5.

CHEMICAL EQUILIBRIUM

1. INTRODUCTION

Attainment of equilibrium in a system indicates a balanced condition of a system.

Balanced condition includes:

(a) Concentration of the components remain constant. It is not necessary for the concentrations to be equal.

(b) Rate of forward reaction=Rate of backward reaction.

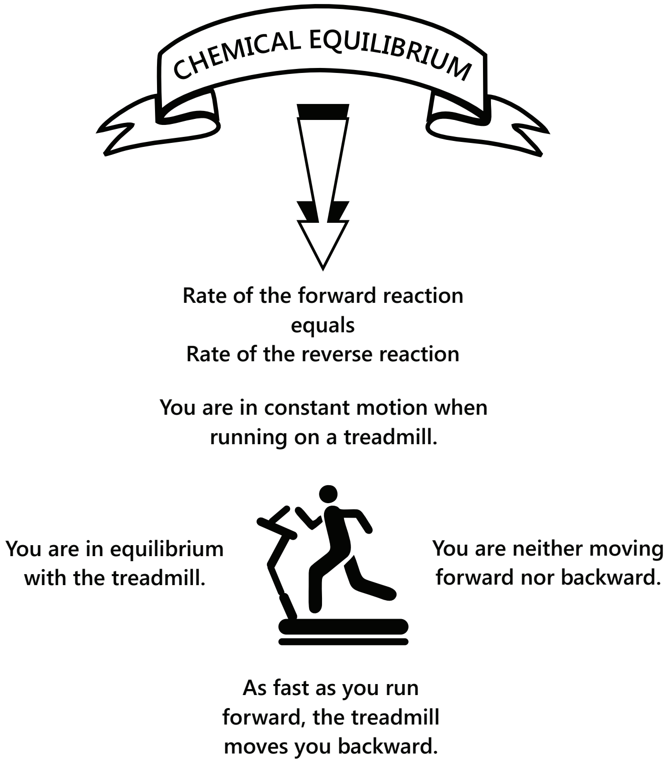


Figure 5.1: Everyday example of equilibrium

If we plot the above condition on a graph, we get,

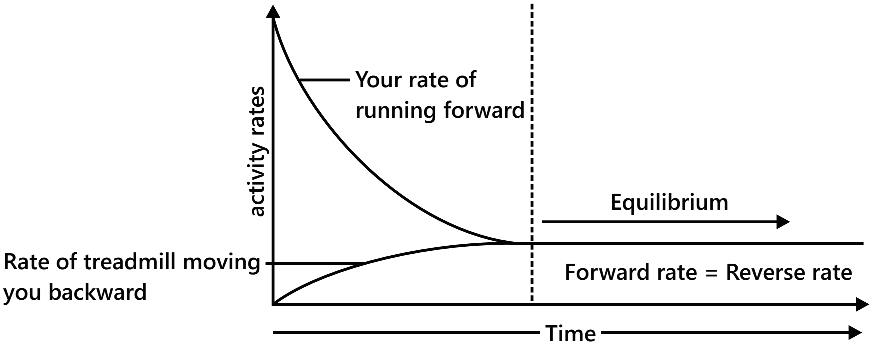


Figure 5.2: Attainment of equilibrium

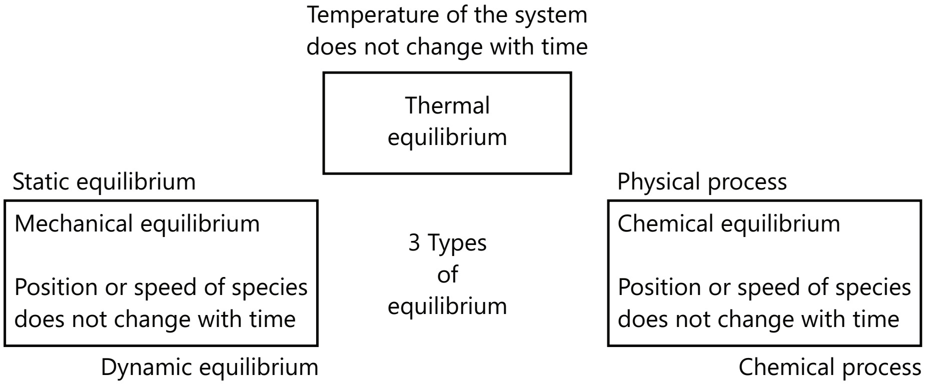


Figure 5.3: Types of equilibrium

Various examples of equilibrium-

(a) Inside a bottle of fizzy cold drink

- **(i)** There is carbon dioxide (CO_2) dissolved in the liquid
- **(ii)** The space between the liquid and the cap also contains CO_2 gas CO_2 moves constantly from the liquid to the gas phase, and from the gas phase into the liquid maintaining the equilibrium $CO_2(g) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq)$

(b) While learning to ride a bicycle, one applies a large amount of force on the pedals in order to balance. This itself imposes a backward pressure on the leg muscles in the form of pain. But, once the balance is attained, the magnitude of the force to be applied becomes less and constant at one point, thereby easing the pain. Thus, equilibrium is maintained.

(c) Running needs a lot of energy and to produce energy, one's body needs to consume a lot of oxygen, for which the heart pumps/beats more than the normal. Once we stop running, our heart beats slow down and come to normal, but do not stop. There is a constant beating rate maintained and thus energy-oxygen equilibrium is maintained.

(d) A staircase which is built against a wall remains so with the passage of time posing as a good example of Static equilibrium.

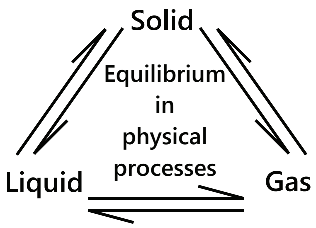
CONCEPTS

A system is said to be in thermodynamic equilibrium when pressure, temperature and concentrations of species do not change with time.

Neeraj Toshniwal (JEE 2009, AIR)

2. EQUILIBRIUM IN PHYSICAL PROCESSES

The equilibrium involving physical processes are referred to as physical equilibrium. The physical equilibrium involving change in state may be of the following three types.



2.1 Solid-Liquid Equilibrium

Process: Melting of a crystalline solid attains equilibrium under 1 atmospheric pressure at a certain temperature, wherein the temperature is termed as the melting or freezing point of that solid.

Changes: On application of constant heat to the equilibrium mixture, solid gets converted to liquid. But if the mixture is kept in an insulated thermos flask, a dynamic equilibrium, (i.e. both the states would be constant) would be maintained.

Example: Let us consider ice and water at 273 K (melting point of ice), taken in a perfectly insulated thermos flask. The temperature as well as the masses of ice and water remains constant. Since there is no change in mass of ice and water, the number of molecules going from ice into water, is equal to the number of molecules of water going into ice.

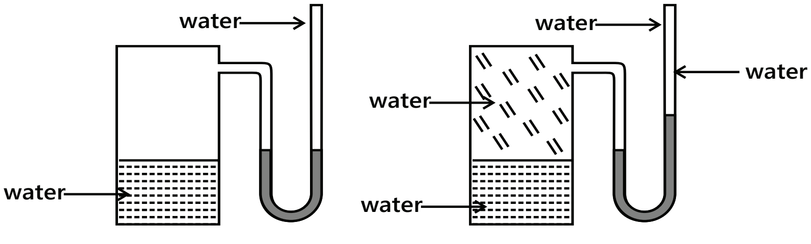
Rate of melting = Rate of freezing

2.2 Liquid – Gas Equilibrium

Process: Evaporation of water in an evacuated vessel gives vapour formation with a gradual decrease in the water level.

Changes: Equilibrium is attained wherein a constant level is observed after a certain time. This is dynamic in nature. In beginning, rate of evaporation is more and hence water vapour concentration increases, which in turn condenses back into the liquid. As the concentration of water vapours increases, rate of condensation also increases. At equilibrium, rate of evaporation is equal to rate of condensation.

$\therefore$ Rate of evaporation = Rate of condensation.



(a) **(b)**

Figure 5.4: Evaporation of water in a closed vessel (a) initial stage (b) equilibrium stage

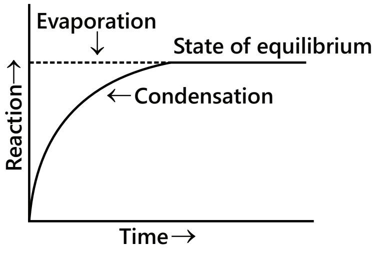


Figure 5.5: Attainment of liquid - vapour equilibrium

2.3 Solid – Vapour Equilibrium

Process: Sublimation occurs when solid turns into vapour phase.

Example: (with explanation of changes): A piece of solid iodine kept in a closed vessel, fills with violet vapour in sometime. Intensity of colour goes on increasing with time and attains a constant violet shade which indicates the equilibrium position. This point gives the sublimation and condensation processes in balance.

Represented as:

I_2 (solid) $\rightleftharpoons$ I_2 (vapour)

Other examples showing this kind of equilibrium are:

Camphor (solid) $\rightleftharpoons$ Camphor (vapour)

NH_4Cl (solid) $\rightleftharpoons$ NH_4Cl (vapour

2.4 Equilibrium Involving Dissolution of Solids or Gases in Liquids

Solids in Liquids

Condition: A saturated solution is the one in which no more solute can be dissolved in a given amount of solvent. The added solute poses as a precipitate.

The amount of solute required to prepare a saturated solution in a given quantity of solvent is known as solubility of the solute at a particular temperature.

This state is dynamic equilibrium.

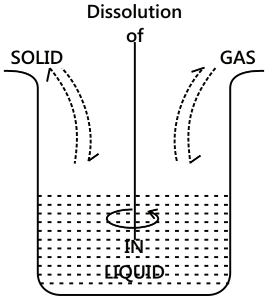


Figure 5.6: Equilibrium involving dissolution of solid or gases in liquids

Example: Addition of sugar to water remains undissolved in a saturated sugar solution.

Sugar (in solution) $\rightleftharpoons$ Sugar (solid)

The dynamic nature of equilibrium can be demonstrated by adding radioactive sugar into a saturated solution of non-radioactive sugar.

It is observed that the solution dissolves some radioactive sugar. This shows that even at equilibrium, the process of dissolution and precipitation are taking place. This means that equilibrium is dynamic in nature. However, at equilibrium:

Rate of dissolution = Rate of precipitation.

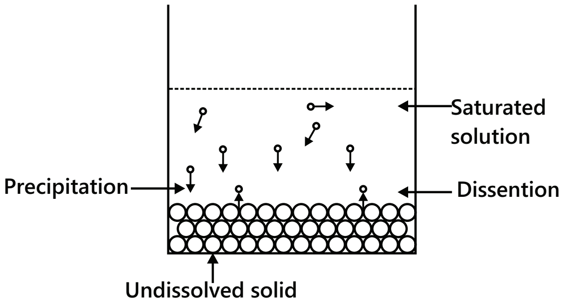


Figure 5.7: Attainment of solid - liquid equilibrium

Gases in Liquids

Condition: Certain liquids dissolve gases at a particular temperature to a certain extent. This suggests that a state of equilibrium exists between molecules in the gaseous state and the molecules dissolved in the liquid.

Example: Carbon dioxide dissolved in soda water.

The following equilibrium exists:
$CO_2(g) \rightleftharpoons CO_2(solution)$

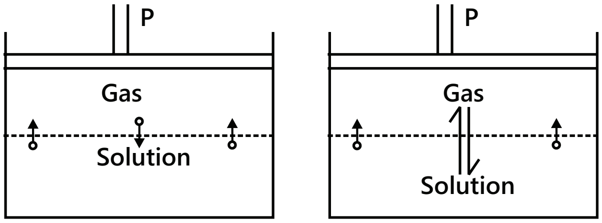


Figure 5.8: Attainment of equilibrium in a gas-liquid system

At equilibrium, the rate at which gas molecules pass into the solution becomes equal to the rate at which dissolved gas molecules come back into the gaseous phase. This is shown in the Fig.

General Characteristics of Physical equilibria:

(a) The system should be closed wherein no exchange of matter takes place with the surroundings.

(b) Irrespective of the side from which a process starts, a stable dynamic condition exists.

(c) The constant concentration keeps the other measurable properties of the system constant.

(d) On reaching the equilibrium at a particular temperature, the concentration of the reacting species reaches a constant value.

(e) The extent of the reaction before reaching equilibrium is given by the magnitude of concentration related expressions.

CONCEPTS

Table 5.1: Examples of physical equilibrium and their constants

Physical Equilibrium	Constant
1. Liquid $\rightleftharpoons$ Vapour equilibrium	Vapour pressure
2. Solid $\rightleftharpoons$ Liquid equilibrium - Coexist at only one temperature (1 atm) i.e. the melting point, without any heat exchange with the surroundings.	Mass
3. Dissolution	
a. Solids in Liquids b. Gases in Liquids - Concentration of a gas in liquid proportionately changes with the pressure of the gas above the liquid.	Solubility at a given temperature Concentration of a gas in liquid proportionately changes with the pressure of the gas above the liquid.

Nikhil Khandelwal (JEE 2009, AIR 94)

2.5 Equilibrium in our Daily Life

(a) On a windy day, the clothes dry quickly since the moving breeze takes away the water vapour, making the clothes lose more water to the surroundings, in order to re-establish the equilibrium.

(b) Perspiration is seen more on a humid day which evaporates on sitting under a fan. The presence of water vapour in the surroundings prevents the loss of water from the skin while the moving air of the fan carries away the humid air enabling the loss of water from the skin and maintaining the equilibrium.

(c) Transport of oxygen by haemoglobin in blood. Oxygen breathed in combines with the haemoglobin according to the equilibrium: $Hb\ (s) + O_2(g) \rightleftharpoons HbO_2(s)$

When it reaches the tissues, the pressure of oxygen is low over there. To readjust the equilibrium, oxyhaemoglobin gives up oxygen. When it returns to lungs where the pressure of oxygen is high more of oxyhaemoglobin is formed.

(d) Removal of CO_2 from tissues by blood. The equilibrium is:

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO^-{}_3(aq)$$

As partial pressure of CO_2 is high in the tissues, CO_2 dissolves in the blood. In the lungs, as partial pressure of CO_2 is low, it is released from the blood.

(e) Sweets cause tooth decay. Enamel coatings on the teeth consist of an insoluble substance called as hydroxyapatite, $Ca_5(PO_4)_3(OH)$.

The following equation shows the equilibrium between the substance and its ions.

$$Ca_5(PO_4)_3(OH)_{(s)} \underset{\text{Remineralisation}}{\overset{\text{Demineralisation}}{\rightleftarrows}} 5Ca^{2+} + 3PO_4^{3-} + OH^-$$

3. EQUILIBRIA IN CHEMICAL PROCESS

3.1 Irreversible 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.

(a) **(i)** Thermal decomposition of ammonium nitrite, $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(b) Precipitation reaction,

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

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

(c) Neutralisation reactions: $\underset{\text{Strong acid}}{H_2SO_4} + \underset{\text{Strong base}}{2NaOH} \longrightarrow Na_2SO_4 + 2H_2O$

3.2 Reversible Reactions

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 ($\longrightarrow$) or sign of equality (=) is replaced by two half arrow ($\rightleftharpoons$) 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:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Steamed Iron!!!

Q. When steam is passed over heated iron fillings in an open tube, Iron is completely converted into its oxide but when the tube is closed, some Iron remains unreacted. Why?

Sol: Iron reacts with steam to form an oxide of iron (Fe_3O_4) and H_2 gas. When the tube is open, H_2 escapes and reverse reaction cannot occur but when the tube is closed, reverse reaction, i. e., reaction between Fe_3O_4 and H_2 also occurs forming iron and H_2O vapour and ultimately equilibrium is attained.

CONCEPTS

Student's prior experience of reactions that proceed to completion appears to have influenced their conception of equilibrium reactions; many students failed to discriminate clearly between the characteristics of completion reactions and reversible reactions. Try to change your mind set in this case.

Saurabh Gupta (JEE 2010, AIR 443)

3.2.1 Heterogeneous Reactions

The reversible reaction in which more than one phase is present is called heterogeneous reaction.

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

$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$

$$2Na_2O_2(s) + 2H_2O(\ell) \rightleftharpoons 4NaOH(\ell) + O_2(g)$$

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

3.2.2 Homogeneous Reactions

The reversible reaction in which only one phase is present, i.e. all the reactions and products are in the same physical state is called homogeneous reaction.

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

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

CONCEPTS

A reaction is said to be irreversible when

- Either of the product separates out as solid, e.g.

  $$AgNO_3 + KCl \longrightarrow AgCl\downarrow + KNO_3$$

  $$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4\downarrow + 2KNO_3$$

- Either of the product escapes out as gas, e.g. $CaCO_3 \longrightarrow CaO + CO_2\uparrow$

  However, if the above reaction is carried out in closed container i.e., leaving no scope for gas to escape out, the reaction shows reversible nature.

Neeraj Toshniwal (JEE 2009, AIR 94)

3.3 Dynamic Nature of Chemical Equilibrium

Dynamic nature is characterized by constant change, activity, or progress.

Thus, chemical equilibrium is dynamic in nature.

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

The measurable properties of the system such as pressure, density, colour or concentration remain constant under a certain set of conditions.

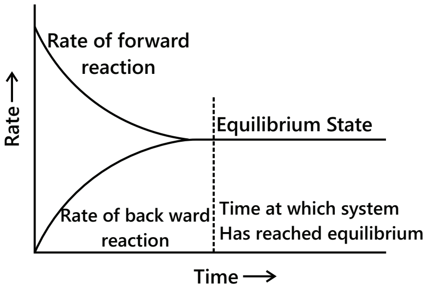


Figure 5.9: Dynamic nature of chemical equilibrium

3.4 Characteristics of Equilibrium State

(i) A system needs to be always closed to achieve equilibrium since an open system allows the escape of the formed products which prevents the backward reaction.

(ii) Chemical equilibrium, at a given temperature, is characterized 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.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

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,

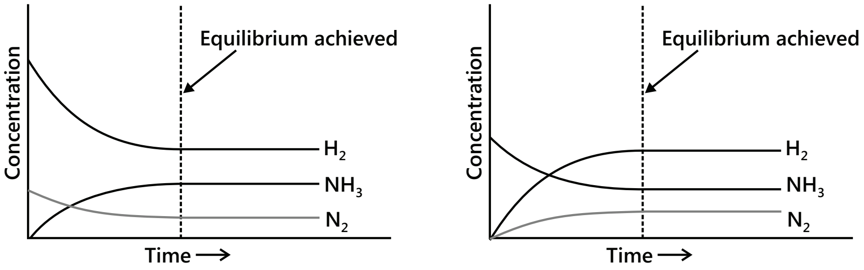


Figure 5.10: Attainment of equilibrium from either side of the reaction

(iv) Presence of catalyst never affects the equilibrium but it helps in attaining it rapidly.

(v) The reactions move with the same speed exhibiting the dynamic nature.

CONCEPTS

- Chemical equilibrium is the state at which concentration of either of reactants or products do not change with time. It is attained when the rate of forward reaction becomes equal to the rate of backward reaction.
- Chemical equilibria are dynamic in nature. It can be approached from either side.
- The gaseous phase chemical equilibrium is attained only if a reaction is made in a closed container, either at constant pressure or at constant volume.

Misconception: Equilibrium is the state where the rates of the forward and reverse reactions are equal, not when the rates reach zero. (Common misconception: Nothing happens at equilibrium.

Aman Gour (JEE 2012, AIR 230)

4. LAW OF MASS ACTION

The term active mass (a) is directly proportional to concentration (in molarity or molality), i.e. $a \propto c_M$ or $a \propto c_m$

Active mass refers to the actual mass of reactants which takes part in a particular reaction.

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

where, f and γ are activity coefficients; Also in terms of mole fraction, activity = activity coefficient (γ) × mole fraction.

Thus, if rate $\propto$ active mass also, rate $\propto$ concentration in mol/litre.

Consider a general reaction at equilibrium, $n_1A + n_2B \rightleftharpoons m_1Z + m_2Y + \ldots\ldots$

Therefore, rate of forward reaction $\propto [A]_0^{n_1}[B]_0^{n_2}\ldots\ldots$

$$r_f = K_f[A]_0^{n_1}[B]_0^{n_2}\ldots\ldots \qquad \ldots \text{(i)}$$

where, K_f is rate constant for forward reaction.

Similarly, rate of backward reaction $\propto [Z]_0^{m_1}[Y]_0^{m_2}$

$$r_b = K_b[Z]_0^{m_1}[Y]_0^{m_2} \qquad \ldots \text{(ii)}$$

where, K_b is rate constant for backward reaction.

At equilibrium, rate of forward reaction = rate of backward reaction, i.e. $r_f = r_b$

$$K_f[A]_{eq.}^{n_1}[B]_{eq.}^{n_2}\ldots\ldots = K_b[Z]_{eq.}^{m_1}[Y]_{eq.}^{m_2}\ldots\ldots \quad \text{or } K_c = \frac{K_f}{K_b} = \frac{[Z]_{eq.}^{m_1}[Y]_{eq.}^{m_2}\ldots.}{[A]_{eq.}^{n_1}[B]_{eq.}^{n_2}} \qquad \ldots \text{(iii)}$$

Remember: By convention, the active masses of the products are written in the numerator and those of the reactants in the denominator.

CONCEPTS

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

- Initial concentration of the reactants involved.
- The presence of a catalyst.
- The direction from which the equilibrium has been attained.
- The presence of inert materials.
- The equilibrium expression for a given reaction is independent of the reaction mechanism.
- The equilibrium state is one of minimum Gibbs energy (G) (free energy). Gibbs energy is the energy associated with a chemical reaction that can be used to do work.
- K_c does not change with time. It has one unique or definite value for a given reaction at a given temperature and it depends only on temperature.
- If a reversible reaction has an exceedingly small value of Kc, adding a catalyst would be of little help.
- The concentrations of pure solid and liquid must be ignored while writing the equilibrium constant expression.

