)$
At equilibrium	$(1-x)$	$2x$	x

$$K_p=(p_{NH_3})^2\times p_{CO_2}$$

$$2.9\times10^{-5}=(2x)^2\times x=4x^3$$

$$x = \left(\frac{2.9\times10^{-5}}{4}\right)^{1/3} = 0.0194 \text{ atm}$$

Total pressure $= 2x + x = 3x = 3\times0.0194 = 0.0582$ atm

Example 28. *In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at 100°C, the equilibrium mixture on analysis shows that 54.3% of the acid is esterified. Calculate the equilibrium constant of this reaction.*

Solution:

$$\begin{array}{lcccc} & CH_3COOH(l) + & C_2H_5OH(l) \rightleftharpoons & CH_3COOC_2H_5(l) + & H_2O(l) \\ \text{Initial} & 1 & 1 & 0 & 1 \\ \text{At equilibrium} & 1-x & 1-x & x & 1+x \\ & 1-0.543 & 1-0.543 & 0.543 & 1+0.543 \end{array}$$

Given, $x = 0.543$.

Applying law of mass action,

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{0.543\times1.543}{0.457\times0.457} = 4.0$$

Example 29. *The equilibrium constant for the reaction,* $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ *is 4. What will be the composition of the equilibrium mixture when one mole of acetic acid is taken along with 4 moles of ethyl alcohol?*

Solution:

$$\begin{array}{lcccc} & CH_3COOH(l) + & C_2H_5OH(l) \rightleftharpoons & CH_3COOC_2H_5(l) + & H_2O(l) \\ \text{Initial} & 1 & 4 & 0 & 0 \\ \text{At equilibrium} & 1-x & 4-x & x & x \end{array}$$

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{x^2}{(1-x)(4-x)} = 4$$

$$x^2 = 4(1-x)(4-x)$$

$$= 4[4-5x+x^2]$$

$$= 16-20x+4x^2$$

or

$$3x^2-20x+16=0$$

$$x = \frac{20\pm\sqrt{400-192}}{6} = \frac{20\pm14.42}{6}$$

$$x = 0.93 \quad \text{or} \quad 5.7366$$

The value 5.7366 is not possible, hence $x = 0.93$

Thus, the composition of mixture at equilibrium is

$[CH_3COOH] = (1-0.93) = 0.07$ mole

$[C_2H_5OH] = (4-0.93) = 3.07$ mole

$[CH_3COOC_2H_5] = 0.93$ mole

$[H_2O] = 0.93$ mole

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. For the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the value of K_c at 500°C is 0.1. When the equilibrium concentrations of both the reactants is 0.5 mol, what is the value of K_p at the same temperature? (KCET 2005)

(a) 0.5 (b) 0.1 (c) 0.01 (d) 0.025

[**Ans.** (b)]

[**Hint:** $K_p = K_c(RT)^{\Delta n}$

Since, $\Delta n = 0$, hence, $K_p = K_c$]

8. $A(g) + 3B(g) \rightleftharpoons 4C(g)$, initial concentration of A is equal to that of B. The equilibrium concentrations of A and C are equal. K_c of the reaction will be:

(a) 0.08 (b) 0.8 (c) 8 (d) 80

(e) 1/8

[**Ans.** (c)]

[**Hint:**

$$\begin{array}{lccc} & A(g) + & 3B(g) \rightleftharpoons & 4C(g) \\ t=0 & a & a & 0 \\ t_{eq.} & a-x & a-3x & 4x \end{array}$$

$a - x = 4x$ given

$a = 5x$

$$K_c = \frac{[C]^4}{[A][B]^3} = \frac{[4x]^4}{[4x][2x]^3} = \frac{256}{32} = 8]$$

9. For a hypothetical reaction:

$$4A(g) + 5B(g) \rightleftharpoons 4P(g) + 6Q(g)$$

The equilibrium constant K_c has units:

(a) $mol\ L^{-1}$ (b) $mol^{-1}\ L$

(c) $(mol\ L^{-1})^{-2}$ (d) unitless

[**Ans.** (a)]

[**Hint:** Unit of $K_c = (mol\ L^{-1})^{\Delta n}$

$= (mol\ L^{-1})^1 = mol\ L^{-1}$]

10. Starting with 1 mol of O_2; 2 mol of SO_2, the equilibrium for the formation of $SO_3(g)$ was established at a certain temperature. If V is the volume of the vessel and $2x$ is the number of moles of SO_3 present, the equilibrium constant will be:

(a) $\dfrac{x^2V}{(1-x)^3}$ (b) $\dfrac{4x^2}{(2-x)(1-x)}$

(c) $\dfrac{(1-x)^3}{2V}$ (d) $\dfrac{x^2}{(2-x)(1-x)}$

[**Ans.** (a)]

[**Hint:**

$$\begin{array}{lccc} & 2SO_2(g) + & O_2(g) \rightleftharpoons & 2SO_3(g) \\ t=0 & 2 & 1 & 0 \\ t_{eq.} & \left[\dfrac{2-2x}{V}\right] & \left[\dfrac{1-x}{V}\right] & \left[\dfrac{2x}{V}\right] \end{array}$$

$$\therefore K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[2x/V]^2}{\left[\dfrac{2-2x}{V}\right]^2\left[\dfrac{1-x}{V}\right]} = \frac{x^2V}{(1-x)^3}]$$

11. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $K = 47.6$, if the initial number of moles of each reactant and product is 1 mole, then at equilibrium: [JEE (Orissa) 2006]

(a) $[I_2] = [H_2]; [I_2] > [HI]$ (b) $[I_2] < [H_2]; [I_2] = [HI]$

(c) $[I_2] = [H_2]; [I_2] < [HI]$ (d) $[I_2] > [H_2]; [I_2] = [HI]$

[**Ans.** (c)]

[**Hint:** $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

$[H_2] = [I_2]$ will be same at equilibrium, since it is same at initial state.

$$K_c = \frac{[HI]^2}{[I_2]^2}$$

$$K_c[I_2]^2 = [HI]^2$$
$$47.6[I_2]^2 = [HI]^2$$
$$\therefore \quad [I_2] < [HI]]$$

12. In a closed vessel of volume V, a mol of nitrogen and b mol of oxygen are made to react to give nitric oxide, according to the reaction:

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

If at equilibrium, $2x$ mol of NO are obtained, then: [BV (Pune) 2006]

(a) $K_c = \dfrac{4x^2}{(a-x)(b-x)} \times \dfrac{1}{V}$

(b) $K_c = \dfrac{4x^2}{(a-x)(b-x)} \times V$

(c) $K_c = \dfrac{x^2}{(a-x)(b-x)} \times V$

(d) $K_c = \dfrac{4x^2}{(a-x)(b-x)}$

[Ans. (d)]

[Hint:

$$\begin{array}{cccc} & N_2(g) & + \; O_2(g) \rightleftharpoons & 2NO(g) \\ t=0 & a & b & 0 \\ t_{eq.} & \dfrac{(a-x)}{V} & \left(\dfrac{b-x}{V}\right) & \dfrac{2x}{V} \end{array}$$

$$K_c = \frac{\left(\dfrac{2x}{V}\right)^2}{\left(\dfrac{a-x}{V}\right)\left(\dfrac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}]$$

13. Equivalent amounts of H_2 and I_2 are heated in a closed till equilibrium is obtained. If 80% of the hydrogen can be converted to HI, the K_c at this temperature is: (VITEEE 2007)

(a) 64 (b) 16 (c) 0.25 (d) 4

[Ans. (a)]

[Hint:

$$\begin{array}{cccc} & H_2(g) & + \; I_2(g) \rightleftharpoons & 2HI(g) \\ t=0 & 1 & 1 & 0 \\ t_{eq.} & \dfrac{1-0.8}{V} & \dfrac{1-0.8}{V} & \dfrac{2\times 0.8}{V} \end{array}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left[\dfrac{1.6}{V}\right]^2}{\dfrac{0.2}{V}\times\dfrac{0.2}{V}} = 64]$$

14. Equimolar concentration of H_2 and I_2 are heated to equilibrium in a 2 litre flask. At equilibrium, the forward and backward rate constants are found to be equal. What percentage of initial concentration of H_2 has reacted at equilibrium? [PMT (Kerala) 2008]

(a) 33% (b) 66%

(c) 50% (d) 40%

(e) 20%

[Ans. (a)]

[Hint :

$$\begin{array}{cccc} & H_2(g) & + \; I_2(g) \rightleftharpoons & 2HI(g) \\ t_0 & 1 & 1 & 0 \\ t_{eq.} & \dfrac{1-x}{2} & \dfrac{1-x}{2} & \dfrac{2x}{2} \end{array}$$

$$K = \frac{k_f}{k_b} = 1 = \frac{[HI]^2}{[H_2][I_2]} = \frac{(x)^2}{\left(\dfrac{1-x}{2}\right)\left(\dfrac{1-x}{2}\right)}$$

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

$$1 = \frac{2x}{1-x}$$

$$x = 0.33$$

% of H_2 reacted = 33]

9.8 LE CHATELIER'S PRINCIPLE

There are three main factors which can change the state of equilibrium in a reversible system. These are concentration, pressure and temperature. Le Chatelier, a French chemist, presented a qualitative principle known as Le Chatelier's principle which can describe the effect of change in concentration, pressure and temperature on any reversible system whether physical or chemical.

According to this principle, **if a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.**

Or

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way as to annul the effect of that change.

(a) Change in concentration: If an additional amount of any reactant or product is added to the system, the stress is relieved as the reaction that consumes the added substance occurs more rapidly than its reverse reaction, *i.e.*, if any of the reactants is added, the rate of forward reaction increases and if any of the products is added, the rate of backward reaction increases.

In general, in a chemical equilibrium, increasing the concentrations of the reactants results in shifting the equilibrium in favour of products while increasing concentrations of the products results in shifting the equilibrium in favour of reactants.

(b) Change in pressure: If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The total number of moles per unit volume will now be more than before. According to Le Chatelier's principle, the equilibrium will shift in the direction in which there is decrease in number of moles, *i.e.*, towards the direction in which there is decrease in volume.

In general, **an increase in pressure applied to a system at equilibrium, favours the reaction in the direction that produces smaller number of moles of gases and a decrease in pressure favours the opposite reaction.** If there is no change in number of moles of gases in a reaction, a pressure change does not affect the equilibrium.

(c) Change in temperature: A chemical reaction (reversible) involves two opposing reactions, forward and backward. If one reaction is endothermic, the other will be exothermic in nature. When heat energy is added by raising temperature, the system can relieve itself from the stress if the reaction which absorbs heat moves faster, *i.e.*, **endothermic reaction is always favoured with increase of temperature.**

Conclusions:

(i) Increase in concentration of any substance favours the reaction in which it is used up.

(ii) High pressure is favourable for the reaction in which there is decrease in volume.

(iii) A rise in temperature favours the endothermic reaction.

(d) Role of catalyst: Positive catalyst increases the rate of both forward and backward reactions equally; the equilibrium will be attained in less time, *i.e.*, same amount of product will be formed in less time.

On the other hand, negative catalyst lowers the rate of both forward and backward reactions equally. Same amount of product will be formed in more time.

Catalyst does not affect equilibrium constant and heat of reaction.

Summary of Le Chatelier's Principle

Effect of inert gas addition

Condition		Effect
$\Delta V = 0, V = \text{Constant}$	$\Delta n = 0, +\text{ve or } -\text{ve}$	No effect
$\Delta V \neq 0, V \neq \text{Constant}$	$\Delta n = 0$	No effect
$\Delta V \neq 0, V \neq \text{Constant}$	$\Delta n > 0$	Forward shift
$\Delta V \neq 0, V \neq \text{Constant}$	$\Delta n < 0$	Backward shift

where, Δn = number of gaseous moles of product − number of gaseous moles of reactant

Effect of temperature and pressure

	Nature of reaction	Effect of increased temperature	Δn; Side with fewer mole of gas	Effect of increase in P
1.	Exothermic	backward shift	0; neither	no shift
2.	Exothermic	backward shift	–ve; right	forward shift
3.	Endothermic	forward shift	–ve; right	forward shift
4.	Endothermic	forward shift	+ve; left	backward shift
5.	Exothermic	backward shift	+ve; left	backward shift
6.	Exothermic	backward shift	–ve; right	forward shift
7.	Endothermic	forward shift	+ve; left	backward shift
8.	Endothermic	forward shift	+ve; left	backward shift

Application of Le Chatelier's Principle

(a) Formation of HI:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + 3000 \text{ cal}$$

Effect of concentration: When concentration of H_2 or I_2 is increased at equilibrium, the system moves in a direction which decreases the concentration, *i.e.*, the rate of forward reaction increases thereby increasing the concentration of HI.

Effect of pressure: As there is no change in the number of moles in the reaction, the equilibrium state remains unaffected by change of pressure.

Effect of temperature: By increasing temperature, the equilibrium state shifts towards the reaction which moves with absorption of heat. The formation of HI is an exothermic reaction. Thus, the backward reaction moves faster when temperature is increased.

In short, we can say that the favourable conditions for greater yield of HI are:

(i) High concentrations of H_2 and I_2 and

(ii) Low temperature.

(b) Formation of nitric oxide:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43200 \text{ cal}$$

Effect of concentration: When concentration of N_2 or O_2 is increased, the system moves in a direction in which N_2 or O_2 is used up, *i.e.*, rate of forward reaction increases thereby increasing the concentration of NO.

Effect of pressure: In the formation of nitric oxide, the number of moles remains the same, *i.e.*, no change in volume occurs. Consequently, the equilibrium state is not affected by any change in pressure.

Effect of temperature: The formation of NO is endothermic in nature. If the temperature is raised, the equilibrium shifts in the direction in which heat is absorbed. The concentration of NO will, therefore, be higher at higher temperature.

Thus, favourable conditions for greater yield of nitric oxide are:

(i) High concentrations of N_2 and O_2 and

(ii) High temperature

(c) Dissociation of PCl_5:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) - 15000 \text{ cal}$$

Effect of concentration: When concentration of PCl_5 is increased at equilibrium, the rate of forward reaction increases as to decrease the added concentration. Thus, more of PCl_3 and Cl_2 are formed.

Effect of pressure: The volume increases in the dissociation of PCl_5. When pressure is increased, the system moves in the direction in which there is decrease in volume. Thus, high pressure does not favour dissociation of PCl_5.

Effect of temperature: The dissociation of PCl_5 is an endothermic reaction. Thus, increase of temperature favours the dissociation.

Thus, favourable conditions for dissociation of PCl_5 are:

(i) High concentration of PCl_5,

(ii) Low pressure and

(iii) High temperature.

(d) Formation of ammonia:

$$N_2(g) + 3H_2(g) \overset{Fe}{\rightleftharpoons} 2NH_3(g); \Delta H = -22.4 \text{ kcal/mol}$$

(i) At high pressure reaction will shift in forward direction to form more product.

(ii) When concentration of N_2 and H_2 is raised or concentration of NH_3 is lowered, then again the equilibrium shifts in forward direction to form more ammonia.

If concentration of only one reactant is raised, then again the equilibrium shifts in forward direction till the other reactant is available for reaction.

(iii) The reaction shifts in forward direction at low temperature. But at very low temperature the rate of reaction becomes very low; thus moderate temperature is favourable for this reaction.

9.9 APPLICATION OF LE CHATELIER'S PRINCIPLE TO PHYSICAL EQUILIBRIA

(i) Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Gas

When temperature is raised, the above equilibrium shifts in forward direction.

(ii) Effect of pressure on boiling point: When pressure is raised, condensation of vapour takes place. Thus, vapour pressure is lowered. Now more heat is required to equate vapour pressure with atmospheric pressure as a result of which boiling point increases.

(iii) Effect of pressure on melting point: There are two types of solids:

(a) Solids whose volume decreases on melting, *e.g.*, ice, diamond, carborundum, magnesium nitride and quartz.

$$\text{Solid (higher volume)} \rightleftharpoons \text{Liquid (lower volume)}$$

The process of melting is facilitated at high pressure, thus melting point is lowered.

(b) Solids whose volume increases on melting, *e.g.*, Fe, Cu, Ag, Au, etc.

$$\text{Solid (lower volume)} \rightleftharpoons \text{Liquid (higher volume)}$$

In this case the process of melting become difficult at high pressure; thus melting point becomes high.

(c) Solubility of substances: When solid substances are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).

$$\text{KCl} + aq. \rightleftharpoons \text{KCl}(aq.) - \text{heat}$$

In such cases, solubility increases with increase in temperature. Consider the case of KOH; when this is dissolved, heat is evolved.

$$\text{KOH} + aq. \rightleftharpoons \text{KOH}(aq.) + \text{heat}$$

In such cases, solubility decreases with increase in temperature.

(d) Solubility of gases in liquids: When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

15. Consider the following reversible reaction at equilibrium:

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g); \ \Delta H = +24.7 \text{ kJ}$$

which one of the following changes in conditions will lead to maximum decomposition of $H_2O(g)$?

(a) Increasing both temperature and pressure

(b) Decreasing temperature and increasing pressure

(c) Increasing temperature and decreasing pressure

(d) Increasing temperature at constant pressure

(e) Increasing pressure at constant temperature

[**Ans.** (c)]

[**Hint:** Reaction is endothermic and $\Delta n > 0$, hence, the formation of product will be favoured by increasing the temperature and decreasing the pressure.]

16. The exothermic formation of ClF_3 is represented by the equation:

$$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g); \ \Delta H = -329 \text{ kJ}$$

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3? (AIEEE 2005)

(a) Increasing the temperature

(b) Removing Cl_2

(c) Increasing the volume of the container

(d) Adding F_2

[**Ans.** (d)]

[**Hint:** Equilibrium will shift in forward direction by increasing the concentration of reactant.]

17. Which among the following reactions will be favoured at low pressure?

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

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

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

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

[**Ans.** (c)]

[**Hint:** On lowering the pressure, equilibrium favours the direction of higher volume.]

18. At constant pressure, the addition of argon to:

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

will:

(a) shift the equilibrium in forward direction

(b) shift the equilibrium in backward direction

(c) not affect the equilibrium

(d) stop the reaction

[**Ans.** (b)]

[**Hint:** If volume is not constant, the addition of inert gas favours the direction where volume is increasing.]

19. The equilibrium reaction that is not influenced by volume change at constant temperature is: [CET (J&K) 2006]

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

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

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

(d) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

[**Ans.** (a)]

[**Hint:** When, $\Delta n = 0$, there is no effect of pressure and volume change on the equilibrium.]

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

What is the effect of the increase of temperature on the equilibrium of the reaction? (KCET 2008)

(a) Equilibrium is unaltered

(b) Reaction rate does not change

(c) Equilibrium is shifted to the left

(d) Equilibrium is shifted to the right

[**Ans.** (c)]

[**Hint:** The given reaction is exothermic, therefore, the equilibrium will shift in backward direction by the increase of temperature.]

9.10 CALCULATION OF DEGREE OF DISSOCIATION FROM DENSITY MEASUREMENTS

Degree of dissociation is defined as the fraction of one molecule dissociated. It is denoted by x or α. Its value is always less than 1. When the value becomes equal to 1, it is said that the substance is completely dissociated.

The degree of dissociation in the case of second type of reactions (reversible) is determined by measuring density of reaction mixture at equilibrium.

Consider the general reversible reaction,

	A	$\rightleftharpoons$ nB
Initial no. of moles	1	0
No. of moles at equilibrium	$(1-x)$	nx

Total number of moles at equilibrium $= (1-x)+nx$

$$= 1+(n-1)x$$

Let the initial volume be V litre. Thus, the volume at equilibrium

$$= [1+(n-1)x]V.$$

Let 'd' be the observed vapour density at a particular temperature when degree of dissociation is 'x' and D be the vapour density when there is no dissociation. Again,

$$D \propto \frac{1}{V} \quad \text{... (i)}$$

and

$$d \propto \frac{1}{[1+(n-1)x]V} \quad \text{... (ii)}$$

Dividing eq. (i) by eq. (ii),

$$\frac{D}{d} = 1+(n-1)x$$

or

$$\frac{D}{d} - 1 = (n-1)x$$

or

$$\frac{D-d}{d} = (n-1)x$$

or

$$x = \frac{D-d}{(n-1)d} \quad \text{... (iii)}$$

$$x = \frac{M-m}{(n-1)m}$$

where, M = initial molecular mass

m = molecular mass at equilibrium.

In the dissociation of PCl_5, NH_4Cl and N_2O_4, the value of $n = 2$.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

$$N_2O_4 \rightleftharpoons 2NO_2$$

So,

$$x = \frac{D-d}{(2-1)d} = \frac{D-d}{d}$$

Calculation of Degree of Reaction using Pressure-Temperature Determination

Let us consider the following gaseous reaction:

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

Initial pressure and temperature are P_1 and T_1. At equilibrium, pressure and temperature are P_2 and T_2 respectively. The volume of vessel is constant, equal to 'V'.

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g) +$	$Cl_2(g)$	n	V	T	P
$t=0$	a	0	0	a	V	T_1	P_1
$t_{eq.}$	$a-ax$	ax	ax	$a+ax$	V	T_2	P_2

Initial state $\quad P_1V = aRT_1 \quad$ ... (i)

Equilibrium state $\quad P_2V = (a+ax)RT_2 \quad$ ... (ii)

Dividing equation (i) by eq. (ii), we get

$$\frac{P_1}{P_2} = \frac{T_1}{(1+x)T_2}$$

$$(1+x) = \frac{T_1P_2}{T_2P_1}$$

$$x = \frac{T_1P_2 - T_2P_1}{T_2P_1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

21. At equilibrium:

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

the observed molecular weight of N_2O_4 is 80 g mol^{-1} at 350 K. The percentage dissociation of $N_2O_4(g)$ at 350 K is:

[PMT Kerala [illegible]]

(a) 10% (b) 15% (c) 20% (d) 18%

(e) 13%

[**Ans.** (b)]

[**Hint:** Degree of dissociation may be calculated as,

$$x = \frac{M-m}{(n-1)m} \qquad \because n = 2 \text{ (number of gas moles produced by 1 mol reactant)}$$

$$= \frac{92-80}{(2-1)80} \qquad (M = 92, m = 80)$$

$$= \frac{12}{80} = 0.15$$

Percentage dissociation = 0.15 × 100 = 15]

22. The vapour density of PCl_5 is 104.25 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:

(a) 6.8% (b) 68% (c) 46% (d) 64%

[**Ans.** (b)]

[**Hint:** The reaction is:

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

$$n = 2$$

$$\alpha = \frac{D-d}{(n-1)d} = \frac{104.25-62}{(2-1)\times 62}$$

$$= 0.68$$

Percentage dissociation = 0.68 × 100 = 68%]

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *At a certain temperature, equilibrium constant (K_c) is 16 for the reaction:*

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

If we take one mole of each of the four gases in one litre container, what would be the equilibrium concentration of NO and NO_2?

Solution:

	$SO_2(g)$ +	$NO_2(g) \rightleftharpoons$	$SO_3(g)$ +	$NO(g)$
Initial concentration	1	1	1	1
Equilibrium concentration	$1-x$	$1-x$	$1+x$	$1+x$

Applying law of mass action,

$$K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = 16$$

$$\frac{1+x}{1-x} = 4 \text{ or } 1+x = 4-4x$$

or $$5x = 3, \text{ i.e., } x = \frac{3}{5} = 0.6$$

Conc. of NO_2 at equilibrium $= (1-0.6) = 0.4$ mole

Conc. of NO at equilibrium $= (1+0.6) = 1.6$ mole

Example 2. *At 817°C, K_p for the reaction between $CO_2(g)$ and excess of hot graphite (s) is 10 atm.*

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

(b) At what total pressure does the gas contain 5% CO_2 by volume? (IIT 2000)

Solution: (a) $CO_2(g) + C(s) \rightleftharpoons 2CO(g); K_p = 10$ atm

Given: $p_{CO(g)} + p_{CO_2(g)} = 5$ atm

Let $p_{CO(g)} = x$ atm

So, $p_{CO_2(g)} = (5-x)$ atm

$$K_p = \frac{[p_{CO}]^2}{p_{CO_2}} = \frac{x^2}{(5-x)}$$

or $$10 = \frac{x^2}{(5-x)}$$

or $$x^2 + 10x - 50 = 0$$

On solving, we get

$$x = 3.66$$

$$p_{CO(g)} = 3.66 \text{ atm}$$

or Mole fraction CO at equilibrium = 73.2% (by volume)

$$p_{CO_2(g)} = 1.34 \text{ atm}$$

or Mole fraction CO_2 at equilibrium = 26.8% (by volume)

(b) Let the total pressure be P atm

Given, % CO_2 (by volume) = 5 and % CO (by volume) = 95

$$p_{CO_2} = \frac{5}{100} \times P = 0.05P \text{ and } p_{CO} = \frac{95}{100} \times P = 0.95P$$

$$K_p = 10 = \frac{[p_{CO}]^2}{p_{CO_2}} = \frac{0.95P \times 0.95P}{0.05P} = 18.05P$$

or $$P = 0.554 \text{ atm}$$

Example 3. *At 700 K, CO_2 and H_2 react to form CO and H_2O. For this process K_c is 0.11. If a mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated to 700 K.*

(i) Find out the amount of each gas at equilibrium state.

(ii) After equilibrium is reached another 0.34 mole of CO_2 and 0.34 mole of H_2 are added to the reaction mixture. Find the composition of the mixture at the new equilibrium state.

Solution: (i)

	$CO_2(g)$ +	$H_2(g) \rightleftharpoons$	$CO(g)$ +	$H_2O(g)$
Initial no. of moles	0.45	0.45	0	0
of moles at equilibrium	$0.45-x$	$0.45-x$	x	x

Applying law of mass action,

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{x \times x}{(0.45-x)(0.45-x)} = \frac{x^2}{(0.45-x)^2} = 0.11$$

So, $$\frac{x}{(0.45-x)} = 0.33$$

$$x = 0.11$$

At equilibrium, $[CO_2] = [H_2] = 0.34$ mole

$[CO] = [H_2O] = 0.11$ mole

(ii)

	CO_2 +	$H_2 \rightleftharpoons$	CO +	H_2O
Initial moles	$0.34 + 0.34$ $= 0.68$	$0.34 + 0.34$ $= 0.68$	0.11	0.11
At equilibrium	$0.68-y$	$0.68-y$	$0.11+y$	$0.11+y$

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{(0.11+y)(0.11+y)}{(0.68-y)(0.68-y)} = 0.11$$

or $$\frac{0.11+y}{0.68-y} = 0.33$$

or $$0.11 + y = 0.33 \times 0.68 - 0.33y$$

or $$y = 0.086$$

At equilibrium, $[CO] = [H_2O] = 0.11 + 0.086 = 0.196$ mole

$[CO_2] = [H_2] = 0.68 - 0.086 = 0.594$ mole

Example 4. *A mixture of SO_3, SO_2 and O_2 gases is maintained in a 10 litre flask at a temperature at which the equilibrium constant for the reaction is 100:*

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

(i) If the number of moles of SO_2 and SO_3 in the flask are equal, how many moles of O_2 are present?

(ii) If the number of moles of SO_3 in the flask is twice the number of moles of SO_2, how many moles of oxygen are present?