Vaibhav Krishnan (JEE 2009, AIR 22)

Misconception

(a) Many students confuse rate of reaction with extent of reaction.

  (i) Rate of Reaction: The **reaction rate** (rate of reaction) or **speed of reaction** for a reactant or product in a particular reaction is intuitively defined as how fast or slow a reaction takes place.

  (ii) Extent of Reaction: The **extent of reaction** is a quantity that measures the extent in which the reaction proceeds. It is usually denoted by the Greek letter ξ. The extent of a reaction has units of amount (moles).

(b) Equilibrium constants can change with temperature when the activation energies of forward and reverse reactions are different. (Common misconception: Equilibrium constants are constant under all conditions.)

(c) The rate of the forward reaction increases with time from the mixing of the reactants until equilibrium is established. But note that this is not so.

Key Concepts

(a) The magnitude of K equilibrium constant is a measure of the extent to which a given reaction has taken place at equilibrium.

(b) The higher value of equilibrium constant ($\simeq 10^3$) for a reaction indicates that the reaction proceeds more in forward direction. A very high value of equilibrium constant ($> 10^3$) such as:

$H_2 + Br_2 \rightleftharpoons 2HBr$; $K_c = 5.4 \times 10^{18}$ or $H_2 + Cl_2 \rightleftharpoons 2HCl$; $K_c = 4.0 \times 10^{31}$ shows that reaction has gone almost to completion.

(c) The lower values of equilibrium constant ($< 10^{-3}$) for a reaction indicates that the reaction proceeds more in backward direction. A way low value of such as $N_2 + O_2 \rightleftharpoons 2NO$; $K_c = 4.8 \times 10^{-31}$ shows that reaction does not proceed significantly in forward direction,

(d) The intermediate value of K_c (10^3 to 10^{-3}) shows that concentrations of products and reactants are comparable.

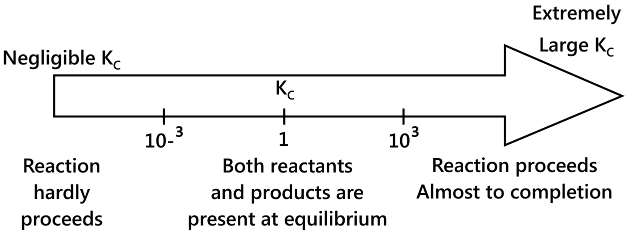


Figure 5.11: Dependence of extent of reaction on K_c

5. RELATIONSHIP BETWEEN K_P AND K_C

A gaseous reaction consists of particle gaseous species which exert an individual pressure, called as partial pressure which is taken into account for the measure of the equilibrium constant called K_p.

Consider gaseous reaction, $nA(g) + mB(g) \rightleftharpoons aY(g) + bZ(g)$

where,

P_A = partial pressure of A

P_B = partial pressure of B

P_Y = partial pressure of Y

P_Z = partial pressure of Z

$$K_p = \frac{(P_Y)^a (P_Z)^b}{(P_A)^n (P_B)^m}$$

Considering the gas equation, $PV = nRT$ or $P = \frac{n}{V} RT$

$$\therefore\ P = CRT \left[\frac{n}{V} = C \text{ i.e. concentration}\right]$$

Substituting in the K_p expression, we get,

$$K_p = \frac{(C_Y RT)^a (C_Z RT)^b}{(C_A RT)^n (C_B RT)^m} \quad = \frac{(C_Y)^a (C_Z)^b RT^{(a+b)-(n+m)}}{(C_A)^n (C_B)^m}$$

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

Δn = total no. of molecules of gaseous products − total no. of molecules of gaseous reactants.

CONCEPTS

Equilibrium constant in terms of mole fractions (K_x)

Consider the general gaseous reaction: $aA + bB \rightleftharpoons cC + dD$

If at equilibrium, the mole fractions of A, B, C and D are x_A, x_B, x_C and x_D respectively then

$$K_x = \frac{x_C^c . x_D^d}{x_A^a . x_B^b}.$$

Similar to the relation between K_p and K_c, we have $K_p = K_x(P)^{\Delta n}$

Nikhil Khandelwal (JEE 2009, AIR 94)

Illustration 1: Write equilibrium constant for the each **(JEE MAIN)**

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

(B) $KClO_3(s) \rightleftharpoons KCl(s) + (3/2)O_2(g)$

(C) $CaC_2(s) + 5O_2(g) \rightleftharpoons 2CaCO_3(s) + 2CO_2(g)$

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

(E) $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$

Sol: Use K_p and K_c expression wherever necessary.

(A) $K_c = \frac{[NO_2]^2}{[N_2O_4]}; K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})}$

(B) $K_c = [O_2]^{3/2}; K_p = (P_{O_2})^{3/2}$

(C) $K_c = \frac{[CO_2]^2}{[O_2]^5}; k_p = \frac{P_{CO_2}}{P_{O_2}{}^5}$

(D) $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}; K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

(E) $K_c = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$

Illustration 2: The equilibrium constant K_c for the gaseous phase reaction at 523 K: $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ is 23.10 litre mol^{-1}. Calculate K_p at 503 K. **(JEE MAIN)**

Sol: $PCl_3 + Cl_2 \rightleftharpoons PCl_5$;

Use $K_p = K_c(RT)^{\Delta n}$ using the given K_c.

The formula to calculate K_p is as follows,

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

Values of K_c, R and T is known, we have to calculate Δ^n

$\Delta n = 1 - 2 = -1$

$K_p = K_c(RT)^{-1}$;

Substituting the values in above equation,

$$k_p = \frac{23.10}{0.0821 \times 503} = 0.5593 \text{ atm}^{-1}$$

Illustration 3: The rate of reversible reaction (change in concentration per second):

$PtCl_4^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3]^- + Cl^-$; was observed at 0.3 ionic strength at 25°C and noticed that

$$\frac{\Delta[PtCl_4^{2-}]}{\Delta t} = 3.0 \times 10^{-5}[PtCl_4^{2-}] - 1.1 \times 10^{-3}\ [Pt(H_2O)Cl_3]^-[Cl^-]$$ **(JEE ADVANCED)**

Calculate

(A) Rate constant for forward and backward reaction.

(B) The equilibrium constant for the complexation of fourth Cl^- at 0.3 ionic strength.

Sol: Observe the data properly and use the rate constants to find equilibrium constant.

(A) Rate constant for forward reaction ⇒ $K_f = 3.0 \times 10^{-5}\ \text{sec}^{-1}$

Rate constant for backward reaction ⇒ $K_b = 1.1 \times 10^{-3}$ litre $\text{mol}^{-1}\ \text{sec}^{-1}$

(B) Equilibrium constant for the complexation of fourth Cl– is equilibrium, i.e. K_c for backward reaction is:

$$K_c = \frac{K_b}{K_f} = \frac{1.1 \times 10^{-3}}{3.0 \times 10^{-5}} = 36.66 \text{ litre mol}^{-1}$$

Illustration 4: Determine K_c for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2^2}Br(g) \rightleftharpoons NOBr(g)$ from the following data at 298 K.

The equilibrium constant 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 2.6×10^{30} and 1.2 respectively. **(JEE MAIN)**

Sol: Frame a net reaction for the formation of NOBr from the given data and apply K_c.

The net reaction is, $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br(g) \rightleftharpoons NOBr(g)$

Equilibrium constant is given by, $K_{C(net)} = \dfrac{[NOBr]}{[N_2]^{1/2}[O_2]^{1/2}[Br_2]^{1/2}}$

Considering the given equations:

$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; Equilibrium constant $= 2.6 \times 10^{30}$

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; Equilibrium constant $= \dfrac{1}{2.6 \times 10^{30}}$

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

Equilibrium constant $= \left(\dfrac{1}{2.6 \times 10^{30}}\right)^{1/2} = 6.2 \times 10^{-16}$

$$\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} = K_c' = 6.2 \times 10^{-16} \qquad \text{.... (i)}$$

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

$$\frac{[NOBr]}{[NO][Br_2]^{1/2}} = K_c^{''} = 1.2 \qquad \text{... (ii)}$$

Multiplying i and ii equations

$$\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} \times \frac{[NOBr]}{[NO][Br_2]^{1/2}} = K_c^{'} \times K_c^{''} = 6.2 \times 10^{-16} \times 1.2$$

or $$\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}[Br_2]^{1/2}} = K_{c(net)} = 7.68 \times 10^{-16}$$

6. EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

According to the Arrhenius equation, $k = Ae^{-E/RT}$ ... (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, $\log\left(\frac{k_{f_2}}{k_{f_1}}\right) = -\frac{E_f}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$ ... (iii)

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

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

$$\log\left(\frac{k_{f_2}/k_{b_2}}{k_{f_1}/k_{b_1}}\right) = -\frac{(E_f - E_b)}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{ or } \log\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (v)}$$

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 $T_2(T_2 > T_1)$. This equation is known as integrated form of van't Hoff isochore.

The differential form of van't Hoff isochore is: $\frac{d}{dt}\ln K_c = \frac{\Delta H}{RT^2}$ ... (12)

CONCEPTS

Equilibrium constants can change with temperature when the activation energies of forward and reverse reactions are different.

(Common misconception: Equilibrium constants are constant under all conditions.)

Aman Gour (JEE 2012, AIR 230)

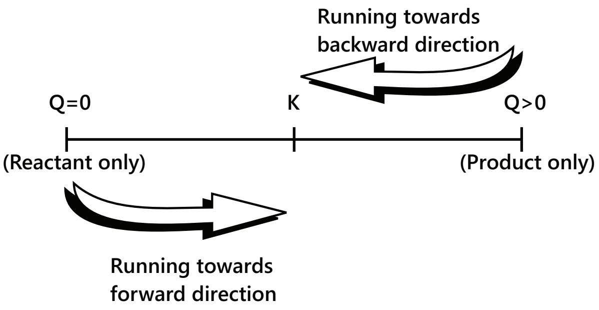


Figure 5.12: Relation between reaction quotient and equilibrium constant

7. REACTION QUOTIENT OR MASS ACTION RATIO

Table 5.2: Prediction of direction of reaction by using reaction quotient

Assume the reaction: A + B $\rightleftharpoons$ C + D	
$Q = \frac{[C][D]}{[A][B]}$	Q can be Q_c or Q_p Q_c = Concentration in moles/litre Q_p = Concentration in partial pressure
$Q_c = K_c$ or $Q_p = K_p$	Reaction attains equilibrium
$Q_c < K_c$ or $Q_p < K_p$	Forward reaction proceeds faster
$Q_c > K_c$ or $Q_p > K_p$	Backward reaction proceeds faster

Illustration 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 300°C. What will be the equilibrium constant at 500°C if heat of reaction in this temperature range is –25.14 kcal **(JEE MAIN)**

Sol: Apply $\log\frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$ i.e. the modified Arrhenius equation.

Given,

$K_{p1} = 1.0 \times 10^{-4}$;

$\Delta H = -22$ kcal

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

$T_1 = 300 + 273 = 573$ K,

$T_2 = 500 + 273 = 773$ K

Using the following relation, new equilibrium constant can be calculated.

Substituting the values,

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

$$\log\frac{K_{p_1}}{(1.0\times10^{-4})} = \frac{-22}{2.303\times2\times10^{-3}}\left[\frac{773-573}{773\times573}\right] = -4-2.1567=-6.1567$$

$K_{p_2} = 6.97 \times 10^{-7}$ atm^{-2}

Illustration 6: For the reaction, $A + B \rightleftharpoons 3C$ at 25°, a 3 litre vessel contains 1, 2, 5 moles of A, B and C respectively. Predict the direction of reaction if: (a) K_c for the reaction is 10; (b) K_c for the reaction is 20.83 **(JEE MAIN)**

Sol: Remember $\text{Concentration} = \dfrac{\text{no. of moles}}{\text{Volume}}$. Use this expression and calculate Q, reaction quotient. Compare with the given K_c and predict the direction.

$A + B \rightleftharpoons 3C$

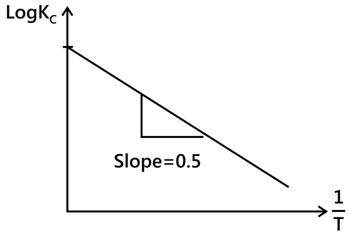
Before reaction, $[A]_0 = 1/3$

$$\text{Thus, } Q = \frac{[C]_0^3}{[A]_0[B]_0} = \frac{4^5 \times 3 \times 3}{3^3 \times 1 \times 2} = \frac{5^3}{3 \times 1 \times 2} = \frac{125}{6} = 20.83$$

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

(b) $Q = K_c$, thus reaction is in equilibrium

Illustration 7: A graph plotted between log10 K_c and 1/T is straight line with intercept 10 and slope equal to 0.5. **(JEE ADVANCED)**



Calculate:

(i) Pre-exponential factor A.

(ii) Heat of reaction at 298 K.

(iii) Equilibrium constant at 298 K.

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

Sol: Using the plotted graph and the graph related expressions, calculate the different parameters.

van't Hoff isochore is: $\log_{10}K = \log_{10}A - \dfrac{\Delta H}{2.303RT}$

(i) Thus, intercept = $\log_{10}A = 10$; $A = 10^{10}$

(ii) Also, slope = $\tan\theta = 0.5 = -\dfrac{\Delta H}{2.303R}$ $\quad \therefore \Delta H = -9.573\text{ks mol}$

(iii) Also, $\log_{10}K = 10 + \dfrac{2.303}{2.303 \times 2 \times 298}$; $K \simeq 1.0 \times 10^{10}$

Illustration 8: The following reaction has attained equilibrium $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, $\Delta H° = -92.0 \text{ kJ mol}^{-1}$ what will happen if

(i) Volume of the reaction vessel is suddenly reduced to half?

(ii) The partial pressure of hydrogen is suddenly doubled?

(iii) An inert gas is added to the system? **(JEE ADVANCED)**

Sol: Application of Le-Chatelier's principle and the use of Q_c will answer the conditions.

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2}, K_p = \frac{p_{CH_3OH}}{p_{CO} \times p_{H_2}^2}$$

(i) When volume of the vessel is reduced to half, the concentration of each reactant or product becomes double.

Thus, $Q_c = \dfrac{2[CH_3OH]}{2[CO]\times\{2[H_2]\}^2} = \dfrac{1}{4}K_c$

As $Q_C < K_c$, equilibrium will shift in the forward direction, producing more of CH_3OH to make QC = K_c.

(ii) As volume remains constant, molar concentrations will not change. Hence, there is no effect on the state of equilibrium.

8. STANDARD FREE ENERGY CHANGE OF A REACTION AND ITS EQUILIBRIUM CONSTANT

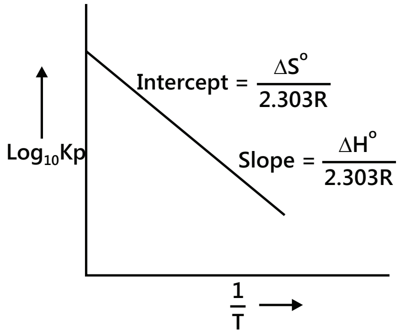
Energy is the driving force for reactions. The standard free energy of a substance represents the free energy change associated with the formation of the substance from the elements in their most stable forms as they exist under the standard conditions of 1 atm pressure and 298K.

ΔG° =Difference in free energy of the reaction when all the reactants and products are in the standard state (1 atmospheric pressure and 298 K)

K_c or K_p = 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 $\Delta G^o = -2.303\ RT \log K_p$ (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 Law 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.

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

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

CONCEPTS

(a) The catalyst never affects ΔG^o of the reaction at equilibrium.

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

(ii) If $\Delta G^\circ > 0$,(+ ve), then $K_c < 1$. So, reverse reaction is possible, i.e., less concentration of products of equilibrium state.

(iii) If $\Delta G^\circ < 0$, (– ve), then $K_c > 1$.

So, forward reaction is possible where a large concentration of products is observed till the point of equilibrium is attained.

(c) A negative ΔG° never indicates the complete transformation of the reactants into products. Similarly, a positive ΔG° does not indicate the absence of product formation.

Neeraj Toshniwal (JEE 2009, AIR 21)

Illustration 9: For the equilibrium, $N_2O_4 \rightleftharpoons 2NO_2$; $(G^{\circ}_{N_2O_4})_{298} = 150 kJ/mol$ and $(G^{\circ}_{NO_2})_{298} = 75 kJ/mol$

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

(B) Find the direction of reaction and concentrations at equilibrium. **(JEE MAIN)**

Sol: Use the expression relating Gibb's free energy and the equilibrium constant. By observing the sign of ΔG, direction of the reaction can be predicted. The same values will be used to calculate the concentrations.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
(A) Concentration at t = 0	5		5

$[G^{\circ}_{N_2O_4}]_{298K} = 100 kJmol^{-1}, [G^{\circ}_{NO_2}]_{298K} = 50 kJmol^{-1}$

ΔG° for reaction = $2 \times G^{\circ}_{NO_2} - G^{\circ}_{N_2O_4} = 2 \times 75 - 150 = 0$

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

$\Delta G = 0 + 2.303 \times 8.314 \times 10^{-3} \times 298 \times \log \frac{5^2}{5}$; $\Delta G = +3.99$ kJ

Since, ΔG = + ve and thus, reaction will not proceed in forward direction. It will take place in backward direction.

(B) Also for reverse reaction,

	$2NO_2$	$\rightleftharpoons$	N_2O_4
Conc. at t = 0	5		5
Conc. at equilibrium	$(5 - 2x)$		$(5 + x)$

At equilibrium, ΔG = 0; Also, ΔG° = 0

∴ From $\Delta G^{\circ} = -2.303\ RT \log K$; $K_c = 1$

Thus, $K_c = \frac{5+x}{(5-2x)^2} = 1$ ∴ x = 1.25

Thus, $[NO_2]_{at}$ eq.= 5 – 2.50 = 2.5 mol litre^{-1}

$[N_2O_4]_{at}$ eq. = 5 + 1.25 = 6.25 mol litre^{-1}

Illustration 10: Calculate K_p at 298 K for the gas-phase reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ from the following data. **(JEE MAIN)**

	CO	**H_2O**	**CO_2**	**H_2**
ΔH°f (kJ/mole)	–120.5	–241.8	–383.5	0
S° (J/mole. K)	177.6	188.7	215.6	130.4

Sol: According to the given reaction, calculate ΔH°f and ΔS° from the available data.Use it in the equation $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$. One gets ΔG°, through which one can calculate K_p by using the equation, $\Delta G^{\circ} = -2.303\ RT \log K_p$.

For the given reaction,

$\Delta H^{\circ} = [\Delta H^{\circ}_f(CO_2) + \Delta H^{\circ}_f(H_2)] - [\Delta H^{\circ}_f(CO) + \Delta H^{\circ}_f(H_2O)] = (-383.5 + 0) - (-120.5 - 241.8) = -21.2\ kJ = -21200$ J/mole.

$\Delta S^{\circ} = [S^{\circ}(CO_2) + H^{\circ}(H_2)] - [H^{\circ}(CO) + S^{\circ}(H_2O)] = (215.6 + 130.4) - (177.6 + 188.7) = -20.9$ J/mole.

Applying the thermodynamic equation,

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -21200 - 298 \times (-20.9) = -14978$ J.

Now, we have, $\Delta G^\circ = -2.\ 303\ RT \log K_p$

$-14978 = -2.303 \times 8.314 \times 298 \times \log K_p$

$\log K_p = 2.6254$

$\therefore K_p = 4.16 \times 10^2$

Illustration 11: The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g/litre at 288 K and 1.84 g/litre at 348 K. Calculate the enthalpy of reaction: $N_2O_4 \rightleftharpoons 2NO_2$. Also calculate the standard entropy change during the reaction at 348 K. **(JEE AVANCED)**

Sol: Use the density to calculate concentration; Arrhenius expression for enthalpy and free energy expression for entropy.