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

At equilibrium, let the number of moles of each of SO_2 and SO_3 be n_1 and of oxygen n_2, i.e.,

$$[SO_2] = \frac{n_1}{10}$$

$$[O_2] = \frac{n_2}{10}$$

$$[SO_3] = \frac{n_1}{10}$$

Applying law of mass action,

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\frac{n_1}{10}\right)^2}{\left(\frac{n_1}{10}\right)^2\left(\frac{n_2}{10}\right)} = 100$$

or $$n_2 = 0.1 \text{ mole}$$

Oxygen = 0.1 mole

(ii) Let the number of moles of SO_2 be $= n_1$

So, number of moles of $SO_3 = 2n_1$

Let the number of moles of oxygen be $= n_2$

$$K_c = \frac{\left(\frac{2n_1}{10}\right)^2}{\left(\frac{n_1}{10}\right)^2\left(\frac{n_2}{10}\right)} \text{ or } 100 = \frac{40}{n_2}$$

$$n_2 = 0.4 \text{ mole}$$

Oxygen = 0.4 mole

Example 5. *At 250°C and 1 atmospheric pressure, the vapour density of PCl_5 is 57.9. Calculate (i) K_p for the reaction,*

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

at 250°C, (ii) the percentage dissociation when pressure is doubled.

Solution: (i) Mol. mass of $PCl_5 = 208.5$

$$\text{Vapour density, } D = \frac{208.5}{2} = 104.25$$

Observed vapour density, $d = 57.9$

$$\text{Degree of dissociation, } \alpha = \frac{D-d}{d} = \frac{104.25 - 57.9}{57.9}$$

$$= 0.80$$

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g)$ +	$Cl_2(g)$
At equilibrium	$1-\alpha$	α	α
	$(1-0.80)$	0.80	0.80

Total number of moles $= (1+\alpha) = (1+0.80) = 1.80$

$$\text{Partial pressure of } PCl_5 = \frac{0.2}{1.80} \times 1 = \frac{1}{9}$$

$$\text{Partial pressure of } PCl_3 = \frac{0.80}{1.80} \times 1 = \frac{4}{9}$$

$$\text{Partial pressure of } Cl_2 = \frac{0.80}{1.80} \times 1 = \frac{4}{9}$$

So, $$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{4/9 \times 4/9}{1/9} = \frac{16}{9} = 1.78$$

(ii) Let the degree of dissociation be α when pressure is 2 atmospheres.

At equilibrium

$$p_{PCl_5} = \frac{(1-\alpha)}{(1+\alpha)} \cdot P = \frac{(1-\alpha)}{(1+\alpha)} \times 2$$

$$p_{PCl_3} = \frac{\alpha}{(1+\alpha)} \cdot P = \frac{\alpha}{(1+\alpha)} \times 2$$

$$p_{Cl_2} = \frac{\alpha}{(1+\alpha)} \cdot P = \frac{\alpha}{(1+\alpha)} \times 2$$

$$K_p = \frac{\frac{\alpha}{(1+\alpha)} \times 2 \times \frac{\alpha}{(1+\alpha)} \times 2}{\frac{(1-\alpha)}{(1+\alpha)} \times 2} = \frac{\alpha^2}{(1-\alpha^2)} \times 2 = 1.78$$

or $$\frac{\alpha^2}{(1-\alpha^2)} = 0.89$$

or $$\alpha^2 = 0.89 - 0.89\alpha^2$$

or $$1.89\alpha^2 = 0.89$$

$$\alpha^2 = \frac{0.89}{1.89}$$

$$\alpha = 0.686$$

Thus, PCl_5 is 68.6% dissociated.

Example 6. *For the reaction,*

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

hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of CO(g) and a catalyst, until the pressure is 4.92 atmosphere. At this point 0.1 mole of $CH_3OH(g)$ is formed. Calculate the equilibrium constants K_p and K_c. (IIT 1990)

Solution: Let the number of moles of hydrogen introduced be m moles.

Total moles of CO and hydrogen $= 0.2 + m$

Applying, $PV = nRT$

$$P = 4.92 \text{ atm}, \; V = 5 \text{ litre}, \; R = 0.082,$$

$$T = (273 + 327) = 600 \text{ K}$$

$$4.92 \times 5 = 0.082 \times 600 \times (0.2 + m)$$

or $$0.2 + m = \frac{4.92 \times 5}{0.082 \times 600}$$

or $$m = 0.3 \text{ mole}$$

	$CO(g)$ +	$2H_2(g) \rightleftharpoons$	$CH_3OH(g)$	
	$0.2 - x$	$0.3 - 2x$	x	(No. of moles
or	$0.2 - 0.1$	$0.3 - 0.2$	0.1	at equilibrium)
or	0.1	0.1	0.1	
	$\frac{0.1}{5}$	$\frac{0.1}{5}$	$\frac{0.1}{5}$	(Active masses)

Applying law of mass action,

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{\frac{0.1}{5}}{\frac{0.1}{5} \times \left(\frac{0.1}{5}\right)^2} = 2500\,\text{mol}^{-2}\,\text{L}^2$$

We know that, $K_p = K_c(RT)^{\Delta n}, \Delta n = -2$

or $K_p = 2500(0.082 \times 600)^{-2}$

or $$K_p = \frac{2500}{49.2 \times 49.2} = 1.0327\,\text{atm}^{-2}$$

Example 7. *When sulphur in the form of S_8 is heated at 900 K the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2. Find the value of equilibrium constant for this reaction.*

Solution: $S_8(g) \rightleftharpoons 4S_2(g)$

	$S_8(g)$	$4S_2(g)$
Initial mole	1	0
At equilibrium	$1-x$	$4x$
	$(1-0.29)$ $= 0.71$	(4×0.29) $= 1.16$

Applying law of mass action,

$$K_p = \frac{[p_{S_2}]^4}{[p_{S_8}]} = \frac{(1.16)^4}{0.71} = 2.5582\,\text{atm}^3$$

Example 8. *For the equilibrium,*

$$AB(g) \rightleftharpoons A(g) + B(g),$$

K_p is equal to four times the total pressure. Calculate the number of moles of A formed.

Solution: Let the total equilibrium pressure be $= P$ atm

Given, $K_p = 4P$

Let the start be made with 1 mole of $AB(g)$ and the degree of dissociation be x.

	$AB(g) \rightleftharpoons$	$A(g) +$	$B(g)$
At equilibrium	$1-x$	x	x

Total moles at equilibrium $= 1 - x + x + x = 1 + x$

Thus, p_A = Partial pressure of $A = \frac{x}{1+x} \cdot P$

p_B = Partial pressure of $B = \frac{x}{1+x} \cdot P$

p_{AB} = Partial pressure of $AB = \frac{1-x}{1+x} \cdot P$

Applying the law of mass action,

$$K_p = \frac{p_A \times p_B}{p_{AB}} = \frac{\left(\frac{x}{1+x} \cdot P\right)\left(\frac{x}{1+x} \cdot P\right)}{\left(\frac{1-x}{1+x} \cdot P\right)}$$

So, $$4P = \frac{x^2}{1-x^2} \cdot P$$

or $4 - 4x^2 = x^2$

or $5x^2 = 4$

or $x = \frac{2}{\sqrt{5}}$

Hence, number of moles of A formed $= \frac{2}{\sqrt{5}}$ times initial moles of AB taken

Example 9. *0.15 mole of CO taken in a 2.5 litre flask is maintained at 705 K along with a catalyst so that the following reaction can take place:*

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

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. (IIT 1993)

Solution: (i) Let the total number of moles of gases be n at equilibrium.

Applying equation, $PV = nRT$

Given, $P = 8.5$ atm; $V = 2.5$ L;

$R = 0.0821\,\text{atm L mol}^{-1}\,\text{K}^{-1}$ and $T = 705$ K

$$n = \frac{8.5 \times 2.5}{0.0821 \times 705} = 0.367\,\text{mol}$$

	$CO(g) +$	$2H_2(g)$	$\rightleftharpoons CH_3OH(g)$
Initial mole	0.15	$(nH_2)_0$	0
At equilibrium	$0.15 - x$	$[(nH_2)_0 - 2x]$	$x = 0.08$

Number of moles of CO at equilibrium

$= (0.15 - 0.08) = 0.07$ mole

Number of moles of H_2 at equilibrium

= total moles − moles of CO − moles of CH_3OH

$= (0.367 - 0.07 - 0.08)$

$= 0.217$ mole

Applying law of mass action,

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{\frac{0.08}{2.5}}{\frac{0.07}{2.5} \times \left(\frac{0.217}{2.5}\right)^2} = 151.6\,\text{mol}^{-2}\,\text{L}^2$$

Now, $K_p = K_c(RT)^{\Delta n} = 151.6 \times (0.0821 \times 705)^{-2}$

$= 0.045\,\text{atm}^{-2}$

(ii) Since, $[(n_{H_2})_0 - 2x] = 0.217$

or $(n_{H_2})_0 = 0.217 + 2 \times 0.08$

$= 0.377$ mole

$(n_{CO})_0 = 0.15$

Total moles $(n_0) = 0.377 + 0.15 = 0.527$

Hence, $$p_0 = \frac{n_0RT}{V} = \frac{0.527 \times 0.0821 \times 705}{2.5}$$

$= 12.20$ atm

Example 10. *The equilibrium constant for the reaction,*

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

at 986°C is 0.63. A mixture of 1.0 mole of water vapour and 3.0 mole of CO is allowed to come to equilibrium. The equilibrium pressure is 2.0 atm.

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

(*ii*) *Calculate the partial pressures of gases in equilibrium mixture.* (IIT 1992)

Solution: (i) In the given reaction, $\Delta n = 0$, hence, $K_c = K_p$

$$\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$$

$$\text{At equilibrium} \quad (3-x) \quad (1-x) \quad x \quad x$$

Applying law of mass action,

$$\frac{x \times x}{(3-x)(1-x)} = 0.63$$

$$x^2 = 0.63(3 - 4x + x^2)$$

$$0.37x^2 + 2.52x - 1.89 = 0$$

or

$$x^2 + 6.81x - 5.1 = 0$$

$$x = \frac{-6.81 \pm [6.81 \times 6.81 - 4 \times (-5.1)]^{1/2}}{2} = 0.68 \text{ mole} = \mathrm{H_2}$$

(ii) Partial pressure of $\mathrm{CO_2}$ = partial pressure of $\mathrm{H_2}$

$$= \text{mole fraction} \times \text{total pressure}$$

$$= \frac{0.68}{4} \times 2 = 0.34 \text{ atm}$$

$$\text{Partial pressure of CO}(g) = \frac{(3 - 0.68)}{4} \times 2 = 1.16 \text{ atm}$$

$$\text{Partial pressure of } \mathrm{H_2O}(g) = \frac{(1 - 0.68)}{4} \times 2 = 0.16 \text{ atm}$$

Example 11. *The equilibrium constant K_p for the reaction,*

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

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

Solution: The system in the initial stage does not contain $\mathrm{SO_2}$. $\mathrm{SO_3}$ will, thus, decompose to form $\mathrm{SO_2}$ and $\mathrm{O_2}$ until equilibrium is reached. The partial pressure of $\mathrm{SO_3}$ will decrease. Let the decrease in partial pressure be $2x$.

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

$$\text{At equilibrium} \quad (2x) \quad (2+x) \quad (1-2x)$$

Applying law of mass action,

$$K_p = \frac{(1-2x)^2}{(2x)^2(2+x)} \qquad (2+x) \rightarrow 2$$

$$900 = \frac{(1-2x)^2}{8x^2}$$

or

$$\frac{1-2x}{x} = 84.85$$

or

$$x = 0.0115 \text{ atm}$$

Thus, the partial pressures at equilibrium are:

$$p_{\mathrm{SO_2}} = 2 \times 0.0115 = 0.023 \text{ atm}$$

$$p_{\mathrm{O_2}} = 2 + 0.0115 = 2.0115 \text{ atm}$$

$$p_{\mathrm{SO_3}} = 1 - 2 \times 0.0115 = 0.977 \text{ atm}$$

Example 12. *What is the concentration of CO in equilibrium at 25°C in a sample of a gas originally containing 1.00 $mol\,L^{-1}$ of CO_2? For the dissociation of CO_2 at 25°C, $K_c = 2.96 \times 10^{-92}$.*

Solution:

$$2\mathrm{CO_2}(g) \rightleftharpoons 2\mathrm{CO}(g) + \mathrm{O_2}(g)$$

$$\text{At equilibrium} \quad (1-2x) \quad (2x) \quad (x)$$

Applying law of mass action,

$$K_c = \frac{[\mathrm{O_2}][\mathrm{CO}]^2}{[\mathrm{CO_2}]^2} = \frac{x \times (2x)^2}{(1-2x)^2} = 2.96 \times 10^{-92}$$

It can be assumed that $1 - 2x \approx 1.0$ as K_c is very small.

So,

$$4x^3 = 2.96 \times 10^{-92}$$

or

$$x = 1.95 \times 10^{-31} \text{ mol L}^{-1}$$

$$[\mathrm{CO}] = 2x = 2 \times 1.95 \times 10^{-31}$$

$$= 3.90 \times 10^{-31} \text{ mol L}^{-1}$$

Example 13. *Ammonia is heated at 15 atm from 27°C to 347°C assuming volume constant. The new pressure becomes 50 atm at equilibrium. Calculate % of NH_3 actually decomposed.* (MLNR [illegible])

Solution: Pressure of $\mathrm{NH_3}$ at 27°C = 15 atm

Pressure of $\mathrm{NH_3}$ at 347°C = P atm

$$\frac{P}{620} = \frac{15}{300}$$

$$P = 31 \text{ atm}$$

Let a moles of ammonia be present. Total pressure at equilibrium = 50 atm

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

$$\text{At equilibrium} \quad (a-2x) \quad x \quad 3x$$

$$\text{Total moles} \quad a - 2x + x + 3x = a + 2x$$

$$\frac{\text{Initial number of moles}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure}}{\text{Equilibrium pressure}}$$

$$\frac{a}{(a+2x)} = \frac{31}{50}$$

$$x = \frac{19}{62}a$$

$$\text{Amount of ammonia decomposed} = 2x = 2 \times \frac{19}{62}a = \frac{19}{31}a$$

$$\%\text{ of ammonia decomposed} = \frac{19 \times a}{31 \times a} \times 100$$

$$= 61.3$$

Example 14. *Calculate the per cent dissociation of $H_2S(g)$ if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1000 K for the reaction,*

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

The value of K_c is 1.0×10^{-6}.

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

$$\begin{array}{llll} \text{At equilibrium} & (0.1-x) & x & x/2 \\ \text{Molar conc.} & \dfrac{(0.1-x)}{0.4} & \dfrac{x}{0.4} & \dfrac{x}{0.8} \end{array}$$

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left(\frac{x}{0.4}\right)^2\left(\frac{x}{0.8}\right)}{\left(\frac{0.1-x}{0.4}\right)^2} = 1.0 \times 10^{-6}$$

or
$$\frac{x^3}{0.8(0.1-x)^2} = 1.0 \times 10^{-6}$$

as x is very small; $0.1 - x \rightarrow 0.1$

$$\frac{x^3}{0.8 \times (0.1)^2} = 1.0 \times 10^{-6}$$

$$x^3 = 8 \times 10^{-9}$$

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

So, per cent dissociation $= \dfrac{2 \times 10^{-3}}{0.1} \times 100 = 2.0$

Example 15. *The vapour density (hydrogen = 1) of a mixture containing NO_2 and N_2O_4 is 38.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 grams of the mixture.* (MLNR 1993)

Solution: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At equilibrium $(1-x)$ $\quad 2x$

$$x \text{ (degree of dissociation)} = \frac{D-d}{(n-1)d}$$

Given, $d = 38.3$, $D = \dfrac{\text{Mol. mass of } N_2O_4}{2} = \dfrac{92}{2} = 46$, $n = 2$

So, $x = \dfrac{46 - 38.3}{38.3} = 0.2$

At equilibrium, amount of $N_2O_4 = 1 - 0.2 = 0.8$ mol

and amount of $NO_2 = 2 \times 0.2 = 0.4$ mol

Mass of the mixture $= 0.8 \times 92 + 0.4 \times 46$

$= 73.6 + 18.4 = 92.0$ g

Since, 92 gram of the mixture contains = 0.4 mol NO_2

So,

100 gram of the mixture contains $= \dfrac{0.4 \times 100}{92} = 0.43$ mol NO_2

Example 16. *At temperature T, the compound $AB_2(g)$ dissociates according to the reaction,*

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation, x, which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant, K_p and the total pressure, P. (IIT 1994)

Solution: $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

At equilibrium $(1-x)$ $\quad x$ $\quad x/2$

Total moles at equilibrium $= 1 - x + x + x/2$

$$= \frac{2+x}{2}$$

$$p_{AB_2} = \frac{2(1-x)}{(2+x)} \cdot P;\ p_{AB} = \frac{2x}{(2+x)} \cdot P;\ p_{B_2} = \frac{x}{(2+x)} \cdot P;$$

$$K_p = \frac{(p_{AB})^2(p_{B_2})}{(p_{AB_2})^2} = \frac{\left[\frac{2x}{(2+x)}P\right]^2\left(\frac{x}{2+x}\right)P}{\left(\frac{2(1-x)}{(2+x)}P\right)^2}$$

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

As x is very small, $(2+x) \rightarrow 2$ and $(1-x) \rightarrow 1$.

So,
$$K_p = \frac{x^3P}{2}$$

or
$$x^3 = \frac{2K_p}{P}$$

or
$$x = \left(\frac{2K_p}{P}\right)^{1/3}$$

Example 17. *At 25°C and one atmospheric pressure, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are 0.7 and 0.3 atmosphere, respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25°C and at a total pressure of 10 atmospheres.* (MLNR 1990)

Solution: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At equilibrium $\quad 0.7 \quad 0.3$ atm

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{0.3 \times 0.3}{0.7} = 0.1285 \text{ atm}$$

Let the degree of dissociation of N_2O_4 be x when total pressure is 10 atmosphere.

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

At equilibrium $(1-x)$ $\quad 2x$

Total number of moles $= 1 - x + 2x = 1 + x$

$$p_{N_2O_4} = \frac{(1-x)}{(1+x)} \times 10;\ p_{NO_2} = \frac{2x}{(1+x)} \times 10$$

$$K_p = 0.1285 = \frac{\left(\frac{2x}{1+x}\right)^2 \times 10^2}{\left(\frac{1-x}{1+x}\right) \times 10} = \frac{40x^2}{1-x^2}$$

Since, x is very small, $(1-x^2) \rightarrow 1$

So,
$$x^2 = \frac{0.1285}{40}$$

or
$$x = 0.0566$$

$$p_{N_2O_4} = \frac{(1-x)}{(1+x)} \times 10 = \frac{1-0.0566}{1+0.0566} \times 10 = \frac{0.9436 \times 10}{1.0566} = 8.93 \text{ atm}$$

$$p_{NO_2} = \frac{2x}{(1+x)} \times 10 = \frac{2 \times 0.0566}{1+0.0566} \times 10 = \frac{0.1132}{1.0566} \times 10 = 1.07 \text{ atm}$$

Example 18. *At 450°C, the equilibrium constant, K_p, for the reaction,*

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

was found to be 1.6×10^{-5} at a pressure of 200 atm. If N_2 and H_2 are taken in 1 : 3 ratio what is % of NH_3 formed at this temperature?

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

At equilibrium $(1-x) \quad (3-3x) \quad 2x$

Total number of moles $= 1 - x + 3 - 3x + 2x = 4 - 2x$

$$p_{N_2} = \frac{(1-x)}{(4-2x)} P;\ p_{H_2} = \frac{(3-3x)}{(4-2x)} P;\ p_{NH_3} = \frac{2x}{(4-2x)} P$$

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3} = \frac{\left(\frac{2x}{4-2x} P\right)^2}{\left(\frac{1-x}{4-2x} P\right)\left(\frac{3-3x}{4-2x} P\right)^3}$$

$$= \frac{4x^2(4-2x)^2}{(1-x) \times 27 \times (1-x)^3 P^2}$$

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

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

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

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

or $x = 0.30$

Moles of ammonia formed $= 2 \times 0.30 = 0.60$

Total moles at equilibrium $= (4 - 2x) = (4 - 2 \times 0.30) = 3.40$

$$\% \text{ of } NH_3 \text{ at equilibrium} = \frac{0.60}{3.40} \times 100 = 17.64$$

Example 19. *A mixture of SO_2 and O_2 at 1 atmosphere in the ratio of 2 : 1 is passed through a catalyst at 1170°C for attainment of equilibrium. The exit gas is found to contain 87% SO_3 by volume. Calculate K_p for the reaction,*

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

Solution: The volume of SO_2 and O_2 at equilibrium

$$= (100 - 87) = 13 \text{ mL}$$

$$\text{Volume of } SO_2 = \frac{2}{3} \times 13 = 8.67 \text{ mL}$$

$$\text{Volume of oxygen} = \frac{1}{3} \times 13 = 4.33 \text{ mL}$$

$$p_{SO_3} = \frac{87}{100} \times 1 = 0.87 \text{ atm}$$

$$p_{SO_2} = \frac{8.67}{100} \times 1 = 0.0867 \text{ atm}$$

$$p_{O_2} = \frac{4.33}{100} \times 1 = 0.0433 \text{ atm}$$

$$K_p = \frac{p_{SO_3}}{p_{SO_2} \times (p_{O_2})^{1/2}} = \frac{0.87}{(0.0867) \times (0.0433)^{1/2}}$$

$$= \frac{0.87}{(0.0867) \times 0.208}$$

$$= 48.24 \text{ atm}^{-1/2}$$

Example 20. *N_2O_4 dissociates as,*

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

at 55°C and one atmosphere % decomposition of N_2O_4 is 50.3%. At what pressure and same temperature, the equilibrium mixture has the ratio of $N_2O_4 : NO_2$ as 1 : 8?

Solution:

Case I: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At equilibrium $(1-x) \quad 2x$

$$p_{N_2O_4} = \frac{(1-x)}{(1+x)} \times P;\ p_{NO_2} = \frac{2x}{(1+x)} \times P$$

$$K_p = \frac{\left(\frac{2x}{1+x} \cdot P\right)^2}{\left(\frac{1-x}{1+x} \cdot P\right)} = \frac{4x^2 P}{(1-x^2)}$$

Given, $x = 0.503$ and $P = 1$

$$K_p = 1.3548 \text{ atm}$$

Case II: $N_2O_4 \rightleftharpoons 2NO_2$

$(1-x) \quad 2x$

Given, $$\frac{(1-x)}{2x} = \frac{1}{8}$$

$$x = 0.8$$

Let the new pressure be P atm.

$$K_p = \frac{4x^2 P}{(1-x^2)} = \frac{4 \times 0.8 \times 0.8 \times P}{(1+0.8)(1-0.8)} = 1.3548$$

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

Example 21. *At 627°C and one atmosphere SO_3 is partially dissociated into SO_2 and O_2 by the reaction,*

$$SO_3(g) \rightleftharpoons SO_2(g) + 1/2O_2(g).$$

The density of the equilibrium mixture is 0.925 g L^{-1}. What is the degree of dissociation?

Solution: Let the molecular mass of the mixture at equilibrium be M_{mix}.

Applying the relation,

$$M_{mix} = \frac{dRT}{P} = \frac{0.925 \times 0.0821 \times 900}{1}$$

$$= 68.348$$

Molecular mass of $SO_3 = 80$

Vapour density of $SO_3, D = \frac{80}{2} = 40$

Vapour density of mixture, $d = \frac{68.348}{2} = 34.174$

Let the degree of dissociation be x.

$$x = \frac{D-d}{(n-1)d} = \frac{40-34.174}{\left(\frac{3}{2}-1\right)\times 34.174} = \frac{5.826\times 2}{34.174} = 0.34$$

or $x = 34\%$ dissociated

i.e., SO_3 is 34% dissociated.

Example 22. *Density of equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 384 K is 1.84 g dm^{-3}. Calculate the equilibrium constant of the reaction.*

$$N_2O_4 \rightleftharpoons 2NO_2$$

Solution: We know that,

$$Pm = dRT$$

$$1\times m = 1.84\times 0.0821\times 384$$

$$m = 29\times 2$$

Vapour density (d) at equilibrium = 29

Initial vapour density = $M/2 = 92/2 = 46$

$$x = \frac{D-d}{(n-1)\,d} = \frac{46-29}{29} = 0.586$$

$$\begin{array}{llll} & N_2O_4 \rightleftharpoons & 2NO_2 & \\ t=0 & 1 & 0 & \\ t_{eq.} & 1-x & 2x & (\text{Total moles} = 1+x) \end{array}$$

$$p_{N_2O_4} = \frac{1-x}{1+x}\times P;\ p_{NO_2} = \frac{2x}{1+x}\times P$$

$$K_p = \frac{4x^2P}{1-x^2} = \frac{4\times(0.586)^2\times 1}{1-(0.586)^2} = 2.09\ \text{atm}$$

Example 23. *For the reaction,*

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

show that degree of dissociation of NH_3 is given as:

$$\alpha = \left[1+\frac{3\sqrt{3}}{4}\frac{p}{K_p}\right]^{-1/2}$$

where, 'p' is equilibrium pressure. If K_p of the above reaction is 78.1 *atm at* 400°*C, calculate K_c.*

Solution:

$$\begin{array}{lcccc} & NH_3(g) \rightleftharpoons & \frac{1}{2}N_2 + & \frac{3}{2}H_2(g) & \text{Total moles} \\ t=0 & 1 & 0 & 0 & 1 \\ t_{eq.} & 1-\alpha & \alpha/2 & 3\alpha/2 & 1+\alpha \\ p_i & \left(\frac{1-\alpha}{1+\alpha}\right)p & \left(\frac{\alpha}{2(1+\alpha)}\right)p & \left(\frac{3\alpha}{2(1+\alpha)}\right)p & (P_i \rightarrow \text{partial pressure}) \end{array}$$

$$K_p = \frac{[N_2]^{1/2}[H_2]^{3/2}}{[NH_3]}$$

$$= \frac{\left[\frac{\alpha}{2(1+\alpha)}p\right]^{1/2}\left[\frac{3\alpha}{2(1+\alpha)}p\right]^{3/2}}{\left[\frac{1-\alpha}{1+\alpha}p\right]} = \frac{p\alpha^2\sqrt{27}}{4(1-\alpha^2)}$$

Solving for α, we get $\alpha = \left[1+\frac{3\sqrt{3}}{4}\frac{p}{K_p}\right]^{-1/2}$

K_c can be calculated by using $K_p = K_c(RT)^{\Delta n}$

$K_p = 78.1; T = 673\,\text{K};\ \Delta n = 1$

Example 24. *The equilibrium constant K_p for the reaction,*

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

is 1.64×10^{-4} *at* 400°*C and* 0.144×10^{-4} *at* 500°*C. Calculate the mean heat of formation of 1 mole of NH_3 from its elements in this temperature range.*

Solution: We know that, $\log\frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

$$\log\frac{0.144}{1.64} = \frac{\Delta H}{2.303\times 1.987\times 10^{-3}}\left(\frac{1}{673}-\frac{1}{773}\right)$$

$$\Delta H = -25.14\ \text{kcal for 2 mole}$$

$$= -12.57\ \text{kcal mol}^{-1}$$

Example 25. *When limestone is heated, quicklime is formed according to the equation,*

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

The experiment was carried out in the temperature range 800–900°C. Equilibrium constant K_p follows the relation,

$$\log K_p = 7.282 - 8500/T$$

where, T is temperature in Kelvin. At what temperature the decomposition will give $CO_2(g)$ *at 1 atm?*

Solution: $K_p = p_{CO_2} = 1$

$$\log K_p = 7.282 - \frac{8500}{T}$$

$$\log 1 = 7.282 - \frac{8500}{T}$$

$$T = \frac{8500}{7.282} = 1167.26\,\text{K}$$

$$= 894.26°\text{C}$$

Example 26. *Equilibrium constant for the reaction of iodine with propane according to the following equation was determined.*

Some results obtained at 545 K were as given ahead:

Initial Pressures (mm Hg)			Equilibrium Pressures (mm)	
I_2	C_3H_6	HI	HI	C_3H_5I
23.9	505.8	0	1.80	1.80
16.1	355.3	1.62	2.27	0.645

Calculate equilibrium constant according to the following equation,

$$I_2(g) + C_3H_6(g) \rightleftharpoons C_3H_5I(g) + HI(g)$$

Solution: Ist experiment:

$$\begin{array}{lccccc} & I_2(g) & + & C_3H_6(g) & \rightleftharpoons & C_3H_5I(g) + HI(g) \\ t=0 & 23.9 & & 505.8 & & 0 \qquad 0 \\ t_{eq.} & (23.9-1.8) & & (505.8-1.8) & & 1.80 \qquad 1.80 \end{array}$$

$$K_p = \frac{p_{C_3H_5I} \times p_{HI}}{p_{I_2} \times p_{C_3H_6}} = \frac{1.8 \times 1.8}{22.1 \times 504} = 2.9 \times 10^{-4}$$

Similarly, solve for second experiment.

Example 27. *At 817°C K_p for the reaction between CO_2 and excess hot graphite to form $2CO(g)$ is 10.*

(*i*) *What is the analysis (mole fraction) of the gases at equilibrium at 817°C and a total pressure of 4 atm? What is the partial pressure of CO_2 at equilibrium?*

(*ii*) *At what total pressure will the gas mixture have 6% CO_2 by volume?*

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

$$\begin{array}{lcc} t=0 & 1 & 0 \\ t_{eq.} & 1-\alpha & 2\alpha \\ p_{eq.} & \left(\frac{1-\alpha}{1+\alpha}\right)p & \left(\frac{2\alpha}{1+\alpha}\right)p \end{array}$$

$$K_p = \frac{4\alpha^2 p}{1-\alpha^2};\ 10 = \frac{4\alpha^2 4}{1-\alpha^2}$$

On solving, we get $\alpha = 0.62$

$$x_{CO_2} = \frac{1-\alpha}{1+\alpha} = \frac{1-0.62}{1+0.62} = 0.2345 = 23.45\% \text{ (by volume)}$$

$$x_{CO} = 0.7655 = 76.55\% \text{ (by volume)}$$

$$p_{CO_2} = (0.2345 \times 4.0) \text{ atm} = 0.938 \text{ atm}$$

(ii) Let the total pressure be P atm.

$$K_p = 10 = \frac{[p_{CO}]^2}{p_{CO_2}} = \frac{0.94 \times P \times 0.94 \times P}{0.06 \times P}$$

$$P = 0.68 \text{ atm}$$

Example 28. *Ammonia under a pressure of 20 atm at 127°C is heated to 327°C in a closed vessel. Under these conditions NH_3 is partially decomposed to N_2 and H_2 according to the equation:*

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

After decomposition at constant volume in a vessel the pressure increases to 45 atm. What is the percentage of ammonia dissociated?

Solution:

$$\begin{array}{lccccccc} & 2NH_3(g) \rightleftharpoons & N_2(g) + & 3H_2(g) & n & P & V & T \\ t=0 & a & 0 & 0 & a & 20 & V & 400 \\ t_{eq.} & a - a\alpha & a\alpha/2 & 3a\alpha/2 & a + a\alpha & 40 & V & 600 \end{array}$$

$$V = \frac{nRT}{P} = \frac{a \times R \times 400}{20} \qquad \text{... (1)}$$

$$V = \frac{nRT}{P} = \frac{a(1+\alpha) \times R \times 600}{45} \qquad \text{... (2)}$$

On dividing, we get $1 = \dfrac{400 \times 45}{(1+\alpha)20 \times 600}$

$$\alpha = 0.5$$

Percentage dissociation of $NH_3 = 50$

Example 29. *When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_c and K_p for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?* (IIT 1999)

Solution: $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$$\text{Moles of } NH_4HS = \frac{3.06}{51} = 0.06$$

Degree of dissociation = 0.3

At equilibrium,

$$[NH_3(g)] = \frac{0.3 \times 0.06}{2};\quad [H_2S(g)] = \frac{0.3}{2} \times 0.06$$

$$K_c = [NH_3(g)][H_2S(g)] = \frac{0.3 \times 0.06 \times 0.3 \times 0.06}{2 \times 2}$$

$$= 8.1 \times 10^{-5}$$

Now applying,

$$K_p = K_c(RT)^{\Delta n} = 8.1 \times 10^{-5} \times (0.082 \times 300)^2$$

$$= 0.049$$

Since, NH_4HS is solid, so it causes no change in equilibrium.

Example 30. *At 540 K, 0.10 mole of PCl_5 are heated in a 8 litre flask. The pressure of equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.* (IIT 1998)

Solution: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$$\begin{array}{lccc} \text{At equilibrium (mole)} & (0.1-x) & x & x \end{array}$$

Total number of moles, $n = (0.1-x) + x + x = (0.1+x)$

$$PV = nRT$$

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

or

$$x = 0.08$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x^2}{(0.1-x) \times 8}$$

$$= \frac{0.08 \times 0.08}{(0.1-0.08)8} = 4 \times 10^{-2} \text{ mol L}^{-1}$$

$$K_p = K_c(RT)^{\Delta n} = K_c\, RT\ (\Delta n = +1)$$

$$= 4 \times 10^{-2} \times 0.082 \times 540 = 1.77 \text{ atm}$$

Example 31. *At 817°C, K_p for the reaction between $CO_2(g)$ and excess hot graphite(s) is 10 atm.*

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

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

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

At equilibrium $(5-x)$ atm $\quad x$ atm

$$K_p = \frac{[CO]^2}{[CO_2]} = \frac{x^2}{(5-x)}$$

$$10 = \frac{x^2}{5-x}$$

$$x^2 = 50 - 10x$$

$$x^2 + 10x - 50 = 0$$

$$x = \frac{-10 \pm \sqrt{100+200}}{2} = 3.66$$

i.e., $p_{CO} = 3.66$ atm; $p_{CO_2} = 1.34$ atm

$$\text{Concentration of CO} = \frac{p}{RT} = \frac{3.66}{0.0821 \times 1090} = 0.041 \text{ mol litre}^{-1}$$

$$\text{Concentration of CO}_2 = \frac{p}{RT} = \frac{1.34}{0.0821 \times 1090} = 0.015 \text{ mol litre}^{-1}$$

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

$$\begin{array}{llll} t=0 & 1 & 0 & 0 \\ t_{eq.} & 1-\alpha & & 2\alpha \\ p_i & \frac{1-\alpha}{1+\alpha}p & & \frac{2\alpha}{1+\alpha}p \end{array}$$

$$K_p = \frac{\left[\frac{2\alpha}{1+\alpha}p\right]^2}{\left[\frac{1-\alpha}{1+\alpha}p\right]} = \frac{4\alpha^2 p}{1-\alpha^2} \quad \text{... (i)}$$

$$\frac{5}{100} = \frac{1-\alpha}{1+\alpha}$$

$$\alpha = 0.95$$

$$\therefore \text{ From eq. (i), } 10 = \frac{4 \times (0.95)^2}{1-(0.95)^2} \times p$$

$$p = 0.27 \text{ atm}$$

Example 32. *The value of K_p is 1×10^{-3} atm^{-1} at 25°C for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$. A flask contains NO at 0.02 atm and at 25°C. Calculate the mole of Cl_2 that must be added if 1% of the NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 mole of gas produces 1 atm pressure at 25°C. (Ignore probable association of NO to N_2O_2).* (IIT 2001)

Solution: $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$

$$\begin{array}{llll} t=0 & 0.02 & 0 & 0 \\ t_{eq.} & \frac{0.02 \times 99}{100} & p & \frac{0.02 \times 1}{100} \end{array}$$

$$K_p = \frac{[p_{NOCl}]^2}{[p_{NO}]^2[p_{Cl_2}]} = \frac{(0.02 \times 0.01)^2}{(0.99 \times 0.02)^2 \times p} = 10^{-3}$$

$$\therefore \quad p = 0.102 \text{ atm}$$

$$PV = nRT$$

$$0.102 \times V = n \times R \times T \quad \text{... (i)}$$

$$1 \times V = 0.2 \times R \times T \quad \text{... (ii)}$$

From eqs. (i) and (ii), $n = 0.0204$ (no. of moles of Cl_2 at equilibrium)

Pressure of Cl_2 involved in reaction

$$= \frac{1}{2} \times \text{pressure of NOCl}$$

$$= \frac{1}{2} \times \frac{0.02}{100} = 0.0001 \text{ atm}$$

$$PV = nRT$$

$$0.0001 \times V = n \times RT \quad \text{... (iii)}$$

From eqs. (ii) and (iii), $n = 2 \times 10^{-5}$ (moles of Cl_2 involved in reaction)

Initial moles of Cl_2 taken $= 0.0204 + 2 \times 10^{-5}$

$= 0.02042$

Example 33. *In the following equilibrium,*

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

when 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given : $\Delta G^\circ_{f\,N_2O_4} = 100\,kJ, \Delta G^\circ_{f\,NO_2} = 50\,kJ$

(*a*) *Find ΔG of the reaction at 298 K.*

(*b*) *Find the direction of the reaction.* (IIT 2004)

Solution: $$\text{Reaction Quotient} = \frac{[p_{NO_2}]^2}{p_{N_2O_4}} = \frac{100}{10} = 10$$

$$\Delta G^\circ_{\text{reaction}} = 2\Delta G^\circ_{f\,NO_2} - \Delta G^\circ_{f\,N_2O_4}$$

$$= 2 \times 50 - 100 = 0$$

We know that, $\Delta G = \Delta G^\circ - 2.303\,RT \log Q_p$

$= 0 - 2.303 \times 8.314 \times 298 \log 10$

$= -5705.8\text{ J} = -5.705\text{ kJ}$

Negative value shows that reaction will be in forward direction..

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Irreversible and reversible reactions: Chemical reactions can be classified as irreversible and reversible reactions. The reactions which move in one direction only are called **irreversible reactions.** In these reactions products do not react to produce original reactants. In such reactions an arrow (→) is placed between reactants and products. The chemical reactions which take place in both directions under similar conditions are called **reversible reactions.** In such reactions products also react with each other to produce reactants again. The sign ($\rightleftharpoons$) is placed between reactants and products.

2. Chemical equilibrium: Chemical equilibrium is the most important characteristic property of reversible reactions. It is the state at which both forward and backward reactions occur at the same speed.

At equilibrium state,

Rate of forward reaction = Rate of backward reaction

At equilibrium state, the concentrations of the reactants and products do not change with time. The following are the characteristics of the equilibrium state:

(i) It can be achieved only if the reversible reaction is carried out in a closed space.

(ii) It is characterised by constancy of certain properties such as concentration, pressure, density, colour, etc.

(iii) It can be attained from either side of the reaction.

(iv) It can be attained in lesser time by use of a catalyst.

(v) It is dynamic in nature, *i.e.*, reaction does not stop, but both the forward and backward reactions move with the same speed.

(vi) Change of pressure, concentration or temperature favours one of the reaction and thus shifts the equilibrium point in one direction.

Reversible chemical reactions are classified into two types:

(i) **Heterogeneous reactions:** The reversible reactions in which more than one-phase is present.

(ii) **Homogeneous reactions:** The reversible reactions in which only one-phase is present. These are further classified into three types:

(a) When there is no change in the number of molecules, $i.e., \Delta n = 0$.

(b) When there is an increase in the number of molecules, $i.e., \Delta n = +\text{ve}$.

(c) When there is a decrease in the number of molecules, $i.e., \Delta n = -\text{ve}$.

3. Law of chemical equilibrium (Application of law of mass action): Consider the general homogeneous reversible reaction in which equilibrium has been attained at a certain temperature.

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3 + \ldots$$

Rate of forward reaction = Rate of backward reaction

$$k_f[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots = k_b[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots$$

or
$$\frac{\{[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots\}}{\{[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots\}} = \frac{k_f}{k_b} = K_c$$

The equilibrium constant, K_c, at a given temperature, is the ratio of rate constants of forward and backward reactions. It is also defined as the ratio between the molar concentrations of the products to the molar concentrations of the reactants with each concentration term raised to the power equal to stoichiometric coefficient in the balanced chemical equation.

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

(i) Initial concentration of reactants.

(ii) The direction from which equilibrium has been attained.

(iii) The presence of a catalyst.

(iv) The presence of inert materials.

The value of equilibrium constant depends upon the following factors:

(i) **The mode of representation of the reaction:** Consider the reversible reaction,

$$A + B \rightleftharpoons C + D$$

$$K_c = \frac{[C][D]}{[A][B]}$$

The products are made the reactants, *i.e.*, the reaction is reversed:

$$C + D \rightleftharpoons A + B$$

$$K'_c = \frac{[A][B]}{[C][D]}$$

So, $$K'_c = \frac{1}{K_c}$$

(ii) **Stoichiometric representation of a chemical equation:** The value of equilibrium constant will be numerically different if the reaction can be written with the help of two or more stoichiometric equations.

i.e., $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$; $K_c = \frac{[N_2][O_2]^2}{[NO_2]^2}$

or $NO_2(g) \rightleftharpoons (1/2)N_2(g) + O_2(g)$; $K'_c = \frac{[N_2]^{1/2}[O_2]}{[NO_2]}$

Thus, $$K'_c = \sqrt{K_c}$$

(iii) **Use of partial pressures:** When the reactants and products are in gaseous state, the partial pressures can be used instead of concentrations at a definite temperature.

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3 + \ldots$$

$$K_p = \frac{(p_{B_1})^{n_1}(p_{B_2})^{n_2}(p_{B_3})^{n_3}\ldots}{(p_{A_1})^{m_1}(p_{A_2})^{m_2}(p_{A_3})^{m_3}\ldots}$$

$$K_p = K_c(RT)^{\Delta n}$$

where, Δn = total number of molecules of products − total number of molecules of reactants.

When, $\Delta n = 0$, $K_p = K_c$;
$\Delta n = +\text{ve}$, $K_p > K_c$;
and $\Delta n = -\text{ve}$, $K_p < K_c$;

(iv) Temperature: The value of equilibrium constant changes with temperature. The values of equilibrium constants at two different temperatures are related by the following equation:

$$\log K_2 - \log K_1 = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad T_2 > T_1$$

When, $\Delta H = 0$, *i.e.*, heat of reaction at constant volume is zero,
$K_2 = K_1$
When, $\Delta H = +\text{ve}$, *i.e.*, endothermic reaction,
$K_2 > K_1$
and when, $\Delta H = -\text{ve}$, *i.e.*, exothermic reaction
$K_2 < K_1$

Units of equilibrium constant: Partial pressures are measured in terms of atmospheres. Therefore, units of K_p will be $(\text{atm})^{\Delta n}$. Since, concentrations are measured in terms of moles per litre, the units of K_c are $(\text{mol L}^{-1})^{\Delta n}$.

K_p and K_c will be pure numbers when, $\Delta n = 0$.

4. Equilibrium expressions for some reactions:

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

Initially	a	b	0
At equilibrium	$(a-x)$	$(b-x)$	$(2x)$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(a-x)(b-x)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{[p_{HI}]^2}{p_{H_2} \times p_{I_2}} = \frac{\dfrac{(2x)^2}{(a+b)^2}P^2}{\left(\dfrac{a-x}{a+b}\cdot P\right)\left(\dfrac{b-x}{a+b}\cdot P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

So, $K_c = K_p$

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

Initially	a	0	0
At equilibrium	$(a-x)$	$x/2$	$x/2$

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2}$$

(c)
$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initially	a	b	0	0
At equil.	$(a-x)$	$(b-x)$	x	x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{x^2}{(a-x)(b-x)}$$

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

Initially	a	0	0
At equilibrium	$(a-x)$	x	x
Active masses	$\frac{(a-x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\dfrac{x}{V} \times \dfrac{x}{V}}{\dfrac{(a-x)}{V}} = \frac{x^2}{(a-x)V}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\dfrac{x}{a+x}\cdot P\right) \times \left(\dfrac{x}{a+x}\cdot P\right)}{\left(\dfrac{a-x}{a+x}\cdot P\right)} = \frac{x^2P}{(a+x)(a-x)}$$

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

Initially	a	b	0
At equilibrium	$(a-x)$	$(b-3x)$	$2x$
Active masses	$\left(\frac{a-x}{V}\right)$	$\left(\frac{b-3x}{V}\right)$	$\left(\frac{2x}{V}\right)$

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

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3} = \frac{\left[\dfrac{2x}{(a+b-2x)}P\right]^2}{\left[\dfrac{(a-x)}{(a+b-2x)}P\right]\left[\dfrac{(b-3x)}{(a+b-2x)}P\right]^3}$$

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

5. Activation energies for the forward and backward reactions: Both forward and backward reactions follow the same path and from the same activated complex. However, the activation energies of both reactions are different.

$$\Delta E = E_a\ (f) - E_a\ (b)$$

For exothermic reaction, $E_a\ (f) < E_a\ (b)$, *i.e.*, $\Delta E = -\text{ ve}$

For endothermic reaction, $E_a\ (f) > E_a\ (b)$, *i.e.*, $\Delta E = +\text{ ve}$

Threshold energy = Energy of reactants + Activation energy of forward reaction

Threshold energy = Energy of products + Activation energy of backward reaction

6. Standard free energy change of a reaction and its equilibrium constant are related to each other at temperature *T* by the following relation:

$$\Delta G° = -2.303RT \log K_p$$
$$\Delta G° = \Delta H° - T\Delta S°$$

When, $\Delta G° = -\text{ve}$, the value of equilibrium constant will be large positive quantity and when $\Delta G°$ is positive, the value of K is less than 1, *i.e.*, low concentration of products at equilibrium state.

7. Degree of dissociation from density measurements: Degree of dissociation in the case of reversible reactions in which there is increase in the number of molecules can be determined by measuring density of the reaction mixture at equilibrium. Let d be the observed density at a particular temperature when degree of dissociation is x and D be the vapour density when there is no dissociation.

$x = \frac{D-d}{(n-1)d}$; where, n is the number of molecules of products.

8. Heterogeneous equilibria: Law of mass action can also be applied to the heterogeneous system. In such systems the concentrations of pure solids and liquids are not considered in equilibrium expressions.

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

$$K_p = \frac{p_{CO} \times p_{H_2}}{p_{H_2O}} \quad \text{or} \quad K_c = \frac{[CO][H_2]}{[H_2O]}$$

i.e., concentration of $C(s)$ is not taken into account.

9. Le Chatelier's principle: It is a qualitative principle which can describe the effect of change in concentration, pressure and temperature on the reversible system whether physical or chemical. It is stated as "If the system at equilibrium is subjected to a change of any one of the factors such as concentration, temperature or pressure, the system adjusts itself in such a way as to annul the effect of that change." The following conclusions have been derived from this principle:

(i) Increase in concentration of any substance favours the reaction in which it is used up.

(ii) High pressure is favourable for the reaction in which there is decrease in volume.

(iii) A rise in temperature favours the endothermic reaction.

Applications of Le Chatelier's Principle

(i) Ice water system (melting of ice):

$$\text{Ice} + \text{Heat} \rightleftharpoons \text{Water}$$

It is an endothermic process and there is decrease in volume. Thus, the favourable conditions for melting of ice are:
(a) High temperature and (b) High pressure.

(ii) Solubility of gases in liquids: When a gas dissolves in a liquid, there is decrease in volume. Thus, increase in pressure will favour the dissolution of a gas in liquid.

(iii) Formation of nitric oxide:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43200 \text{ calorie}$$

In this chemical reaction, there is no change in the number of molecules and heat is absorbed (endothermic). Thus, favourable conditions for greater yields of NO are:

(a) High concentrations of N_2 and O_2,
(b) High temperature and
(c) No effect of pressure and catalyst.

(iv) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22400$ calorie: The reaction involves decrease in number of molecules and evolution of heat (exothermic). The favourable conditions are:

(a) High concentrations of N_2 and H_2,
(b) High pressure and
(c) Low temperature.

To speed up the rate of reaction at low temperature, a suitable catalyst is always employed.

Questions

1. Match List I (Equations) with List II (Type of Processes) and select the correct option:

List-I (Equations)	List-II (Type of Processes)
(a) $K_p > Q$	(i) Non-spontaneous
(b) $\Delta G^\circ < RT \log_e Q$	(ii) Equilibrium
(c) $K_p = Q$	(iii) Spontaneous and endothermic
(d) $T > \frac{\Delta H}{\Delta S}$	(iv) Spontaneous

(A) a = (i); b = (ii); c = (iii); d = (iv)
(B) a = (iii); b = (iv); c = (ii); d = (i)
(C) a = (iv); b = (i); c = (ii); d = (iii)
(D) a = (ii); b = (i); c = (iv); d = (iii) **[CBSE (PMT) 2010]**

[**Hint:** When $K_p > Q$; rate of forward reaction > rate of backward reaction, *i.e.*, process is spontaneous.

When $\Delta G^\circ < RT \log_e Q$, ΔG° is positive, thus reaction is non spontaneous.

When $K_p = Q$, reaction is at equilibrium.

When $T\Delta S > \Delta H$, ΔG will be negative only when ΔH = +ve, thus is spontaneous and endothermic.]

2. **Matrix-Matching Problems (For IIT Aspirants):**

[A] Match the Column-I with Column-II:

Column-I	Column-II
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(p) Unaffected by inert gas addition
(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	(q) Forward shift by rise in pressure and backward shift by inert gas addition
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(r) Unaffected by increase in pressure
(d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(s) Backward shift by rise in pressure and forward shift by inert gas addition

[B] Match the reactions in the Column-I with the units of equilibrium constant in Column-II:

Column-I	Column-II
(a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	(p) mol L
(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(q) Unitless
(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(r) atm
(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(s) $(atm)^{-2}$

[C] Match the reactions of the Column-I with the factors in Column-II:

Column-I	Column-II
(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (Exothermic)	(p) Forward shift by rise in pressure
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ (Exothermic)	(q) Unaffected by change in pressure
(c) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ (Endothermic)	(r) Forward shift by rise in temperature
(d) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ (Endothermic)	(s) Forward shift by lowering the temperature

[D] Match the reactions of the Column-I with the relations in Column-II:

Column-I	Column-II
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(p) $K_p = K_c(RT)$
(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(q) $K_p = K_c(RT)^2$
(c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(r) $K_p = K_c(RT)^{-2}$
(d) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$	(s) $K_p = K_c$

[E] Match the List-I with List-II:

List-I	List-II
(a) $Q = K$	(p) Reaction is nearer to completion
(b) $Q < K$	(q) Reaction is not at equilibrium
(c) $Q > K$	(r) Reaction is fast in forward direction
(d) $K >>> 1$	(s) Reaction at equilibrium

[F] Match the List-I with List-II:

List-I (Reaction)	List-II (K_p/K_c)
(a) $A_2(g) + 3B_2(g) \rightleftharpoons 2AB_3(g)$	(p) $(RT)^{-2}$
(b) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$	(q) $(RT)^0$
(c) $A(s) + \frac{3}{2}B_2(g) \rightleftharpoons AB_3(g)$	(r) $(RT)^{1/2}$
(d) $AB_2(g) \rightleftharpoons AB(g) + \frac{1}{2}B_2(g)$	(s) $(RT)^{-1/2}$

Answers

1. (C) (a = iv); (b = i); (c = ii); (d = iii)
2. [A] (a–p, r); (b–p, r); (c–q); (d–s)
   [B] (a–p, r); (b–p, r); (c–q); (d–s)
   [C] (a–p, s); (b–p, s); (c–q, r); (d–p, r)
   [D] (a–s); (b–r); (c–p); (d–q)
   [E] (a–s); (b–q, r); (c–q); (d–p)
   [F] (a–p); (b–q); (c–s); (d–r)

• PRACTICE PROBLEMS •

1. K_c for the reaction, $NH_3(g) \rightleftharpoons 1/2N_2(g) + 3/2\,H_2(g)$, at 298 K is 5.2×10^{-5}. What is the value of K_c at 298 K for the reaction,

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

[**Hint:** K_c' for reaction $1/2\,N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3$ is $\frac{1}{K_c}$,

i.e., $\frac{1}{5.2 \times 10^{-5}}$

K_c for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, will be $= (K_c')^2$

$$= \left[\frac{1}{5.2 \times 10^{-5}}\right]^2 = 3.7 \times 10^8\ ]$$

2. The value of K_p for the reaction,

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g),$$

is 0.035 atm at 400°C, when the partial pressures are expressed in atmosphere. Calculate the value of K_c for the same reaction.
[**Ans.** 6.342×10^{-4} mol L^{-1}]

3. For the reaction,

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

the equilibrium constant $K_c = 2.52 \times 10^{-2}$ at 27°C; calculate K_p. (Given, $R = 0.082$ litre-atm deg^{-1} mol^{-1})
[**Ans.** 61.99×10^{-2}]

4. If K_p for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, is 1.64×10^{-4} atm^{-2} at 400°C. What will be the equilibrium constant at 500°C, if heat of reaction in this temperature range is – 105185.8 joule?
[**Ans.** 1.44×10^{-5} atm]

5. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_p = 0.157$ atm at 300 K. Calculate the value of K_c for the same reaction at the same temperature.
[**Ans.** 6.38×10^{-3} mol L^{-1}]

6. For the reaction, $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$, the value of K_c is 1.7×10^{12} at 300 K. Calculate the equilibrium constants for the following reactions at 300 K:

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

and $$SO_3(g) \rightleftharpoons SO_2(g) + 1/2O_2(g)$$

[**Ans.** 2.89×10^{24}, 5.88×10^{-13}]

7. Determine K_p for the following reactions:

(a) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$; $K_c = 23.2$ at 600 K

(b) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $K_c = 4.62 \times 10^{-3}$ M at 298 K

(c) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $K_c = 2.8 \times 10^2$ M^{-1} at 1000 K

[**Ans.** (a) 23.2 (b) 11.45 kPa (c) 0.0337 kPa]

8. From the following data at 1000 K:

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g); \quad K_1 = 0.329$$
$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g); \quad K_2 = 2.24 \times 10^{22}$$

Calculate the equilibrium constant for the following reaction:

$$2COCl_2(g) + O_2(g) \rightleftharpoons 2CO_2(g) + Cl_2(g)$$

[**Ans.** 2.43×10^{21}]

9. For the reaction, $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$, K_p is 32 (atm)$^{-1/2}$ at 800 K and ΔH for the reaction is −187.9 kJ mol^{-1}. Calculate its value at 900 K, if it is assumed that ΔH remains constant over this range of temperature.
[**Ans.** 1.387 atm$^{-1/2}$]

10. The equilibrium constants for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, at 1727°C and 2227°C are 4.08×10^{-4} and 3.6×10^{-3} respectively. Calculate the enthalpy change for the reaction. (Given, $R = 1.987$ cal.)
[**Ans.** 43273 cal]

11. Calculate the equilibrium constant (K_p) for the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, at 1300 K from the following data: $C(s) + 2H_2O(g) \rightleftharpoons CO_2(g) + 2H_2(g)$;

K_p (1300 K) = 3.9 atm

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

K_p (1300 K) = 0.7 atm

[**Ans.** 1.91 atm]

[**Hint:** $$\frac{[CO]^2}{[CO_2]} = K_{p\,(\text{net})} = \frac{[CO]^2[H_2O]^2}{[H_2]^2[CO_2]^2} \times \frac{[H_2]^2[CO_2]}{[H_2O]^2} = (0.7)^2 \times 3.9\,]$$

12. The standard equilibrium constant for the reaction,

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

is 1.8×10^{-7} at 298 K. Calculate its $\Delta G°$ value.
[**Ans.** 38.49 kJ mol^{-1}]

13. For the equilibrium, $Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$, equilibrium constants are 3.98×10^{-4} and 1.41×10^{-2} respectively at 350 K and 400 K. Calculate the standard enthalpy of decomposition.
[**Ans.** 83.06 kJ/mol]

14. The equilibrium constant for the reaction,

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

at 715 K is 6.0×10^{-2}. If in a particular reaction, there are 0.25 mol L^{-1} of H_2 and 0.06 mol L^{-1} of NH_3 present, calculate the concentration of N_2 at equilibrium.