$N_2O_4 \rightleftharpoons 2NO_2\ ;\ PV = \frac{w}{m}RT$

$\therefore m_{mix} = \frac{w}{m}.RT = \frac{dRT}{P} = \frac{3.62}{1\,atm} \times 0.08 \times 288 = 85.69$. Let a mole N_2O_4 and (1 – a) mole of NO_2 exist at equilibrium

$\therefore a \times 82 + (1 - a) \times 46 = 85.6; \quad a = 0.86$

$\therefore [n_{N_2O_4}] = 0.86$ mole and $[n_{NO_2}] = 0.14$ mole

$$\therefore K_p = \frac{0.14 \times 0.14}{0.86} \times \left[\frac{1}{1}\right]^1 = 0.0228 \text{ atm at 288 K}$$

Case II: $m_{mix} = 1.84 \times 0.0821 \times 248 = 82.57$

Let a' mole of N_2O_4 and (1 – a') mole of NO_2 exist at equilibrium

$\therefore a' \times 92 + (1 - a') \times 46 = 52.57$

$\therefore a' = 0.14$

$\therefore [n_{N_2O_4}] = 0.14\ [n_{NO_2}] = 0.86$

$$\therefore K_p = \frac{0.86 \times 0.86}{0.14} \times \left[\frac{1}{1}\right]^1 = 5.283 \text{ atm at 348 K}$$

$$\text{Now, } 2.303 \log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^o}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\therefore 2.303 \log \frac{5.283}{0.0228} = \frac{\Delta H^o}{2} - \left[\frac{348 - 288}{348 \times 288}\right]$$

$\therefore \Delta H^\circ = 18195.6$ cal $= 18.196$ kcal

Also, $-\Delta G^\circ = 2.303 \times 2 \times 348 \times \log 5.283$

$\therefore \Delta G^\circ = -2.303 \times 2 \times 348 \times \log 5.283 = -1158.7$ cal $= -1.1587$ kcal

$$\therefore \Delta S^\circ = \frac{\Delta H^o - \Delta G^o}{T} = \frac{18196 + 1158.7}{348} = 55.62 \text{ cal}$$

9. APPLICATIONS OF LAW OF MASS ACTION

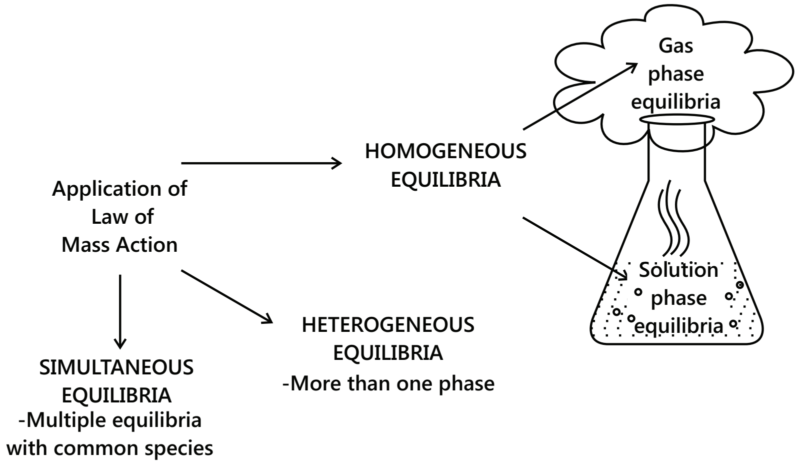


Figure 5.13: Application of law of mass action to different types of equilibria

9.1 Homogeneous Equilibria

These are of two types

(i) Gaseous phase equilibria: This type of equilibria involves following cases:

Table 5.3: Gaseous phase equilibria

Formation Equilibria							
Δn =0 [vol.='V' L]				Δn ≠0 [vol.='V' L]			
Cond.	No. of moles			Cond.	No. of moles		
	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$		$N_2(g)$	$+3H_2(g)$ $\rightleftharpoons$	$2NH_3(g)$
t = 0	a	b	0	t = 0	a	b	0
EQM	(a-x)	(b-x)	2x	EQM	(a-x)	(b-x)	2x
CONC.	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$	CONC.	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$
$K_c = \frac{4x^2}{(a-x)(b-x)}$				$K_c = \frac{4x^2V^2}{(a-x)(b-3x)^3}$			
Total Pressure of gases at eqm. = P_T				Eqm. Pressure = P Total moles at eqm.= (a-x)+(b – 3x) + 2x = a+ b -2x			
Partial pressure =Tot. pressure × Mole fraction (P_T) $K_P = \frac{\left[\frac{n_{HI}}{\sum n}\right]^2 \times P_T^2}{\left[\frac{n_{H2}}{\sum n}\right] \times P_T \times \left[\frac{n_{I_2}}{\sum n}\right] \times P_T} = \frac{(n_{HI})^2}{nH_2 \times n_{I_2}}$ $K_P = \frac{4x^2}{(a-x)(b-x)}$				$K_P = \frac{(n_{NH_3})^2}{n_{N_2}(n_{H_2})^3} \times \left[\frac{P}{\sum n}\right]^{-2}$ $= \frac{(2x)^2}{(a-x)(b-3x)^3}\left[\frac{P}{(a+b-2x)}\right]^{-2}$ $K_P = \frac{4x^2(a+b-2x)^2}{P^2(a-x)(b-3x)^3}$			

Dissociation Equilibria							
Δn = 0 [vol.='V' L]				Δn ≠0 [vol.='V' L]			
Cond.	No. of moles			Cond.	No. of moles		
	$2HI(g) \rightarrow H_2(g) + I_2(g)$				$NH_3(g) \longrightarrow N_2 + 3H_2(g)$		
t = 0	1	0	0	t = 0	1	0	0
EQM	(1-x)	x/2	x/2	EQM	(1-x)	x/2	x/2
	X= Degree of Dissociation				X= Degree of Dissociation		
CONC.	$\frac{(1-x)}{V}$	$\frac{x}{2V}$	$\frac{x}{2V}$	CONC.	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$
$K_c = \frac{x^2}{4(1-x)^2}$				$K_c = \frac{\frac{x}{2V}\left(\frac{3x}{2V}\right)^3}{\left(\frac{1-x}{V}\right)^2} = \frac{27x^4}{16V^2(1-x)^2}$			
Eqm. Pressure = P Total moles = (1- x) + x/2 + x/2=1				Eqm. Pressure =P Total moles = (1- x) + x/2 + 3x/2v			
$K_P = \frac{n_{H_2} \times \left(n_{I_2}\right)^3}{(n_{HI})^2} \times \left[\frac{P}{\Sigma n}\right]^{-2} = \frac{x^2}{4(1-x)^2}$				$K_P = \frac{n_{N_2} \times \left(n_{H_2}\right)^3}{(n_{NH_3})^2} \times \left[\frac{P}{\Sigma n}\right]^{-2} = \frac{\frac{x}{2} \times \left(\frac{3x}{2}\right)^3}{(1-x)^2} \times \left[\frac{P}{(1+x)}\right]^2$ $K_P = \frac{27 \times P^2}{16(1-x^2)^2}$			

(ii) Solution phase equilibria: Here, the reactants and products are in the solution/aqueous phase, represented as follows,

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

In such cases, only K_c exists.

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

9.2 Heterogeneous Equilibria

More than one phase existence is seen for the reactants and the products.

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

$$K_p = P'_{CO_2} = n_{CO_2} \times \left(\frac{P}{\Sigma n}\right)^1$$

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

The constants in the multiple phases

(a) Pure solids and pure liquids do not undergo any change in their concentration, along with the progress of the reaction.

(b) Thus, in heterogeneous equilibria, their concentration is considered as unity.

9.3 Simultaneous Equilibria

When all the products that are not inert but present in the reacting mixture cannot be expressed in terms of one equilibrium reaction, we must consider simultaneous equilibrium reactions are occurring. In such cases, thermodynamic conditions remains same for all the equilibrium system.

Illustration 12: There occurs following equilibria in one container. If 100 mole/litre of but-1-yne is taken in flask, calculate the value of K_{c_1}, K_{c_2} and K_{c_3}.

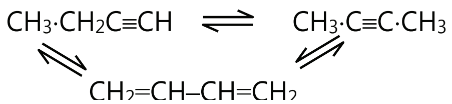
$CH_3.\ CH_2.\ C \equiv CH(g) \rightleftarrows CH_3C \equiv C.\ CH_3(g)\ ;\ K_{c_1}$

$CH_3.\ CH_2.\ C \equiv CH(g) \rightleftharpoons CH_2 = CH - CH = CH_2(g)\ ;\ K_{c_2}$

$CH_3.\ C \equiv C.\ CH_3(g) \rightleftharpoons CH_2 = CH - CH = CH_2(g)\ ;\ K_{c_3}$ **(JEE MAIN)**

Sol: Using the concentration of 100 mole/litre and the K_c expression, substitute the values.

The overall reaction may be written as



Let x mol/litre of 1,3-butadiene and y mole/litre of but-2-yne are formed then

$[CH_3CH_2.\ C \equiv CH] = 100 - x - y$

$[CH_3\ .\ C \equiv CH_3] = y$

$[CH_2 = CH - CH = CH_2] = x$

$$\therefore\ K_{c_1} = \frac{y}{100 - x - y}$$

Illustration 13: The equilibrium concentration of A, B and C for the reaction are $A \rightleftharpoons B + C$ 4.2, 2.1 and 2.1 moles/L respectively at 25°C. If 2 moles per-litre of A are removed, calculate the equilibrium concentration of A, B and C at the same temperature. **(JEE MAIN)**

Sol: Using the expression of K and the given number of moles, calculate the case after deduction of the concentrations.

For equilibrium:	A	$\rightleftharpoons$ B	+ C
Concentration at equilibrium	4.2	2.1	2.1

$$K = \frac{2.1 \times 2.1}{4.2} = 1.05$$

Now suppose the initial concentration is 'a' moles/L and ‘x’ moles/L of A changed to the products at equilibrium

conc. of A at eqb. = (a – x) = 4.2

and conc. of B or C at eqb = x = 2.1

∴ Initial conc. of A = a = (a – x) + x = 4.2 + 2.1 = 6.3 moles/L

Since 2 moles per litre of A are removed, the initial concentration of A will be (6.3 – 2) i. e., 4.3 moles per litre.

Suppose x' moles/L of a will change to the product when the new equilibrium is attained.

Initial concentration

$$\begin{array}{ccc} A & \rightleftharpoons B & +C \\ (4.3-x') & x' & x' \end{array}$$ Concentration at equilibrium

$\therefore\ K=\dfrac{x'\cdot x'}{4.3-x'}=1.05$ (K remains the same as the temperature is not change)

On solving, we get x' = 1.48

$\therefore$ At equilibrium,

[A] = 4.3 – 1.48 = 2.81 moles/litre

[B] = 1.48 moles/litre,

[C] = 1.48 moles/litre.

Illustration 14: A flask containing 0.50 atm of ammonia contains some solid NH_4HS which undergoes dissociation according to $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$. Calculate the pressure of NH_3 and H_2S at equilibrium (K_p = 0. 11). Also, calculate the total pressure. **(JEE ADVANCED)**

Sol: Apply law of mass action and using the partial pressure equation, calculate the total pressure. Since 1 mole of solid NH_4HS, on dissociation, produces 1 mole of NH_3 and 1 mole of H_2S, the partial pressure of NH_3 should be equal to that of H_2S if the flask contains no other substances. Let this be X atm.

But as the flask contains 0. 50 atm of NH_3 besides solid NH_4HS, the partial pressure of NH_3 will be (0.50 + X) atm.

Now, for the equilibrium, $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$K_p = p_{NH_3} \times p_{H_2S}$ As NH_4HS is solid, it includes the constant active mass of NH_4HS

0.11 = (0.5 + X) × X

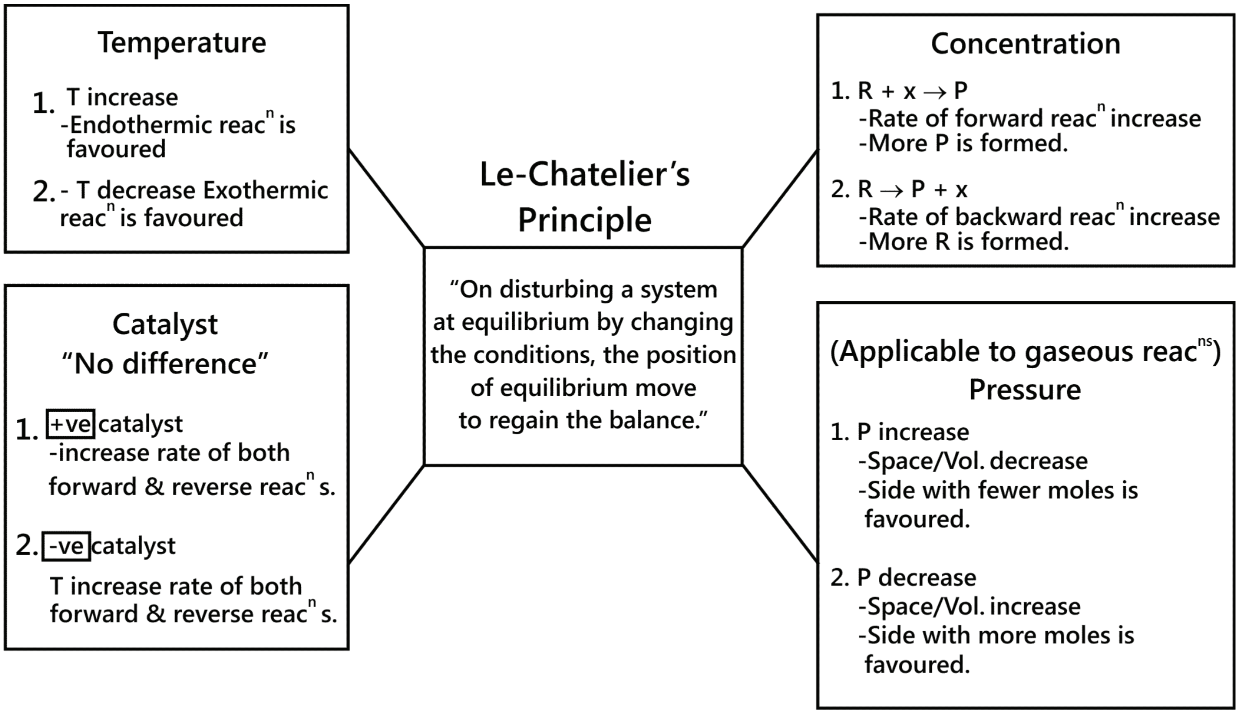
X = 0.17

$\therefore\ p_{NH_3} = 0.50 + 0.17 = 0.67$ atm

$p_{H_2S} = 0.17 atm$

Total pressure = $p_{NH_3} + p_{H_2S} = 0.84$ atm.

10. LE CHATELIER'S PRINCIPLE



Flowchart 5.1: Le-Chatelier's principle

CONCEPTS

- Equilibrium tends to oppose a change. (Misconception: The rate of the favoured reaction increases but the rate of the other reaction decreases.)
- Le Chatelier's Rule.

  (Misconception: Students sometimes have a hard time getting the idea that Le Chatelier's Rule is about perturbing an equilibrium state, driving the system to a new equilibrium state.)
- It doesn't matter how much of a solid is present when it is at equilibrium with a surrounding solution. The concentrations of the aqueous species will still end up being the same. (Misconception: Students usually think that if you add more solid, the equilibrium concentrations of the aqueous species will go up. This is a misapplication of Le Chatelier's Rule.)

Effect of adding an inert gas

An inert gas (or noble gas) such as helium is one that does not react with other elements or compounds. At constant volume, addition of this inert gas does not affect the equilibrium.

According to Dalton's law, the partial pressures of the other gases remains same, which itself is the reason for the unchanged equilibrium.

But on increasing the volume, the partial pressures of all gases would decrease, resulting in a shift towards the side with the greater number of moles of gas.

CONCEPTS

Table 5.4: Summary of Le chateliers Rule

Conditions	Forward Direction	No Effect	Backward Direction
$\Delta v = 0$ $v = \text{constant}$	×	✓ $\Delta v = 0$ $= +$ $= -$	×
$\Delta v \neq 0$ $v \neq \text{constant}$ Δn = (no. of gaseous moles of product) — (no. of gaseous moles of reat.)	×	✓ $\Delta v = 0$	×
	✓ $\Delta v = 0$	×	×
	×	×	$\Delta v < 0$

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

Table 5.5: Effect of temperature and pressure

Nature of Reaction	Effect of ↑ T	Δn	Side with fewer mole	Effect of ↑ P
Exothermic	Backward Shift	0	Neither	No Shift
		–ve	Right	Forward
		+ve	Left	Backward
		–ve	Right	Forward
Endothermic	Forward Shift	–ve	Right	Forward
		+ve	Left	Forward
		0	Neither	No Shift

Systems will tend to attain a state of lower potential energy i.e. enthalpy if nothing else is acting upon them. A chemical reaction will always favour the side (reactants or products) with minimum enthalpy if no other factors are considered.

Saurabh Gupta (JEE 2010, AIR 443)

10.1 Applications of Le Chatelier's Principle to Physical Equilibrium

(a) Effect of Pressure on Boiling Point: Water $\rightleftharpoons$ vapour; An increases in pressure will favour backward reaction, i.e., the reaction in which volume decreases ($V_{vapour} > V_w$). Thus more water will exist at equilibrium, i.e., boiling point of water (solvent) increases with increases in pressure.

(b) Effect of Pressure on Melting Points

(i) For, Ice $\rightleftharpoons$ water equilibrium: An increase in pressure will favour forward reaction because V_{ice} is greater then V_{water}. Thus, more and more ice will melt or the m. pt. of ice is lowered with increases in pressure.

(ii) For, solid $\rightleftharpoons$ liquid equilibrium: An increases in pressure will favour backward reaction because $V_{(l)} > V_{(s)}$ and thus, more solid will exist at equilibrium, i.e., m. pt. of solid increases with increases in pressure.

(c) Effect of Pressure on Solubility of Gases: Gas + Solvent $\rightleftharpoons$ Solution (and $V_f > V_b$) where, V_f is volume of left hand side components and V_b is volume of right hand side components.

An increase in pressure will favour forward reaction and thus, solubility of gas increases with increase in pressure. Dissolution of water soluble gas in water is always exothermic (ΔH = – ve) and spontaneous (ΔG=–ve). It is thus evident form $\Delta G = \Delta H - T\Delta S$, that ΔS will be – ve or entropy decreases on dissolution or if ΔS = + ve then $T\Delta S < \Delta H$.

(d) Effect of Temperature on Solubility of Solids

(i) Solute + Solvent $\rightleftharpoons$ Solution ; ΔH = -ve

An increases in temperature always favours endothermic process and thus, solute having endothermic dissolution (e.g., urea, glucose) show an increases in their solubility with temperature, e.g., urea, glucose.

(ii) Solute + Solvent $\rightleftharpoons$ Solution ; ΔH = + ve

Accordingly, solute having exothermic dissolution (e.g., lime, acids) show a decrease in their solubility with temperature.

CONCEPTS

- The critical temperature and critical pressure for liquid H_2O, i. e., water is 647.15 K and 218 atm respectively. Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Vapour

  These three phases exist in equilibrium at a point called as triple point of water seen at 0.0098° C and 4.58 mm pressure.
- A solid-solid heterogeneous system cannot be studied using Le Chatelier's principle.
- Heat absorption takes place when hydrated salts like $CuSO_4 . 5H_2O$, $CH_2O . 6H_2O$ are dissolved in water i.e. , ΔH_{sol} = + ve.
- An exceptional case of NaOH whose solubility increases with temperature but expels out heat.

Neeraj Toshniwal (JEE 2009, AIR)

11. CALCULATION OF DEGREE OF DISSOCIATION

Definition: Defined as the fraction of one molecule dissociated.

Expressed as: x or α having a value always less than 1. Complete dissociation is achieved when the value becomes 1.

General Reversible Reaction

$$A \rightleftharpoons nB$$

Initial moles	1	0
Equilibrium moles	(1 –x)	nx
Conc.	$\frac{1-x}{v}$	$\frac{nx}{v}$

Total no. of moles = 1 – x + nx

= 1 + x(n -1)

$$D \alpha \frac{1}{v}$$

D = vapour density when no dissociation occurs

$$d \alpha \frac{1}{[1+(n-1)x]v}$$

d = vapour density when

x = degree of dissociation

Dividing the above equations,

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

$x=\frac{M-m}{(n-1)m}$ where, M = initial molecular mass and m = molecular mass at equilibrium

Calculation of Degree of Reaction Using Pressure-Temperature Determination

Consider the following gaseous reaction:

P_1 = Initial pressure	At equilibrium,
T_1 = Initial temperature	Pressure = P_2
Volume of vessel = 'V'	Temperature = T_2

	PCl_5 (g) $\rightleftharpoons$	PCl_3 (g)	Cl_2 (g)
t=0	a	0	0
t=eq.	a-ax	ax	ax

Initial $P_1V = aRt_1$ state

equilibrium

State $P_2V = (a + ax)\,RT_2$

Dividing the above equations, we get

$$\frac{P_1}{P_2}=\frac{T_1}{(1+x)T_2} \qquad (1+x)=\frac{P_2T_1}{P_1T_2} \Rightarrow x=\frac{P_2T_1-P_1T_2}{P_1T_2}$$

Illustration 15: $2N_2O(g) + O_2(g) \rightleftharpoons 4NO\,(g)\,;\ \Delta H > 0.$

What will be the effect on equilibrium when **(JEE ADVANCED)**

(A) Volume of the vessel increases? (B) Temperature decreases? **[AIPMT 2008]**

Sol: Apply Le-Chatelier's principle.

(A) For the given reaction, $K = \frac{[NO]^4}{[N_2O]^2[O_2]}$

- When volume of the vessel increases, number of moles per unit volume (i. e. molar concentration) of each reactant and product decreases. As there are 4 concentration terms in the numerator but 3 concentration terms in the denominator, to keep K constant, the decrease in [N2O] and [O2] should be more i. e. , equilibrium will shift in the forward direction.
- Alternatively, increases in volume of the vessel means decreases in pressure. As forward reaction is accompanied by increases in the number of moles (i. e., increase of pressure) decreases in pressure will favour forward reaction (according to Le Chatelier's principle.).

(B) As ΔH is + ve, i. e., reaction is endothermic, decrease of temperature will favour direction in which heat is absorbed, i. e., backward direction.

Illustration 16: The vapour density (hydrogen = 1) of a mixture containing NO_2 and N_2O_4 is 35.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 grams of the mixture. **(JEE ADVANCED) [MLNR 1993]**

Sol: Use vapour density to calculate molar mass and then calculate the individual concentration of the species.

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

$$x\ (\text{degree of dissociation}) = \frac{D-d}{(n-1)d}$$

Given, d = 35.3, D = $\frac{\text{Mol. mass of } N_2O_4}{2} = \frac{92}{2} = 46, n = 2$; So $x = \frac{46-35.3}{35.3} = 0.303$

At equilibrium, amount of N_2O_4 =1 – 0.308 = 0.70 mol and amount of NO_2 = 2 × 0.308 = 0.606 mol

Mass of mixture = 0.7 × 92 + 0.606 × 46 = 64.4 × 27.9 = 92.3 g

Since, 92.3 gram of the mixture contains = 0.606 mol NO_2

So, 100 gram of the mixture contains = $\frac{0.606 \times 100}{92.3} \approx 0.65$ mole NO_2

Illustration 17: 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. **(JEE MAIN)**

(A) Calculate K_c and K_p for the reaction at 27°C.