[**Ans.** $[N_2] = 3.84$ mol L^{-1}]

15. One mole of H_2O and one mole of CO were heated in a 10 litre closed vessel at 1260 K. At equilibrium, 40% of water was found to react in the equation,

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

Calculate the equilibrium constant of the reaction.

[**Ans.** 0.44]

[**Hint:** $\underset{(1-0.4)}{H_2O(g)} + \underset{(1-0.4)}{CO(g)} \rightleftharpoons \underset{0.4}{CO_2(g)} + \underset{0.4}{H_2(g)}$ (at equilibrium)]

16. Two moles of PCl_5 were introduced in a 2 litre flask and heated at 600 K to attain equilibrium. PCl_5 was found to be 40% dissociated into PCl_3 and Cl_2. Calculate the value of K_c.

[**Ans.** $K_c = 0.267$ mole L^{-1}]

17. 0.1 mole of PCl_5 is heated in a litre vessel at 533 K. Determine the concentration of various species present at equilibrium, if the equilibrium constant for the dissociation of PCl_5 at 533 K is 0.414.

[**Ans.** $[PCl_5] = 0.0531$ mol L^{-1}; $[PCl_3] = 0.0469$ mol L^{-1}; $[Cl_2] = 0.0469$ mol L^{-1}]

18. At 1000 K, the equilibrium constant, K_c, for the reaction,

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

is equal to 3.04. If 1 mole of CO and 1 mole of Cl_2 are introduced into a 1 litre box at 1000 K, what will be the final concentration of $COCl_2$ at equilibrium?

[**Ans.** $[COCl_2] = 0.568$ mol L^{-1}]

19. Given, that $K_c = 13.7$ at 546 K for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, calculate what pressure will develop in a 10 litre box at equilibrium at 546 K when 1.00 mole of PCl_5 is injected into the empty box?

[**Ans.** $P = 8.93$ atm]

[**Hint:** First determine degree of dissociation, then evaluate the total pressure by applying, $P = \frac{n}{V}RT$ where, $n = 1 + \alpha$.]

20. In the following reaction,

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

the amounts of H_2, I_2 and HI are 7.8 g, 203.2 g and 1638.4 g respectively at equilibrium at a certain temperature. Calculate the equilibrium constant of the reaction.

[**Ans.** 0.019]

21. Concentrations of two reactants A and B are 0.8 mol L^{-1} each. On mixing the two, the reaction sets in at a slow rate to form C and D.

$$A + B \rightleftharpoons C + D$$

At equilibrium, concentration of C was found to be 0.60 mol L^{-1}. Calculate the equilibrium constant.

[**Ans.** $K_c = 9$]

22. 15 moles of hydrogen reacting with 5.2 moles of iodine form 10 g mole of hydrogen iodide. Calculate the equilibrium constant of the reaction.

[**Ans.** $K_c = 50$]

23. In the dissociation of HI, it is found that 20% of the acid is dissociated when equilibrium is reached. Calculate the value of K_p for the equilibrium,

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

[**Ans.** $K_p = 1.56 \times 10^{-2}$]

24. The equilibrium constant of the reaction,

$$A + B \rightleftharpoons C + D$$

is unity. What per cent of A will be transformed if three moles of A are mixed with 5 moles of B?

[**Ans.** 62.5%]

[**Hint:** At equilibrium,

$$\underset{(3-x)}{A} + \underset{(5-x)}{B} \rightleftharpoons \underset{x}{C} + \underset{x}{D}$$

Find the value of x. % of A transformed $= \frac{x}{3} \times 100$]

25. 2 moles of A and 3 moles of B are mixed and the reaction is carried at 400°C according to the equation,

$$A + B \rightleftharpoons 2C$$

the equilibrium constant of the reaction is 4. Find the concentration of C at equilibrium.

[**Ans.** 2.4 mole]

26. A combination of hydrogen and iodine is carried out by heating 60 mL of hydrogen and 42 mL of iodine in a closed vessel. At equilibrium 28 mL of hydroiodic acid is present in the vessel. Calculate the degree of dissociation of HI.

[**Hint:** $\underset{(60-14)}{H_2(g)} + \underset{(42-14)}{I_2(g)} \rightleftharpoons \underset{28 \text{ mL}}{2HI(g)}$ At equilibrium

$$K_c = \frac{28 \times 28}{46 \times 28} = \frac{14}{23}$$

$\underset{1-x}{2HI(g)} \rightleftharpoons \underset{x/2}{H_2(g)} + \underset{x/2}{I_2(g)}$ (x is the degree of [illegible]iation)

$$K_c' = \frac{x/2 \times x/2}{(1-x)^2} = \text{[illegible]}$$

or

$$\frac{x}{2(1-x} \quad \sqrt{\frac{23}{14}} = 1.2817$$

$$x = 0.72]$$

27. One mole of H_2, 2 moles of I_2 and 3 moles of HI are injected in a one litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium when K_c is 45.9?

[**Ans.** $[H_2] = 0.316$ mol L^{-1}, $[I_2] = 1.316$ mol L^{-1}, $[HI] = 4.368$ mol L^{-1}]

[**Hint:** $\underset{(1-x)}{H_2(g)} + \underset{(2-x)}{I_2(g)} \rightleftharpoons \underset{(3+2x)}{2HI(g)}$ At equilibrium

$$K_c = \frac{(3+2x)^2}{(1-x)(2-x)} = 45.9,$$

On solving, $x = 0.684$ mole]

28. Four moles of hydrogen iodide were taken in a 10 litre flask kept at 800 K. When equilibrium was attained, the mixture was found to contain 0.42 mole of iodine. Calculate the equilibrium constant for dissociation of HI.

[**Ans.** $K_c = 1.76 \times 10^{-2}$]

29. The equilibrium constant, K_c, for the reaction,

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

is 56.8 at 800 K. When the mixture was analysed, it was found to contain 0.316 mol/L HI at 800 K. What are the concentrations of H_2 and I_2 at equilibrium? (Assume that initial concentrations of H_2 and I_2 were the same.)

[**Ans.** $[H_2] = [I_2] = 0.0419 \text{ mol L}^{-1}$]

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

[**Ans.** 0.96 atm]

31. The reaction of the formation of phosgene gas from CO and Cl_2 is as follows:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

In an experiment, starting with equimolecular CO and Cl_2 in a 250 mL flask, the equilibrium mixture on analysis is found to contain 0.05 mole CO, 0.05 mole Cl_2 and 0.15 mole $COCl_2$. Calculate the equilibrium constant of the reaction.

[**Ans.** $K_c = 15 \text{ mol}^{-1}\text{L}$]

32. At 35°C and 1 atmospheric pressure, N_2O_4 is 27.2% dissociated into NO_2. What is the value of K_p under these conditions?

[**Ans.** $K_p = 0.3195$ atm]

33. Nitrogen and hydrogen are added to a 5 litre flask under pressure. The flask was sealed and heated. The equilibrium mixture contained 19.0 g of ammonia, 0.16 g of hydrogen and 3.4 g of nitrogen. Calculate the equilibrium constant, K_c, of the reaction:

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

[**Ans.** $K_c = 5.02 \times 10^5 \text{ mol}^{-2}\text{L}^2$]

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

[**Hint:** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$K_p = \frac{(p_{NO_2})^2}{(p_{N_2O_4})} = \frac{(1.1)^2}{0.28} = 4.32 \text{ atm}$$

When the volume is doubled, the pressure becomes half and the system again adjusts to achieve equilibrium.

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

$$\left(\frac{0.28}{2} - x\right)\left(\frac{1.1}{2} + 2x\right)$$

$$(0.14 - x)\,(0.55 + 2x)$$

$$K_p = \frac{(0.55 + 2x)^2}{(0.14 - x)} = 4.32$$

$$x = 0.045$$

$$p_{N_2O_4} = (0.14 - 0.045) = 0.095 \text{ atm}$$

$$p_{NO_2} = (0.55 + 2 \times 0.045) = 0.64 \text{ atm}]$$

35. At 21.5°C and a total pressure of 0.0787 atm, N_2O_4 is 48.3% dissociated into NO_2. At what total pressure will the per cent dissociation be 10.0%?

[**Ans.** 2.37 atm]

[**Hint:** First calculate the value of K_p and then evaluate the pressure by applying,

$$K_p = \frac{\left(\frac{0.2}{1.1}\right)^2 P^2}{\left(\frac{0.9}{1.1}\right) P} = 0.0959\,]$$

36. At 3000 K, chlorine gas dissociates into chlorine atoms in an equilibrium reaction for which $K = 0.37$. What is the concentration of chlorine atoms in a vessel that originally contained 1.0 mol L^{-1} of molecular chlorine?

[**Ans.** $[Cl] = 0.54 \text{ mol L}^{-1}$]

37. The equilibrium constant K_p for the reaction,

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

at 1500°C is 120. If N_2 and O_2 at an initial pressure of 0.25 atm each are maintained at 1500°C till equilibrium is established, calculate the partial pressure of N_2, O_2 and NO in the equilibrium mixture.

[**Ans.** $p_{N_2} = p_{O_2} = 0.04$; $p_{NO} = 0.42$ atm]

38. Find K_p for the following reaction,

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

If sulphuryl chloride decomposes to the extent of 91.2% at 102°C and total pressure 1 atmosphere.

[**Ans.** $K_p = 4.94$ atm]

39. If carbon dioxide is 2% dissociated at 1800°C and 1 atmospheric pressure,

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

Calculate K_p for the reaction.

[**Ans.** $K_p = 4.12 \times 10^{-6}$ atm]

40. At a certain temperature, K_c for the reaction,

$$POCl_3(g) \rightleftharpoons POCl(g) + Cl_2(g)$$

is 0.30. If 0.6 mole of $POCl_3$ is placed in a closed vessel of 3.0 litre capacity at this temperature, what percentage of it will be dissociated when equilibrium is established?

[**Ans.** 68.5%]

41. A reaction carried out by 1 mole of N_2 and 3 moles of H_2 shows at equilibrium the mole fraction of NH_3 as 0.012 at 500°C and total pressure 10 atmosphere; calculate K_p. Also report the pressure at which mole percentage of NH_3 in equilibrium mixture increased to 10.4.

[**Ans.** $K_p = 1.431 \times 10^{-5} \text{ atm}^{-2}$; $P = 105.41$ atm]

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

[**Ans.** $K_p = 0.425$ atm; degree of dissociation = 0.1025]

43. The vapour density of PCl_5 at 200°C and 252°C are 70.2 and 57.2 respectively at one atmosphere. Calculate its value of dissociation constant at these temperatures.

[**Ans.** $K_p = 0.307, 1.19$]

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

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

[**Ans.** $NH_3 = 0.83$ atm; $H_2S = 0.33$ atm] **(MLNR 1994)**

[**Hint:** $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

At equilibrium $\qquad x + 0.5 \qquad x$

$$K_p = (x + 0.5)x = 0.11\,]$$

45. $SnO_2(s) + 2H_2(g) \rightleftharpoons 2H_2O_{(steam)} + Sn(s)$

For the above reaction find K_p, if at 900 K, the equilibrium mixture contains 45% H_2 by volume.

[Ans. $K_p = 1.5$]

46. The equilibrium constant for the reaction is 9.40 at 900°C.

$$S_2(g) + C(s) \rightleftharpoons CS_2(g)$$

Calculate the pressure of two gases at equilibrium, when 1.42 atm of S_2 and excess of $C(s)$ come to equilibrium.

[Ans. $p_{CS_2} = 1.28$ atm; $p_{S_2} = 0.14$ atm]

47. For the reaction,

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

$K_p = 1.16$ atm at 800°C. If 20.0 g of $CaCO_3$ were kept in a 10 litre container and heated up to 800°C, what percentage of $CaCO_3$ would remain unreacted at equilibrium?

[Ans. 34%]

[Hint: $K_p = p_{CO_2} = 1.16$ atm

$$n = \frac{p_{CO_2} \times V}{RT} = \frac{1.16 \times 10}{0.0821 \times 1073} = 0.132 \text{ mol}$$

$$\text{Initial amount of } CaCO_3 = \frac{20.0}{100} = 0.2 \text{ mol}$$

$$\text{Unreacted } CaCO_3 = 0.2 - 0.132 = 0.068 \text{ mol}$$

$$\% \text{ unreacted } CaCO_3 = \frac{0.068}{0.2} \times 100 = 34]$$

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

[Ans. $K_p = 16$ atm]

49. A mixture of 0.373 atm of $NO(g)$ and 0.310 atm of $Cl_2(g)$ is prepared at 500°C. The reaction, $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl$, occurs. The total pressure at equilibrium is 0.544 atm. Determine K_p of the reaction.

[Ans. $K_p = 50.08\ atm^{-1}$]

50. For the reaction,

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

at a given temperature, K_c is 9.0. What must be the volume of a flask if the mixture of 2.0 moles each of A, B and C is obtained at equilibrium?

[Ans. $V = 6$ litre]

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

[Hint: $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

Initial 0.6 0.2

Since, equilibrium constant is very high the reaction will be complete and bromine is consumed.

Thus, 0.2 mole of Br_2 and 0.2 mole of H_2 will be consumed to produce 0.4 mole of HBr. This can be calculated by applying law of mass action.

$$\frac{[HBr]^2}{[H_2][Br_2]} = K \text{ or } \frac{4x^2}{(0.6-x)(0.2-x)} = 5 \times 10^8$$

$$x = 0.6 \text{ or } 0.2$$

The value of x cannot be more than 0.2 as Br_2 is a limiting reactant. Thus, when reaction is complete,

$H_2 = (0.6 - 0.2) = 0.4$ mol; $Br_2 = 0$; HBr = 0.4 mol

At this point some HBr will dissociate.

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$$

At equilibrium $(0.4 - 2x)$ $(0.4 + x)$ (x)

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

or $$\frac{0.4x}{0.4} = 2 \times 10^{-10} (\text{since, } x \text{ is very small})$$

or $$x = 2 \times 10^{-10}$$

$[Br_2] = 2 \times 10^{-10}$ mol; $[H_2] = 0.4$ mol; [HBr] = 0.4 mol]

52. One mole of H_2, two moles of I_2 and three moles of HI are injected in a 1 litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 490°C? The equilibrium constant for the reaction at 490°C is 45.9.

[Ans. $[H_2] = 0.316$; $[I_2] = 1.316$; [HI] = 4.36 mol]

53. Solid ammonium carbamate dissociates to give ammonia and carbon dioxide as follows:

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

At equilibrium, ammonia is added such that partial pressure of NH_3 now equals to the original total pressure. Calculate the ratio of total pressure now to the original total pressure.

[Ans. $^{31}/_{27}$]

54. Two solid compounds A and C dissociate into gaseous product at temperature T as follows:

(i) $A(s) \rightleftharpoons B(g) + D(g)$

(ii) $C(s) \rightleftharpoons E(g) + D(g)$

At 20°C, pressure over excess solid A is 50 atm and that over excess solid C is 68 atm. Find the total pressure of the gases over the solid mixture.

[Ans. 84.38 atm]

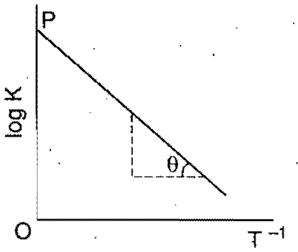
55. Variation of equilibrium constant K with temperature T is given by van't Hoff equation,

$$\log K = \log A - \frac{\Delta H°}{2.303\,RT}$$

A graph between $\log K$ and T^{-1} was a straight line as shown in the figure and having $\theta = \tan^{-1}(0.5)$ and $OP = 10$. Calculate:

(a) $\Delta H°$ (standard heat of reaction) when $T = 298$ K,

(b) A (pre-exponential factor),



(c) Equilibrium constant K at 298 K,

(d) K at 798 K, if $\Delta H°$ is independent of temperature.

[Ans. (a) 9.574 J mol^{-1}; (b) $A = 10^{10}$; (c) 9.96×10^9; (d) 9.98×10^9]

[**Hint:** (a) $\log K = \log A - \dfrac{\Delta H^\circ}{2.303RT}$

It is equation of straight line of the type $y = c + mx$

$$\text{Slope '}m\text{'} = \tan\theta = \frac{\Delta H^\circ}{2.303R}$$

$$0.5 = \frac{\Delta H^\circ}{2.303 \times 8.314}$$

$$\Delta H^\circ = 9.574 \text{ J mol}^{-1}$$

(b) Intercept 'c' $= \log A = 10$

$$\therefore \quad A = 10^{10}$$

(c) $$\log K = 10 - \frac{9.574}{2.303 \times 8.314 \times 298}$$

$$K = 9.96 \times 10^{9}$$

(d) $$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log \frac{K_2}{9.96 \times 10^9} = \frac{9.574}{2.303 \times 8.314}\left(\frac{1}{298} - \frac{1}{798}\right)$$

On solving, $K_2 = 9.98 \times 10^{9}$]

56. When 0.112 mole of NO and 18.22 g of bromine are placed in a 1.00 L reaction vessel and sealed, the mixture is heated to 350 K and the following equilibrium is established:

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

If the equilibrium concentration of nitrosyl bromide is 0.0824 M, what is K_c?

[**Ans.** 106.74]

[**Hint:**

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g); \; n_{Br_2} = \frac{18.22}{160} = 0.1138$$

$$\begin{array}{llll} t=0 & 0.112 & 0.1138 & 0 \\ t_{eq.} & \left[\frac{0.112-2x}{1}\right] & \left[\frac{0.1138-x}{1}\right] & \frac{2x}{1} \end{array}$$

$$2x = 0.0824$$

$$\therefore \quad [NO] = 0.112 - 2x$$

$$= 0.112 - 0.0824 = 0.0296\, M$$

$$[Br_2] = 0.1138 - \frac{0.0824}{2} = 0.0726\, M$$

$$K_c = \frac{[NOBr]^2}{[NO]^2[Br_2]} = \frac{[0.0824]^2}{[0.0296]^2[0.0726]} = 106.74\,]$$

57. Solid ammonium carbamate is put into a closed container and allowed to come to equilibrium with the gaseous products at 35°C, the total pressure is found to be 0.30 atmospheres. What is the value of K_p for this reaction at 35°C?

[**Ans.** 4×10^{-3}]

58. K_p for the equilibrium of,

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

at 1000°C is 0.403, if $CO(g)$, at a pressure of 1.0 atm and excess of $FeO(s)$ are placed in a container at 1000°C. What are the pressures of $CO(g)$ and $CO_2(g)$ when the equilibrium is attained?

[**Ans.** $p_{CO} = 0.713$ atm; $p_{CO_2} = 0.287$ atm]

59. A mixture of 1.0 mole of sulphur and 0.2 mole of hydrogen is heated at 90°C in a one litre flask. The equilibrium constant for the formation of hydrogen sulphide, $H_2(g) + S(s) \rightleftharpoons H_2S(g)$ is 6.8×10^{-2}. Calculate the partial pressure of H_2S at equilibrium.

[**Ans.** $p_{H_2S} = 0.397$ atm]

[**Hint:** First determine the initial pressure of H_2 by applying

$$p_0 = \frac{n}{V} \cdot RT = 5.953 \text{ atm}]$$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. A reversible reaction is one which:
(a) proceeds in one direction
(b) proceeds in both directions
(c) proceeds spontaneously
(d) all the statements are wrong

2. An example of reversible reaction is:
(a) $Pb(NO_3)_2 + 2NaI = PbI_2 + 2NaNO_3$
(b) $AgNO_3 + HCl = AgCl + HNO_3$
(c) $2Na + 2H_2O = 2NaOH + H_2$
(d) $KNO_3 + NaCl = KCl + NaNO_3$

3. Which one of the following is not a reversible reaction?
(a) $2HI(g) = H_2(g) + I_2(g)$
(b) $PCl_5(g) = PCl_3(g) + Cl_2(g)$
(c) $2KClO_3(s) = 2KCl(s) + 3O_2(g)$
(d) $CaCO_3(s) = CaO(s) + CO_2(g)$

4. Which one is not correct for a reversible reaction?
(a) The reaction is never completed
(b) The reactants are present in the initial stage but after that the reactants and products are always present in the reaction mixture
(c) At equilibrium only products are present
(d) When the reaction is carried out in closed space, it attains equilibrium state after suitable time

5. The law of mass action was proposed by:
(a) Guldberg and Waage (b) Le Chatelier and Braun
(c) Kossel and Lewis (d) van't Hoff

6. The rate at which a substance reacts, depends on its:
(a) active mass (b) molecular mass
(c) equivalent mass (d) total volume

7. Active mass is defined as:
(a) number of g equivalent per unit volume
(b) number of g mol per litre
(c) amount of substance in gram per unit volume
(d) number of g mole in 100 litre

8. 8.50 g of NH_3 is present in 250 mL volume. Its active mass is:
(a) 1.0 M L^{-1} (b) 0.5 M L^{-1} (c) 1.5 M L^{-1} (d) 2.0 M L^{-1}

9. Theory of 'active mass' indicates that the rate of a chemical reaction is directly proportional to the: **[PET (MP) 1990]**

(a) equilibrium constant (b) properties of reactants
(c) volume of apparatus (d) concentration of reactants

10. The state of equilibrium refers to: **[PMT (Pb.) 1993]**

(a) state of rest (b) dynamic state
(c) stationary state (d) state of inertness

11. In a reversible chemical reaction equilibrium is said to have been established when the:

(a) concentrations of reactants and products are equal
(b) opposing reactions cease
(c) speeds of opposing reactions become equal
(d) temperatures of opposing reactions are equal

12. A chemical reaction, $A \rightleftharpoons B$, is said to be in equilibrium when:

(a) rate of forward reaction is equal to rate of backward reaction
(b) conversion of A to B is only 50% complete
(c) complete conversion of A to B has taken place
(d) only 25% conversion of A to B has taken place

13. The reaction between barium chloride and sodium sulphate goes to completion because:

(a) barium sulphate is almost insoluble
(b) the solubility of barium chloride decreases
(c) lattice energy of barium sulphate is very high
(d) the reaction is irreversible in nature

14. What is the equilibrium constant expression for the reaction,

$$P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)?$$

(Jamia Millia Islamia Engg. Ent. 2007; UPSEE 2007)

(a) $K_c = \dfrac{[P_4O_{10}]}{[P_4]\,[O_2]^5}$ (b) $K_c = \dfrac{[P_4O_{10}]}{5\,[P_4]\,[O_2]}$

(c) $K_c = [O_2]^5$ (d) $K_c = \dfrac{1}{[O_2]^5}$

15. Equilibrium constant for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, is correctly given by the expression:

(a) $K_c = \dfrac{[H_2][I_2]}{[HI]}$ (b) $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

(c) $K_c = \dfrac{[HI]}{[H_2][I_2]}$ (d) $K_c = \dfrac{[2HI]}{[H_2][I_2]}$

16. Equilibrium constant for the reaction, $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$, is correctly given by the expression:

(a) $K = \dfrac{[NOCl]^2}{[NO]^2[Cl_2]}$ (b) $K = \dfrac{[2NOCl]}{[2NO][Cl_2]}$

(c) $K = \dfrac{[NO]^2 + [Cl_2]}{[NOCl]}$ (d) $K = \dfrac{[NO]^2[Cl_2]}{[NOCl]^2}$

17. For the system, $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant is: **[JEE (WB) 2007]**

(a) $\dfrac{[A]^3[B]^2}{[C]}$ (b) $\dfrac{[C]}{[A]^3[B]^2}$ (c) $\dfrac{[A]^2[B]^3}{[C]}$ (d) $\dfrac{[C]}{[A][B]}$

18. The equilibrium constants of the reactions,

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

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

are K_1 and K_2 respectively. The relationship between K_1 and K_2 is:

(a) $K_1 = K_2$ (b) $K_2^2 = K_1$
(c) $K_1^2 = K_2$ (d) $K_2 = \sqrt{K_1}$

19. The equilibrium constant for the given reaction is 100.

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

What is the equilibrium constant for the reaction given below:

$$NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$$

(EAMCET 2009)

(a) 10 (b) 1
(c) 0.1 (d) 0.01

20. For the reaction, $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$, $K_c = 1.8 \times 10^{-6}$ at 185°C. The value of K_c at 185°C for the reaction;

$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$ is: **(MLNR 1993)**

(a) 0.9×10^6 (b) 1.95×10^{-3}
(c) 1.95×10^3 (d) 7.5×10^2

21. The equilibrium constant for the synthesis of HI at 490°C is 50.0. The value of K for the dissociation of HI will be: **(IIT 1990)**

(a) 0.02 (b) 50.0 (c) 0.50 (d) 0.20

22. Consider the following equilibrium,

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

$$2SO_3(g) \overset{K_2}{\rightleftharpoons} 2SO_2(g) + O_2(g)$$

What is the relation between K_1 and K_2? **[PET (MP) 1993]**

(a) $K_1 = \dfrac{1}{K_2}$ (b) $K_1 = \dfrac{1}{\sqrt{K_2}}$ (c) $K_1 = K_2$ (d) $K_1 = \dfrac{1}{K_2^2}$

23. For the reaction $AB(g) \rightleftharpoons A(g) + B(g)$, AB is 33%, dissociated at a total pressure of P. Therefore, P is related to K_p by one of the following option: **[AMU (Med.) 2010]**

(a) $P = K_p$ (b) $P = 3K_p$
(c) $P = 4K_p$ (d) $P = 8K_p$

[Hint:

$$\begin{array}{cccc} & AB(g) \rightleftharpoons & A(g) + & B(g) \\ t_0 & 1 & 0 & 0 \\ t_{eq} & 1-\frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{array}$$

$$p_{AB} = \frac{2/3}{4/3} \times p = \frac{p}{2};$$

$$p_A = p_B = \frac{1/3}{4/3} \times p = \frac{p}{4}$$

$$K_p = \frac{\frac{p}{4} \times \frac{p}{4}}{\frac{p}{2}} = \frac{p}{8}$$

$p = 8K_p$ **]**

24. For a system, $A + 2B \rightleftharpoons C$, the equilibrium concentrations are $[A] = 0.06$, $[B] = 0.12$ and $[C] = 0.216$. The K_c for the reaction is:

(a) 125 (b) 415
(c) 4×10^{-3} (d) 250

25. The equilibrium concentrations of x, y and yx_2 are 4, 2 and 2 respectively for the equilibrium $2x + y \rightleftharpoons yx_2$. The value of equilibrium constant, K_c is: **(EAMCET 1990)**
(a) 0.625 (b) 6.25 (c) 0.0625 (d) 62.5

26. 4 mole of A are mixed with 4 mole of B when 2 mole of C are formed at equilibrium, according to the reaction,

$$A + B \rightleftharpoons C + D$$

the equilibrium constant is: **(CPMT 1992)**
(a) $\sqrt{2}$ (b) 2 (c) 1 (d) 4

27. If the equilibrium constant of the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 0.25, the equilibrium constant of $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, under similar conditions, will be:
(a) 4.0 (b) 3.0 (c) 2.0 (d) 1.0

28. HI was heated in a sealed tube at 400°C till the equilibrium was reached. HI was found to be 22% decomposed. The equilibrium constant for dissociation is:
(a) 1.99 (b) 0.0199 (c) 0.0796 (d) 0.282

29. For a reversible reaction if the concentrations of the reactants are doubled at a definite temperature, then equilibrium constant will: **(CPMT 1990; MLNR 1992)**
(a) also be doubled (b) be halved
(c) become one-fourth (d) remain the same

30. In a reversible gaseous system, molar concentrations (active masses) of reactants and products are proportional to:
(a) partial pressure
(b) total pressure
(c) amounts of reactants and products
(d) none of the above

31. At 3000 K, the equilibrium partial pressure of CO_2, CO and O_2 are 0.6, 0.4 and 0.2 atmospheres respectively. K_p for the reaction,

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g) \text{ is :}$$

[BHU (Mains) 2010]
(a) 0.088 (b) 0.0533 (c) 0.133 (d) 0.177

32. Equilibrium constant depends on:
(a) the actual quantities of reactants and products
(b) the presence of a catalyst
(c) temperature
(d) the presence of inert material

33. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant, K_p, changes with:
(a) total pressure
(b) catalyst
(c) the amounts of H_2 and I_2 taken
(d) temperature

34. $$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The equilibrium constant of the above reaction is 6.4 at 300 K. If 0.25 mole each of H_2 and I_2 are added to the system, the equilibrium constant will be: **(CET Karnataka 2009)**
(a) 0.8 (b) 3.2 (c) 1.6 (d) 6.4

35. 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 reaction :

$$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$$

will be : **[BHU (Screening) 2010]**
(a) 6.66×10^{-3} (b) 0.30
(c) 3.30 (d) 150

[Hint:

$$\begin{array}{llll} & Fe^{3+} + & SCN^- \rightleftharpoons & FeSCN^{2+} \\ t_0 & 3.1 & 3.2 & 0 \\ t_{eq.} & \frac{0.1}{1} & \frac{0.2}{1} & \frac{3}{1} \end{array}$$

$$K_c = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

$$= \frac{3}{0.1 \times 0.2} = 150]$$

36. K_p and K'_p are the equilibrium constants of the two reactions, given below:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

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

Therefore, K_p and K'_p are related by **[AMU (PMT) 2009]**
(a) $K_p = K'^2_p$ (b) $K_p = \sqrt{K'_p}$
(c) $K_p = 2K'_p$ (d) $K_p = K'_p$

37. In which of the following equilibrium K_c and K_p are not equal? **[CBSE (PMT) 2010]**
(a) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
(b) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(d) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$

38. Select the correct statement from the following:
(a) equilibrium constant changes with addition of a catalyst
(b) catalyst increases the rate of forward reaction
(c) the ratio of mixture at equilibrium does not change by catalyst
(d) catalysts are active only in solution

39. In which of the following, the reaction proceeds towards completion? **(MLNR 1990)**
(a) $K = 1$ (b) $K = 10^{-2}$
(c) $K = 10$ (d) $K = 10^3$

40. For the following reaction at 250°C, the value of K_c is 26, then the value of K_p at the same temperature will be:
$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ **(MLNR 1990; CBSE 1993)**
(a) 0.57 (b) 0.61 (c) 0.83 (d) 0.91

41. In the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the amounts of PCl_5, PCl_3 and Cl_2 are 2 mole each at equilibrium and the total pressure is 3 atmospheres. The equilibrium constant, K_p, is: **(IIT 1991)**
(a) 1 atm (b) 2 atm (c) 3 atm (d) 1.5 atm

42. In which of the following K_p is less than K_c?
(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
(b) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(c) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
(d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

43. For a reversible reaction, the rate constants for the forward and backward reactions are 2.38×10^{-4} and 8.15×10^{-5} respectively. The equilibrium constant for the reaction is:
(a) 0.342 (b) 2.92
(c) 0.292 (d) 3.42

44. The equilibrium constant in a reversible reaction at a given temperature:

(a) depends on the initial concentration of the reactants
(b) depends on the concentration of products at equilibrium
(c) it is not characteristic of the reaction
(d) does not depend on initial concentrations

45. 1.0 g mole of ethyl alcohol and 1.0 g mole of acetic acid are mixed. At equilibrium 0.666 g mole of the ester is present. The value of equilibrium constant is: **[PET (MP) 1993]**

(a) $\frac{1}{4}$ (b) $\frac{1}{2}$ (c) 2 (d) 4

46. The equilibrium constant of the reaction,

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

is 4. If one mole of each of acetic acid and ethyl alcohol are heated in presence of a little concentrated H_2SO_4, at equilibrium the amount of ester present is: **[PET (MP) 1992]**

(a) 1 mole (b) 2 mole
(c) $\frac{2}{3}$ mole (d) $\frac{1}{2}$ mole

47. If different quantities of ethanol and acetic acid are used in the following reversible reaction,

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

the equilibrium constant will have values which will be?

(a) Different in all cases
(b) Same in all cases
(c) Higher in cases where higher concentration of ethanol is used
(d) Higher in cases where higher concentration of acetic acid is used

48. The reaction,

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

is begun with concentration of A and B both at initial value of 1M. 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 : **[CBSE (PMT) 2010]**

(a) $[(0.75)^3(0.25)] \div [(1.00)^2(1.00)]$
(b) $[(0.75)^3(0.25)] \div [(0.50)^2(0.75)]$
(c) $[(0.75)^3(0.25)] \div [(0.50)^2(0.25)]$
(d) $[(0.75)^3(0.25)] \div [(0.75)^2(0.25)]$

[Hint:

$$\begin{array}{lccccccc} & 2A(g) & + & B(g) & \rightleftharpoons & 3C(g) & + & D(g) \\ t_0 & 1 & & 1 & & 0 & & 0 \\ t_{eq.} & 0.50 & & 0.75 & & 0.75 & & 0.25 \end{array}$$

$$K = \frac{[C]^3[D]}{[A]^2[B]} = \frac{(0.75)^3(0.25)}{(0.50)^2(0.75)}$$ **]**

49. The decomposition of N_2O_4 to NO_2 is carried at 280 K in chloroform. When equilibrium has been established, 0.2 mole of N_2O_4 and 2×10^{-3} mole of NO_2 are present in 2 litre solution. The equilibrium constant for the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, is:

(a) 1×10^{-2} (b) 2×10^{-3}
(c) 1×10^{-5} (d) 2×10^{-5}

50. The unit of equilibrium constant, K_c, for the reaction $A + B \rightleftharpoons C$ would be:

(a) mol^{-1} L (b) mol L^{-1} (c) mol L (d) no unit

51. For which of the following reactions does the equilibrium constant depend on the units of concentration?

(a) $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$
(b) $C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$
(c) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(d) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

52. The units of K_p in the following reaction are:

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

(a) atm (b) atm^{-2} (c) atm^2 (d) atm^{-1}

53. The equilibrium of formation of phosgene is represented as:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

The reaction is carried out in a 500 mL flask. At equilibrium 0.3 mole of phosgene, 0.1 mole of CO and 0.1 mole of Cl_2 are present. The equilibrium constant of the reaction is:

(a) 30 (b) 15 (c) 5 (d) 3

54. In an equilibrium reaction, for which $\Delta G^\circ = 0$, the equilibrium constant K should be equal to:

(a) zero (b) 10 (c) 1 (d) 2

55. The equilibrium constant K_p for the homogeneous gaseous reaction is 10^{-3}. The standard Gibbs free energy change ΔG° for the reaction at 27°C (using $R = 2$ cal K^{-1} mol^{-1}) is:

(a) zero (b) − 1.8 kcal
(c) − 4.154 kcal (d) + 4.154 kcal

56. At 500 K, the equilibrium constant for reaction *cis*-$C_2H_2Cl_2 \rightleftharpoons$ *trans*-$C_2H_2Cl_2$ is 0.6. At the same temperature, the equilibrium constant for the reaction *trans*-$C_2H_2Cl_2 \rightleftharpoons$ *cis*-$C_2H_2Cl_2$, will be:

(a) 1.67 (b) 0.6 (c) 1.76 (d) 1.64

57. Which one of the following oxides is most stable? The equilibrium constants are given at the same temperature:

(a) $2N_2O_5(g) \rightleftharpoons 2N_2(g) + 5O_2(g)$; $K = 1.2 \times 10^{34}$
(b) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$; $K = 3.5 \times 10^{35}$
(c) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; $K = 2.2 \times 10^{30}$
(d) $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$; $K = 6.71 \times 10^{16}$

58. In a chemical equilibrium, $K_c = K_p$ when: **[CEE (Bihar) 1992]**

(a) the number of molecules entering into a reaction is more than the number of molecules produced
(b) the number of molecules entering into the reaction is equal to the number of molecules produced
(c) the number of molecules entering into the reaction is less to the number of molecules produced
(d) none of the above

59. In a general reaction, $A + B \rightleftharpoons AB$, which value of equilibrium constant most favours the production of AB?

(a) 9.0×10^{-3} (b) 3.5×10^{-3}
(c) 4.0×10^{-7} (d) 4.0×10^{-12}

60. During thermal dissociation of a gas, the vapour density:

(a) remains the same
(b) increases
(c) decreases
(d) increases in some cases and decreases in others

61. The vapour density of fully dissociated NH_4Cl would be:
(a) less than half of the vapour density of pure NH_4Cl
(b) double of the vapour density of pure NH_4Cl
(c) half of the vapour density of pure NH_4Cl
(d) one-third of the vapour density of pure NH_4Cl

62. In the dissociation of $2HI \rightleftharpoons H_2 + I_2$, the degree of dissociation will be affected by:
(a) increase of temperature (b) addition of an inert gas
(c) addition of H_2 and I_2 (d) increase of pressure

63. In lime kilns, the following reversible reaction,

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

proceeds to completion because of: **(CPMT 1990)**
(a) high temperature
(b) CO_2 escapes
(c) low temperature
(d) molecular mass of CaO is less than that of $CaCO_3$

64. The equilibrium constant for the reaction,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g), \text{ is:}$$

(a) $K_c = \dfrac{1}{[CO_2]}$ (b) $K_c = [CO_2]$
(c) $K_c = \dfrac{[CaO][CO_2]}{[CaCO_3]}$ (d) $K_c = \dfrac{[CaCO_3]}{[CaO][CO_2]}$

65. For the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressure of CO_2 and CO are 2.0 and 4.0 atm, respectively, at equilibrium. The K_p of the reaction is: **(IIT 1992)**
(a) 0.5 (b) 4.0
(c) 32.0 (d) 8.0

66. Iron fillings and water were placed in a 5 litre vessel and sealed. The tank was heated to 1000°C. Upon analysis the tank was found to contain 1.1 g of hydrogen and 42.5 g of water vapour. If the reaction in the tank is represented by,

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

the value of equilibrium constant, K_c, is:
(a) 30 (b) 0.03
(c) 3 (d) 0.003

67. Ammonium hydrogen sulphide is contained in a closed vessel at 313 K when total pressure at equilibrium is found to be 0.8 atm. The value of K_p for the reaction, $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ is:
(a) 0.16 (b) 1.6 (c) 0.016 (d) 16

68. Variation of K with temperature as given by van't Hoff equation can be written as:
(a) $\log \dfrac{K_2}{K_1} = -\dfrac{\Delta H}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$
(b) $\log \dfrac{K_2}{K_1} = \dfrac{\Delta H}{2.303R}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$
(c) $\log \dfrac{K_2}{K_1} = -\dfrac{\Delta H}{2.303R}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$
(d) none of the above

69. When any system in equilibrium is subjected to a change in pressure, concentration or temperature, the equilibrium is shifted in the direction which tends to undo the effect of the change. This statement is known as:
(a) First law of thermodynamics
(b) Le Chatelier's principle
(c) Hess's law
(d) Ostwald's law

70. Le Chatelier's principle is applicable to:
(a) only homogeneous chemical reversible reactions
(b) only heterogeneous chemical reversible reactions
(c) only physical equilibria
(d) all systems, chemical or physical, in equilibrium

71. In the melting of ice, which one of the conditions will be more favourable?
(a) High temperature and high pressure
(b) Low temperature and low pressure
(c) Low temperature and high pressure
(d) High temperature and low pressure

72. Solubility of a gas in liquid increases on:
(a) addition of a catalyst (b) decreasing of pressure
(c) increasing of pressure (d) increasing of temperature

73. When KOH is dissolved in water, heat is evolved. If the temperature is raised, the solubility of KOH:
(a) increases (b) decreases
(c) remains the same (d) cannot be predicted

74. The yield of product in the reaction,

$$A_2(g) + 2B(g) \rightleftharpoons C(g) + Q \text{ kJ}$$

would be higher at:
(a) low temperature and high pressure
(b) high temperature and high pressure
(c) low temperature and low pressure
(d) high temperature and low pressure

75. Manufacture of ammonia from the elements is represented by,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22.4 \text{ kcal}$$

The maximum yield of ammonia will be obtained when the process is made to take place:
(a) at low pressure and high temperature
(b) at low pressure and low temperature
(c) at high pressure and high temperature
(d) at high pressure and low temperature

76. In the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + X$ cal, most favourable conditions of temperature and pressure for greater yield of SO_3 are:
(a) low temperature and low pressure
(b) high temperature and low pressure
(c) high temperature and high pressure
(d) low temperature and high pressure

77. What is the direction of a reversible reaction when one of the products of the reaction is removed?
(a) The reaction moves towards right hand side
(b) The reaction moves towards left hand side
(c) The reaction moves equally on both the sides
(d) The reaction stops

78. In the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -93.6$ kJ, the yield of ammonia does not increase when:
(a) pressure is increased
(b) pressure is decreased
(c) temperature is lowered
(d) volume of the reaction vessel is decreased

79. A cylinder provided with a piston has some PCl_5 which is in equilibrium with PCl_3 and Cl_2. The system is compressed with the help of piston. Indicate the correct statement:
(a) some more PCl_5 will decompose
(b) the system remains unaffected
(c) PCl_3 and Cl_2 will combine to form PCl_5
(d) explosion occurs

80. In the manufacture of nitric oxide, the forward reaction is favoured by:
(a) high pressure (b) low pressure
(c) high temperature (d) low temperature

81. The reaction,
$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g); \Delta H = -32.7 \text{ kcal}$$
is carried out in a vessel. The equilibrium concentration of C_2H_4 can be increased by:
(a) increasing the temperature
(b) decreasing the pressure
(c) removing some hydrogen
(d) all of these

82. In an exothermic reaction, a 10°C rise in temperature will: **[PMT (Bangalore) 1993]**
(a) decrease the value of equilibrium constant
(b) double the value of equilibrium constant
(c) not produce any change in equilibrium constant
(d) produce some increase in equilibrium constant

83. If K_p for a reaction,
$$A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$$
is 0.05 atm at 1000 K, its K_c in terms of R will be:
(a) $20000\,R$ (b) $0.02\,R$ (c) $5 \times 10^{-5}\,R$ (d) $\frac{5 \times 10^{-5}}{R}$

84. Consider the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ in closed container at equilibrium. What would be the effect of addition of $CaCO_3$ on the equilibrium concentration of CO_2? **(AIIMS 1991)**
(a) Increases
(b) Decreases
(c) Remains unaffected
(d) Data is not sufficient to predict it

85. XY_2 dissociates as:
$$XY_2(g) \rightleftharpoons XY(g) + Y(g)$$
Initial pressure of XY_2 is 600 mm Hg. The total pressure at equilibrium is 800 mm Hg. Assuming volume of system to remain constant, the value of K_p is: **(BHU 1992)**
(a) 50 (b) 100 (c) 200 (d) 400

[Hint: $XY_2(g) \rightleftharpoons XY(g) + Y(g)$
$600 - x \quad x \quad x$
$600 + x = 800$ or $x = 200$]

86. Which of the following reactions will be favoured at low pressure?
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

87. According to Le Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause the: **(MLNR 1990)**
(a) amount of solid to decrease
(b) amount of liquid to decrease
(c) temperature to rise
(d) temperature to fall

88. For the reaction:
$$2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$$
two moles each of A and B were taken into a flask. The following must always be true when the system attained equilibrium:
(a) $[A] = [B]$ (b) $[A] < [B]$
(c) $[B] = [C]$ (d) $[A] > [B]$

89. In a vessel containing SO_3, SO_2 and O_2 at equilibrium, some helium gas is introduced so that total pressure increases while temperature and volume remain the same. According to Le Chatelier's principle, the dissociation of SO_3: **(MLNR 1991)**
(a) increases (b) decreases
(c) remains unaltered (d) changes unpredictably

90. The equilibrium, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas, helium, is introduced. Which of the following statements is correct?
(a) Concentrations of SO_2Cl_2, SO_2 and Cl_2 do not change
(b) More Cl_2 is formed
(c) Concentration of SO_2 is reduced
(d) More SO_2Cl_2 is formed

91. 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 % dissociation of N_2O_4 is:
(a) 40 (b) 57
(c) 67 (d) 87

92. K_p/K_c for the reaction, $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ is:
(a) RT (b) $\frac{1}{\sqrt{RT}}$ (c) $\sqrt{RT}$ (d) 1

93. For the reactions,
$A \rightleftharpoons B, K_c = 1$; $B \rightleftharpoons C, K_c = 3$; $C \rightleftharpoons D, K_c = 5$
K_c for the reaction $A \rightleftharpoons D$ is:
(a) 15 (b) 5 (c) 3 (d) 1

[Hint: $\frac{[B]}{[A]} = 1$; $\frac{[C]}{[B]} = 3$; $\frac{[D]}{[C]} = 5$,

Multiplying all the three, $\frac{[D]}{[A]} = 1 \times 3 \times 5$]

94. The equilibrium constant of the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 50. If the volume of the container is reduced to one half of its original value, the equilibrium constant will be:
(a) 25 (b) 50
(c) 75 (d) 100

95. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
The above equilibrium when subjected to pressure: **[PMT (Raj.) 1992]**
(a) remains unaffected
(b) proceeds in the backward direction
(c) proceeds in the forward direction
(d) none of the above

96. Reaction, $A + B \longrightarrow C + D + 38$ kcal has activation energy 20 kcal. Activation energy for the reaction, $C + D \longrightarrow A + B$ is: **[PMT (Pb.) 1993]**

(a) 20 kcal (b) –20 kcal

(c) 18 kcal (d) 58 kcal

97. The equilibrium constant for the reaction,

$$CaSO_4 \cdot 5H_2O(s) \rightleftharpoons CaSO_4 \cdot 3H_2O(s) + 2H_2O(g),$$

is equal to:

(a) $\dfrac{[CaSO_4 \cdot 3H_2O][H_2O]^2}{[CaSO_4 \cdot 5H_2O]}$ (b) $\dfrac{[CaSO_4 \cdot 3H_2O]}{[CaSO_4 \cdot 5H_2O]}$

(c) $[H_2O]^2$ (d) $[H_2O]$

98. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is:

(a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm

99. The equilibrium constant for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 4.0×10^{-4} at 2000 K. In the presence of a catalyst the equilibrium is attained ten times faster. Therefore, the equilibrium constant in presence of the catalyst at 2000 K is: **(MLNR 1994)**

(a) 4×10^{-4}

(b) 40×10^{-4}

(c) 4×10^{-2}

(d) difficult to compute without more data

100. The equilibrium constant for a reaction, $A + B \rightleftharpoons C + D$ is 1×10^{-2} at 298 K and is 2 at 273 K. The chemical process resulting in the formation of C and D is:

(a) exothermic

(b) endothermic

(c) unpredictable

(d) there is no relationship between ΔH and K

101. The equilibrium constant for the reaction, $A + B \rightleftharpoons C + D$ is 2.85 at room temperature and 1.4×10^{-2} at 698 K. This shows that forward reaction is:

(a) exothermic

(b) endothermic

(c) unpredictable

(d) there is no relationship between ΔH and K

102. If E_f and E_r are the activation energies of forward and backward reactions and the reaction is known to be exothermic, then:

(a) $E_f > E_r$

(b) $E_f < E_r$

(c) $E_f = E_r$

(d) no relation can be given between E_f and E_r

103. K_p for a reaction at 25°C is 10 atm. The activation energy for forward and reverse reactions are 12 and 20 kJ/mol respectively. The K_c for the reaction at 40°C will be:

(a) $4.33 \times 10^{-1}\ M$ (b) $3.33 \times 10^{-2}\ M$

(c) $3.33 \times 10^{-1}\ M$ (d) $4.33 \times 10^{-2}\ M$

104. Concentration of pure solid and liquid is not included in the expression of equilibrium constant because:

(a) solid and liquid concentrations are independent of their quantities

(b) solid and liquids react slowly

(c) solid and liquids at equilibrium do not interact with gaseous phase

(d) the molecules of solids and liquids cannot migrate to the gaseous phase

105. For an equilibrium reaction involving gases, the forward reaction is first order while the reverse reaction is second order. The units of K_p for forward equilibrium is:

(a) atm (b) atm^2 (c) atm^{-1} (d) atm^{-2}

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

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation 'x' which is small as compared to unity. The expression for K_p, in terms of 'x' and total pressure 'P' is

(a) $\dfrac{Px^3}{2}$ (b) $\dfrac{Px^2}{3}$

(c) $\dfrac{Px^3}{3}$ (d) $\dfrac{Px^2}{2}$

107. 40% mixture of 0.2 mole of N_2 and 0.6 mole of H_2 react to give NH_3 according to the equation:

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

at constant temperature and pressure. Then the ratio of the final volume to the initial volume of gases is:

(a) 4 : 5 (b) 5 : 4

(c) 7 : 10 (d) 8 : 5

108. 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:

(a) PCl_5 is greater (b) PCl_3 remains unchanged

(c) PCl_5 is less (d) Cl_2 is greater

109. For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$, the equilibrium constant K_c at 25°C is 4×10^{-19}; then Ag^+ concentration in a solution which has 0.1 M KCN and 0.03 M $AgNO_3$ is:

(a) 7.5×10^{18} (b) 7.5×10^{-18}

(c) 7.5×10^{19} (d) 7.5×10^{-19}

110. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium:

(a) addition of $NaNO_2$ favours reverse reaction

(b) addition of $NaNO_2$ favours forward reaction

(c) increasing temperature favours forward reaction

(d) decreasing pressure favours reverse reaction

111. For the reaction,

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

which one is the correct representation?

(a) $K_p = [p_{H_2O}]^2$ (b) $K_c = [H_2O]^2$

(c) $K_p = K_c(RT)^2$ (d) All of these

112. Which one is the correct representation for,

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

(a) $K_p = \dfrac{[p_{SO_3}]^2}{[p_{SO_2}]^2[p_{O_2}]}$

(b) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

(c) $K_p = \dfrac{[n_{SO_3}]^2}{[n_{SO_2}]^2[n_{O_2}]} \times \left[\dfrac{P}{\text{Total mole}}\right]^{-1}$

(d) All of the above

113. For the reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \textbf{(IIT 1991)}$$

The forward reaction at constant temperature is favoured by:

(a) introducing inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) none of the above

114. In a flask colourless N_2O_4 is in equilibrium with brown coloured NO_2. At equilibrium, when the flask is heated to 100°C the brown colour deepens and on cooling, the brown colour became less coloured. The change in enthalpy ΔH for the system is: **(KCET 1993)**

(a) negative (b) positive (c) zero (d) not defined

115. Le Chatelier's principle is not applicable to:

(a) $Fe(s) + S(s) \rightleftharpoons FeS(s)$
(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

116. Densities of diamond and graphite are 3.5 and 2.3 g/mL respectively. Increase in pressure on the equilibrium $C_{\text{diamond}} \rightleftharpoons C_{\text{graphite}}$:

(a) favours backward reaction
(b) favours forward reaction
(c) has no effect
(d) increases the reaction rate

117. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ in a vessel, after the addition of equal number of moles of N_2 and H_2 equilibrium state is achieved. Which of the following is correct?