(B) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

Sol: Use the stepwise calculation of the concentration of the reacting species following the decomposition and apply Le-Chatelier's principle.

$$\begin{array}{llccc} & & NH_4HS(s) \rightleftharpoons & NH_3(s) \ + & H_2S(g) \\ \text{(A)} & \text{Initial amt} & 3.06g = 3.06/51\text{mole} = 0.06\text{mole} & & \\ & \text{At eqm} & 0.06 - \frac{30}{100} \times 0.06 & 0.018\text{ mole} & 0.018\text{ mole} \\ & & = 0.06 - 0.018 & & \\ & & = 0.042\text{mole} & & \end{array}$$

$$\begin{array}{lccc} & NH_4HS(s) \rightleftharpoons & NH_3(s)\ + & H_2S(g) \\ \text{Eqm. conc.} & 1 & 0.018/2 & 0.018/2 \\ \text{(being solid)} & & = 0.009 & = 0.009\text{molL}^{-1} \end{array}$$

$$K_c = \frac{[NH_3][H_2S]}{[NH_4HS]} = \frac{0.009 \times 0.009}{1} = 8.1 \times 10^{-5} \left(\left[NH_4HS(s)\right] = 1\right)$$

$$K_p = K_c(RT)^{\Delta n_g} = 8.1 \times 10^{-5} \times (0.082 \times 500)^2 = 40.5 \qquad (\Delta n_g = 2 - 0 = 2)$$

(B) As K_c = $[NH_3]$ $[H_2S]$ and does not depend upon the amount of $NH_4HS(s)$, hence there will be no effect on equilibrium when more solid NH_4HS is added.

Illustration 18: Ammonium carbamate when heated to 200°C gives a mixture of NH_3 and CO_2 vapours with a density of 15.0. What is the degree of dissociation of ammonium carbonate?

(a) 3/2 (b) 1/2 (c) 2 (d) 1 (e) 5/2 **(JEE MAIN)**

Sol: Write down the decomposition of ammonium carbamate, noting down the dissociated values of the reacting species. Using the vapour density, calculate degree of dissociation.

$$\begin{array}{lccc} & NH_2COONH_4 & \longrightarrow & 2NH_3 + CO_2 \\ \text{Initial 1 mole, After disso.} & 1-\alpha & & 2\alpha \quad \alpha \\ \text{Total} = 1+2\alpha & & & \end{array}$$

$$\text{Theoretical density (D)} \propto \frac{1}{v};\ \text{Observed density (d)} \propto \frac{1}{(1+2\alpha)V} \quad \therefore \frac{D}{d} = 1+2\alpha \text{ or } \alpha = \frac{1}{2}\left(\frac{D-d}{d}\right) = \frac{1}{2}\left(\frac{48-15.0}{15.0}\right) = 1.1$$

PROBLEM-SOLVING TACTICS

(a) The equilibrium constant expression depends on the stoichiometry of the balanced reaction.

Table 5.6: Variation of Equilibrium Constant with Stoichiometric Coefficient

When the equation is	The new Equilibrium constant is
Reversed	1/K
Divided by 2	$\sqrt{K}$
Multiplied by 2	K^2
Divided into 2 steps	$K = K_1 \times K_2$

Case I: If $\Delta n(g) = 0$, $K_p = K_c$

Case II: If $\Delta n(g) = +ve$, $K_p > K_c$

Case III: If $\Delta n(g) = -ve$, $K_p < K_c$

Retain in Memory

For Δn, count only the gaseous species.

Δn may be positive, negative, zero, integer or a fraction. If $\Delta n = 0$, $K_p = K_c$.

Units of K_p and K_c

Unit of K_p = (unit of pressure)$^{\Delta n}$

Unit of K_c = (unit of concentration)$^{\Delta n}$

If $\Delta n = 0$; K_p or K_c have no units.

(b) If the partial pressures are taken in atmospheres, the value of R to be used in the above equation will be 0.0821 litre atmospheres/degree/mole. Temperature T will, of course be in degree Kelvin (K). If pressure is expressed in bars, R = 0.0831 litre bar K^{-1} mol^{-1}. (1 bar = 10^5 Pa = 10^5 Nm^{-2} = 0.987 atm). If the given value of K_p or K_c is dimensionless, use R = 0.0831 L bar K^{-1} mol^{-1}.

(c) Effect of temperature on equilibrium constant:

Case I: If $\Delta H = 0$, i.e. neither heat is evolved nor

absorbed, then $2.303\log_{10}\left(\frac{K_2}{K_1}\right) = 0$ or $\frac{K_2}{K_1} = 1$ or $K_2 = K_1$

i.e. equilibrium constant remains same at different temperature.

Case II: If ΔH = +ve, i.e., heat is absorbed during the course of reaction, then

$$2.303 \log \left(\frac{K_2}{K_1}\right) = +\text{ve} \quad \text{or} \quad \log K_2 > \log K_1 \text{ or } K_2 > K_1$$

i. e. , equilibrium constant increases with increase in temperature.

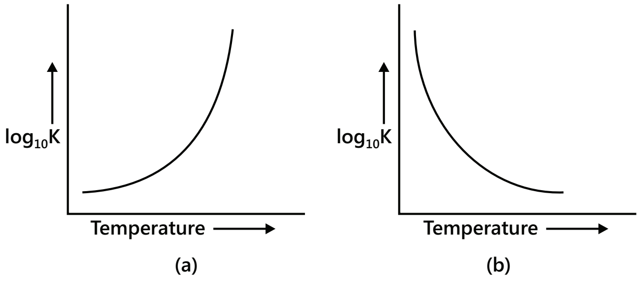


Figure 5.14: Plots of log K versus T
(a) Endothermic reaction (b) Exothermic reaction

Case III: If ΔH = – ve, i.e.heat is evolved during the course of reaction, then

$$2.303 \log \left(\frac{K_2}{K_1}\right) = -\text{ve} \quad \text{or} \quad \log K_2 < \log K_1 \text{ or } K_2 < K_1$$

i.e., equilibrium constant decreases with increase in temperature.

POINTS TO REMEMBER

Effect of adding an inert gas:

- An inert gas (or noble gas) such as helium is one that does not react with other elements or compounds. At constant volume, addition of this inert gas does not affect the equilibrium.
- According to Dalton's law, the partial pressures of the other gases remains same, which itself is the reason for the unchanged equilibrium.
- But on increasing the volume, the partial pressures of all gases would decrease, resulting in a shift towards the side with the greater number of moles of gas.

Factors affecting the state of Equilibrium

Conditions	**Shifts the Equilibrium**
Increase in concentration of reactants	Forward direction
Increase in concentration of any product	Backward direction
Increase in temperature	In direction of endothermic reaction
Decrease in temperature	Direction of exothermic reaction
Increase in pressure	In direction of less number of gaseous moles
Decrease in pressure	In direction of large number of moles

Effect of temperature and Pressure :

Nature of Reaction	**Effect of increase in T**	Δn	**Side with fewer mole**	**Side with fewer mole**	**Effect of increase on P**
Exothermic concentration of reactants	Backward shift	0	Neither	neither	No shift
		-ve	Right	Forward	Forward
		+ve	Left	Backward	Backward
		-ve	Right	Forward	Forward
Endothermic concentration of any product	Forward shift	-ve	Right	Right	Forward
		+ve	Left	Forward	Forward
		0	Neither	No Shift	No shift

SOLVED EXAMPLES

JEE Main/Boards

Example 1: A 10.0 litre vessel contains 2 moles of B at 100 K. How many moles of C should be added to drive the following backward reaction practically to completion?

$$A(s) \rightleftharpoons B(s) + 2C(g)\ ;\ K_p = 16\ atm^2$$

Sol: Using the given K_p, calculate the partial pressure of gas C and use it to get the no. of moles. Using the reaction, moles of C can be found.

$K_p = [p_c]^2 = 16$; $P_c = 4$ atm

Using ideal gas equation, for C,

pV = nRT

$4 \times 10 = n_c \times 0.0821 \times 100$

$$n_c = \frac{0.0821 \times 100}{4 \times 10}$$

$n_c = 4.\ 872$ moles

By looking at the given equation, stoichiometry for B and C should be in the ration 1:2

Thus 2 moles of B shall combine with 4 moles of C to give back A.

In order to drive the backward reaction almost to completion total number of moles required will be = 4.872 + 4 = 8.872

Example 2: (a) For which of the following reactions, K_p is equal to K_c?

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

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

(iii) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Sol: Use equation $K_p = K_c(RT)^{\Delta n}$ to solve the above.

In order to calculate K_p, we have to use the formula, $K_p = K_c(RT)^{\Delta n}$

For reaction $H_2 + I_2 \rightleftharpoons 2HI$ only $\Delta n = 2 - 2 = 0$

For this reaction $(RT)^{\Delta n} = 0$

Thus $K_p = K_c$

Example 3: For which of the following cases does the reaction go farthest to completion:

$K = 1$, $K = 10^{10}$, $K = 10^{-10}$?

Sol: More the value of the ratio of [product]/[reactant], farther the reaction will go.

The reaction having $K=10^{10}$ will go farthest to completion because the ratio [product]/[reactant] is maximum in this case.

Example 4: Both metal Mg and Fe can reduce the metal copper from a solution having copper ions (Cu^{2+}), according to the equilibria:

$$Mg(s) + Cu^{2+} \rightleftharpoons Mg^{2+} + Cu(s)\ ;\ K_1 = 6 \times 10^{90}$$

$$Fe(s) + Cu^{2+} \rightleftharpoons Fe^{2+} + Cu(s);\ K_2 = 3 \times 10^{26}$$

Which metal will remove cupric ions from the solution to a greater extent?

Sol:

- As we know greater the value of K forward reaction is more feasible.
- Since $K_1 > K_2$, the product in the first reaction is much more favoured than in the second one.
- Mg thus removes more Cu^{2+} from solution than does Fe.

(K_1 and K_2 include the constant concentration of the solid species.)

Example 5: Two moles of PCl_5 were heated to 327ºC in a closed two litre vessel and when equilibrium was achieved, PCl_5 was found to be 40% dissociated into PCl_3 and Cl_2. Calculate the equilibrium constants K_p and K_c for this reaction,

Sol: Amount of reacting species and the product can be calculated and then apply the 40% dissociation. Accordingly solve K_p and K_c by using $K_p = K_c(RT)^{\Delta n}$

Reaction for dissociation of PCl_5:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Given: Amount of PCl_5 (initially) = 2 moles

Percentage dissociation at equilibrium = 40%

∴ No. of moles of PCI5 dissociated at equilibrium

$$= \frac{40}{100} \times 2 = 0.8\ \text{mole}$$

∴ Amounts of PCl_5, PCl_3 and Cl_2 at equilibrium will be

PCl_5 = 2 – 0.8 = 1.2 mole

[From the reaction, 1 mole of PCl_5 on dissociation gives 1 mole of PCl_3 and 1 mole of Cl_2]

∴ PCl_3 = 0.8 mole

∴ Cl = 0.8 mole

In order to calculate K_c we have to calculate molar concentration of reactant and product at equilibrium.

(Given: volume of vessel = 2 litre)

Thus,

$$[PCl_5] = \frac{1.2}{2} = 0.6\,molL^{-1},$$

$$[PCl_3] = \frac{0.8}{2} = 0.4\,molL^{-1}$$

And $[Cl_2] = \frac{0.8}{2} = 0.4\,molL^{-1}$

Applying the law of chemical equilibrium to the dissociation equilibrium, we get

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.4molL^{-1} \times 0.4\,molL^{-1}}{0.6\,molL^{-1}}$$

$K_c = 0.267$ mole L^{-1}

As we have calculated the value of K_c we can now calculate value of K_p using the following equation.

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

Now, $\Delta n = n_p = n_r = 2 – 1 = 1$ mole

∴ $K_p = K_c(RT)$

T = 327 + 273 = 600 K

R = 0.0821 L atm K^{-1} mol^{-1}

∴ K_p = 0.267mol L^{-1} × 0.0821 L atm $K^{-1}mol^{-1}$ × 600 K = 13.15 atm

Example 6: AB_2 dissociates as: $AB_2(g) \rightleftharpoons AB(g) + B(g)$.

If the initial pressure is 500 mm of Hg and the total pressure at equilibrium is 700 mm of Hg, calculate K_p for the reaction.

Sol: Using partial pressure concepts in the given reaction, calculate the partial pressure and then apply K_p expression.

After dissociation, suppose the decreases in the pressure of AB_2 at equilibrium is p mm. Then

$$\begin{array}{llll} \text{Initially at equil} & AB_{2(g)} \rightleftarrows & AB_{(g)} & +B_{(g)} \\ & 500 & 0 & 0 \\ & 500-P & P & P \end{array}$$

$$PT = 500 - P + P + P = 500 + P$$

$$\therefore 700 = 500 + P \therefore P = 200\ MM$$

$$\therefore P_{AB_2} = 500 - 200 = 300\ mm$$

$$\therefore K_p = \frac{P_{AB} \times P_B}{P_{AB_2}} = \frac{200 \times 200}{300} = 133.33\ mm$$

Example 7: The degree of dissociation of PCl_5 at a certain temperature and pressure is 0.2. Calculate the pressure at which it will be half (50%) dissociated at the same temperature.

Sol: Using the reaction and the given degree of dissociation, frame the partial pressure equations and solve by using K_p.

Suppose α is the degree of dissociation, then

$$\begin{array}{llll} & PCl_5 \rightleftharpoons & PCl_3 & +Cl_2 \\ \text{Initial conc.} & 1\text{mole} & 0 & 0 \\ \text{At. Equilibrium} & 1-\alpha & \alpha & \alpha \end{array}$$

∴ Total number of moles at equilibrium

= 1 – α + α + α = 1 + α

If P is the total pressure at equilibrium, then partial pressures will be

$$p_{PCl_3} = \frac{\alpha}{1+\alpha}P,\quad p_{Cl_2} = \frac{\alpha}{1+\alpha}P,$$

$$p_{PCl_5} = \frac{1-\alpha}{1+\alpha}P\ ;\ K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

Substituting the values in above equation,

$$= \frac{\left(\frac{\alpha}{1+\alpha}P\right) \times \left(\frac{\alpha}{1+\alpha}P\right)}{\left(\frac{1-\alpha}{1+\alpha}.P\right)}$$

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

We are given that at P = 1 atm, a = 0. 2.

$$\text{Hence, } K_p = \frac{(0.2)^2}{1-(0.2)^2} \times 1 \ \therefore K_p = 0.042$$

At 50%, dissociation i. e. α = 0.5,

Suppose total pressure is P'. Then

$$A(g)+2B(g)\longrightarrow C(g)$$

$$0.042=\frac{(0.5)^2}{1-(0.5)^2}\times p$$

P' = 0.1272 atm

Example 8: A vessel at 1000 K contains carbon dioxide with a pressure of 0.4 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K if the total pressure at equilibrium is 0.7 atm.

Sol: Frame the reaction. Using the total pressure and the partial pressure concept, solve for K. The chemical reaction for the above transformation is:

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

Suppose decrease in pressure of CO_2 after reaction = p atm

Final pressure = 0.7

Then increase in pressure due to CO = 2 p

Final pressure=(0.4 – p)+2p = 0.4+p= 0.7 atm

∴ p = 0.3 atm. Hence, we have

$$p_{CO_2}=0.4-0.3=0.1\text{ atm}$$

p_{CO} = 2 × 0.3 = 0.6 atm

$$K=\frac{p_{CO}^2}{p_{CO_2}^2}=\frac{(0.6)^2}{0.1}=3.6$$

Example 9: Two solids A and C dissociate into gas products as follows;

$A(s) \rightleftharpoons B(g) + D(g)$; K_{p_1} = 400

$C(s) \rightleftharpoons E(g) + D(g)$; K_{p_2} = 900

At 25° C, the pressure over excess solid A only is 400 atm, and that over solid C only is 60 atm. Find the pressure over solid mixture.

Sol: Arrange the stepwise conversion and using the given values of K_p, frame for partial pressure and solve for solid mixture pressure.

- When two solids A and C are taken together in a closed container, both decompose to give gases B, D and E.
- As D is the common gas, the dissociation of both the solids A and C shall be suppressed.
- Suppose that the partial pressures of B and D due to dissociation of only A are p_1 atm each, and the partial pressures of E and D due to dissociation of only C are p_2 atm each.

$A(s) \rightleftharpoons B(g) + D(g)$; $K_{p_1} = 400\ p_1p_1$

$C(s) \rightleftharpoons E(g) + D(g)$; $K_{p_2} = 900\ p_2p_2$

$K_{p_1} = p_B \cdot p_D = p_1(p_1 + p_2) = 400$ . . . (i)

and $K_{p_2} = p_E \cdot p_D = p_2(p_1 + p_2) = 900$ . . . (ii)

Solving equation. (1) and (2),

p_1 = 11.097 and p_2 = 24.96 atm.

∴ pressure over solid mixture = $2(p_1 + p_2)$

= 2(11.097 + 24.96) = 72.114 atm.

Example 10: The equilibrium constant of the reaction, $H_2(g)+I_2(g)\rightleftharpoons 2HI(g)$ at 426° C is 65.5, what will be the value of the equilibrium constant

(a) if the reaction is reversed, and

(b) if the given reaction is represented as

$3H_2 + 3I_2 \rightleftharpoons 6HI$?

Sol: Using 1/K and $(K)^n$, solve the above.

(a) The reverse reaction of the given reaction is

$2HI \rightleftharpoons H_2 + I_2$

(**Remember:** If the reaction is reversed equilibrium constant is given by 1/ k)

$$\therefore \text{ Equilibrium constant} = \frac{1}{65.5} = 0.0152$$

(b) The reaction $3H_2 + 3I_2 \rightleftharpoons 6HI$ has been obtained by multiplying the reaction $H_2 + I_2 \rightleftharpoons 2HI$ by 3.

(**Remember:** if the reaction is multiplied by n,

then equilibrium constant = $(K)^n$)

Hence, K = $(65.5)^3$ =281011.

Example 11: A mixture of 1. 62 mol of N_2, 1.20 mol of H_2 and 9.24 mole of NH_3 is introduced into a 20 L reaction vessel at 500K. At this temperature, the equilibrium constant, K_c for the reaction, $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$ is 1.7×10^2.

Predict the direction of reaction.

Sol: Calculate the concentration of each species in the reaction and then solve for Q_c.

For a general reaction $aA + bB \rightleftharpoons cC + dD$

$$\begin{array}{ccccc} N_2(g) & + & 3H_2(g) & \rightleftharpoons & 2NH_3(g) \\ \frac{1.62}{20} & & \frac{1.20}{20} & & \frac{9.24}{20} \end{array}$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{(0.462)^2}{(0.081)(0.08)^3} = 4.9\times10^3$$

For the given reaction, K_c

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is $= 1.7\times10^2$

As $Q_c > K_c$, the net reaction will be in the backward direction.

Example 12: What is the effect of reducing the volume on the system described below?

$$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$$

Sol:

- This can be explained on the basis of Le Chatelier's principle.
- On reducing the volume, the pressure will increase.
- By Le Chatelier's principle equilibrium will shift to the side accompanied by decrease of pressure, i.e. decrease in the number of gaseous moles, i.e. backward direction.

Example 13: In the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at equilibrium, helium gas is injected into the vessel without disturbing the overall pressure of the system. What will be the effect on the equilibrium?

Sol: Application of Le-Chatelier's principle.

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

- Since pressure is kept constant, volume will increase.
- Hence, molar concentration of NH_3, N_2 and H_2 will decrease.
- As there are two concentration terms in numerator and four concentration terms in the denominator, to keep K_c constant, decrease in NH_3 should be more, i.e., equilibrium will shift in the backward direction.

Example 14: A liquid is in equilibrium with its vapour in a sealed container at fixed temperature. The volume of the container is suddenly increased.

(a) What is the initial effect of the change on vapour pressure?

(b) How do rates of evaporation and condensation change initially?

(c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

Sol: (a) As volume is increased, the vapour pressure will decrease because the same amount of vapour are now distributed in larger space. Number of molecules striking the wall of container decreases and thus pressure decreases.

(b) As the vessel is sealed, the rate of evaporation remains constant at constant temperature. However, the rate of condensation will be low initially because there are fewer molecules per unit volume in the vapour phase and hence the number of collisions per unit time with the liquid surface decreases.

(c) When equilibrium is restored, Rate of evaporation = rate of condensation. The final vapour pressure =Initial pressure because vapour pressure of a liquid depends only on temperature and not volume.

Example 15: The following system is in equilibrium:

$$SO_2Cl_2 + \text{Heat} \rightleftharpoons SO_2 + Cl_2$$

What will happen to the temperature of the system if some Cl_2 is added into it at constant volume?

Sol: Temperature will increase. Backward direction will be more feasible. Thus equilibrium will shift in the backward direction producing more heat.

Example 16: Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression.

Sol: This can be explained by considering density of pure solid or pure liquid.

$$[\text{Pure liquid}] \text{ or } [\text{Pure solid}] = \frac{\text{No. of moles}}{\text{Volume in L}}$$

$$\text{No of moles= Mass/ Mol. Mass} = \frac{\text{Mass / mol.mass}}{\text{Volume}}$$

$$= \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Mol.mass}} = \frac{\text{Density}}{\text{Mol.mass}}$$

- Density of a pure liquid or pure solid is constant at constant temperature and molecular mass is also constant, therefore, their molar concentrations are constant and are ignored into the equilibrium constant.

JEE Advanced/Boards

Example 1: One mole of nitrogen is mixed with 3 moles of hydrogen in 4-litre container. If 0.50 % 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_c for the following equilibrium? $\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

Sol: Using the reaction, calculate equilibrium concentration and K_c. Apply the formula for the next reaction and solve the new K_c.

	N_2		$3H_2$	$\rightleftharpoons$	$NH_3(g)$
Initial moles	1	+	3		0
Moles at equilibrium	$(1-0.0050)$		$(3-0.0050)$		(2×0.0050)
Molar concentration at equilibrium	$\frac{0.9950}{4}$		$\frac{2.9950}{4}$		$\frac{0.01}{4}$

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

$$=\frac{\left(\frac{0.01}{4}\right)^2}{\left(\frac{0.9950}{4}\right)\left(\frac{2.9950}{4}\right)^3}\frac{6.25x10^{-6}}{(0.2487)x(0.1044)}$$

$$=6.0\times10^{-5}(mol/L)^{-2}$$

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

We can see that the above reaction has been obtained by multiplying the equation

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

Thus, the new equilibrium constant = $(6.0 \times 10^{-5})^{1/2}$

K_c = 7.7x 10-3$(mole/litre)^{-1}$

Example 2: Would 1% CO_2 in the air be sufficient to prevent any loss in weight when Ag_2CO_3 is dried at 120°C? $Ag_2CO_3(s)$ is dried at 120°C? $Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$; kp = 0. 0095 at 120°C. How low would the partial pressure of CO_2 have to be to promote this reaction at 120°C?

Sol: $K_p=\frac{p_{Ag_2O}\times p_{CO_2}}{p_{Ag_2CO_3}}=p_{CO_2}$

$\therefore\ p_{CO_2}=0.0095\,atm$ = constant at 120°C.

- Thus, if Ag_2CO_3 is taken in a closed container, a small amount of it would decompose to give CO_2 gas until the partial pressure of CO_2 reaches 0.0095 atm.
- As this is the equilibrium pressure of CO_2, the decomposition would then stop.
- Now since partial pressure of CO_2 in air is 0.01 atm ($\because$ CO_2 is 1% in air) which is much greater than 0. 0095 atm, the equilibrium would practically shift to the left-hand side completely, or in other words, there would be no loss in weight of Ag_2CO_3 (by decomposition) if placed in air containing 1% CO_2.
- Further, if the partial pressure of CO_2 in air is less than the equilibrium pressure of 0.0095 atm, the decomposition of Ag_2CO_3 would continue till the CO_2 pressure around Ag_2CO_3 becomes 0.0095 atm.

Example 3: In the preparation of quick lime from limestone, the reaction is

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

Experiments carried out between 850°C and 950°C led to a set of K_p values fitting an empirical equation

$\log K_p = 7.282 - \frac{8500}{T}$

where T is the absolute temperature. If the reaction is carried out in quiet air, what temperature would be predicted from this equation for complete decomposition of the limestone?

Sol: For the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_p = p_{CO_2}$

the decomposition of $CaCO_3$ in quiet air, would continue till the pressure developed due to CO_2 equals 1 atm (atmospheric pressure).

$\therefore$ when the decomposition is complete K_p = 1atm

Substituting K_p in the given empirical equation,

$\log 1 = 7.282 - \frac{8500}{T} = 0.$

T = 1167 K = 894° C

Example 4: 0.0785 g of selenium vapour occupying a volume of 105 mL of 600° C exerts a pressure of 160 mm. The selenium is in a state of equilibrium according to the reaction $Se_6(g) \rightleftharpoons 3Se_2(g)$.

Calculate (a) degree of dissociation of selenium, (b) K_p, and (c) K_c; (Se = 79)

Sol: Using $\left(\frac{p_1V_1}{T_1}=\frac{p_2V_2}{T_2}\right)$, find

1. Volume at NTP
2. No. of moles
3. Molar mass
4. Vapour density
5. Degree of dissociation
6. Using reaction, find moles at equilibrium and then solve for K_p and K_c from

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

(a) Volume at NTP = $\frac{160}{760}\times\frac{105}{873}\times 273\text{mL}$

$= 6.9216 \left(\frac{p_1V_1}{T_1}=\frac{p_2V_2}{T_2}\right)$

$\therefore$ Moles at NTP = $\frac{6.9216}{22400}$ . . .

Let the observed molecular weight of selenium be M.

$\therefore$ No. of moles = $\frac{0.0785}{M}$

Hence, $\frac{0.0785}{M}=\frac{6.9216}{22400}$

M = 254.04

$\therefore$ Observed vapour density = $\frac{254.04}{2}=127.02$

Theoretical vapour density = $\frac{79\times 6}{2}=237$

(mol. wt. of Se_6 = 79 × 6)

(i.e., when there is no diss.)

Since 1 molecule of selenium produces 3 molecules

$\therefore$ n = 3

Substituting the above values in Eqn.(4), we get

Degree of dissociation of Se_6 $=\frac{(237-127.02)}{(3-1)\times 127.02}$

$=\frac{190.98}{254.04}=0.43$

(b)

	$Se_6(g) \rightleftharpoons$	$3Se_2(g)$
Initial moles(suppose)	1	0
Moles at eqm.	$(1-x)$	$3x$

(x = deg. of diss.)

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

$$K_p = \frac{p_{Se_2}^3}{p_{Se_6}} = \frac{\left(\frac{3x}{1+2x}\times p\right)^3}{\left(\frac{1-x}{1+2x}\times p\right)} = \frac{27x^3}{(1+2x)^2(1-x)}\times p^2$$

Substituting the values of x = 0.43 and p = $\frac{160}{760}$ atm,

K_p = 0.8970

(c) $K_p = K_c(RT)^{\Delta n}$ . . . . . (Eqn. 3)

$0.8970 = K_c\,(0.08821 \times 973)^2$

$(\Delta n = 3 - 1 = 2)$

$K_c = \frac{0.8970}{(0.821\times 973)^2} = 1.40\times 10^{-4}$

Example 5: An equilibrium mixture, $CO(g) + H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$, present in a vessel of one litre capacity at 1000 K was found to contain 0.4 mole of CO, 0.3 mole of H_2O, 0.2 mole of CO_2 and 0.6 mole of H_2. If it is desired to increase the concentration of CO to 0.6 mole by adding CO_2 into the vessel, how many moles of it must be added into equilibrium mixture at constant temperature in order to get this change?

Sol: Step-1 To calculate K_c of the reaction.

$$Kc = \frac{[CO(g)][H_2(g)]}{[CO(g)][H_2O(g)]} = \frac{0.2\times 0.6}{0.4\times 0.3} = 1$$

Step-2 To calculate extra CO_2 to be added:

Suppose X mole of extra CO_2 is added

Then writing the reverse reaction, we have

	CO_2 +	H_2 $\rightleftharpoons$	CO +	H_2O
Initial moles after add^n	$(0.2+x)$	0.6	0.4	0.3
Moles (Molar conc.) = at new Equilibrium	$(0.2+x$ $-0.2)$ $=x$	$(0.6$ $-0.2)$ $=0.4$	$(0.4$ $+0.2)$ $=0.6$	$(0.3$ $+0.2)$ $=0.5$

(V = 1 L) (Given)

$K_c' = \frac{1}{K_c} = \frac{0.6\times 0.5}{x\times 0.4} = 1 \quad \therefore x = \frac{0.6\times 05}{0.4} = 0.75$

Example 6: Ammonium carbamate decomposes as $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. In a closed vessel containing ammonium carbamate in equilibrium, NH_3 is added such that the partial pressure of NH_3 now equals original total pressure. Calculate the ratio of total pressure now to the original pressure.

Sol: Let us assume that initial pressure of the mixture is P. Thus, pressure is due to NH_3 and CO_2 which are present in the ratio of 2 : 1. (from the reaction)

Thus, $p_{NH_3} = \frac{2}{3}P,\ p_{CO_2} = \frac{1}{3}P$

$$K_P = (p_{NH_3})^2(p_{CO_2})^2 = \left(\frac{2}{3}P\right)^2\left(\frac{1}{3}P\right) = \frac{4}{27}P^3$$

After adding NH_3, partial pressure of NH_3 equals the original total pressure

p_{NH_3} = P (given)

$\therefore P^2 \times p_{CO_2}$

$= K_p = \frac{4}{27}P^3$ or $p_{CO_2} = \frac{4}{27}P$

$\therefore$ Total pressure now $= p_{NH_3} + p_{CO_2} = P + \frac{4}{27}P = \frac{31}{27}P$

$= \frac{31}{27}$

Example 7: An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.23 and 1.4 atm respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the two gases.

Sol: Step-1: Calculate K_p

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Equilibrium pressure	0.23	1.4atm

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{(1.4\text{atm})^2}{0.23\text{atm}} = 8.52\text{atm}$$

Step-2: Calculation of new equilibrium pressures:

According to Boyle's law, volume increases pressure decreases.

Thus on doubling the volume, pressure will decrease to half.

As pressure decreases, equilibrium will shift to the side accompanied by increase in the number of mole, i.e. forward direction.

This means that pressure of N_2O_4 will decrease while that of NO_2 will increase

Let us assume that decrease in pressure of N_2O_4 = p.

Then

	N_2O_4 $\rightleftharpoons$	$2NO_2$
Initial pressure	$\frac{0.23}{2}$atm	$\frac{1.4}{2}$atm
New eq pre	$\left(\frac{0.23}{2} - p\right)$atm	$\left(\frac{1.4}{2} + p\right)$atm

$$K_p = \frac{(0.70 + 2p)^2}{(0.115 - p)} = 8.52\text{atm} \text{ (Calculate above)}$$

$0.49 + 4p^2 + 2.8p = 0.9798 - 8.52p$

$4p^2 + 11.32p - 0.4898 = 0$

$$p = \frac{-11.32 \pm \sqrt{128.14 + 7.83}}{8} = 0.042\text{atm}\cdot$$

(minus value is neglected)

(For quadratic equation $ax^2 + bx + c = 0$,

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$)

$\therefore$ New equilibrium pressures will be

$p_{N_2O_4} = 0.115 - 0.042 = 0.072$ atm,

$p_{NO_2} = 0.70 + 2 \times 0.042 = 0.113$ atm

Example 8: At some temperature and under a pressure of 4 atm, PCl_5 is 20% dissociated. Calculate the pressure at which PCl_5 will be 40% dissociated, temperature remaining same.

Sol: Split into case 1 and case 2 where in case 1, 20% dissociation and in case 2, 40% dissociation is applied.

Case 1: When PCl_5 is 20% dissociated

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
At eq. (mole)	$1 - 0.2$ $= 0.8$	0.2	0.2

Total no. of moles = 0.8 + 0.2 + 0.2 = 1.2mole

$p_{PCl_5} = \frac{0.8}{1.2} \times 4\,\text{atm}$,

$p_{PCl_3} = \frac{0.2}{1.2} \times 4\,\text{atm}$,

$p_{Cl_2} = \frac{0.2}{1.2} \times 4\,\text{atm}$

$$K_p = \frac{\frac{0.8}{1.2} \times \frac{0.8}{1.2}}{\frac{3.2}{1.2}} = 0.166$$

Case 2: When PCl_5 is 40% dissociated. Suppose total pressure = P atm. Then,

	PCl_5	$\rightleftharpoons PCl_3$	$+\ Cl_2$
Initial mole	1	0	0
Eqm mole	$1-0.4$ $=0.6$	0.4	0.4

Total no. of moles = 0.6 + 0. 4 + 0. 4= 1.4 moles

$$p_{PCl_5} = \frac{0.6}{1.4}\times P \text{ atm}, \; p_{PCl_3} = \frac{0.4}{1.2}\times P\text{atm}, \; P_{Cl_2} = \frac{0.4}{1.2}\times P\text{atm}$$

$$K_p = \frac{\frac{0.4}{1.4}P\times\frac{0.4}{1.4}P}{\frac{0.6}{1.4}P} = \frac{0.4}{1.4}\times\frac{0.4}{0.6}P = 0.1904P$$

$K_p = 0.166$

Which gives P = 0. 87 atm

But $K_p = 0.166$

$\therefore$ P = 0.8 atm

JEE Main/Boards

Exercise 1

Q.1 When 46 g of I_2 and Ig or H_2 are heated at equilibrium at 450°C, the equilibrium mixture contained 1.9g of I_2. How many moles of I_2 and HI are present at equilibrium?

Q.2 A two litre flask contains 1.4 gm nitrogen and 1.0 gm hydrogen. The ratio of active mass of nitrogen and hydrogen would be?

Q.3 In the reaction: $A + B \rightleftharpoons C + D$ the initial concentration of A is double the initial concentration of B. At equilibrium the concentration of B was found to be one third of the concentration of C. The value of equilibrium constant is?

Q.4 The value of K_c for the reaction: $A + 3B \rightleftharpoons 2C$ at 400°C is 0.1768. Calculate the value of K_p?

Q.5 Two moles of ammonia was introduced in an evacuated vessel of 1 litre capacity. At high temperature the gas undergoes particle dissociation according to the equation:

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

At equilibrium the concentration of ammonia was found be 1 mole. What is the value of 'K'?

Q.6 What will be the expressions of formation of PCl_5 for K_p and K_c?

Q.7 4.0 gms of hydrogen react with 9.023 × 10^{23} molecules of chorine to form HCL gas. The total pressure after the reaction was found to be 700 mm. What will be the partial pressure of HCl?

Q.8 The equilibrium constant K for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 16. What would be value of equilibrium constant 'K' for the reaction:

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

Q.9 1.0 mole of PCl_3 (g) and 2.0 moles of Cl_2 (g) were placed in a 3 litre flask and heated to 400 K. When equilibrium was established, only 0.70 mole of $PCl_3(g)$ remained. What is the value of equilibrium constant for the reaction: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ at 400 K ?

Q.10 For the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

The moles of each component PCl_5, PCl_3 and Cl_2 at equilibrium were found to be 2. If the total pressure is 3 atm. What will be the value of K_p?

Q.11 For the reaction $H_2 + I_2 \rightleftharpoons 2HI$

The value of equilibrium constant is 9.0. Calculate the degree of dissociation of HI?

Q.12 For the reaction $N_2 + H_2 \rightleftharpoons 2NH_3$, N_2: H_2 where taken in the ratio of 1:3. Up to the points of equilibrium 50% each reactant has been reacted. If total pressure at equilibrium is P. Calculate the partial pressure of ammonia?

Q.13 In a reaction vessel of 2 litre capacity 3 mole N_2 reacts with 2 moles of O_2 to produce 1 mole of NO. What is the molar concentration of N2 equilibrium?

Q.14 At 300 K, K_p for the reaction:

$SO_2(g) \ = \ 1/2O_2(g) \rightleftharpoons SO_3(g)$ is 1.7×10^{-12}

Calculate K_p and K_c for the reaction

$2SO_3(g) \rightleftharpoons 2SO_2 + O_2(g)$ at 300 K?

Q.15 2.0 g mol of PCl_5 were heated in a 3 litre capacity vessel. At equilibrium 50% PCl_5 is dissociated. What will be the dissociation constant of the reaction?

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

Q.16 What should be the equilibrium constant K_2 for the reaction $2C \rightleftharpoons A \ + \ 3B$, if the equilibrium constant for the reaction $A \ + \ 3B \rightleftharpoons 2C$ is K_1?

Q.17 If the value of K_c for $P \ + \ Q \rightleftharpoons R \ + \ S$ is 10^{-2} and that of K_f is 10^{-1} the rate constant for the backward reaction will be.

Q.18 If the concentration of B is increased at fixed temperature, in the reaction, $A + 2B \rightleftharpoons C + 3D$ the equilibrium constant of backward reaction.

Q.19 In reaction $A + B \rightleftharpoons C + D$, if concentration of A in increased four times and concentration of B is halved, the rate of reaction will become.

Q.20 The value of for the reaction K_p^0 for the reaction $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$ is 8.32 at 873 K and 1 bare pressure. Calculate K_p^0, K_{c^o} and K_x for

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

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

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

Q.21 A mixture of hydrogen and iodine (molecular ratio is 2:1) is reacted to form HI. Calculate total moles at equilibrium?

Q.22 The vapour density for dissociation of PCl_5 at 250°C is 57.9. What will be the value of amount of dissociation, if molecular weight of PCl_5 is 208.5?

Q.23 In the reaction, $PCl_5 \rightleftharpoons PCl_3 + \ Cl_2$, a moles of PCI5 are initially taken. If the amount x gets dissociated and total pressure is P, the value of $P_{PCl_3} \times P^{-1}$ will be

Q.24 In the following reaction

$2A(g) \ + \ B(g) \rightleftharpoons 3C(g) \ + \ D(g)$ two moles each of A and B are initially taken in a one-litre flask. What will be the [A] – [D]?

Q.25 What of the following effect will occur when CN^- is added in the reaction, $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$, at equilibrium?

Q.26 In the reaction,

$CH_3COOH(I) \ + \ C_2H_5OH(I) \rightleftharpoons H_2O(I)$, the concentration of product can be increased when?

Q.27 What happens when pressure is increased in the equilibrium system, Ice $\rightleftharpoons$ Water?

Q.28 A vessel at 1000 K contains CO_2 with a pressures of 0.5 atmosphere. Some of the CO_2 in converted into CO on addition on graphite. Calculate the value of K, if total pressure at equilibrium is 0.8 atmosphere.

Q.29 At a certain temperature equilibrium constant (K_c) is 16 for the reaction: $SO_2(g) + NO_2(g) \longrightarrow SO_3(g) + NO(g)$. If we take 1 mole of each of the four gases in 1 litre vessel, what is equilibrium concentration of NO and NO_2?

Q.30 For the formation of ammonia the equilibrium constant data at 673 K and 773 K respectively are 1.64×10^{-4} and 1.44×10^{-5} respectively. Calculate heat of the reaction. Given R = 8.314 $JK^{-1}\ mol^{-1}$.

Q.31 K_c for the reaction $N_2O_4 \rightleftharpoons 2NH_2$ in chloroform at 291 K is 1.14. Calculate the free energy change of the reaction when the concentration of the two gases are 0.5 mol dm-3 each at the same temperature. (R = 0.082 lit atm K^{-1} mol^{-1})

Q.32 Calculate the pressure of CO_2 gas at 700K in the heterogeneous equilibrium reaction

$CaCO_3(s) \rightleftharpoons CaO(s) + \ CO_2(g)$ if ΔG^o for this reaction is 130.2 kJ mol^{-1}.

Q.33 For the equilibrium

$NiO(s) + CO(g) \rightleftharpoons Ni(s) + CP_2(g)$, ΔG° (J mol^{-1}) $= -20,700 - 11.97\,T$. Calculate the temperature at which will contain 400 ppm (parts per million) of carbon monoxide.

Exercise 2

Single Correct Choice Type

Q.1 Which is false?

(A) The greater the concentration of the substance involved in a reaction, the lower the speed of the reaction

(B) The dissociation of weak electrolyte is a reversible reaction

(C) The presence of free ions facilities chemical changes

(D) All of the above

Q.2 Chemical equations convey quantitative information on the:

(A) Type of atoms/molecules taking part in the reaction

(B) Relative number of moles of reactants and products involved in the reaction

(C) Number of atoms/molecules of the reactants and products involved in the reaction

(D) Quantity of reactant consumed and quantity of product formed.

Q.3 In the thermal decomposition of potassium chlorate given as:

$2KClO_3 \longrightarrow 2KCl + 3O_2$, law of mass action:

(A) Can be applied

(B) Cannot be applied

(C) Can be applied at low temperature

(D) Can be applied at high temperature and pressure

Q.4 In which of the following, the reaction proceeds towards completion?

(A) $K = 1$ (B) $K = 10$ (C) $K = 10^2$ (D) $K = 10^3$

Q.5 A reversible chemical reaction having two reactants in equilibrium. If the concentration of the reactants are doubled, then the equilibrium constant will:

(A) Be halved (B) Also be doubled

(C) Remains the same (D) None of these

Q.6 Pure ammonia is placed in a vessel at temperature where its dissociation constant (α) is appreciable. At equilibrium:

(A) K_p does not change significantly with pressure

(B) α does not change with pressure

(C) Concentration of NH_3 does not change with pressure

(D) Concentration of H_2 is less than that of N_2

Q.7 2 moles of PCl_5 were heated vessel of 2 L capacity. At equilibrium 40% of PCl_5 is dissociated into PCl_3 and Cl_2. The value of equilibrium constant is:

(A) 0.266 (B) 0.366 (C) 2.66 (D) 3.66

Q.8 The decomposition of N_2O_4 and NO_2 is carried out 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 L solution. The equilibrium constant for reaction, $N_2O_4 \rightleftharpoons 2NO_2$ is:

(A) 1×10^{-2} (B) 1×10^{-3} (C) 1×10^{-4} (D) 1×10^{-5}

Q.9 $A + B \rightleftharpoons C + D$. If finally 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 reaction?

(A) 2 (B) 4 (C) $\frac{2}{3}$ (D) $\frac{4}{5}$

Q.10 In the reaction, $N_2O_4 \rightleftharpoons 2NO_2$, α is that part of N_2O_4 which dissociates, then the number of moles at equilibrium will be:

(A) 1 (B) 3 (C) $(1 + \alpha)$ (D) $(1 - \alpha)^2$

Q.11 A mixture of 0.3 mole of H_2 and 0.3 mole of I_2 is allowed to react in a 10 L evacuated flask at 500°C. The reaction is $H_2 + I_2 \rightleftharpoons 2HI$, the K is found to be 64. The amount of unreacted at equilibrium is:

(A) 0.03 mole (B) 0.06 mole

(C) 0.09 mole (D) 3.6 moles

Q.12 In a chemical equilibrium, the rate constant of the backward reaction is 7.5×10^{-4} and the equilibrium constant is 1.5. So, the rate constant of the forward reaction is:

(A) 1.125×10^{-3} (B) 2.225×10^{-3}

(C) 3.335×10^{-5} (D) 1.125×10^{-1}

Q.13 28 g of N_2 and 6 g of H_2 were kept at C in 1 L vessel, the equilibrium mixture contained 27.54 g of NH_3. The approximate value of K_c for the above reaction can be (in $mol^{-2}\ L^2$):

(A) 25 (B) 50 (C) 75 (D) 100

Q.14 The equilibrium concentration of X, Y and XY_2 are 4, 2 and 2 moles respectively for the equilibrium, $2X + Y \rightleftharpoons YX_2$. The value of K_c is:

(A) 0.625 (B) 0.0625 (C) 0.00625 (D) 6.25

Q.15 An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonia hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for decomposition at this temperature is:

(A) 0.11 (B) 0.22 (C) 0.33 (D) 0.44

Q.16 A reaction is, $A + B \longrightarrow C + D$, Initially we start with equal concentration of A, and B. At equilibrium we find the moles of C is two times of A. What is the equilibrium constant of the reaction?