(a) $[H_2] = [N_2]$ (b) $[H_2] < [N_2]$
(c) $[H_2] > [N_2]$ (d) $[H_2] > [NH_3]$

118. If pressure is applied to the equilibrium of solid $\rightleftharpoons$ liquid, the melting point of the solid:

(a) will not change
(b) may increase or decrease depending upon its nature
(c) will always increase
(d) will always decrease

119. If concentrations of N_2, H_2 and NH_3 are 1, 2 and 3 respectively, their concentration at equilibrium will be:

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

(a)	$(1-x)$	$(2-3x)$	$2x$
(b)	$(1-x/3)$	$(2-x)$	$2x/3$
(c)	$(1-x)$	$(2-x)$	$(3+x)$
(d)	$(1-x)$	$(2-3x)$	$(3+2x)$

120. A reaction attains equilibrium, when the free energy change is:

(a) zero (b) positive and large
(c) negative and small (d) negative and large

121. If 340 g of a mixture of N_2 and H_2 in the correct ratio gave a 20% yield of NH_3, the mass produced would be:

(a) 16 g (b) 17 g (c) 20 g (d) 68 g

122. If the pressure of N_2 / H_2 mixture in a closed apparatus is 100 atm and 20% of the mixture then reacts, the pressure at the same temperature would be:

(a) 100 (b) 90 (c) 85 (d) 80

123. The equilibrium constants 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:

(a) endothermic (b) exothermic
(c) fast (d) slow

124. If the concentration of OH^- ions in the reaction:

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq.) + 3OH^-(aq.)$$

is decreased by $\frac{1}{4}$ times, then equilibrium concentration of Fe^{3+} will increase by: **[CBSE (PMT) 2008]**

(a) 64 times (b) 4 times (c) 8 times (d) 16 times

125. K_c for $A + B \rightleftharpoons C + D$ is 10 at 25°C. If a container contains 1, 2, 3 and 4 mol per litre of A, B, C and D respectively at 25°C, the reaction shall:

(a) proceed from left to right (b) proceed from right to left
(c) be at equilibrium (d) none of these

126. In the preparation of CaO from $CaCO_3$ using the equilibrium,

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

K_p is expressed as:

$$\log K_p = 7.282 - \frac{8500}{T}$$

For complete decomposition of $CaCO_3$ the temperature in celsius to be used is:

(a) 1167 (b) 894
(c) 8500 (d) 850

127. To the system,

$$LaCl_3(s) + H_2O(g) \rightleftharpoons LaClO(s) + 2HCl(g) - \text{heat}$$

already at equilibrium, more water vapour is added without altering T or V of the system. When equilibrium is re-established, the pressure of water vapour is doubled. The pressure of HCl present in the system increases by a factor of:

(a) 2 (b) $2^{1/2}$ (c) 3 (d) 4

128. For the chemical reaction,

$$3X(g) + Y(g) \rightleftharpoons X_3Y(g)$$

the amount of X_3Y at equilibrium is affected by: **(IIT 1999)**

(a) temperature and pressure
(b) temperature only
(c) pressure only
(d) temperature, pressure and catalyst

129. In a 500 mL capacity vessel CO and Cl_2 are mixed to form $COCl_2$. At equilibrium, it contains 0.2 mole of $COCl_2$ and 0.1 mole of each of CO and Cl_2. The equilibrium constant K_c for reaction, $CO + Cl_2 \rightleftharpoons COCl_2$ is: **(CBSE 1998)**

(a) 5 (b) 10 (c) 15 (d) 20

130. The partial pressures of CH_3OH, CO and H_2 in the equilibrium mixture for the reaction,

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

at 427°C are 2.0, 1.0 and 0.1 atm respectively. The value of K_p for the decomposition of CH_3OH into CO and H_2 is:

(IIT 1999)

(a) 1×10^2 atm (b) 2×10^2 atm^{-1}

(c) 50 atm^2 (d) 5×10^{-3} atm^2

131. 8 mole of a gas AB_3 are introduced into a 1.0 dm^3 vessel. It dissociates as:

$$2AB_3(g) \rightleftharpoons A_2(g) + 3B_2(g)$$

At equilibrium, 2 mole of A_2 are found to be present. The equilibrium constant of the reaction is: **(IIT 1997)**

(a) 2 mol^2 L^{-2} (b) 3 mol^2 L^{-2}

(c) 27 mol^2 L^{-2} (d) 36 mol^2 L^{-2}

132. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction,

$$N_2O_4 \rightleftharpoons 2NO_2$$

is expressed by:

$$K_p = \frac{4x^2P}{(1-x^2)}$$

Where, P = pressure, x = extent of decomposition. Which one of the following statements is true? **[IIT (Screening) 2000]**

(a) K_p increases with increase of P

(b) K_p increases with increase of x

(c) K_p increases with decrease of x

(d) K_p remains constant with change in P and x

133. Consider the reactions,

$$NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g) \qquad K_1$$

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_2$$

Give the equilibrium constant for the formation of N_2O_4 from N_2 and O_2: **(DCE 2006)**

(a) $\frac{1}{K_1^2}\times\frac{1}{K_2}$ (b) $\frac{1}{2K_1}+\frac{1}{K_2}$ (c) $\sqrt{\frac{1}{K_1K_2}}$ (d) $\frac{K_2}{K_1}$

[**Hint:** $NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)\ K_1$

$$\therefore \quad N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \qquad K = \frac{1}{K_1^2} \qquad \text{... (i)}$$

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_2$$

$$\therefore \quad 2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K = \frac{1}{K_2} \qquad \text{... (ii)}$$

Adding eqs. (i) and (ii),

$$N_2(g) + 2O_2(g) \rightleftharpoons N_2O_4(g) \qquad K = \frac{1}{K_1^2}\times\frac{1}{K_2}$$]

134. Phosphorous pentachloride dissociates as follows:

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

If total pressure at equilibrium is P and the degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be: **(AIEEE 2006)**

(a) $\left(\frac{x}{x+1}\right)P$ (b) $\left(\frac{2x}{1-x}\right)P$ (c) $\left(\frac{x}{x-1}\right)P$ (d) $\left(\frac{x}{1-x}\right)P$

135. At $t = 0$ a vessel (volume 1 litre) contains 1 mole N_2, 3 mole H_2 and 2 mole NH_3. The value of K_c for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 17.5 L^2 mol^{-2}. Then:

(a) total gaseous weight at equilibrium is more than 68 g

(b) total number of moles (gaseous) at equilibrium are more than 6 moles

(c) $\frac{dM}{dt}$ is +ve for $t \in (0, T_{eq.})$ where, M is average molar mass of the reaction mixture

(d) total gaseous weight at equilibrium is less than 68 g

136. A vessel (volume = 2 L) contains 60 g of water gas. When steam is passed through the vessel, the reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$ occurs and equilibrium is attained:

(a) $\frac{n(H_2)}{n(CO)} < 1$ (at equilibrium)

(b) $n(H_2) + n(CO) = 4$ (at any instant)

(c) $\frac{dM}{dt} > 0$ (where, M is average molar mass of gas mixture before the attainment of equilibrium)

(d) $\frac{dM}{dt} < 0$

137. A vessel contains CO_2 and CO with pressures 2 atm and 3 atm respectively at 27°C. At a temperature of 2727°C, the reaction $2CO(g) \rightleftharpoons CO_2(g) + C(s)$ occurs and equilibrium is attained. If the equilibrium pressure is 45 atm, then:

(a) $K_p = 2/9$ atm^{-1}

(b) $p_{CO} : p_{CO_2} = 4:5$ at equilibrium

(c) $K_p = 16$ atm^{-1}

(d) % dissociation of CO = 0.333

138. A vessel (volume 8.2 L) contains $H_2(g)$ at 2 atm pressure. When $H_2S(g)$ at a pressure of 4 atm is introduced into the vessel, the reaction, $8H_2S(g) \rightleftharpoons 8H_2(g) + S_8(s)$ occurs at a temperature of 2000 K. It is found that:

$$\left[\frac{n(H_2)}{n(H_2S)}\right]_{\text{at equilibrium}} = \left[\frac{n(H_2S)}{n(H_2)}\right]_{\text{at } t=0}$$

(a) maximum weight of solid formed is 32 g

(b) maximum weight of solid formed is 0.32 g

(c) $K_p = K_c\,RT$

(d) $K_c = 256$

139. $N_2(g)$ and $H_2(g)$ are taken in a vessel in mass ratio of 7 : 1. The only reaction $N_2 + 2H_2 \rightleftharpoons N_2H_4(g)$ occurs. Pressure due to N_2H_4 at equilibrium is 0.2 times of total pressure 'P'. Then at equilibrium:

(a) partial pressure of $N_2 = 2P/15$

(b) partial pressure of $H_2 = 8P/25$

(c) $2p_{N_2} = p_{H_2}$

(d) $p_{N_2} = 2p_{H_2}$

140. In the equilibrium, $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$ at 2000 K and 10 atm pressure, % Cl_2 = % SO_2 = 40 by volume. Then:

(a) $K_p = 2$ atm

(b) $\frac{n(SO_2Cl_2)}{n(SO_2)} = \frac{1}{4}$ at equilibrium

(c) $K_p = 8$ atm

(d) $n(SOCl_2) = n(SO_2) = n(Cl_2)$

141. A 20 litre box contains O_3 and O_2 at equilibrium at 202 K. $K_p = 2\times 10^{14}$ for $2O_3 \rightleftharpoons 3O_2$. Assume that $p_{O_2} >> p_{O_3}$ and total pressure is 8 atm; the partial pressure of O_3 is:

(a) exactly 1.6×10^{-6} atm

(b) sufficiently less than 1.6×10^{-6} atm

(c) slightly more than 1.6×10^{-6} atm

(d) very slightly less than 1.6×10^{-6} atm

142. For the reactions, $A \rightleftharpoons B, B \rightleftharpoons C$ and $C \rightleftharpoons D$, equilibrium constants are K_1, K_2 and K_3 respectively. What is the value of equilibrium constant for $A \rightleftharpoons D$?

(a) $K_1 + K_2 + K_3$ (b) $K_1 \times K_2 \times K_3$

(c) $K_1K_2/3$ (d) None of these

143. $AO \rightleftharpoons \left(\frac{1}{2}\right) A_2 + \left(\frac{1}{2}\right) O_2; K = 5 \times 10^5$

$BO \rightleftharpoons \left(\frac{1}{2}\right) B_2 + \left(\frac{1}{2}\right) O_2; K = 1.10 \times 10^{12}$

$CO \rightleftharpoons \left(\frac{1}{2}\right) C_2 + \left(\frac{1}{2}\right) O_2; K = 2.3 \times 10^{18}$

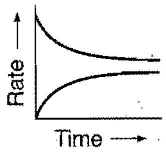
$DO \rightleftharpoons \left(\frac{1}{2}\right) D_2 + \left(\frac{1}{2}\right) O_2; K = 1.4 \times 10^{21}$

Which oxide is most stable?

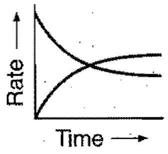
(a) AO (b) BO (c) CO (d) DO

144. Which graph will show equilibrium condition?

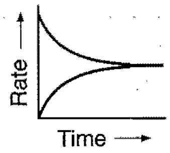
(a)



(b)



(c)



(d) None of these

145. For the reaction, $N_2 + O_2 \rightleftharpoons 2NO$ equilibrium constant $K_c = 2$. Degrees of dissociation of N_2 and O_2 are:

(a) $\frac{1}{1+\sqrt{2}}, \frac{1}{1-\sqrt{2}}$ (b) $\frac{1}{1-\sqrt{2}}, \frac{1}{1+\sqrt{2}}$

(c) both are $\frac{1}{1+\sqrt{2}}$ (d) $\frac{2}{1+\sqrt{2}}, \frac{2}{1-\sqrt{2}}$

146. $A \rightleftharpoons 2B, K_p$; $C \rightleftharpoons D + E, K_{p'}$. If degrees of dissociation of A and C are same and $K_p = 2K_{p'}$, then the ratio of total pressure $p/p' = ?$

(a) 1/2 (b) 1/3 (c) 1/4 (d) 2

147. Equilibrium constants for four different reactions are given as: $K_1 = 10^6$, $K_2 = 10^{-4}$, $K_3 = 10$, $K_4 = 1$. Which reaction will take maximum time to attain equilibrium?

(a) $K_1 = 10^6$ (b) $K_2 = 10^{-4}$

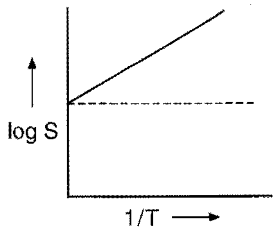
(c) $K_3 = 10$ (d) $K_4 = 1$

148. Solubility of a solute in water is dependent on temperature as given by,

$S = Ae^{-\Delta H/RT}$ where, ΔH = heat of solution

Solute + $H_2O(l) \rightleftharpoons$ Solution; $\Delta H = \pm x$

For a given solution, variation of log S with temperature is shown graphically. Hence, solute is:

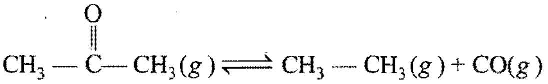


(a) $CuSO_4 \cdot 5H_2O$

(b) NaCl

(c) sucrose

(d) CaO

149. 

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3(g) \rightleftharpoons CH_3-CH_3(g) + CO(g)$$

Initial pressure of CH_3COCH_3 is 100 mm. When equilibrium is achieved, the mole fraction of $CO(g)$ is 1/3 hence, K_p is:

(a) 100 mm (b) 50 mm (c) 25 mm (d) 150 mm

150. In which of the following equilibrium, change in the volume of the system does not alter the number of moles? **(AIEEE 2002)**

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

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

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

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

151. What are the most favourable conditions for the reaction;

$$SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g); \ \Delta H^\circ = -\text{ve}$$

to occur? **[DPMT 2002; JEE (Orissa) 2[illegible]]**

(a) low temp. and high press. (b) low temp. and low press.

(c) high temp. and low press. (d) high temp. and high press.

152. Consider the following reactions in which all the reactants and products are in gaseous state

$$2PQ \rightleftharpoons P_2 + Q_2; \ K_1 = 2.5 \times 10^5$$

$$PQ + \frac{1}{2}R_2 \rightleftharpoons PQR \ ; \ K_2 = 5 \times 10^{-3}$$

The value of K_3 for the equilibrium:

$\frac{1}{2}P_2 + \frac{1}{2}Q_2 + \frac{1}{2}R_2 \rightleftharpoons PQR$ is: **[PET (Kerala) 2010]**

(a) 2.5×10^{-3} (b) 2.5×10^3

(c) 1.0×10^{-5} (d) 5×10^3

(e) 5×10^{-3}

[Hint: $\frac{1}{2}P_2 + \frac{1}{2}Q_2 \rightleftharpoons PQ$ $\quad K = \frac{1}{K_1^{1/2}}$

$PQ + \frac{1}{2}R_2 \rightleftharpoons PQR$ $\quad K_2$

$\frac{1}{2}P_2 + \frac{1}{2}Q + \frac{1}{2}R_2 \rightleftharpoons PQR$ $\quad K_3 = \frac{1}{K_1^{1/2}} \times K_2$

$$= \frac{5 \times 10^{-3}}{(2.5 \times 10^5)^{1/2}}$$

$= 1 \times 10^{-5}$]

153. Consider the following equilibrium in a closed container,

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

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)? **(IIT 2002)**

(a) neither K_p nor 'α' changes

(b) both K_p and 'α' change

(c) K_p changes but 'α' does not

(d) K_p does not change but 'α' changes

154. For the reaction, $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, the position of equilibrium can be shifted to the right by: **[PET (MP) 2004]**

(a) doubling the volume

(b) increasing the temperature

(c) addition of equimolar quantities of PCl_3 and PCl_5

(d) addition of Cl_2 at constant volume

155. The most favourable condition for the manufacture of NH_3 is: **[CECE (Bihar) 2004]**

(a) high temperature and high pressure

(b) low temperature and low pressure

(c) high temperature and low pressure

(d) low temperature and high pressure

156. The chemical equilibrium of a reversible reaction is not influenced by: **(KCET 2004)**

(a) catalyst (b) pressure

(c) temperature (d) concentration

157. Which of the following change will shift the reaction in forward direction?

$$I_2(g) \rightleftharpoons 2I(g); \Delta H^\circ = +150 \text{ kJ}$$ **(AIIMS 2004)**

(a) Increase in total pressure

(b) Increase in temperature

(c) Increase in concentration of I

(d) Decrease in concentration of I_2

158. For the reaction, $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, the $\frac{K_p}{K_c}$ is equal to: **(AIEEE 2004)**

(a) $1/RT$ (b) RT (c) $\sqrt{RT}$ (d) 1

159. The equilibrium constant 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: **(AIEEE 2004)**

(a) 2.5×10^2 (b) 50 (c) 4×10^{-4} (d) 0.02

160. 2 moles of N_2 are mixed with 6 moles of H_2 in a closed vessel of one litre capacity. If 50% N_2 is converted into NH_3 at equilibrium, the value of K_c for the reaction,

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

[PMT (Kerala) 2004]

(a) 4/27 (b) 27/4

(c) 1/27 (d) 27

(e) 9

161. 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 mol/litre of H_2 is consumed at equilibrium, the correct expression of K_p is: **[JEE (Orissa) 2005]**

(a) $\frac{x^2}{(1-x)^2}$ (b) $\frac{(1+x)^2}{(1-x)^2}$ (c) $\frac{x^2}{(2+x)^2}$ (d) $\frac{x^2}{1-x^2}$

162. Partial pressure of O_2 in the reaction,

$$2Ag_2O(s) \rightleftharpoons 4Ag(s) + O_2(g)$$

is: **(DCE 2005)**

(a) K_p (b) $\sqrt{K_p}$ (c) $\sqrt[3]{K_p}$ (d) $2K_p$

163. Two moles of PCl_5 are heated in a closed vessel of 2 litre capacity. When the equilibrium is attained 40% of it has been found to be dissociated. What is the value of K_c in mol/dm^3? **[PET (Kerala) 2005]**

(a) 0.532 (b) 0.266 (c) 0.133 (d) 0.174

(e) 0.25

[Hint:

$$\begin{array}{llll} & PCl_5(g) \rightleftharpoons & PCl_3(g) + & Cl_2(g) \\ t=0 & 2 & 0 & 0 \\ t_{eq.} & \frac{2-0.8}{2} & \frac{0.8}{2} & \frac{0.8}{2} \end{array}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{0.8}{2} \times \frac{0.8}{2}}{\frac{1.2}{2}} = \frac{0.64}{2.4} = 0.266]$$

164. For the reaction:

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

$K_c = 1.8 \times 10^{-6}$ at 184°C

$R = 0.0831 \text{ kJ K}^{-1} \text{ mol}^{-1}$

when, K_p and K_c are compared at 184°C it is found that: **(AIEEE 2005)**

(a) K_p is greater than K_c

(b) K_p is less than K_c

(c) $K_p = K_c$

(d) whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure

[Hint: $K_p = K_c\,(RT)^{\Delta n}$

$\Delta n = 3 - 2 = 1$

$K_p = K_c\,(RT)^1$

$\therefore \quad K_p > K_c$]

165. $NH_4COONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. If equilibrium pressure is 3 atm for the above reaction; K_p will be: **(DPMT 2005)**

(a) 4 (b) 27 (c) 4/27 (d) 1/27

[Hint: $p_{NH_3} : p_{CO_2} = 2:1$

$\therefore \quad p_{NH_3} = 2$ atm; $p_{CO_2} = 1$ atm

$K_p = [p_{NH_3}]^2[p_{CO_2}] = 2^2 \times 1 = 4$]

166. $A + B \rightleftharpoons C + D$. If initially the concentration of A and B are both equal but at equilibrium, concentration of D will be twice of that of A, then what will be the equilibrium constant of the reaction? **[BHU (Pre.) 2005; JIPMER 2006]**

(a) $\frac{4}{9}$ (b) $\frac{9}{4}$ (c) $\frac{1}{9}$ (d) 4

[Hint:

$$\begin{array}{lllll} & A + & B \rightleftharpoons & C + & D \\ t=0 & a & a & 0 & 0 \\ t_{eq.} & a-x & a-x & x & x \end{array}$$

$x = 2(a-x)$

$3x = 2a$

$$K = \frac{x \times x}{(a-x)(a-x)} = \frac{x \times x}{\frac{x}{2} \times \frac{x}{2}} = 4]$$

167. 15 moles of H_2 and 5.2 moles of I_2 are mixed and allowed to attain equilibrium at 500°C. At equilibrium, the concentration of HI is found to be 10 moles. The equilibrium constant for the formation of HI is: **(KCET 2005)**

(a) 50 (b) 15 (c) 100 (d) 25

[**Hint:**
$$\begin{array}{lcccc} & H_2 & + & I_2 \rightleftharpoons & 2HI \\ t=0 & 15 & & 5.2 & 0 \\ t_{eq.} & 15-5 & & 5.2-5 & 10 \end{array}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{100}{10\times 0.2} = 50]$$

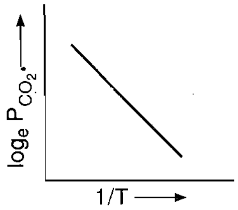
168. For the reaction: $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, K_c at 427°C is 3×10^6 L mol^{-1}. The value of K_p is nearly: **(AIIMS 2005)**

(a) 7.5×10^{-5} (b) 2.5×10^{-5} (c) 2.5×10^{-4} (d) 1.75×10^{-4}

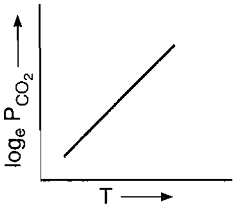
169. For the chemical equilibrium,

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

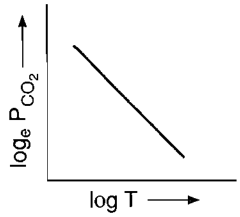
ΔH_r° can be determined from which one of the following plots? **(AIIMS 2005)**



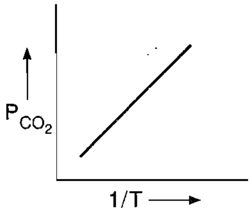
(a)



(b)



(c)



(d)

[**Hint:** $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_p = P_{CO_2}$$

According to Arrhenius equation:

$$K = Ae^{-\Delta H_r^\circ/RT}$$

$$\log K_p = \log A - \frac{\Delta H_r^\circ}{2.303RT}$$

$$\log P_{CO_2} = \log A - \frac{\Delta H_r^\circ}{2.303R}\frac{1}{T} \quad \text{... (i)}$$

$$Y = C + MX$$

Graph (a) represents (i) and its slope will be used to determine the heat of the reaction.]

170. In gaseous reversible reaction,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) + \text{Heat}$$

If pressure is increased, then the equilibrium constant would be: **[UGET (Manipal, Medical) 2006]**

(a) unchanged
(b) increased
(c) decreased
(d) sometimes increased, sometimes decreased

171. If the equilibrium constant for the reaction,

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

at 750 K is 49, then the equilibrium constant for the reaction,

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

at the same temperature is: **[PMT (Kerala) 2006]**

(a) 1/49 (b) 49 (c) 7 (d) 49^2
(e) 1/7

172. The equilibrium constant for the reaction,

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

is $K_c = 4.9\times 10^{-2}$.

The value of K_c for the reaction,

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

will be: **(AIEEE 2006)**

(a) 416 (b) 2.40×10^{-3}
(c) 9.8×10^{-2} (d) 4.9×10^{-2}

[**Hint:** $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$; $K_c = 4.9\times 10^{-2}$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $K_c = \left(\frac{1}{4.9\times 10^{-2}}\right)^2$

$= 416.5 \approx 416$]

173. For a reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 721 K, the value of equilibrium constant is 50. If 0.5 mol each of H_2 and I_2 is added to the system, the value of equilibrium constant will be: **[VMMC (Safdarjung) 2006]**

(a) 40 (b) 60 (c) 50 (d) 30

[**Hint:** Equilibrium constant does not change on adding the reactant.]

174. In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, in a 2 litre flask 0.4 mole of each H_2 and I_2 are taken. At equilibrium 0.5 mole of HI are formed. What will be the value of equilibrium constant K_c? **[PMT (Raj.) 2006]**

(a) 20.2 (b) 25.4 (c) 0.284 (d) 11.1

175. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant K_p changes with: **(VITEEE 2007)**

(a) total pressure (b) catalyst
(c) the amount of H_2 and I_2 (d) temperature

176. Given the equilibrium system,

$$NH_4Cl(s) \rightleftharpoons NH_4^+(aq.) + Cl^-(aq.)$$
$$(\Delta H^\circ = +3.5 \text{ kcal/mol})$$

what change will shift the equilibrium to the right? **(VITEEE 2007)**

(a) Decreasing the temperature
(b) Increasing the temperature
(c) Dissolving NaCl crystals in equilibrium mixture
(d) Dissolving NH_4NO_3 crystals in the equilibrium mixture

177. The equilibrium constant (K_p) for the decomposition of gaseous H_2O:

$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$ is related to degree of dissociation (α) at a total pressure P is given by: **[PMT (Kerala) 2007]**

(a) $K_p = \dfrac{\alpha^3 P^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$ (b) $K_p = \dfrac{\alpha^3 P^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(c) $K_p = \dfrac{\alpha^{3/2} P^2}{(1-\alpha)(2+\alpha)^{1/2}}$ (d) $K_p = \dfrac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(e) $K_p = \dfrac{\alpha^2 P}{\sqrt{2}}$

[**Hint:** $H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$

$t=0$	1	0	0
$t_{eq.}$	$1-\alpha$	α	$\alpha/2$

$$\Sigma n = 1-\alpha+\alpha+\frac{\alpha}{2} = 1+\frac{\alpha}{2} = \left(\frac{2+\alpha}{2}\right)$$

$$K_p = \frac{n_{H_2} \times n_{O_2}^{1/2}}{n_{H_2O}} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n}$$

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

$$= \frac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}]$$

178. The equilibrium constant for the reaction,
$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ is 2×10^{-6} at 185° C
Then, the equilibrium constant for the reaction,
$4NO(g) + 2O_2(g) \rightleftharpoons 4NO_2(g)$ at the same temperature would be: **[PET (Kerala) 2007]**

(a) 2.5×10^{-5} (b) 4×10^{-12} (c) 2.5×10^{11} (d) 2×10^{6}
(e) 5×10^{5}

179. 1 mole of H_2 and 2 mole of I_2 are taken initially in a 2 L vessel. The number of moles H_2 at equilibrium is 0.2. Then, the number of moles of I_2 and HI at equilibrium are: **[PMT (Raj.) 2007]**

(a) 1.2, 1.6 (b) 1.8, 1.0 (c) 0.4, 2.4 (d) 0.8, 2.0

180. 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 as compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure P is:

(a) $(2K_p/P)^{1/2}$ (b) K_p/P (c) $2K_p/P$ (d) $(2K_p/P)^{1/3}$ **[CBSE (PMT) 2008]**

[**Hint :** $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

t_0	2	0	0	
$t_{eq.}$	$2(1-x)$	$2x$	x	Total moles $= 2+x$
Partial pressure	$\frac{2(1-x)}{2+x} \times P$	$\frac{2x}{2+x} \times P$	$\frac{x}{2+x} \times P$	

$$K_p = \frac{p_{AB}^2 \times p_{B_2}}{(p_{AB_2})^2} = \frac{\left[\frac{2}{(2+x)}P\right]^2 \left[\frac{xP}{(2+x)}\right]}{\left[\frac{2(1-x)}{2+x} \times P\right]^2}$$

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

$(2+x) \approx 2, (1-x) \approx 1$

$K_p = \dfrac{Px^3}{2}$ $\therefore x = (2K_p/P)^{1/3}$]

181. In which of the following reactions, the concentration of the product is higher than the concentration of reactant at equilibrium ? (K = equilibrium constant) **(AIIMS 2008)**

(a) $A \rightleftharpoons B$; $K = 0.001$ (b) $M \rightleftharpoons N$; $K = 10$
(c) $X \rightleftharpoons Y$; $K = 0.005$ (d) $R \rightleftharpoons P$; $K = 0.01$

182. 1.6 mole of $PCl_5(g)$ is placed in 4 dm^3 closed vessel. When the temperature is raised to 500 K, it decomposes and at equilibrium 1.2 mole of $PCl_5(g)$ remains. What is the K_c value for the decomposition of $PCl_5(g)$ to $PCl_3(g)$ and $Cl_2(g)$ at 500K? **[PET (Kerala) 2008]**

(a) 0.013 (b) 0.050 (c) 0.033 (d) 0.067
(e) 0.045

183. Consider the following statements regarding chemical equilibrium:

1. For the gaseous reaction, the equilibrium can be established in open vessel.
2. The state of equilibrium is dynamic in nature.
3. If temperature is kept constant, the colour of the reacting system changes with time.