(A) 2 (B) 4 (C) $\frac{1}{2}$ (D) $\frac{1}{4}$

Q.17 9.2 g of N_2O_4(g) is taken in a closed 1 L vessel and heated till the following equilibrium is reached.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$. At equilibrium, 50% N_2O_4(g) is dissociated. What is the equilibrium constant (in mol/L) (molecular weight of N_2O_4 = 92).

(A) 0.1 (B) 0.2 (C) 0.3 (D) 0.4

Q.18 In Haber process, 30 L of dihydrogen and 30 L of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end?

(A) 10 L NH_3, 25 L NH_3, 15 L

(B) 20 L NH_3, 20 L NH_3, 20 L

(C) 20 L NH_3, 25 L NH_3, 15 L

(D) 20 L NH_3, 10 L NH_3, 30 L

Q.19 3.2 moles of hydrogen iodine were heated in a sealed bulb at 444°C till the equilibrium state was reached. Its degree of dissociation at this temperature was found to be 22%. The number of moles of hydrogen iodine present at equilibrium are:

(A) 1.876 (B) 2.496 (C) 3.235 (D) 4.126

Q.20 56 g of nitrogen and 8 g hydrogen gas heated in a closed vessel. At equilibrium, 34 g of ammonia are present. The equilibrium number of moles of nitrogen, hydrogen and ammonia are, respectively:

(A) 1, 1, 2 (B) 1, 2, 2 (C) 2, 1, 1 (D) 2, 2, 1

Q.21 The reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is carried out in a 1 dm^3 vessel and 2 dm^3 vessel respectively. The ratio of the reaction velocities will be:

(A) 1 : 4 (B) 2 : 4 (C) 1 : 8 (D) 8 : 1

Q.22 When $NaNO_3$ is heated in a closed vessel, O_2 is liberated and $NaNO_2$ is left behind. At equilibrium:

(i) Addition of $NaNO_3$ favours forward reaction

(ii) Addition of $NaNO_2$ favours backward reaction

(iii) Increasing pressure favours reverse reaction

(iv) Increasing temperature favours forward reaction

(A) (i), (ii), (iii) (B) (ii), (iii), (iv)

(C) (i), (iii), (iv) (D) (i), (ii), (iii), (iv)

Q.23 5 moles of SO_2 and 5 moles of O_2 are allowed to react to form SO_3 in a closed vessel. At the equilibrium stage 60% of SO_2 is used up. The total number of moles of SO_2, O_2 and SO_3 in the vessel now is:

(A) 8.5 (B) 9.5 (C) 10 (D) 10.5

Q.24 K for the synthesis of HI is 50. K for the dissociation of HI is:

(A) 0.2 (B) 0.02 (C) 0.4 (D) 0.04

Q.25 For which of the following reactions $K_p = K_c$?

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

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

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

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

Q.26 In which of the following reaction $K_p > K_c$

(A) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (B) $H_2 + I_2 \rightleftharpoons 2HI$

(C) $2SO_3 \rightleftharpoons O_2 + 2SO_2$ (D) $PCl_3 + Cl_2 \rightleftharpoons PCl_5$

Q.27 The equilibrium constant (K_p) for the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 16. If the volume of the container is reduced to one half its original volume, the value of K_p for the reaction at the same temperature will be:

(A) 8 (B) 16 (C) 32 (D) 64

Q.28 For the reversible reaction, $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c with concentration in mol L^{-1}, is:

(A) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$ (B) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{2}}$

(C) $\dfrac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$ (D) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$

Q.29 A chemical reaction is catalysed by a catalyst X. Hence, X:

(A) Reduce enthalpy of the reaction

(B) Decreases rates constant of the reaction

(C) Increases rate constant of the reaction

(D) Does not affect equilibrium constant of reaction

Q.30 Phosphorus pentachloride dissociate as follows, in a closed reaction vessel, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of   is x, the partial pressure of   will be:

(A) $\left(\dfrac{x}{x+1}\right)P$ (B) $\left(\dfrac{2x}{1-x}\right)P$ (C) $\left(\dfrac{x}{x-1}\right)P$ (D) $\left(\dfrac{x}{1-x}\right)P$

Q.31 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:

(A) 416 (B) 2.40×10^{-3} (C) 9.8×10^{-2} (D) 4.9×10^{-2}

Previous Years' Questions

Q.1 For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ At a given temperature, the equilibrium amount of CO_2(g) can be increased by ***[1998]***

(A) Adding a suitable catalyst

(B) Adding an inert gas

(C) Decreasing the volume of the container

(D) Increasing the amount CO (g)

Q.2 At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by

$K_p = \dfrac{(4x^2P)}{(1-x^2)}$, where P = pressure, x = extent of decomposing. Which one of the following statements is true ***[2001]***

(A) K_p increases with increase of P

(B) K_p increases with increases of x

(C) K_p increases with increases of x

(D) K_n remains constant with change in P & x

Q.3 Ammonia under a pressure of 15 atm at 27°C is heated to 437°C in a closed vessel in the presence of a catalyst. Under the conditions, NH_3 is partially decomposed according to the equation, $2NH_3 \rightleftharpoons N_2 + 3H_2$. The vessel is such that the volume remains effectively constant whereas pressure increases to 50 atm. Calculate the percentage of NH_3 actually decomposed. ***[2001]***

(A) 65% (B) 61.3% (C) 62.5% (D) 64%

Q.4 The partial pressure of CH_3OH CO and H_2 in the equilibrium mixture of the reaction $CO + 2H_2 \rightleftharpoons CH_3OH$ at 427° Care 2.0, 1.0 and 0.1 atm respectively. The value of K_p for the decomposition of CH_3OH to CO and H_2 is ***[1999]***

(A) 1×10^2 atm (B) 2×10^2 atm^{-1}

(C) 50 atm^2 (D) 5×10^{-3} atm^2

Q.5 For the gas phase reaction $C_2H_4 + H_2 \rightleftharpoons C_2H_6$. Carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by ***[1984]***

(A) Increasing the temperature

(B) Decreasing the pressure

(C) Removing some H_2

(D) Adding some C_2H_6

Q.6 When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium ***[1986]***

(A) Addition of $NaNO_2$ favours reverse reaction.

(B) Addition of $NaNO_3$ favours forward reaction.

(C) Increasing temperature favours forwarded reaction

(D) Increasing pressure favours reverse reaction

Q.7 For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

The forward reaction at constant temperature is favored by ***[1991]***

(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

Q.8 When two reactants, A and B are mixed to give products, C and D, the reaction quotient, (Q) at the initial stages of the reaction ***[2000]***

(A) Is zero (B) Decreases with time

(C) Is independent of time (D) Increases with time

Each of the questions given below consists of two statements, an assertion (Assertion) and reason (Reason). Select the number corresponding to the appropriate alternative as follows

(A) If both assertion and reason are true and reason is the correct explanation of assertion.

(B) If both assertion and reason are true and reason is not the correct explanation of assertion.

(C) If assertion is true but reason is false.

(D) If assertion is false but reason is true.

Q.9 Assertion: Effect of temperature on K_c or K_p depends on enthalpy change. ***[1993]***

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

Q.10 Assertion: For a gaseous reaction,

$xA + yB \rightleftharpoons lC + mD$, $K_p = K_c$. ***[1996]***

Reason: Concentration of gaseous reactant is taken to be unity.

Q.11 Assertion: Ice $\rightleftharpoons$ water, if pressure is applied water will evaporate. ***[1986]***

Reason: Increases of pressure pushes the equilibrium towards the side in which number of gaseous mole decreases.

Q.12 For the following three reactions a, b and c, equilibrium constants are given: ***[2008]***

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

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

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

Which of the following relations is correct?

(A) $K_1\sqrt{K_2} = K_3$ (B) $K_2\,K_3 = K_1$

(C) $K_3 = K_1 . K_2$ (D) $K_3 . K_2^3 = K_1^2$

Q.13 The equilibrium constant (K_c) for the reaction at temperature T is $N_2(g) + O_2(g) \rightarrow 2NO(g)$. The value of K_c for the reaction, $NO(g) \rightarrow \tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g)$ at the same temperature is: ***[2012]***

(A) 0.02 (B) 25×10^2 (C) 4×10^{-4} (D) 50.0

Q.14 For the reaction $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$, if $K_P = K_C(RT)^x$ where the symbols have usual meaning then the value of x is (assuming ideality) ***[2014]***

(A) -1 (B) $-\frac{1}{2}$ (C) $\frac{1}{2}$ (D) 1

Q.15 The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}, [B] = 2$ and $[C] = \frac{1}{2}$. The reaction proceeds in the: [R = 8.314 J/K/mol, e = 2.718] ***[2015]***

(A) Forward direction because $Q > K_c$

(B) Reverse direction because $Q > K_c$

(C) Forward direction because $Q < K_c$

(D) Reverse direction because $Q < K_c$

JEE Advanced/Boards

Exercise 1

Q.1 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.

Q.2 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, $K_c = 2.96 \times 10^{-92}$.

Q.3 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.

Q.4 Calculate the percent 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}

Q.5 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.

Q.6 At temperature T, the compound $AB_2(g)$ dissociated 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.

Q.7 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.

Q.8 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?

Q.9 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,

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

Q.10 At 627°C and one atmosphere SO_3 is partially dissociated into SO_2 and O_2 by the reaction.

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

The density of the equilibrium mixture is 0.925 g L^{-1}. What is the degree of dissociation?

Q.11 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?

Q.12 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: $\Delta G^o_{f\,N_2O_4} = 100$ kJ, $\Delta G^o_{f\,NO_2} = 50$ kJ

(i) Find ΔG of the reaction at 298 K.

(ii) Find the direction of the reaction

Q.13 Equilibrium constant for the reaction of iodine with propane according to the following was determined.

Some results obtained at 545 K were as given ahead:

Initial Pressure (mm Hg)			**Equilibrium Pressure (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,

$$I_2(g) + C_3H_6(g) \rightleftharpoons C_3H_5I(g) + HI(g)$$

Q.14 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.

Q.15 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 is introduced into the flask?

Q.16 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.

Q.17 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.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Q.18 $2NOBr(g) \longrightarrow 2NO(g)+Br_2(g)$. If nitrosyl bromide (NOBr) is 33.33% dissociation at 25°C and a total pressure of 0.28 atm. Calculate K_p for the dissociation at this temperature.

Q.19 At 30° C, the following equilibrium is established: $H_2(g) + S(g) \longrightarrow H_2S(g)$, $K_p = 6.8 \times 10^{-2}$. If 0.2 mol of hydrogen and 1. 0 mol of sulphur are heated to 90°C in a 1.0 litre vessel, what will be the partial pressure of H_2S at equilibrium?

Q.20 A mixture of 2 moles of CH_4 and 34 gms of H_2S was placed in an evacuated container, which was then heated to and maintained at 727°C. When equilibrium was established in the gaseous reaction $CH_4+2H_2S \rightarrow CS_2+4H_2$ the total pressure in the container was 0.92 atm. & the partial pressure of hydrogen was 0. 2 atm. What was the volume of the container?

Q.21 At 1200° C, the following equilibrium is established between chlorine atoms & molecules:

$$Cl_2(g) \longrightarrow 2Cl(g)$$

The composition of the equilibrium mixture may be determined by measuring the rate of effusion the mixture through a pin hole. It is found that at 1200°C and 1 atm pressure the mixture effuses 1.16 times as fast as krypton effuses under the same condition. Calculate the equilibrium constant K_c.

Q.22 SO_3 decomposes at a temperature of 1000 K and at a total pressure of 1.642 atm. At equilibrium, the density of mixture is 1.28 g/l in a vessel. Find the degree of dissociation of SO_3 for $SO_3(g) \longrightarrow SO_2(g) + 1/2O_2(g)$.

Q.23 Consider the equilibrium: $P(g) + 2Q(g) \rightleftharpoons R(g)$. When the reaction is carried out at a certain temperature, the equilibrium concentration of P and Q are 3M and 4M respectively. When the volume of the vessel is doubled and the equilibrium is allowed to be re-established, the concentration of Q is found to be 3M. Find (i) K_c, (ii) concentration of R at two equilibrium stages.

Exercise 2

Single Correct Choice Type

Q.1 The reaction which proceeds in the forward direction is:

(A) $Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$

(B) $SnCl_4 + Hg_2Cl_2 = SnCl_2 + 2HgCl_2$

(C) $NH_3 + H_2O + NaCl = NH_4Cl + NaOH$

(D) $2CuI + I_2 + 4K^+ = 2Cu^{2+} + 3KI$

Q.2 In $K_p = K_c\left[RT\right]^{\Delta n}$, Δn may have:

(A) +ve values (B) –ve values

(C) Integer or fractional values (D) Either of the above

Q.3 For reaction, $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, the value of K_c at 250°C is 26 mol $litre^{-1}$. The value of K_p at this temperature will be:

(A) 0.61 atm^{-1} (B) 0.57 atm^{-1}

(C) 0.83 atm^{-1} (D) 0.46 atm^{-1}

Q.4 For the reversible reaction, $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in the atmosphere. The corresponding value of K_c, with concentration in mol $litre^{-1}$, is:

(A) $1.44 \times 10^{-5} / (0.082 \times 500)^{-2}$

(B) $1.44 \times 10^{-5} / (8.314 \times 773)^{-2}$

(C) $1.44 \times 10^{-5} / (0.082 \times 773)^{2}$

(D) $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$

Q.5 A cylinder fitted with a movable piston contains liquid water in equilibrium with water vapour at 25°C. Which operation result in a decrease in the equilibrium vapour pressure?

(A) Moving the piston downward a short distance

(B) Removing a small amount of vapour

(C) Removing a small amount of the liquid water

(D) Dissolving salt in the water

Q.6 The volume of the reaction vessel containing an equilibrium mixture in the reaction,

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

Is increases. When equilibrium is restablished:

(A) The amount of SO_2(g) will decrease

(B) The amount of SO_2Cl_2(g) will decrease

(C) The amount of Cl_2(g) will increase

(D) The amount of Cl_2(g) will remain unchanged.

Q.7 For the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, which of the following expression is correct?

(A) $K_p = [CaO][CO_2]/[CaCO_3]$

(B) $K_p = (P_{CaO} \times P_{CO_2})/P_{CaCO_3}$

(C) $K_p = P_{CO_2}$

(D) $K_p = (P_{CaO} + P_{CO_2}/P_{CaCO_3})$

Q.8 Just before a reversible reaction attains equilibrium it is found that:

(A) The velocity of both forward reaction and backward reaction is also increasing

(B) The velocity of the forward reaction is decreasing and that of backward reaction is increasing

(C) The velocity of both forward and backward reaction is decreasing

(D) All of the above

Q.9 Densities of diamond and graphite are 3.5 and 2.3 g/mL respectively. Increase of pressure on the equilibrium $C_{(diamond)} \rightleftharpoons C_{(graphite)}$:

(A) Favours backward reaction

(B) Favours forward reaction

(C) Have no effect

(D) Increases the reaction rate

Q.10 For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ in a vessel, after the addition of equal numbers of mole of N_2 and H_2, equilibrium state is formed. Which of the following is correct?

(A) $[H_2] = [N_2]$

(B) $[H_2] < [N_2]$

(C) $[H_2] > [N_2]$

(D) $[H_2] > [NH_3]$

Q.11 A characteristic feature of reversible reaction is that:

(A) They never proceed to completion

(B) They proceed to completion

(C) They are not complete unless the reactants are removed from sphere of reaction mixture

(D) None of the above

Q.12 An example of reversible reaction is:

(A) $AgNO_3(aq) + HCl(aq) \longrightarrow AgCl(s) + HNO_3(aq)$

(B) $2NA + 2H_2O \longrightarrow 2NaOH + H_2$

(C) $NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

(D) $Pb(NO_3)_2 + 2NaI \longrightarrow PbI_2 + 2NaNO_3$

Q.13 The correct relation between K_p and K_c for the reaction $aX + bY \rightleftharpoons bZ + aW$ is:

(A) $K_p = K_c[Rt]^{a+b}$

(B) $K_p = \frac{K_c}{(a+b)^2}$

(C) $K_p = K_c[RT]$

(D) $K_p = K_c$

Q.14 The reaction that proceeds in the forward direction is:

(A) $SnCl_4 + Hg_2Cl_2 \longrightarrow SnCl_2 + 2HgCl_2$

(B) $NH_4Cl + NaOH \longrightarrow H_2O + NH_3 + NaCl$

(C) $Mn^{2+} + 2H_2O + Cl_2 \longrightarrow MnO_2 + 4H^+ + 2Cl^-$

(D) $S_4O_6^{2-} + 2I^- \longrightarrow 2S_2O_3^{2-} + I_2$

Q.15 Which information can be obtained from Le Chatelier's principle?

(A) Shift in equilibrium position on changing P, T and concentration

(B) Dissociation constant of a weak acid

(C) Energy change in a reaction

(D) Equilibrium constant of a chemical reaction

Q.16 The values of K_{p_1} and K_{p_2} for the reaction:

(i) $X \rightleftharpoons Y + Z$ (ii) $A \rightleftharpoons 2B$

Are in the ratio 9 : 1. Assuming degree of dissociation of X and A and be same, the dissociation pressure at equilibrium (i) and (ii) are in the ratio:

(A) 36 : 1 (B) 1 : 1 (C) 3 : 1 (D) 1 : 9

Q.17 For the equilibrium, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$K_c = \alpha^2 / (1-\alpha)V$, temperature remaining constant:

(A) K_c will increase with the increase in volume

(B) K_c will increase with decrease in volume

(C) K_c will not change with the change in volume

(D) K_c may increase or decrease with the change in volume depending upon its numerical value.

Q.18 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 given statements golds true regarding the equilibrium constant (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

Q.19 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 of the following statements is true?

(A) K_p increases with increase of P

(B) K_p increases with increases of x

(C) K_p increases with decrease of x

(D) K_p remains constant with change in P and x decreases with pressure

Q.20 For the reaction in equilibrium,

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

The concentrations, of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1} respectively. The value of K_c for this reaction is:

(A) 3×10^{-3} mol L^{-1} (B) 3×10^{3} mol L^{-1}

(C) 3.3×10^{2} mol L^{-1} (D) 3×10^{-1} mol L^{-1}

Q.21 1.1 mole of A are mixed with 2.2 mole of B and the mixture is then kept in one litre flask till the equilibrium is attained $A + 2B \rightleftharpoons 2C + D$. At the equilibrium, 0.2 mole of C are formed. The equilibrium constant of the reaction is:

(A) 0.001 (B) 0.002 (C) 0.003 (D) 0.004

Q.22 For the reactions, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 720 K, the value of equilibrium constant is 50, when equilibrium concentration of both H_2 and I_2 is 0.5 M. K_p under the same conditions will be:

(A) 0.02 (B) 0.2 (C) 50 (D) 50 RT

Q.23 The equilibrium constant for a reaction is 1×10^{20} at 300 K. The standard Gibbs energy change for this reaction is:

(A) – 115 kJ (B) + 115 kJ (C) + 166 kJ (D) – 166 kJ

Q.24 The equilibrium constant for the reaction:

$P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$ is:

(A) $K_c = \frac{1}{[O_2]^5}$ (B) $K_c = [O_2]^5$

(C) $K_c = \frac{[P_4O_{10}]}{5[P_4][O_2]}$ (D) $K_c = \frac{[P_4O_{10}]}{5[P_4][O_2]^5}$

Q.25 Eight mole of a gas AB_3 attain equilibrium in a closed container of volume 1 dm^3 as, $2AB_3 \rightleftharpoons A_2(g) + 3B_2(g)$. If at equilibrium 2 mole of A_2 are present then, equilibrium constant is:

(A) 72 mol^2 L^{-2} (B) 36 mol^2 L^{-2}

(C) 3 mol^2 L^{-2} (D) 27 mol^2 L^{-2}

Q.26 The equilibrium constant for the reaction, $N_2(g)+O_2(g)\rightleftharpoons 2NO(g)$ is 4 × 10^{-4} at 2000 K. in presence of a catalyst the equilibrium is attained 10 times faster. Therefore, the equilibrium constant, in presence of the catalyst, at 2000 K is:

(A) 40×10^{-4}

(B) 4×10^{-4}

(C) 4×10^{-3}

(D) Difficult to compute without more data

Q.27 The reaction, $A+2B\rightleftharpoons 2C+D$ was studied using an initial concentration of B which was 1.5 times that of A. But the equilibrium concentrations of A and C were found to be equal. Then the for the equilibrium is:

(A) 4 (B) 8 (C) 6 (D) 0.32

Multiple Correct Choice Type

Q.28 The yield of product in the reaction

$2A(g)+B(g)\rightleftharpoons 2C(g)+QkJ$

Would be lower at:

(A) Low temperature and low pressure

(B) High temperature and high pressure

(C) Low temperature and to high pressure

(D) High temperature and low pressure

Q.29 What is the effect of the reduction of the volume of the system for the equilibrium $2C(s)+O_2(g)\longrightarrow 2CO(g)$?

(A) The equilibrium will be shifted to the left by the increased pressure caused by the reduction in volume

(B) The equilibrium will be shifted to the right by the decreased pressure by the reduction in volume.

(C) The equilibrium will be shifted to the left by the increased pressure caused by the increased in volume.

(D) The equilibrium will be shifted to the right by the increased pressured caused by the reduction in volume.

Q.30 For the reaction $PCl_5(g)\longrightarrow PCl_3(g)+Cl_2(g)$, the forward reaction at constant temperature is favoured by

(A) Introducing an inert gas at constant volume

(B) Introducing chlorine gas at constant volume

(C) Introducing an inert gas at constant pressure

(D) Introducing PCl_5 at constant volume.