Which of the statements given above is/are correct? **(SCRA 2009)**

(a) 1 (b) 2 only
(c) 3 only (d) 2 and 3 only

184. The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium:

$$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$$

would be : **[CBSE (PMT) 2009]**

(a) 3×10^4 (b) 3×10^5
(c) 3×10^{-5} (d) 3×10^{-4}

[**Hint :** Given

(i) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $K_1 = 1.5 \times 10^{-5}$

(ii) $HCN \rightleftharpoons H^+ + CN^-$ $K_2 = 4.5 \times 10^{-10}$

(iii) $H^+ + CN^- \rightleftharpoons HCN$ $K_3 = \dfrac{1}{K_2} = \dfrac{1}{4.5 \times 10^{-10}}$

Adding (i) and (iii) we get

$$CH_3COOH + CN^- \rightleftharpoons CH_3COO^- + HCN$$

$$K = 1.5 \times 10^{-5} \times \frac{1}{4.5 \times 10^{-10}}$$

$$= 3 \times 10^4]$$

185. One mole of N_2O_4 is heated in a flask with a volume of 0.1 dm^3. At equilibrium, 1.708 mole of NO_2 and 0.146 mole of N_2O_4 were found 134°C. The equilibrium constant will be: **(MPPET 2009)**

(a) 250 mol dm^{-3} (b) 300 mol dm^{-3}
(c) 200 mol dm^{-3} (d) 230 mol dm^{-3}

186. What is the effect of a tenfold increase in pressure on K_p in the reaction?

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

At equilibrium : **(EAMCET 2010)**

(a) a tenfold increase (b) a tenfold decrease
(c) no change (d) equal to K_c

Set–2: The Questions given below may have more than one correct answers

1. Unit of equilibrium constant is:
(a) $(\text{mol/L})^{1-n}$ (b) $(\text{mol/L})^{\Delta n}$
(c) $(\text{atm})^{\Delta n}$ (d) all of these

2. Which is/are correct?
(a) $2.303 \log K = -\Delta H^\circ/RT + \Delta S^\circ/R$
(b) $\Delta G^\circ = -2.303RT \log K$
(c) $-2.303 \log K = -\Delta H^\circ/RT^2 + \Delta S^\circ/R$
(d) $2.303 \log K = (1/RT)(\Delta H^\circ + \Delta S^\circ)$

3. For the reaction, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, which is correct representation?
(a) $K_p = (p_{CO_2})$ (b) $K_p = K_c(RT)$
(c) $K_c = (CO_2)/1$ (d) All of these

4. $N_2 + O_2 \rightleftharpoons 2NO, K_1; \left(\frac{1}{2}\right) N_2 + \left(\frac{1}{2}\right) O_2 \rightleftharpoons NO, K_2;$

$2NO \rightleftharpoons N_2 + O_2, K_3; NO \rightleftharpoons \left(\frac{1}{2}\right) N_2 + \left(\frac{1}{2}\right) O_2, K_4$

Correct relation(s) between K_1, K_2, K_3 and K_4 is/are:
(a) $K_1 \times K_3 = 1$ (b) $\sqrt{K_1} \times K_4 = 1$
(c) $\sqrt{K_3} \times K_2 = 1$ (d) none of these

5. For the reaction, $N_2O_4 \rightleftharpoons 2NO_2$, if degree of dissociation of N_2O_4 are 25%, 50%, 75% and 100%, the gradation of observed vapour densities is:
(a) $d_1 > d_2 > d_3 > d_4$ (b) $d_4 > d_3 > d_2 > d_1$
(c) $d_1 = d_2 = d_3 = d_4$ (d) none of these

6. The equation, $\alpha = \frac{D-d}{(n-1)d}$ is correctly matched for:
(a) $A \rightleftharpoons nB/2 + nC/3$ (b) $A \rightleftharpoons nB/3 + (2n/3)C$
(c) $A \rightarrow (n/2)B + (n/4)C$ (d) $A \rightleftharpoons (n/2)B + C$

7. For a reaction, $nA \rightleftharpoons A_n$, degree of dissociation when A trimerises is:
(a) $2\left(\frac{d-D}{d}\right)$ (b) $\frac{3}{2}\left(\frac{d-D}{d}\right)$ (c) $\frac{4}{3}\left(\frac{d-D}{d}\right)$ (d) $2\left(\frac{D-d}{d}\right)$

8. 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 the volume of the container
(e) introducing PCl_5 at constant volume

9. Which of the following will favour the formation of NH_3 by Haber's process?
(a) Increase of temperature (b) Increase of pressure
(c) Addition of catalyst (d) Addition of promoter

10. Which of the following will not affect the value of equilibrium constant of a reaction?
(a) Change in the concentration of the reactants
(b) Change in temperature
(c) Change in pressure
(d) Addition of catalyst

11. Which of the following statements is/are wrong?
(a) At equilibrium, concentrations of reactants and products become constant because the reaction stops
(b) Addition of catalyst speeds up the forward reaction more than the backward reaction
(c) Equilibrium constant of an exothermic reaction decreases with increase of temperature
(d) K_p is always greater than K_c

12. For the gas phase reaction,

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6; \quad \Delta H^\circ = -136.8 \text{ kJ mol}^{-1}$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by: [BHU (Mains) 2008]
(a) increasing the temperature
(b) decreasing the pressure
(c) removing some H_2
(d) adding some C_2H_6

13. When $NaNO_3$ is heated in a closed vessel oxygen is liberated and $NaNO_2$ is left behind. At equilibrium, which are not correct?
(a) Addition of $NaNO_2$ favours reverse reaction
(b) Addition of $NaNO_3$ favours forward reaction
(c) Increasing temperature favours forward reaction
(d) Increasing pressure favours reverse reaction

14. An increase in temperature increases which of the following?
1. The rate constant of a reaction
2. The ionic product of water
3. The equilibrium constant of an exothermic reaction
Select the correct answer using the code given below: (SCRA 2007)
(a) 1 and 2 only (b) 1 and 3 only
(c) 2 and 3 only (d) 1, 2 and 3 only

15. In the following question, more than one answers are correct. Select the correct answer and mark it according to the codes :
Codes : [BHU (Mains) 2010]
(a) 1, 2 and 3 are correct (b) 1 and 2 are correct
(c) 2 and 4 are correct (d) 1 and 3 are correct

Water gas, an industrial fuel, consisting CO and H_2 in equimolar amounts is obtained by passing steam over red-hot carbon in accordance with the reaction :

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g); \quad \Delta H = +130.5 \text{ kJ}$$

The yield of water gas can be increased by
(1) → Reducing the total presure of the system
(2) → Increasing pressure of steam
(3) → Raising the temperature
(4) → Introducing hot carbon

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as **'Assertion' (A)** and **'Reason' (R).** While answering these questions you are required to choose any one of the following four:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).

(b) If both (A) and (R) are correct and (R) is not the correct explanation for (A).

(c) If (A) is correct but (R) is incorrect.

(d) If (A) is incorrect but (R) is correct.

1. (A) K_p can be equal to or less than or even greater than the value of K_c.

   (R) $K_p = K_c\,(RT)^{\Delta n}$

   Relation between K_p and K_c depends on the change in the number of moles of gaseous reactants and products.

2. (A) For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, the equilibrium constant is 'K' then for $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ the equilibrium constant will be $\sqrt{K}$.

   (R) If concentrations are changed to half the equilibrium constant will be halved.

3. (A) A catalyst does not influence the values of equilibrium constant.

   (R) Catalysts influence the rate of both forward and backward reactions equally.

4. (A) The active mass of pure solid and pure liquid is taken unity.

   (R) The active mass of pure solids and liquids depends on density and molecular mass. The density and molecular mass of pure liquids and solids are constant.

5. (A) For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. If more Cl_2 is added the equilibrium will shift in backward direction hence, equilibrium constant will decrease.

   (R) Addition of inert gas to the equilibrium mixture at constant volume, does not alter the equilibrium.

6. (A) At equilibrium $\Delta G = 0$

   (R) $\Delta G^\circ = -RT\log_e K_c$ at equilibrium.

7. (A) At equilibrium $\Delta G = 0$

   (R) The Gibbs free energy of reactants and products decreases and become equal at equilibrium.

8. (A) Equilibrium constant of a reaction changes on changing the stoichiometric coefficients of the reaction.

   (R) The reactions : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ and $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ have same equilibrium constant.

9. (A) The Q_c for the reaction :

   $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ is } Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

   (R) When $Q_c < K_c$, the reaction is not at equilibrium and it will be fast in backward direction.

10. (A) The equilibrium of $[PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)]$ is not affected by changing the volume of container.

    (R) $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

    Equilibrium constant K_c does not depend on the volume of vessel.

11. (A) The reaction : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ will shift in forward direction by increase in pressure.

    (R) On increasing the pressure, the equilibrium will shift in forward direction.

Answers : OBJECTIVE QUESTIONS

- **Set–1**

1. (b) **2.** (d) **3.** (c) **4.** (c) **5.** (a) **6.** (a) **7.** (b) **8.** (d)
9. (d) **10.** (b) **11.** (c) **12.** (a) **13.** (d) **14.** (d) **15.** (b) **16.** (a)
17. (b) **18.** (c) **19.** (c) **20.** (d) **21.** (a) **22.** (b) **23.** (d) **24.** (d)
25. (c) **26.** (c) **27.** (a) **28.** (b) **29.** (d) **30.** (a) **31.** (a) **32.** (c)
33. (d) **34.** (d) **35.** (d) **36.** (b) **37.** (d) **38.** (c) **39.** (d) **40.** (b)
41. (a) **42.** (c) **43.** (b) **44.** (d) **45.** (d) **46.** (c) **47.** (b) **48.** (b)
49. (c) **50.** (a) **51.** (d) **52.** (b) **53.** (b) **54.** (c) **55.** (d) **56.** (a)
57. (d) **58.** (b) **59.** (a) **60.** (c) **61.** (c) **62.** (a) **63.** (b) **64.** (b)
65. (d) **66.** (d) **67.** (a) **68.** (c) **69.** (b) **70.** (d) **71.** (a) **72.** (c)
73. (b) **74.** (a) **75.** (d) **76.** (d) **77.** (a) **78.** (b) **79.** (c) **80.** (c)
81. (d) **82.** (a) **83.** (d) **84.** (c) **85.** (b) **86.** (c) **87.** (a) **88.** (b)
89. (c) **90.** (a) **91.** (d) **92.** (b) **93.** (a) **94.** (b) **95.** (b) **96.** (d)
97. (c) **98.** (b) **99.** (a) **100.** (a) **101.** (a) **102.** (b) **103.** (c) **104.** (a)
105. (a) **106.** (a) **107.** (a) **108.** (c) **109.** (b) **110.** (c) **111.** (d) **112.** (d)
113. (c) **114.** (b) **115.** (a) **116.** (a) **117.** (b) **118.** (b) **119.** (d) **120.** (a)
121. (d) **122.** (b) **123.** (a) **124.** (a) **125.** (a) **126.** (b) **127.** (b) **128.** (a)
129. (b) **130.** (d) **131.** (c) **132.** (d) **133.** (a) **134.** (a) **135.** (c) **136.** (b)
137. (b) **138.** (d) **139.** (c) **140.** (c) **141.** (d) **142.** (b) **143.** (d) **144.** (c)
145. (c) **146.** (a) **147.** (b) **148.** (d) **149.** (b) **150.** (a) **151.** (a) **152.** (c)
153. (d) **154.** (d) **155.** (d) **156.** (a) **157.** (b) **158.** (a) **159.** (b) **160.** (a)
161. (a) **162.** (a) **163.** (b) **164.** (a) **165.** (a) **166.** (d) **167.** (a) **168.** (d)
169. (a) **170.** (a) **171.** (e) **172.** (a) **173.** (c) **174.** (d) **175.** (d) **176.** (b)
177. (d) **178.** (c) **179.** (a) **180.** (d) **181.** (b) **182.** (c) **183.** (d) **184.** (a)
185. (c) **186.** (c)

- **Set–2**

1. (b, c) **2.** (a, b) **3.** (d) **4.** (a, b, c) **5.** (a) **6.** (b) **7.** (b) **8.** (c, d, e)
9. (b, c, d) **10.** (a, b, d) **11.** (a, b, d) **12.** (a, b, c, d) **13.** (a, b, d) **14.** (a) **15.** (a)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (a) **2.** (c) **3.** (a) **4.** (a) **5.** (c) **6.** (b) **7.** (a) **8.** (c)
9. (c) **10.** (d) **11.** (a)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

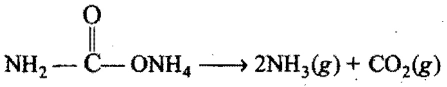
1. Ammonium carbamate when heated to 200°C gives a mixture of NH_3 and CO_2 vapour with a density of 13. What is the degree of dissociation of ammonium carbamate?

[CEE (Kerala) 2004]

(a) $\frac{3}{2}$ (b) $\frac{1}{2}$ (c) 2 (d) 1

(e) $\frac{5}{2}$

[Hint:



$$NH_2-\overset{\overset{\large O}{\|}}{C}-ONH_4 \longrightarrow 2NH_3(g) + CO_2(g)$$

Initial vapour density $D = \frac{\text{Molecular mass}}{2}$

$$= \frac{79}{2} \simeq 39$$

$$\alpha = \frac{D-d}{(n-1)d} = \frac{39-13}{(3-1)\times 13} = \frac{26}{26} = 1$$

here, n = number of moles of product formed by dissociation of 1 mole reactant.]

2. In the heterogeneous equilibrium:

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

what would be the effect of addition of $CaCO_3$ on the equilibrium concentration of CO_2?

(a) Increases (b) Unpredictable

(c) Decreases (d) Remains unaffected

[Hint: Gaseous components are not present on both sides, hence, equilibrium will not be affected on addition of $CaCO_3$

$K_p = p_{CO_2}$ = constant (at constant temperature)]

3. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; if percentage dissociation of N_2O_4 are 25%, 50%, 75% and 100%, then the sequence of observed vapour densities will be:

(a) $d_1 > d_2 > d_3 > d_4$ (b) $d_4 > d_3 > d_2 > d_1$

(c) $d_1 = d_2 = d_3 = d_4$ (d) $(d_1 = d_2) > (d_3 = d_4)$

[Hint: Lesser is the percentage dissociation; greater is the vapour density.]

4. In a system:

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

if the concentration of C at equilibrium is increased by a factor of 2, it will cause the equilibrium concentration of B to change to:

(a) two times the original value

(b) one half of its original value

(c) $2\sqrt{2}$ times the original value

(d) $\frac{1}{2\sqrt{2}}$ times the original value

5. For the decomposition of $NH_3(g)$ in a sealed tube:

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

(a) K_p does not change with pressure

(b) concentration of $H_2(g)$ is less than that of nitrogen

(c) concentration of ammonia does not change with pressure

(d) K_p changes significantly with pressure

6. The equilibrium constant for the decomposition of water,

$$[H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)]$$

is given by:

(a) $K = \frac{\alpha^3 p^{1/2}}{(1-\alpha)(2-\alpha)^{1/2}}$ (b) $K = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(c) $K = \frac{\alpha^3 p^{1/2}}{\sqrt{2}}$ (d) $K = \frac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

7. On heating a mixture of SO_2Cl_2 and CO, two equilibria are simultaneously established:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$
$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

On adding more SO_2 at equilibrium what will happen?

(a) Amount of CO will decrease

(b) Amount of SO_2Cl_2 and $COCl_2$ will increase

(c) Amount of CO will remain unaffected

(d) Amount of SO_2Cl_2 and CO will increase

8. Consider the reactions,

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

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

The addition of an inert gas at constant volume:

(a) will increase the dissociation of PCl_5 as well as N_2O_4

(b) will reduce the dissociation of PCl_5 as well as N_2O_4

(c) will increase the dissociation of PCl_5 and step up the formation of NO_2

(d) will not disturb the equilibrium of the reactions

[Hint: At constant volume, inert gas will not affect any of the equilibrium.]

9. Densities of diamond and graphite are 3.5 and 2.3 g/mL respectively. Increase of pressure on the equilibrium

$$C\,(\text{diamond}) \rightleftharpoons C\,(\text{graphite})$$

(a) favours backward reaction (b) favours forward reaction

(c) has no effect (d) increases the reaction rate

10. A reaction at equilibrium involving 2 moles each of PCl_5, PCl_3 and Cl_2 is maintained at 250°C and a total pressure of 3 atm. The value of K_p is:

(a) 2 (b) 3 (c) 4 (d) 1

[Hint:

$$\begin{array}{lccc} & PCl_5 \rightleftharpoons & PCl_3 + & Cl_2 \\ \text{At equilibrium} & 2 & 2 & 2 \end{array}$$

$$p_{PCl_5} = \frac{2}{6}\times 3,\ p_{PCl_3} = \frac{2}{6}\times 3,\ p_{Cl_2} = \frac{2}{6}\times 3$$

$$K_p = \frac{p_{PCl_3}\times p_{Cl_2}}{p_{PCl_5}} = \frac{1\times 1}{1} = 1]$$

11. In case of gaseous homogeneous reaction, the active mass of the reactant is given by the expression:

(a) $\frac{RT}{P}$ (b) $\frac{P}{RT}$ (c) $\frac{PV}{RT}$ (d) $\frac{n}{V}RT$

[Hint: $PV = nRT$

$$\frac{n}{V} = \frac{P}{RT}$$

$\therefore$ Active mass (mol L^{-1}) $= \frac{P}{RT}$]

12. In the dissociation of $I_2(g)$ at 1000 K in a container of 1 litre:

$$I_2(g) \rightleftharpoons 2I^-(g);\ K_c = 10^{-6}$$

Select the correct relation:

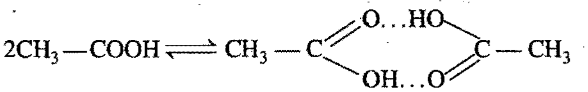
(a) $[I_2] > [I^-]$ (b) $[I_2] < [I^-]$ (c) $[I_2] = [I^-]$ (d) $[I_2] = \frac{1}{2}[I^-]$

[Hint: $K_c = \frac{[I^-]^2}{[I_2]}$

$$10^{-6} = \frac{[I^-]^2}{[I_2]}$$

$\therefore$ $[I_2] > [I^-]$]

13. Acetic acid undergoes dimerisation, when dissolved in benzene


$2CH_3—COOH \rightleftharpoons CH_3—C(=O\ldots HO)(—OH\ldots O=)C—CH_3$

Molecular mass of acetic acid is found 120. Which among the following relation is correct?

(a) $\alpha = 2\left(\frac{D-d}{d}\right)$ (b) $\alpha = 2\left(\frac{D-d}{D}\right)$

(c) $\alpha = 2\left(\frac{d-D}{d}\right)$ (d) $\alpha = \frac{2d}{D-d}$

where, d = Observed vapour density
D = Theoretical vapour density

[Hint: For association of molecule

$$\alpha = \frac{d-D}{d(1-1/n)} = \frac{d-D}{d(1-1/2)}$$

$$= \frac{2(d-D)}{d}]$$

14. The equilibrium:

$$P_4(g) + 6Cl_2(g) \rightleftharpoons 4PCl_3(g)$$

is attained by mixing equal moles of P_4 and Cl_2 in an evacuated vessel. Then at equilibrium:

(a) $[Cl_2] > [PCl_3]$ (b) $[Cl_2] > [P_4]$

(c) $[P_4] > [Cl_2]$ (d) $[PCl_3] > [P_4]$

15. In the reaction: $A + B \rightleftharpoons 2C + D$. The initial concentration of A and B are 1 M each. The value of K_c is 10^8. What is the equilibrium concentration of A?

(a) 2×10^{-4} M (b) 2×10^4 M (c) 0.005 M (d) 0.0025 M

16. For the reaction:

$A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g);\ K_p = 0.05$ atm at 1000 K

The value of K_c is represented by:

(a) $5\times10^{-4}R$ (b) $\frac{5\times10^{-4}}{R}$ (c) $5\times10^{-5}R$ (d) $\frac{5\times10^{-5}}{R}$

[Hint: $K_p = K_c(RT)^{\Delta n}$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{0.05}{(1000\times R)^1} = \frac{5\times10^{-5}}{R}]$$

17. Match the List-I (equilibria) with List-II (conditions) and select the correct answer using the options given below:

List-I	List-II
$P.$ $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	1. High temperature
$Q.$ $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	2. Low temperature
$R.$ $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	3. High pressure
	4. Low pressure
	5. Independent of pressure

	P	Q	R
(a)	1, 3	2, 3	2, 4
(b)	2, 3	1, 4	1, 3
(c)	1, 5	2, 3	2, 4
(d)	2, 4	1, 5	1, 3

18. At constant pressure, the presence of inert gases:

(a) reduces the dissociation of PCl_5

(b) increases the dissociation of PCl_5

(c) does not affect the degree of dissociation of PCl_5

(d) steps up the formation of PCl_5

[Hint: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

On adding inert gas, the equilibrium will shift towards higher volume direction.]

19. Which of the following expressions is correct?

(a) $K_p = K_c\left(\frac{RT}{\Sigma n}\right)^{\Delta n}$ (b) $K_p = K_x\left(\frac{P}{\Sigma n}\right)^{\Delta n}$

(c) $K_p = K_n\left(\frac{P}{\Sigma n}\right)^{\Delta n - 1}$ (d) $K_p = K_c\left(\frac{P}{\Sigma n}\right)^{-\Delta n + 1}$

20. The most stable oxide of nitrogen will be:

(a) $2NO(g) \rightleftharpoons N_2(g) + O_2(g);$ $K = 2.2\times10^{30}$

(b) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g);$ $K = 3.5\times10^{33}$

(c) $2N_2O_5(g) \rightleftharpoons 2N_2(g) + 5O_2(g);$ $K = 1.2\times10^{24}$

(d) $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g);$ $K = 6.7\times10^{16}$

[Hint: Stability constant $= \frac{1}{K}$

$\therefore$ Smaller is the value of equilibrium constant greater is the stability of oxide.]

21. Equilibrium constant for two complexes are:

A: $K_4[Fe(CN)_6]$ 2.6×10^{37} (for dissociation)

B: $K_3[Fe(CN)_6]$ 1.9×10^{17} (for dissociation)

(a) A and B are equally stable(b) A is more stable than B

(c) B is more stable than A (d) the predictable stability

[Hint: Stability $\propto \frac{1}{\text{Equilibrium constant for dissociation}}$]

22. At the equilibrium of the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the observed molar mass of N_2O_4 is 77.70 g. The percentage dissociation of N_2O_4 is:

(a) 28.4 (b) 46.7 (c) 22.4 (d) 18.4

[Hint: $\alpha = \dfrac{M_0 - M}{(n-1)M}$

$$= \frac{92 - 77.7}{(2-1) \times 77.7} = 0.184$$

% Dissociation = 18.4]

23. Consider the following statements :
In the Haber method of synthesis of ammonia
1. Increase of pressure favours the formation of NH_3
2. Decrease of pressure produces more NH_3
3. Increase of temperature dissociates NH_3
4. Addition of inert gas favours the formation of NH_3
Which of the statements given above are correct? (SCRA 2009)
(a) 1 and 3 (b) 2 and 4 (c) 1 and 4 (d) 2 and 3

24. For the decomposition of $PCl_5(g)$ in a closed vessel, the degree of dissociation is α at total pressure P.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g); \quad K_p$$

Which among the following relations is correct?
(a) $\alpha = \sqrt{\dfrac{K_p}{K_p + P}}$ (b) $\alpha = \sqrt{\dfrac{K_p + P}{K_p}}$
(c) $\alpha = \sqrt{K_p + P}$ (d) $\alpha = \dfrac{1}{\sqrt{K_p + P}}$

25. In the decomposition reaction of ammonia:

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

2 moles of NH_3 are introduced in the vessel of 1 litre. At equilibrium, 1 mole NH_3 was left, the value of K_c will be:
(a) 0.75 (b) 0.70 (c) 1.75 (d) 1.70

[Hint:

$$\begin{array}{lccc} & 2NH_3(g) & \rightleftharpoons N_2(g) & + \; 3H_2(g) \\ t=0 & 2 & 0 & 0 \\ t_{eq.} & 1 & 1/2 & 3/2 \end{array}$$

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$= \frac{\frac{1}{2} \times \left(\frac{3}{2}\right)^3}{1^2} = 1.685 \approx 1.7]$$

26. By which of the following relations, the equilibrium constant varies with temperature?
(a) $\ln K_2 - \ln K_1 = \dfrac{\Delta H^\circ}{R} \int_{T_1}^{T_2} d\left(\dfrac{1}{T}\right)$
(b) $\ln K_2 - \ln K_1 = -\dfrac{\Delta H^\circ}{R} \int_{1/T_1}^{1/T_2} d\left(\dfrac{1}{T^2}\right)$
(c) $\ln K_2 - \ln K_1 = -\dfrac{\Delta H^\circ}{R} \int_{T_1}^{T_2} d\left(\dfrac{1}{T}\right)$
(d) $\ln K_2 - \ln K_1 = -\dfrac{\Delta H^\circ}{R} \int_{1/T_2}^{1/T_1} d\left(\dfrac{1}{T}\right)$

27. For dissociation of a gas N_2O_5 as:

$$N_2O_5(g) \rightleftharpoons 2NO_2(g) + \frac{1}{2} O_2(g);$$

If 'D' is the vapour density of equilibrium mixture and P_0 is the initial pressure of $N_2O_5(g)$, then its equilibrium pressure must not be (M is molecular mass of N_2O_5):
(a) $P_0 \dfrac{(M - 2D)}{3D}$ (b) $\dfrac{P_0 M}{3D - M}$
(c) $\dfrac{P_0 M}{2D}$ (d) $\dfrac{2P_0 D}{M}$

28. $SO_3(g)$ is heated in a closed vessel. An equilibrium:

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

is established. The vapour density of the mixture, in which SO_3 is 50% dissociated, is:
(a) 26.5 (b) 35 (c) 42 (d) 55

[Hint: $\alpha = \dfrac{D - d}{(n-1)d}$

$$0.5 = \frac{40 - d}{(2-1)d}$$

$$d = 26.5]$$

29. When $\ln K$ is plotted against $\dfrac{1}{T}$ using the van't Hoff equation, a straight line is expected with a slope equal to:
(a) $\Delta H^\circ / RT$ (b) $-\Delta H^\circ / R$ (c) $\Delta H^\circ / R$ (d) $R / \Delta H^\circ$

30. $AB_2(g)$ dissociates as,

$$AB_2(g) \rightleftharpoons AB(g) + B(g)$$

The initial pressure of AB_2 is 600 mm Hg and total pressure is 800 mm Hg. The equilibrium constant for the reaction will be:
(a) 500 (b) 100 (c) 200 (d) 400

31. For the gaseous reaction,

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6,$$

the equilibrium constant has the units:
(a) $mol^2\ dm^{-3}$ (b) $dm^3\ mol^{-1}$ (c) $dm^{-3}\ mol^{-1}$ (d) $mol\ dm^{-3}$

32. The equilibrium constant for the reaction:

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

is 67.8 at 300 K. The equilibrium constant for the dissociation of HBr is:
(a) 0.0147 (b) 67.8 (c) 33.90 (d) 8.349

[Hint: $K_{\text{dissociation}} = \dfrac{1}{K_{\text{formation}}}$]

33. A large positive value of ΔG° corresponds to which of these?
(a) Small positive K (b) Small negative K
(c) Large positive K (d) Large negative K
[Hint: $\Delta G^\circ = -2.303RT \log K_e$]

34. What is ΔG° for the following reaction?

$$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3(g); \; K_p = 4.42 \times 10^4 \text{ at } 25^\circ C$$

(a) -26.5 kJ mol^{-1} (b) -11.5 kJ mol^{-1}
(c) -2.2 kJ mol^{-1} (d) -0.97 kJ mol^{-1}

35. For the following reaction: $K = 1.7 \times 10^7$ at 25°C

$$Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons [Ag(NH_3)_2]^+$$

what is the value of ΔG° in kJ?
(a) -41.2 (b) -17.9 (c) $+17.9$ (d) $+41.2$

36. If E°_{cell} for a given reaction is negative, which gives the correct relationships for the values of ΔG° and K_{eq}?
(a) $\Delta G^\circ > 0, K_{eq.} < 1$ (b) $\Delta G^\circ > 0, K_{eq.} > 1$
(c) $\Delta G^\circ < 0, K_{eq.} > 1$ (d) $\Delta G^\circ < 0, K_{eq.} < 1$

37. The free energy of formation of NO is 78 kJ mol^{-1} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at 1000 K?

$$\frac{1}{2}N_2(g)+\frac{1}{2}O_2(g) \rightleftharpoons NO(g)$$

(a) 8.4×10^{-5} (b) 7.1×10^{-9} (c) 4.2×10^{-10} (d) 1.7×10^{-19}

38. $$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$$

Given, that the equilibrium constant for the reaction above has a value of 278 at a particular temperature, what is the value of equilibrium constant for the following reaction at same temperature?

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

(a) 1.3×10^{-5} (b) 1.8×10^{-3} (c) 3.6×10^{-3} (d) 6×10^{-2}

39. In which of the following reactions, the increase in volume of the container will favour the formation of products?

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

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

(c) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l)$

(d) $3O_2(g) \rightleftharpoons 2O_3(g)$

40. Consider the reaction, whose $K_c = 33$,

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

If 0.1 mol each of SO_2 and NO_2 are placed in 1 L container, what is the concentration of SO_2 at equilibrium?

(a) 0.003 *M* (b) 0.015 *M* (c) 0.085 *M* (d) 0.097 *M*

41.

Reaction	***K***
$\frac{1}{2}N_2(g)+O_2(g) \rightleftharpoons NO_2(g)$	K_1
$2NO_2(g) \rightleftharpoons N_2O_4(g)$	K_2

Using above equations, write down expression for *K* of the following reaction:

$$N_2O_4(g) \rightleftharpoons N_2(g)+\frac{1}{2}O_2(g)$$

(a) K_1K_2 (b) $\frac{K_2^2}{K_1}$ (c) $\frac{1}{K_2K_1^2}$ (d) $\frac{1}{K_1^2K_2}$

42. Cu^{2+} ions react with Fe^{2+} ions according to the following reaction:

$$Cu^{2+} + 2Fe^{2+} \rightleftharpoons Cu + 2Fe^{3+}$$

At equilibrium, the concentration of Cu^{2+} ions is not changed by the addition of:

(a) Cu^{2+} (b) Fe^{2+} (c) Cu (d) Fe^{3+}

43. Consider this equilibrium, for which $\Delta H < 0$,

$$HgO(s) + 4I^-(aq.) + H_2O(l) \rightleftharpoons HgI_4^{2-} + 2OH^-$$

Which changes will increase the equilibrium concentration of HgI_4^{2-}?