Comprehension Type

Paragraph 1: 10 moles of is heated at 15 atm from 27°C to 347°C assuming volume constant. The pressure at equilibrium is found to be 50 atm. The equilibrium constant for dissociation of

$NH_3 : 2NH_3 \rightleftharpoons N_2+3H_2;\ \Delta H = 91.94\ kJ$

Can be written as; $K_p = \dfrac{P_{N_2}\times\left(P_{H_2}\right)^3}{\left(P_{NH_3}\right)^2}(atm)^2$

Q.31 The degree of dissociation of is:

(A) 61.3% (B) 20% (C) 48% (D) None of these

Q.32 The equilibrium constant for the reaction is:

(A) 7.08×10^2 (B) 3.06×10^2

(C) 7.6×10^2 (D) 1.53×10^3

Q.33 The volume of container in which gas is heated is:

(A) 16.42 litre (B) 8.21 litre (C) 20 litre (D) 15 litre

Paragraph 2: For a reversible reaction at a certain temperature when it is at equilibrium has been attained whether physical or chemical, a change in certain variables might change the state of equilibrium. These variables includes pressure, volume, concentration and temperature. Due to these changes, a system under equilibrium changes its state in such a manner, i.e., the equilibrium moves in forward direction or backward direction, so that the effect of change is annulled. For a gaseous phase endothermic decomposition of phosphorus pentachloride, can be made spontaneous by increasing concentration of PCl_5, lowering the pressure and increasing temperature of the system.

Q.34 Which of the following reactions proceed in forward direction with increase in temperature are:

(A) $H_2(g)+I_2(g)\rightleftharpoons 2HI(g)+3000\ cal$

(B) $N_2(g)+O_2(g)\rightleftharpoons 2NO(g)-43200\ cal$

(C) $N_2(g)+3H_2(g)\rightleftharpoons 2HN_3(g)+22400\ cal$

(D) $C(s)+O_2(g)\longrightarrow CO_2(g)+94300\ cal$

Q.35 The equilibrium, solid $\rightleftharpoons$ liquid $\rightleftharpoons$ gas, will shift in forward direction when:

(A) Temperature is raised (B) Temperature is constant

(C) Temperature is lowered (D) Pressure is increases

Q.36 The change is standard Gibbs energy for a reaction at equilibrium, e.g., $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, on addition of an inert gas at constant pressure and then at constant volume respectively are:

(A) Decreases, no change (B) Increases, no change

(C) No change, no change (D) No change, decreases

Previous Years' Questions

Q.1 For the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_2OH(g)$, true condition is ***[1992]***

(A) $K_p = K_c$ (B) $K_p > K_c$

(C) $K_p < K_c$ (D) $K_c = 0$ but $K_p \neq 0$

Q.2 Which of the following is not favorable for SO_3 formation $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \Delta H = -45.0$ kcal ***[1997]***

(A) High pressure

(B) High temperature

(C) Decreasing SO_3 concentration

(D) Increasing reactant concentration

Q.3 The formation of NO2 in the reaction

$2NO + O_2 \rightleftharpoons 2NO_2 + \text{heat}$ is favoured by ***[1998]***

(A) Low pressure

(B) High pressure

(C) Low temperature

(D) Reduction in the mass of reactant

Q.4 For the gas phase reaction $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ($\Delta H = -32.7$ kcal). Carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by ***[1984]***

(A) Increasing the temperature

(B) Decreasing the pressure

(C) Removing some H_2

(D) Adding some C_2H_6

Q.5 The equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas helium is introduced. Which of the following statements are correct? ***[1989]***

(A) Concentration of SO_2, Cl_2 and SO_2 Cl_2 change

(B) More chlorine is formed

(C) Concentration of SO_2 is reduced

(D) All the above are incorrect

Q.6 For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by ***[2009]***

(A) Temperature and pressure

(B) Temperature only

(C) Pressure only

(D) Temperature, pressure and catalyst

Q.7 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 statement is correct. ***[1989]***

(A) More chlorine is formed

(B) Concentration of SO_2 is reduced

(C) More SO_2Cl_2 is formed

(D) Concentration of SO_2Cl_2, SO_2 and Cl_2 does not

Q.8 In the reaction, $A_2(g) + 4B_2(g) \rightleftharpoons 2AB_4(g)$

$\Delta H < 0$ the formation of AB_4 is will be favoured at ***[1990]***

(A) Low temperature, high pressure

(B) Low temperature, low pressure

(C) Low temperature low pressure

(D) High temperature low pressure

Q.9 For the given equilibrium: ***[2003]***

$2SO_2 + O_2 \rightleftharpoons 2SO_3 + \text{heat}$

The equilibrium reaction proceeds in forward direction when

(A) Oxygen is removed (B) SO_3 is added

(C) Heat is added (D) Oxygen is added

Q.10 Statement-I: For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

Statement-II: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. ***[2008]***

(A) Statement-I is True, statement-II is True; statement-II is correct explanation for statement-I

(B) Statement-I is True, statement-II is True; statement-II is NOT a correct explanation for statement-I

(C) Statement-I is True, statement-II is False

(D) Statement-I is False, statement-II is True

Q.11 The thermal dissociation equilibrium of (s) is studied under different conditions.

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

For this equilibrium, the correct statement(s) is(are) ***[2013]***

(A) ΔH is dependent on T

(B) K is independent of the initial amount of $CaCO_3$

(C) K is dependent on the pressure of CO_2 at a given T

(D) ΔH is independent of the catalyst, if any

Paragraph: Thermal decomposition of gaseous X2 to gaseous X at 298 K takes place according to the following equation:

The standard reaction Gibbs energy, of this reaction is positive. At the start of the reaction, there is one mole of X2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $\beta_{equilibrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given: R = 0.083 L bar K mol^{-1})

Q.12 The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{equilibrium}$, is ***[2016]***

(A) $\dfrac{8\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$

(B) $\dfrac{8\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$

(C) $\dfrac{4\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$

(D) $\dfrac{4\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$

Q.13 The INCORRECT statement among the following, for this reaction, is ***[2016]***

(A) Decrease in the total pressure will result in formation of more moles of gaseous X.

(B) At the start of the reaction, dissociation of gaseous X_2, takes place spontaneously.

(C) $\beta_{equilibrium} = 0.7$.

(D) $K_c < 1$

Questions

JEE Main/Boards

Exercise 1

Q.1 Q.7 Q.8
Q.15 Q.17 Q.22
Q.25 Q.29

Exercise 2

Q.2 Q.6 Q.10
Q.15 Q.17 Q.20
Q.24 Q.29

Previous Years' Questions

Q.1 Q.3 Q.8

JEE Advanced/Boards

Exercise 1

Q.2 Q.6 Q.8
Q.12 Q.15 Q.23

Exercise 2

Q.10 Q.12 Q.18-20

Previous Years' Questions

Q.5 Q.6

Answer Key

JEE Main/Boards

Exercise 1

Q.1 At equilibrium: Mole of I_2 = 0.0075 moles; Mole of HI = 0.347 moles

Q.2 1:10 **Q.3** $K_C = 1.8$ **Q.4** $K_p = 1.64 \times 10^{-4}$ atm **Q.5** $K = 1.7$ mol^2 l^{-2}

Q.6 $\frac{K_p}{K_c} = 1$ **Q.7** Partial pressure of HCl = 600 mm **Q.8** $K' = 0.25$

Q.9 $K_C = 0.76$ **Q.10** $K_p = 1$ atmosphere **Q.11** $x = 2/5$

Q.12 $P_{NH_3} = \frac{1}{3}P$ **Q.13** $[N_2] = 1.\ 25$ **Q.14** $K_p = 3.5 \times 10^{23}$ atm $K_C = 1.4 \times 10^{22}$ mol l^{-1}

Q.15 0.33 **Q.16** $K_2 = \frac{1}{K_1}$ **Q.17** 1000 times of K_c

Q.18 Remains unchanged **Q.19** Double **Q.20** $K_p = K_c = K_x = 0.1202$

Q.21 3 **Q.22** 0.8 **Q.23** $\frac{x}{a+x}$ **Q.24** [A] – [D] = 2 – 3x

Q.25 Increase is the negative log value of concentration of H^+

Q.26 H_2SO_4 is used in the reaction, due to absorption of water where the reaction no more remains reversible. Thus, the reaction proceeds in forward direction only and the product is obtained in larger amounts

Q.27 Melting point of ice decreases **Q.28** 1.2 atmosphere

Q.29 NO_2 = 0.4 mole, NO = 1.6 mole **Q.30** –105.216 kJ

Q.31 –19.67 lit atm **Q.32** $p_{CO_2} = K_p = 1.94 \times 10^{-10}$ atm **Q.33** T = 399 K.

Exercise 2

Single Correct Choice Type

Q.1 A **Q.2** B **Q.3** B **Q.4** D **Q.5** C **Q.6** A **Q.7** A

Q.8 D **Q.9** B **Q.10** C **Q.11** B **Q.12** A **Q.13** C **Q.14** B

Q.15 A **Q.16** B **Q.17** B **Q.18** A **Q.19** B **Q.20** A **Q.21** D

Q.22 D **Q.23** A **Q.24** B **Q.25** B **Q.26** C **Q.27** B **Q.28** A

Q.29 D **Q.30** A **Q.31** A

Previous Years' Questions

Q.1 D **Q.2** D **Q.3** B **Q.4** D **Q.5** A, B, C, D **Q.6** C, D **Q.7** C, D, E

Q.8 A, D **Q.9** C **Q.10** D **Q.11** E **Q.12** C **Q.13** D **Q.14** B

Q.15 B

JEE Advanced/Boards

Exercise 1

Q.1 0.977 atm **Q.2** $= 3.90\times10^{-31}$ mol L^{-1} **Q.3** 61.3 **Q.4** 2.0 **Q.5** 0.43 mol NO_2

Q.6 $x = \left(\frac{2K_p}{P}\right)^{1/3}$ **Q.7** $p_{N_2O_4} = 8.93$ atm; $p_{NO_2} = 1.07$ atm **Q.8** 17.64 **Q.9** $= 48.24\ \text{atm}^{-1/2}$

Q.10 34% **Q.11** 894.26°C

Q.12 –5.705 kJ and Negative value shows that reaction will be in forward direction.

Q.13 2.9×10^{-4} **Q.14** = -12.57 kcal mol-1 **Q.15** 0.049 **Q.16** 1.77 atm

Q.17 2.09 atm **Q.18** $K_p = 0.01$ atm **Q.19** 0.379 atm **Q.20** 300 L

Q.21 6.71×10^{-4} **Q.22** $\alpha = 0.5$ **Q.23** $K_c = 1/12$, [R] = 4 (initial), = 1.5 (final)

Exercise 2

Single Correct Choice Type

Q.1 A **Q.2** D **Q.3** A **Q.4** D **Q.5** D **Q.6** C **Q.7** C

Q.8 B **Q.9** C **Q.10** B **Q.11** A **Q.12** C **Q.13** D **Q.14** B

Q.15 A **Q.16** A **Q.17** C **Q.18** D **Q.19** D **Q.20** A **Q.21** A

Q.22 C **Q.23** A **Q.24** A **Q.25** D **Q.26** B **Q.27** D

Multiple Correct Choice Type

Q.28 A, B, C **Q.29** A, B, C, D **Q.30** C, D

Comprehension Type

Paragraph 1: **Q.31** A **Q.32** D **Q.33** A

Paragraph 2: **Q.34** B **Q.35** A **Q.36** C

Previous Years' Questions

Q.1 C **Q.2** B **Q.3** B, C **Q.4** A, B, C, D **Q.5** D **Q.6** A **Q.7** D

Q.8 A **Q.9** D **Q.10** D **Q.11** A, B, D **Q.12** B **Q.13** C

Solutions

JEE Main/Boards

Exercise 1

Sol 1:

	H_2 +	I_2	$\rightleftharpoons$	2HI
	1 :	1		2
Initial moles	23	0.18		0
Moles of equilibrium		$\frac{1.9}{126\times 2}=$ 0.0075		0.0075×2 $=0.345$

Sol 2:

N_2 :	**H_2**
14 g	1.0 g
$\text{conc.}=\frac{n}{v}$	$\text{conc.}=\frac{n}{v}$
$=\frac{1.4}{28}\times\frac{1}{2}=\frac{1}{40}$	$=\frac{1.0}{2}\times\frac{1}{2}=\frac{1}{4}$
1:10	

Sol 3:

	A +	B $\rightleftharpoons$	C+	D
Initial	2B	B	o	O
Eq^m	2B - x	B - x	x	x
	x			
		$B-x=\frac{1}{3}x$		
Eq^m	$\frac{5x}{3}$	$\frac{x}{3}$	x	x

Sol 4:

$$K_p=K_c(RT)^{\Delta n}=0.1768(0.0821\times 400)^{2-}=1.64\times 10^{-4}$$

Sol 5: Let α be the degree of dissociation:

Hence we have:

$2NH_3(g)\rightleftharpoons$	$N_2(g)+$	$3H_2(g)$
2	0	0
$2-2\alpha$	α	$3\,\alpha$

$$[N_2]=\frac{1}{2},\ [H_2]=\frac{3}{2},\ [NH_3]=1$$

$$\because\ K=\frac{[N_2][H_2]^3}{[NH_3]^2}=\frac{\frac{1}{2}\times\frac{3}{2}\times\frac{3}{2}\times\frac{3}{2}}{1\times 1}=\frac{27}{16}=1.7\ \text{mol}^2\ l^{-2}$$

Sol 6: $PCl_3+Cl_2\rightleftharpoons PCl_5$

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

$\Delta n=1$

$K_c=K_p$

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

Sol 7: $H_2+Cl_2\rightleftharpoons 2HCl$

$\frac{4}{2}$	$\frac{9.023\times 10^{23}}{6.02\times 10^{23}}$	0	Initially
2	$\approx\frac{3}{2}$	0	Initially

3/2 moles of Cl_2 will react with 3/2 moles of H_2 to give $\frac{3}{2}\times 2=3.0$ moles of HCl. So the total number of moles in the reaction.

$$=\left(2-\frac{3}{2}\right)+0+3=3.5$$

Partial pressure of HCl = $\frac{3\times 700}{3.5}=600$ mm

Sol 8: $N_2+3H_2\rightleftharpoons 2NH_3\rightarrow k=16$

$2NH_3\rightleftharpoons N_2+3H_2\rightarrow k^1=\frac{1}{16}$

$\therefore\quad NH_3\rightleftharpoons\frac{1}{2}N_2+\frac{3}{2}H_2\rightarrow k^{11}=\sqrt{\frac{1}{16}}$

Sol 9:

	$\underset{(g)}{PCl_3}$	+	$\underset{(g)}{Cl_2}\rightleftharpoons$	$\underset{(g)}{PCl_5}$
	1	:	1 $\rightarrow$	1
Initial	1/3		2/3	0
Equilibrium	$\frac{0.70}{3}$		$\frac{1.70}{3}$	$\frac{0.30}{3}$

$$K_c = \frac{0.30/3}{\left(\frac{0.70}{3}\right)\left(\frac{1.70}{3}\right)}$$

Sol 10: Total Moles = 2 + 2 + 2 = 6

$$P_{PCl_3} = \frac{2}{6}\times 3 \text{ , } P_{PCl_5} = \frac{2}{6}\times 3 \text{ , } P_{Cl_2} = \frac{2}{6}\times 3$$

$$K_p = \frac{P_{PCl_3}\times P_{Cl_2}}{P_{PCl_5}} = \frac{1\times 1}{1} = 1 \text{ atmosphere}$$

Sol 11: $H_2 + I_2 \rightleftharpoons 2HI$ $\quad K_c = 9$

$\therefore \quad 2HI \rightarrow H_2 + I_2 \quad ; \quad K_c = \frac{1}{9}$

Initial	2	0	0
eq^m	$2-2x$	x	x

$$\therefore \quad K_c' = \frac{x^2}{(2-2x)^2}; (2-2x)^2 = 9x^2$$

$$2-2x = 3x \therefore \quad x = \frac{2}{5}$$

Sol 12:

N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
$1-0.5$		$3-3(0.5)$		2×0.5
0.5		1.5		1.0

$\therefore P_{NH_3} = \frac{1}{3}\times P$ (3 = Total no. of moles)

Sol 13:

	N_2	+	O_2	$\rightarrow$	2NO
Initial	$\frac{3}{2}$		$\frac{2}{2}$		0
eq^m	$\frac{3}{2}-\frac{1}{2}$ = 1.0				$\frac{1}{2}$

Sol 14: T = 300 K

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

$$k_p = 1.7\times 10^{-12}$$

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

$$k_p' = \left(\frac{1}{k_p}\right)^2 = \left(\frac{1}{1.7\times 10^{-12}}\right)^2$$

$$k_p = k_c\,(RT)^{\Delta n}$$

Sol 15:

	PCl_5 $\rightleftharpoons$	PCl_3	+ Cl_2	$\left(\frac{2}{3}\times\frac{50}{100}\right)$
Initial	$\frac{2}{3}$	0	0	
eq^m	$\frac{2}{3}-\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	

$\therefore \quad k_c = 0.33$

Sol 16: $2C \rightleftharpoons A+3B$

$$k_2 = \frac{1}{k_1} \qquad (\because k_1 \Rightarrow A+3B \rightleftharpoons 2C)$$

Sol 17: $P + Q \rightleftharpoons R + S$

$K_c = 10^{-2} \quad ; K_f = 10^{-1}$

$$\because \quad K_c = \frac{K_f}{K_b} \Rightarrow K_b = 10^1$$

Sol 18: $A + 2B \rightleftharpoons C + 3D$

Le-chatlier's principle

Sol 19: Apply law of mass action

Sol 20: In this case

$\Delta n = 0$

$\therefore K_p = K_c = K_x = K$

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

Reaction is reversed and multiplied by two.

$$\therefore K = \frac{(8.32)^2}{8.32} = 8.32$$

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

Reaction is multiplied by 2

$\therefore K = (8.32)^2 = 69.66$

(iii) Since the reaction is reversed, $K = \frac{1}{8.32} = 0.1201$

Sol 21:

$$\begin{array}{lccccc} & H_2 & + & I_2 & \longrightarrow & HI \\ \text{Initial} & 2 & & 1 & & 0 \end{array}$$

Sol 22: Vapour density = 57.9

Molar mass = 208.5

$$\alpha = \frac{D-d}{(n-1)d} \Rightarrow \quad \begin{array}{l} D = \text{initial V.D} \\ d = \text{equilibrium V.D.} = 57.9 \end{array}$$

$$D = \frac{M_{PCl_5}}{2} = \frac{208.5}{2} = 104.25 \ (n = 2)$$

$$\therefore \ \alpha = \frac{104.25 - 57.9}{1 \times 57.9} = 0.8$$

Sol 23:

$$\begin{array}{lccccc} & PCl_5 & \rightleftharpoons & PCl_3 & + & Cl_2 \\ \text{Initial} & \text{"a"} & & o & & O \\ & a\text{-}x & & x & & x \end{array}$$

$\therefore$ Total no. of moles = (a – x) + x + x

= a + x

$$\therefore P_{PCl_5} = \frac{a-x}{a+x}P \ ; \quad P_{PCl_3} = \frac{x}{a+x}P \ ; P_{Cl_2} = \frac{x}{a+x}P$$

$$\therefore \ P_{PCl_3} \times \frac{1}{P} = \frac{x}{a+x}P \times \frac{1}{P} = \frac{x}{a+x}$$

Sol 24:

$$\begin{array}{lcccccc} & \underset{(g)}{2A} + & \underset{(g)}{B} & \rightleftharpoons & \underset{(g)}{3C} & + & \underset{(g)}{D} \\ & 2 & 1 & \longrightarrow & 3 & : & 1 \\ \text{Initial} & 2 & 2 & \longrightarrow & o & & o \\ eq^m & 2-2x & 2 - x & \longrightarrow & 3x & & x \end{array}$$

$$\therefore \ [A] - [D] = 2 - 2x - x = 2 - 3x$$

Sol 25: What of the following effect will occur when CN^- is added in the reaction, $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$, at equilibrium Increase is the negative log value of concentration of H^+.

Sol 26:

$$CH_3COOH(2) + C_2H_5OH\ (l) \rightleftharpoons CH_3\underset{(l)}{COO}C_2H_5 + H_2O(l)$$

Le-chatlier's principle

Sol 27: Le-chatlier's principle when pressure is increased in the equilibrium system of water and ice, Melting point of ice decreases.

Sol 28:

$$\begin{array}{lccc} & CO_2 + C & \rightarrow & 2CO \\ \text{Initial Pressure} & 0.5 & & \\ \text{Final Pressure} & 0.5-x & & 2x \end{array}$$

Total pressure=0.5+x

But the total pressure at equilibrium is 0.8 atm

$$0.5 + x = 0.8$$

$$x = 3\,\text{atm}$$

$$K = \frac{[CO]^2}{[CO_2]} = \frac{6^2}{0.3} = 1.2$$

Sol 29:

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

$$k_c = 16$$

$$\begin{array}{lcccc} \text{Initial} & 1 & 1 & 1 & 1 \\ eq^m & 1\text{-}x & 1\text{-}x & x & x \end{array}$$

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

$$4 - 4x = x \ ; \quad 4 = 5x \qquad 0$$

$$x = \frac{4}{5} = 0.8$$

$\therefore$ eq^m conc. of NO = 0.8

NO_2 = 0.2

Sol 30:

$T_1 = 673k \qquad T_2 = 773k$

$k_1 = 1.64 \times 10^{-4} \qquad k_2 = 1.44 \times 10^{-5}$

$R = 8.314\ Jk^{-1}\ mol^{-1}$

$$\log\frac{k_2}{k_1} = \frac{\Delta H}{2.303R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{(Apply)}$$

Sol 31: $N_2O_4 \rightleftharpoons 2NO_2$

$k_c = 1.14$

$\Delta G = ? \qquad ; R = 0.082\ \text{lit atm}\ k^{-1}\ mol^{-1}$

$T = 291K$

$\Delta G = -RT\ \ln k$ (Apply)

Sol 32: $CaCO_3 \rightleftharpoons \underset{(s)}{CaO} + \underset{(g)}{CO_2}$

$\Delta G^o = 130.2 \text{ k J mol}^{-1}$

$T = 700k$

$\Delta G^o = -RT \ln k$ (Apply)

Sol 33: $\underset{(s)}{NiO} + \underset{(g)}{CO} \rightleftharpoons \underset{(s)}{Ni} + \underset{(g)}{CO_2}$

$\Delta G^o = -20,700 - 11.97T$

$\Delta G^o = -RT \ln k$

$-20,700 - 11.97T = -0.082T \ln k$

Exercise 2

Single Correct Choice Type

Sol 1: (A) As we increases the concentration of substance, then speed of the reaction increases.