I. Increasing the mass of HgO(*s*) present.
II. Increasing $[I^-]$.
III. Adding 1 *M* HCl.

(a) I only (b) II only
(c) II and III only (d) I, II and III

44. Which of the following do not change the value of *K* for a reaction?

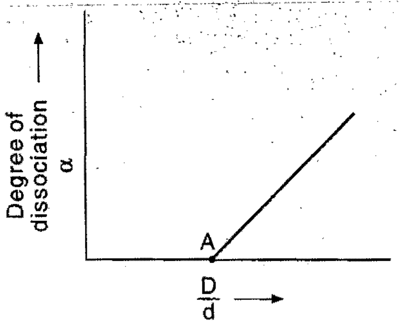
(a) Addition of catalyst
(b) Increase in temperature
(c) Increase in pressure
(d) Removal of one of the products

45. For which of the following reactions at equilibrium at constant temperature doubling the volume will cause a shift to the right?

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(c) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$
(d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

46. In the reaction,

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ if *D* and *d* are the vapour densities at initial stage and at equilibrium then what will be the value of $\frac{D}{d}$ at point *A* in the following graph?



(a) 0 (b) 1.5 (c) 1 (d) 0.5

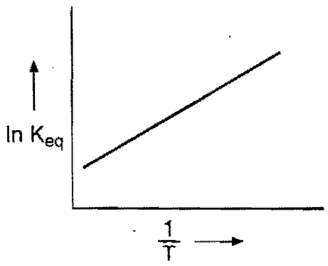
[**Hint:** $$\alpha = \frac{D-d}{(n-1)d}$$

For the given reaction, $n = 2$ and $\alpha = 0$ at *A*

$$\therefore \quad \frac{D-d}{(2-1)d} = 0$$

$$\frac{D}{d} = 1]$$

47. A schematic plot of $\ln K_{eq}$ *versus* inverse of temperature for a reaction is shown below:



The reaction must be:

(a) exothermic
(b) endothermic
(c) one with negligible enthalpy change
(d) highly spontaneous at ordinary temperature

[Hint: We know that, $\frac{d \ln K_{eq.}}{dT} = \frac{\Delta H^\circ}{RT^2}$

$$\therefore \quad \ln K_{eq.} = -\frac{\Delta H^\circ}{RT} + C$$

The plot has positive slope, hence ΔH° will be negative.]

48. The equilibrium:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g),$$

is followed to set-up at 127°C in a closed vessel. The total pressure at equilibrium was 20 atm. The K_c for the reaction is:

(a) $0.092\,M^2$ (b) $0.085\,M^2$
(c) $3.045\,M^2$ (d) none of these

[Hint: $pNH_3 = pH_2S = \frac{20}{2}$ atm

$$K_p = pNH_3 \times pH_2S = 100\text{ atm}^2$$
$$K_p = K_c (RT)^{\Delta n}$$
$$100 = K_c \times (0.0821 \times 400)^2$$
$$K_c = 0.092\,M^2]$$

49. 20% of N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Mixture has the density at equilibrium equal to:

(a) 1.48 g/L (b) 1.84 g/L
(c) 2.25 g/L (d) 3.12 g/L

[Hint: The reaction is:

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

$$n = 2 \text{ and } \alpha = \frac{20}{100} = 0.2$$

$D = 46$, initial vapour density

d = vapour density at equilibrium

$$\alpha = \frac{D - d}{(n-1)d}$$

$$0.2 = \frac{46 - d}{(2-1)d}$$

$$d = 38.3$$

Molar mass equilibrium = 2 × 38.3 = 76.6

$Pm = dRT$ Here, d = density of gas mixture

$$d(\text{mix}) = \frac{Pm}{RT} = \frac{1 \times 76.6}{0.0821 \times 300} = 3.12\text{ g/L}]$$

50. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$; respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is: **(AIEEE 2008)**

(a) 1 : 9 (b) 1 : 36
(c) 1 : 1 (d) 1 : 3

[Hint : $X \rightleftharpoons 2Y$ $\qquad$ $Z \rightleftharpoons P + Q$

$$\begin{array}{lcccccc} & X & 2Y & & Z & P & Q \\ t_0 & 1 & 0 & & 1 & 0 & 0 \\ t_{eq.} & 1-\alpha & 2\alpha & & 1-\alpha & \alpha & \alpha \end{array}$$

$$K_{p_1} = \frac{\left[\frac{2\alpha}{1+\alpha}P_1\right]^2}{\left[\frac{1-\alpha}{1+\alpha}P_1\right]} \qquad K_{p_2} = \frac{\left[\frac{\alpha}{1+\alpha}P_2\right]\left[\frac{\alpha}{1+\alpha}P_2\right]}{\left[\frac{1-\alpha}{1+\alpha}P_2\right]}$$

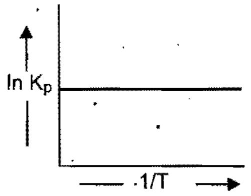
$$= \frac{4\alpha^2 P_1}{1-\alpha^2} \qquad = \frac{\alpha^2 P_2}{1-\alpha^2}$$

$$\frac{K_{p_1}}{K_{p_2}} = \frac{4\alpha^2 P_1}{1-\alpha^2} \Big/ \frac{\alpha^2 P_2}{1-\alpha^2}$$

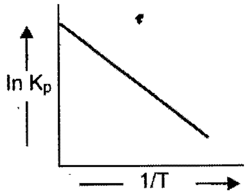
$$\frac{1}{9} = \frac{4P_1}{P_2}$$

$$\frac{P_1}{P_2} = \frac{1}{36}]$$

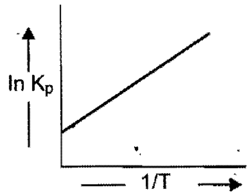
51. Which of the following plots is correct about endothermic reaction ?



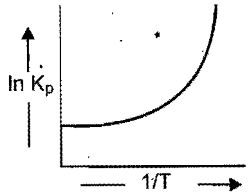
(a)



(b)



(c)



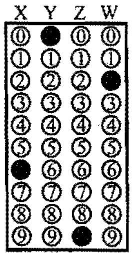
(d)

Answers

1. (d)	**2.** (d)	**3.** (a)	**4.** (d)	**5.** (a)	**6.** (b)	**7.** (d)	**8.** (d)
9. (a)	**10.** (d)	**11.** (b)	**12.** (a)	**13.** (c)	**14.** (c)	**15.** (b)	**16.** (d)
17. (c)	**18.** (b)	**19.** (b)	**20.** (d)	**21.** (c)	**22.** (d)	**23.** (a)	**24.** (a)
25. (d)	**26.** (c)	**27.** (a)	**28.** (a)	**29.** (b)	**30.** (b)	**31.** (b)	**32.** (a)
33. (a)	**34.** (a)	**35.** (a)	**36.** (a)	**37.** (a)	**38.** (d)	**39.** (a)	**40.** (b)
41. (d)	**42.** (c)	**43.** (c)	**44.** (a, c, d)	**45.** (a, b)	**46.** (c)	**47.** (a)	**48.** (a)
49. (d)	**50.** (b)	**51.** (b)					

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. For the reaction:
$$AB(g) \rightleftharpoons A(g) + B(g)$$
AB is 33% dissociated at a total pressure of p. Then, $\frac{p}{K_p}$ will be equal to :
2. If the reaction $A \rightleftharpoons B$, has $\Delta G^\circ = 0$, then its equilibrium constant will be equal to :
3. Consider the following reaction
$$A + B \rightleftharpoons E \qquad K_c = 6$$
$$2B + C \rightleftharpoons 2D \qquad K_c = 4$$
What will be the equilibrium constant (K_c) for the following reaction?
$$A + D \rightleftharpoons E + C$$
4. For the equilibrium of the reaction :
$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g) \quad K_p = 81\ \text{atm}^2$$
Total pressure at equilibrium will be x times the pressure of NH_3.
The value of x will be :
5. Mixing 4 moles of A with 4 moles of B forms 2 moles of C at equilibrium, according to the following reaction :
$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$
The value of equilibrium constant is :
6. A reaction at equilibrium involving 2 mol each of PCl_5, PCl_3, Cl_2 is maintained at 250°C and total pressure of 3 atm. The value of K_p is :
7. For the reaction:
$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$
The initial concentrations of A and B are equal. The equilibrium concentration of C is two times the equilibrium concentration of A. The value of equilibrium constant is :
8. $$N_2 + O_2 \rightleftharpoons 2NO; K_1$$
$$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO; K_2$$
$$2NO \rightleftharpoons N_2 + O_2; K_3$$
$$NO \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2; K_4$$
$$K_1 \times K_3 = x; \quad \sqrt{K_1} \times K_4 = y; \quad \sqrt{K_3} \times K_2 = z$$
What will be the value of xyz?
9. 4.5 moles each of H_2 and I_2 are heated in a sealed 10 L vessel. At equilibrium, 3 mole of HI were found. The equilibrium constant for :
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ is :}$$
10. SO_2Cl_2 and Cl_2 are introduced into a 3 L vessel. Partial pressure of SO_2Cl_2 and Cl_2 at equilibrium are 1 atm and 2 atm respectively. The value of K_p for the following reaction is 10.
$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$
The total pressure in atm at equilibrium would be :

Answers

1. (8) **2.** (1) **3.** (3) **4.** (2) **5.** (1) **6.** (1) **7.** (4) **8.** (1)
9. (1) **10.** (8)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

Phosphorous pentachloride when heated in a sealed tube at 700 *K, it undergoes decomposition as,*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g); \quad K_p = 38\, atm$$

vapour density of the mixture is 74.25.

Answer the following questions:

1. The reaction is:
   (a) endothermic
   (b) exothermic
   (c) may be endothermic or exothermic
   (d) unpredictable
2. Percentage dissociation of PCl_5 may be given as:
   (a) 4.04 (b) 40.4 (c) 44.0 (d) 0.404
3. Equilibrium constant K_c for the reaction will be:
   (a) 0.66 M (b) 0.56 M (c) 0.46 M (d) 0.36 M
4. If pressure is increased then the equilibrium will:
   (a) be unaffected
   (b) shift in backward direction
   (c) shift in forward direction
   (d) cannot be predicted
5. When inert gas is added to the given reversible process then the equilibrium will:
   (a) be unaffected
   (b) shift in backward direction
   (c) shift in forward direction
   (d) cannot be predicted

• Passage 2

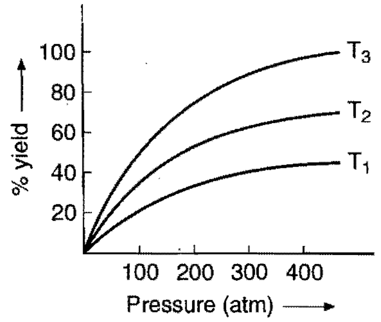
In Haber's process, the ammonia is manufactured according to the following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta H^\circ = -(22.4\, kJ)$$

The pressure inside the chamber is maintained at 200 *atm and temperature at* 500°*C. Generally, this reaction is carried out in presence of Fe catalyst.*

Answer the following questions:

1. If K_p for the given reaction is 1.44×10^{-5}, then the value of K_c will be:
   (a) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ mol L^{-1}
   (b) $\dfrac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$ mol L^{-1}
   (c) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{2}}$ mol L^{-1}
   (d) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$ mol L^{-1}
2. The preparation of ammonia by Haber's process is an exothermic reaction. If the preparation follows the following temperature pressure relationship for its % yield. Then for temperature T_1, T_2 and T_3 the correct option is:



   (a) $T_3 > T_2 > T_1$ (b) $T_1 > T_2 > T_3$
   (c) $T_1 = T_2 = T_3$ (d) nothing could be predicted
   [**Hint:** The % yield will decrease with rise in temperature, since it is exothermic.]
3. 500°C is considered optimum temperature for Haber's process because:
   (a) catalyst has maximum activity at this temperature
   (b) energy required is easily obtained at this temperature
   (c) yield is maximum at this temperature
   (d) rate is fast enough while the yield is also appreciable at this temperature
4. If K_p for the reaction is 1.44×10^{-5}, then the value of K_p for the decomposition of NH_3,
   $$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$
   will be:
   (a) $\sqrt{1.44 \times 10^{-5}}$ (b) $(1.44 \times 10^{-5})^2$
   (c) $\dfrac{1}{1.44 \times 10^{-5}}$ (d) 2.88×10^{-5}
5. 30 litre $H_2(g)$ and 30 litre were taken for the reaction in Haber's process which yields only 50% of the expected ammonia due to reversibility of the reaction. What will be the composition of reaction mixture under the given condition?

	NH_3	N_2	H_2
(a)	20 L	20 L	20 L
(b)	10 L	25 L	15 L
(c)	20 L	10 L	30 L
(d)	20 L	25 L	15 L

• Passage 3

When all the coefficients in a balanced chemical equation are multiplied by a constant factor J, the equilibrium constant (originally K) becomes K^J. Similarly, when balanced equations are added together, the equilibrium constant for the combined process is equal to the product of the equilibrium constants for each step.

Equilibrium constant of the reversed reaction is numerically equal to the reciprocal of the equilibrium constant of the original equation.

Unit of $K_p = (atm)^{\Delta n}$; *Unit of* $K_c = [mol\, L^{-1}]^{\Delta n}$

Answer the following questions:

1. Consider the reactions:

(i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$
(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$
(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$

Which of the following is correct?

(a) $K_3 = K_1/K_2$ (b) $K_3 = K_1^2/K_2^3$
(c) $K_3 = K_1K_2$ (d) $K_3 = K_1\sqrt{K_2}$

2. The equilibrium constants for the following reactions at 1400 K are given:

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g);\ K_1 = 2.1 \times 10^{-13}$$
$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g); K_2 = 1.4 \times 10^{-12}$$

Then, the equilibrium constant K for the reaction,

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

is:

(a) 2.04 (b) 20.5 (c) 2.6 (d) 8.4

3. Given: $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g); K_1$
$2NO_2(g) \rightleftharpoons N_2O_4(g); K_2$
$2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g); K_3$

Which of the following relations is correct?

(a) $K_3 = K_1 / K_2$ (b) $K_3 = K_1 \times K_2$
(c) $K_3 = K_1 + K_2$ (d) $K_3 = \frac{K_1}{\sqrt{K_2}}$

4. H_3PO_4 is a tribasic acid, it undergoes ionization as:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-; K_1$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}; K_2$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}; K_3$$

Then, equilibrium constant for the following reaction will be:

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$$

(a) $K_1K_2K_3$ (b) $\frac{K_1K_2}{K_3}$ (c) $\frac{K_1K_3}{K_2}$ (d) $\frac{K_1K_2}{K_3{}^2}$

5. Consider the two reactions:

$$XeF_6(g) + H_2O(g) \rightleftharpoons XeOF_4(g) + 2HF(g); K_1$$
$$XeO_4(g) + XeF_6(g) \rightleftharpoons XeOF_4(g) + XeO_3F_2(g); K_2$$

Then, the equilibrium constant for the following reaction will be:

$$XeO_4(g) + 2HF(g) \rightleftharpoons XeO_3F_2(g) + H_2O(g)$$

is given by:

(a) K_1/K_2^2 (b) K_1/K_2 (c) K_1^2/K_2 (d) K_2/K_1

• Passage 4

Mass action ratio or reaction quotient Q for a reaction can be calculated using the law of mass action,

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$
$$Q = \frac{[C][D]}{[A][B]}$$

The value of Q decides whether the reaction is at equilibrium or not.

At equilibrium, $Q = K$
For non-equilibrium process, $Q \neq K$

when $Q > K$, reaction will favour backward direction and when $Q < K$, it will favour forward direction.

Answer the following questions:

1. The reaction quotient Q for:

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

is given by $Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed in backward direction, when:

(a) $Q = K_c$ (b) $Q < K_c$ (c) $Q > K_c$ (d) $Q = 0$

2. For the reaction:

$$2A + B \rightleftharpoons 3C \quad \text{at 298 K, } K_c = 49$$

A 3L vessel contains 2, 1 and 3 moles of A, B and C respectively. The reaction at the same temperature:

(a) must proceed in forward direction
(b) must proceed in backward direction
(c) must be in equilibrium
(d) cannot be predicted

3. In a reaction mixture containing H_2, N_2 and NH_3 at partial pressure of 2 atm, 1 atm and 3 atm respectively, the value of K_p at 725 K is 4.28×10^{-5} atm^{-2}. In which direction the net reaction will go?

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

(a) Forward
(b) Backward
(c) No net reaction
(d) Direction cannot be predicted

4. In the following reaction:

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

the equilibrium is not attained. The rate of forward reaction is greater than that of backward reaction. Thus, which of the following is the correct relation between K_p and Q_p?

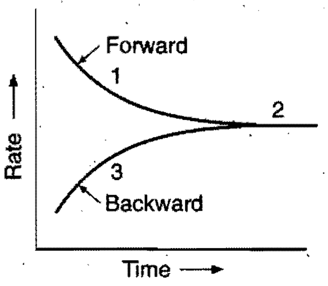
(a) $K_p = Q_p$ (b) $Q_p > K_p$ (c) $Q_p < K_p$ (d) $K_p = Q_p = 1$

5. In the reaction:

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

a graph is plotted to show the variation of rate of forward and backward reactions against time:

Which of following is correct?



	$Q > K$	$Q = K$	$Q < K$
(a)	3	2	1
(b)	1	2	3
(c)	2	3	1
(d)	2	1	3

• Passage 5

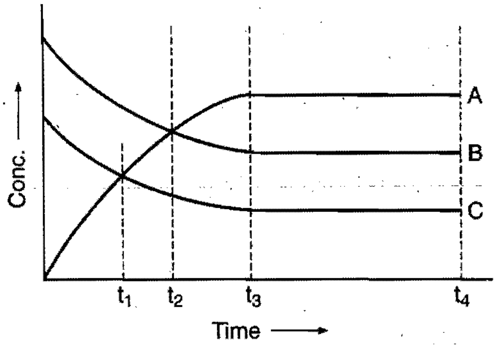
In a reversible chemical reaction, the rate of forward reaction decreases and that of backward reaction increases with the passage of time; at equilibrium the rate of forward and backward reactions become same.

Let us consider the formation of SO_3 in the following reversible reaction:

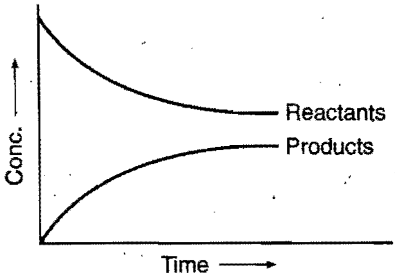
$$2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$$

Following graphs are plotted for this reaction:

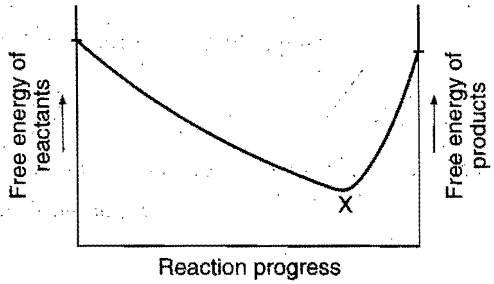
Graph 1



Graph 2



Graph 3



Answer the following questions:

1. In the graph (1), A, B and C respectively are:
   (a) SO_3, SO_2 and O_2 (b) SO_3, O_2 and SO_2
   (c) SO_2, O_2 and SO_3 (d) O_2, SO_2 and SO_3
2. In the graph (1), the equilibrium state is reached at:
   (a) t_1 (b) t_2 (c) t_3 (d) t_4
3. The graph (2) tells us that:
   (a) the reaction is irreversible
   (b) the reaction is reversible
   (c) the reaction is exothermic
   (d) the reaction is endothermic
4. The graph (2) tells us that:
   (a) equilibrium is never achievable
   (b) equilibrium is achieved after the concentrations of reactants and products become equal
   (c) equilibrium is achieved before the concentrations of reactants and products become equal
   (d) none of the above
5. From the graph (3), it can be interpreted that:
   (a) equilibrium is achieved at X
   (b) reaction is nearer to the completion
   (c) $\Delta G = 0$ at X
   (d) all of the above

Answers

Passage 1.	1. (a)	2. (b)	3. (a)	4. (b)	5. (c)
Passage 2.	1. (d)	2. (b)	3. (d)	4. (c)	5. (b)
Passage 3.	1. (c)	2. (d)	3. (b)	4. (a)	5. (d)
Passage 4.	1. (c)	2. (a)	3. (b)	4. (c)	5. (a)
Passage 5.	1. (a)	2. (c)	3. (b)	4. (c)	5. (d)

SELF ASSESSMENT

ASSIGNMENT NO. 9

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. By applying the law of mass action, the equilibrium constant K for the reaction:

$$HA + H_2O \rightleftharpoons H_3^+O + A^- \qquad \text{[CET (J\&K) 2007]}$$

(a) $K = \frac{[HA][H_2O]}{[H_3O^+][A^-]}$ (b) $K = \frac{[H_3^+O][A^-]}{[HA][H_2O]}$

(c) $K = \frac{[H_3^+O][H_2O]}{[A^-][HA]}$ (d) $K = \frac{[HA][A^-]}{[H_2O][H_3O^+]}$

2. For the reaction,

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

When temperature increases: [PMT (Haryana) 2007]

(a) formation of NH_3 increases

(b) formation of NH_3 decreases

(c) concentration of N_2 decreases

(d) concentration of H_2 decreases

3. For the reaction 1 g mole of $CaCO_3$ is enclosed in 5 L container

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K_p = 1.16$ atm at 1073 K then percentage dissociation of $CaCO_3$ is:

(a) 65% (b) 100% (c) 6.5% (d) zero

4. The activation energy for forward and backward reactions are 50 kJ / mol and 40 kJ / mol respectively. If K_1 and K_2 are the equilibrium constants of reaction at temperature T_1 and T_2 respectively and $T_2 > T_1$ then:

(a) $K_1 < K_2$ (b) $K_1 = K_2$ (c) $K_1 > K_2$ (d) $K_2 = K_1^2$

[**Hint:** $\Delta H = E_f - E_b = 50 - 40 = 10$ kJ / mol. In endothermic reactions, equilibrium constant increases with increase in temperature.]

5. Given, $X(g) \rightleftharpoons nY(g)$.

If degree of dissociation is α, then K_c of the reaction in a vessel of 1 litre is:

(a) $\frac{n\alpha^n}{1-\alpha}$ (b) $\frac{n\alpha}{1-\alpha}$ (c) $\frac{(n\alpha)^n}{1+\alpha}$ (d) $\frac{(n\alpha)^n}{1-\alpha}$

6. Consider the following equation in a closed container,

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

at a fixed temperature, the volume of the reaction container is halved, for this change, which of the following statement holds true regarding the K_p and degree of dissociation 'α':

(a) neither K_p nor α changes

(b) both K_p and α change

(c) K_p changes but α does not change

(d) K_p does not change but α changes

7. The reaction, $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ is studied in a vessel of one litre at 250° C. The initial concentration of A was $3x$ and that of B was x. At equilibrium, concentration of C was found to be equal to the equilibrium concentration of B. What is the concentration of D at equilibrium:

(a) $\frac{x}{2}$ (b) $3x - \frac{1}{2}$ (c) $x - \frac{x}{2}$ (d) x

SECTION-II

Multiple Answers Type Objective Questions

8. Equilibrium constant does not depend on:

(a) catalyst (b) temperature

(c) pressure (d) inert gas

9. Which of the following reactions have $K_p < K_c$?

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

(b) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

(c) $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$

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

10. Which of the following reactions are not affected by inert gas addition?

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

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

(In a rigid container of constant volume)

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

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

11. Which of the following are not affected by pressure change?

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

(b) $2NaNO_2(s) + O_2(g) \rightleftharpoons 2NaNO_3(s)$

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

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

12. The reaction,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ (Exothermic)}$$

will shift in forward direction by:

(a) adding SO_3 at constant volume

(b) increasing volume of container

(c) adding SO_2 at constant volume

(d) adding inert gas at constant volume

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.

(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.

(c) Statement-1 is true; statement-2 is false.

(d) Statement-1 is false; statement-2 is true.

13. **Statement-1:** The value of equilibrium constant depends on the stoichiometry of the equation.

Because

Statement-2: The value of equilibrium constant does not change when the equation is multiplied or divided by a number.

14. **Statement-1:** $K_p = K_c$ for all reactions.

Because

Statement-2: K_p and K_c are interrelated by the equation $K_p = K_c(RT)^{\Delta n}$.

15. **Statement-1:** Catalyst does not change the position of equilibrium.

Because

Statement-2: Catalyst only changes the equilibrium time.

16. **Statement-1:** Free energy of both reactants and products are minimum at equilibrium.

Because

Statement-2: The free energy of reactants and products decreases with passage of time and become equal at equilibrium.

17. **Statement-1:** Addition of inert gases at equilibrium will support the dissociation of PCl_5 at constant temperature.

Because

Statement-2: The addition of inert gas at constant volume will not affect the equilibrium.

SECTION-IV

Matrix-Matching Type Questions

This section contains 4 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in List-I have to be matched with statements (p, q, r and s) in List-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s), then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	ⓠ	ⓡ	●
b	ⓟ	●	●	ⓢ
c	●	●	ⓡ	ⓢ
d	ⓟ	ⓠ	ⓡ	●

18. Match the List-I with List-II:

List-I	List-II
(a) $A(g) \rightleftharpoons B(g) + C(g)$	(p) $\alpha = \sqrt{\frac{K_p}{K_p + 4P}}$
(b) $A_2(g) \rightleftharpoons 2A(g)$	(q) $\alpha = \sqrt{\frac{K_p}{P + K_p}}$
(c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(r) $M_{mix} = \frac{M_{reactant}}{1+\alpha}$
(d) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$	(s) Forward shift on decreasing the pressure

19. Match the List-I with List-II:

List-I (Mathematical process)	List-II (New equilibrium constant)
(a) Divided by n	(p) K^n
(b) Multiplied by n	(q) $\frac{1}{K}$
(c) Reaction is reversed	(r) $K_1 \times K_2 \times K_3 \times \ldots \times K_n$
(d) n-equations are added	(s) $(K)^{1/n}$

20. Match the List-I with List-II for the following reaction:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

List-I	List-II
(a) Partial pressure of $NH_4HS(s)$	(p) $p_{NH_3} \times p_{H_2S}$
(b) K_p	(q) $p_{NH_3} + p_{H_2S}$
(c) Total pressure at equilibrium	(r) $(p_{NH_3} \times p_{H_2})(RT)^{-2}$
(d) K_c	(s) Zero

Answers

1. (b) **2.** (b) **3.** (c) **4.** (a) **5.** (d) **6.** (d) **7.** (a) **8.** (a, b, d)
9. (b. d) **10.** (a, b) **11.** (a, b, c) **12.** (a, b) **13.** (c) **14.** (d) **15.** (a) **16.** (a)
17. (b) **18.** (a-q,r,s) (b-p,q,s) (c-q, r,s) (d-p,s) **19.** (a-s) (b-p) (c-q) (d-r)
20. (a-s) (b-p) (c-q) (d-r)