Sol 2: (B) Chemical reaction quantitatively depend on the reactant and product molecule.

Sol 3: (B) In the thermal decomposition of potassium chlorate given as:

$2KClO_3 \longrightarrow 2KCl + 3O_2$, law of mass action cannot be applied.

Sol 4: (D) Those reaction which have more value of K proceeds towards completion.

Sol 5: (C) K_c is a characteristic constant for the given reaction.

Sol 6: (A) K_p is a constant and does not change with pressure.

Sol 7: (A)

$$\begin{array}{llll} PCl_5 \rightleftharpoons & PCl_3 + & Cl_2 & \\ 0 & 0 & 0 & \text{initially} \\ \frac{2\times 60}{100} & \frac{2\times 40}{100} & \frac{2\times 40}{100} & \text{at equilibrium} \end{array}$$

Volume of container = 2 L.

$$K_c = \frac{\frac{2\times 40}{100\times 2} \times \frac{2\times 40}{100\times 2}}{\frac{2\times 60}{100\times 2}} = 0.266$$

Sol 8: (D)

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left[2\times\frac{10^{-3}}{2}\right]}{\left[\frac{0.2}{2}\right]}$$

$$= \frac{10^{-6}}{10^{-1}} = 10^{-5}$$

Sol 9: (B)

$$\begin{array}{llll} A + B \rightleftharpoons & & C + D & \\ x & x & 0 & 0 \\ & & 2x & 2x \end{array}$$

$$K_c = \frac{[C][D]}{[A][B]} = \frac{2x.2x}{x.x} = 4$$

Sol 10: (C)

$$\begin{array}{lll} N_2O_4 \rightleftharpoons & 2NO_2 & \\ 1 & 2 & \text{initially} \\ (1-\alpha) & 2\alpha & \text{at equilibrium} \end{array}$$

Total moles at equilibrium $= (1-\alpha) + 2\alpha$

$= 1 + \alpha$

Sol 11: (B)

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

$$\therefore\ 64 = \frac{x^2}{0.03\times 0.03}$$

$\therefore\ x^2 = 64\times 9\times 10^{-4}$

Or, $x = 8\times 3\times 10^{-2}$

x is the amount of HI at equilibrium amount of I_2 at equilibrium will be:

0.30 – 0.24 = 0.06

Sol 12: (A) $K_c = \frac{k_f}{k_b}$

$\therefore\ k_f = k_c \times k_b = 1.5\times 7.5\times 10^{-4} = 1.125\times 10^{-3}$

Sol 13: (C)

$$\begin{array}{llll} N_2 & + \; 3H_2 & \rightleftharpoons 2NH_3 & \\ 1 & \; 3 & & \\ 1-0.81 & 3-2.43 & 0 & \text{initially} \\ (=0.19) & (=0.57) & 1.62 & \text{at equilibrium} \end{array}$$

Number of moles of $N_2 = \frac{28}{28} = 1 \text{ mol}$

Number of moles of $H_2 = \frac{6}{2} = 3 \text{ mol}$

Number of moles of $NH_3 = \frac{27.54}{17} = 1.62 \text{ mol}$

$$\therefore \; K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[1.62]^2}{[0.19][0.57]^3} = 75$$

Sol 14: (B) $K_c = \frac{[YX_2]}{[X]^2[Y]} = \frac{2}{4\times4\times2} = \frac{1}{16} = 0.0625$

Sol 15: (A)

$$\begin{array}{llll} NH_4HS(s) \rightleftharpoons & NH_3(g) + & H_2S(g) & \\ a & 0.5 \text{ atm} & 0 & \text{initially} \\ (a-x) & 0.5+x & x & \text{at equilibrium} \end{array}$$

Total pressure = 0.5 + 2 x = 0.84

i.e., x = 0.17

$K_p = P_{NH_3}.P_{H_2S} = (0.67)\times(0.17) = 0.1139$

Sol 16: (B)

$$\begin{array}{lll} A+B \rightleftharpoons & C+D & \\ a \quad a & 2a \quad 2a & \text{at equilibrium} \end{array}$$

$$\therefore \; K_c = \frac{[C][D]}{[A][B]}$$

$$= \frac{2a\times2a}{a\times a} = 4.$$

Sol 17: (B)

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{4\times(0.05)^2}{0.05} = 4\times0.05 = 0.2$$

Sol 18: (A)

$$\begin{array}{llll} N_2 \; + & 3H_2 & \rightleftharpoons 2NH_3 & \\ 30 & 30 & 0 & \text{initially} \\ (30-x) & (30-x) & 2x & \text{at equilibrium} \end{array}$$

$2x = 10, \qquad \therefore x = \frac{10}{2} = 5$

$N_2 = 30-5 = 25 \text{ L}$

$H_2 = 30-3\times5 = 15 \text{ L}$

$NH_3 = 2\times5 = 10 \text{ L}$

Sol 19: (B) $\frac{22}{100}\times3.2 = 0.704$

Sol 20: (A)

$$\begin{array}{lllll} N_2 \; + & 3H_2 & \rightleftharpoons \; 2NH_3 & \text{....(1)} & \\ 56 \text{ g} & 8\text{g} & 0\text{g} & & \\ (=2 \text{ mol}) & (=4 \text{ mol}) & (0 \text{ mol}) & \text{initially } (t=0) & \\ (2-1) & (4-3) & 34 \text{ g} & \text{at equilibrium} & \\ =1 & =1 & (=2 \text{ mol}) & & \end{array}$$

According to Eq. (1) 2 moles of ammonia are present and to produce 2 moles of NH_3, we need 1 mole of N_2 and 3 moles of H_2, hence, 2 – 1 = 1 mole of N_2 and 4 – 3 = 1 mole of H_2 are present at equilibrium in vessel.

Sol 21: (D) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

For 1 dm³, $\qquad R = k[SO_2]^2[O_2]$

$$R = k\left[\frac{1}{T}\right]^2\left[\frac{1}{1}\right] = 1$$

For 2 dm³, $\qquad R = k\left[\frac{1}{2}\right]^2\left[\frac{1}{2}\right] = \frac{1}{8}$

So, the ratio is 8 : 1.

Sol 22: (D) When $NaNO_3$ is heated in a closed vessel, O_2 is liberated and $NaNO_2$ is left behind. At equilibrium increasing temperature favours forward reaction

Sol 23: (A) 5 moles of SO_2 and 5 moles of O_2 are allowed to react to form SO_3 in a closed vessel. At the equilibrium stage 60% of SO_2 is used up. The total number of moles of SO_2, O_2 and SO_3 in the vessel now is 8.5.

Sol 24: (B)

K_{c_1} for $H_2 + I_2 \rightleftharpoons 2HI$ is 50

K_{c_2} for $2HI \rightleftharpoons H_2 + I_2$

$$K_{c_1} = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_{c_2} = \frac{[H_2][I_2]}{[HI]^2}$$

On reversing Eq. (i)

$$\frac{1}{K_{c_1}} = \frac{[H_2][I_2]}{[HI]^2}$$

From Eqs. (ii) and (iii)

$$K_{c_2} = \frac{1}{K_{c_1}} = \frac{1}{50} = 0.02$$

Sol 25: (B) $K_p = K_c(RT)^{\Delta n}$

Here, $\Delta n = 2 - 2 = 0$

Sol 26 : (C) $K_p = K_c(RT)^{\Delta n}$

Here, $\Delta n = 3 - 2 = 1$

Sol 27: (B) For reaction, $2SO_3 \rightleftharpoons O_2 + 2SO_2$

Here, $\Delta n = 3 - 2 = 1$, i.e., + ve, thus, K_p is more than K_c

$\left[\because K_p = K_c (RT)^{\Delta n}\right]$

Sol 28: (A)

$$\underbrace{\underset{1}{N_2} + \underset{3}{3H_2}}_{4} \rightleftharpoons \underset{2}{2NH_3}$$

$\Delta n = 2 - 4 = -2$

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

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

$$\therefore \; K_c = \frac{K_p}{(RT)^{-2}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$$

Sol 29: (D) Catalyst does not affect equilibrium constant.

Sol 30: (A) $\underset{(1-x)}{PCl_5(g)} \rightleftharpoons \underset{x}{PCl_3(g)} + \underset{x}{Cl_2(g)}$

Total number of moles at equilibrium

= (1 - x) + x + x

= 1 + x

$$P_{PCl_3} = \left[\frac{x}{1+x}\right] \times P$$

Sol 31: (A) Equilibrium constant for the reaction:

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

$$K_c = \frac{1}{4.9 \times 10^{-2}}$$

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

$$K_c = \left(\frac{1}{4.9 \times 10^{-2}}\right)^2$$

$$= \frac{10^4}{(4.9)^2} = 416.49$$

Previous Years' Questions

Sol 1: (D) According to Le-chatelier's principle

Sol 2: K_p (equilibrium constant) is independent of pressure and concentration.

Sol 3: (B)

$$\begin{array}{cccc} 2NH_3 \rightleftharpoons & N_2 & + & 3H_2 \\ a & 0 & & 0 \\ (a-2x) & x & & 3x \end{array}$$

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

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

$$\therefore \quad \frac{15}{300} = \frac{p}{620}$$

$\therefore$ p = 31 atm

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

a $\propto$ 31 (before equilibrium)

$\therefore$ a + 2x $\propto$ 50 (after equilibrium)

$$\therefore \; \frac{a+2x}{a} = \frac{50}{31}$$

$x = \frac{19}{62}\ a$

$\therefore$ % of NH_3 decomposed = $\frac{2x}{a} \times 1(a)$

$$= \frac{2 \times 19a}{62 \times a} \times 100 = 61.29\%$$

Sol 4: (D) $CH_3OH \rightarrow CO + 2H_2$

$$\frac{[H_2]^2[CO]}{[CH_3OH]} = \frac{0.1 \times 0.1 \times 1}{2} = \frac{0.01}{2} = \frac{10 \times 10^{-3}}{2}$$

Sol 5: (A, B, C, D) According to Le-Chatelier's Principle.

Sol 6: (C, D) $NaNO_3(s) \rightleftharpoons NaNO_2(s) + O_2(g)$, $\Delta H = +$υe

Since reaction is endothermic, forward reaction is favoured by increases in temperature.

$K_p = [PO_2]^{1/2}$. Thus, addition of $NaNO_2$ or $NaNO_3$ does not cause any change in K_p.

Sol 7: (C, D, E) According to Le-Chatelier's principle.

Sol 8: (A, D) Reaction quotient = $\frac{[C][D]}{[A][B]}$

Initial stages (C) = 0 or [D] = 0

So, the value of quotient = $\frac{0}{[A][B]} = 0$ and increases with time.

Sol 9: (C) According to Le-Chatelier's principle endothermic reaction favours increases in temperature. However exothermic reaction favours decreases in temperature.

Sol 10: $Kp = Kc(RT)^{\Delta n}$; where $\Delta n = (l + m) - (x + y)$

Concentration of solids and liquids is taken to be unity.

Sol 11: (E) Increases in pressure favours melting of ice into water because at higher pressure melting point of ice is lowered.

Sol 12: (C) Equation (c)= Equation (a)+Equation (b)

Thus, $K_3 = K_1.K_2$

Sol 13: (D) $N_2 + O_2 \rightleftharpoons 2NO \quad K_c = 4 \times 10^{-4}$

$$NO \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2 \qquad K_c^1 = \sqrt{\frac{1}{K_c}}$$

$$K_c^1 = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$$

Sol 14: (B) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

$K_p = K_c(RT)^x$

$x = \Delta n_g$ = no. of gaseous moles in product – no. of gaseous in reactant

$$= 1 - \left(1 + \frac{1}{2}\right) = 1 - \frac{3}{2} = \frac{-1}{2}$$

Sol 15: (B) $\Delta G = \Delta G^\circ + RT\ \ln Q$

$= 2494.2 + 8.314 \times 300\ \ln\ 4$

= Positive

$\Delta G = RT \ln \frac{Q}{K}$

Since, ΔG is positive so, Q > K so reaction shifts in reverse direction.

JEE Advanced/Boards

Exercise 1

Sol 1: The system in the initial stage does not contain $SO_2.SO_3$ will, thus, decompose to form SO_2 and O_2 until equilibrium is reached. The partial pressure of SO_3 will decrease. Let the decrease in partial pressure be 2x.

$$\begin{array}{lccc} & 2SO_2(g) + & O_2(g) \rightleftharpoons & 2SO_3(g) \\ \text{At equilibrium} & (2x) & (2+x) & (1-2x) \end{array}$$

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 $\quad \frac{1-2x}{x} = 84.85$

Or $\quad x = 0.0115$ atm

Thus, the partial pressure at equilibrium are:

$P_{SO_2} = 2 \times 0.0115 = 0.023$ atm

$P_{O_2} = 2 + 0.0115 = 2.0115$ atm

$P_{SO_3} = 1 - 2 \times 0.0115 = 0.977$ atm

Sol 2:

$$\begin{array}{llll} & 2CO_2(g) \rightleftharpoons & 2CO(g) + & O_2(g) \\ \text{At equilibrium} & (1-2x) & (2x) & (x) \end{array}$$

Applying law of mass action,

$$K_c = \frac{[O_2][CO]^2}{[CO_2]^2} = \frac{x \times (2x)^2}{(1-2x)^2} = 2.96 \times 10^{-92}$$

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 $x = 1.95 \times 10^{-31}$ mol L^{-1}

$[CO] = 2x = 2 \times 1.95 \times 10^{-31}$

$= 3.90 \times 10^{-31}$ mol L^{-1}

Sol 3: Pressure of NH_3 at 27°C = 15 atm

Pressure of NH_3 at 347°C = P atm

$$\frac{P}{620} = \frac{15}{300}$$

P = 31 atm

Let a moles of ammonia be present. Total pressure at equilibrium = 50 atm

$$\begin{array}{llll} & 2NH_3(g) \rightleftharpoons & N_2(g) + & 3H_2(g) \\ \text{At equilibrium} & (a-2x) & x & 3x \end{array}$$

Total moles $a - 2x + x + 3x = a + 2x$

$$\frac{\text{Initial number of moles}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure}}{\text{Equilibrium pressure}}$$

$$\frac{a}{(a+2x)} = \frac{31}{50}$$

$$x = \frac{19}{62} a$$

Amount of ammonia decomposed =

$$2x = 2 \times \frac{19}{62} a = \frac{19}{31} a$$

% of ammonia decomposed $= \frac{19 \times a}{31 \times a} \times 100 = 61.3$

Sol 4: $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

$$\begin{array}{llll} \text{At equilibrium} & (0.1-x) & x & x/2 \\ \text{Molar conc.} & \frac{(0.1-x)}{0.4} & \frac{x}{0.4} & \frac{x}{0.8} \end{array}$$

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left(\frac{x}{0.4}\right)^2\left(\frac{x}{0.8}\right)}{\left(\frac{0.1-x}{0.4}\right)^2} = 1.0 \times 10^{-6}$$

Or $\frac{x^3}{0.8(0.1-x)^2} = 1.0 \times 10^{-6}$

as x is very small; $0.1 - x \to 0.1$

$$\frac{x^3}{0.8 \times (0.1)^2} = 1.0 \times 10^{-6}$$

$x^3 = 8 \times 10^{-9}$

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

So, percent dissociation $= \frac{2 \times 10^{-3}}{0.1} \times 100 = 2.0$

Sol 5:

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

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

Given, $d = 38.3$, $D = \frac{\text{Mol. mass of } N_2O_4}{2} = \frac{92}{2} = 46$, $n = 2$

So, $x = \frac{46 - 38.3}{38.3} = 0.2$

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

$= \frac{0.4 \times 100}{92} = 0.43$ mol NO_2

Sol 6:

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

At equilibrium $(1-x) \quad x \quad x/2$

Total moles at equilibrium = 1 – x + x + x/2 $= \dfrac{2+x}{2}$

$$p_{AB_2} = \frac{2(1-x)}{(2+x)}.P \; ; p_{AB} = \frac{2x}{(2+x)}.P; \; p_{B_2} = \frac{x}{(2+x)}.P;$$

$$K_p = \frac{(p_{AB})^2(p_{B_2})}{(p_{AB_2})^2} = \frac{\left[\dfrac{2x}{(2+x)}P\right]^2\left(\dfrac{x}{2+x}\right)P}{\left(\dfrac{2(1-x)}{(2+x)}P\right)^2}$$

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

As x is very small, $(2+x) \to 2$ and $(1-x) \to 1$.

So, $K_p = \dfrac{x^3P}{2}$

Or $x^3 = \dfrac{2K_p}{P}$

Or $x = \left(\dfrac{2K_p}{P}\right)^{1/3}$

Sol 7:

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

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 $\quad (1-x) \quad 2x$

Total number of moles = 1 – x + 2x = 1 + x

$$P_{N_2O_4} = \frac{(1-x)}{(1+x)} \times 10 \; ; \; p_{NO_2} = \frac{2x}{(1+x)} \times 10$$

$$K_p = 0.1285 = \frac{\left(\dfrac{2x}{1+x}\right)^2 \times 10^2}{\left(\dfrac{1-x}{1+x}\right) \times 10} = \frac{40\,x^2}{1-x^2}$$

Since, x is very small, $(1-x^2) \to 1$

So, $\quad x^2 = \dfrac{0.1285}{40}$

Or $\quad x = 0.0566$

$$p_{N_2O_4} = \frac{(1-x)}{(1+x)} \times 10 = \frac{1-0.0566}{1+0.0566} \times 10 = \frac{0.9436 \times 10}{1.0566}$$

= 8.93 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 atm

Sol 8:

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

At equilibrium $\quad (1-x) \quad (3-3x) \quad 2x$

Total number of moles = 1 – x + 3 – 3x + 2x = 4 – 2x

$$p_{N_2} = \frac{(1-x)}{(4-2x)}P; \; p_{H_2} = \frac{(3-3x)}{(4-2x)}P; \; p_{NH_3} = \frac{2x}{(4-2x)}P$$

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3} = \frac{\left(\dfrac{2x}{4-2x}P\right)^2}{\left(\dfrac{1-x}{4-2x}P\right)\left(\dfrac{3-3x}{4-2x}P\right)^3}$$

$$= \frac{4x^2(4-2x)^2}{(1-x) \times 27 \times (1-x)^3 P^2}$$

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

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 $\quad x = 0.30$

Moles of ammonia formed = $2 \times 0.30 = 0.60$

Total moles at equilibrium =

$(4-2x) = (4 - 2 \times 0.30) = 3.40$

% of NH_3 at equilibrium = $\frac{0.60}{3.40}\times 100 = 17.64$

Sol 9: The volume of SO_2 and O_2 at equilibrium

= (100 - 87) = 13 mL

Volume of $SO_2 = \frac{2}{3}\times 13 = 8.67$ mL

Volume of oxygen = $\frac{1}{3}\times 13 = 4.33$ mL

$$p_{SO_3} = \frac{87}{100}\times 1 = 0.87 \text{ atm}$$

$$p_{SO_2} = \frac{8.67}{100}\times 1 = 0.0867 \text{ atm}$$

$$p_{O_2} = \frac{4.33}{100}\times 1 = 0.0433 \text{ atm}$$

$$K_p = \frac{p_{SO_3}}{p_{SO_2}\times\left(p_{O_2}\right)^{1/2}} = \frac{0.87}{\left(0.0867\right)\times\left(0.0433\right)^{1/2}}$$

$$= \frac{0.87}{\left(0.0867\right)\times 0.208} = 48.24 \text{ atm}^{-1/2}$$

Sol 10: 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.

$$x = \frac{D-d}{\left(n-1\right)d} = \frac{40-34.174}{\left(\frac{3}{2}-1\right)\times 34.174} = \frac{5.826\times 2}{34.174} = 0.34$$

Or x = 34 % dissociated

i.e., SO_3 is 34% dissociated.

Sol 11: $K_p = p_{CO_2} = 1$

$$\log K_p = 7.282 - \frac{8500}{T}$$

$$\log 1 = 7.282 - \frac{8500}{T}$$

$$T = \frac{8500}{7.282} = 1167.26 \text{ K} = 894.26^\circ\text{C}$$

Sol 12: Reaction Quotient = $\frac{\left[p_{NO_2}\right]^2}{p_{N_2O_4}} = \frac{100}{10} = 10$

$$\Delta G^o_{reaction} = 2\,\Delta\,G^o_{f\,NO_2} - \Delta\,G^o_{f\,N_2O_4}$$

$$= 2\times 50 - 100 = 0$$

We know that, $\Delta G = \Delta G^\circ - 2.303\text{ RT}\log Q_p$

$$= 0 - 2.303\times 8.314\times 298\log 10$$

$$= -5705.8 \text{ J} = -5.705 \text{ kJ}$$

Negative value shows that reaction will be in forward direction.

Sol 13: Ist experiment:

$$\begin{array}{lccccc} & I_2(g) & + & C_3H_6(g) & \rightleftharpoons & C_3H_5I(g) + HI(g) \\ t=0 & 23.9 & & 505.8 & & 0 \qquad 0 \\ t_{eq.} & \left(23.9-1.8\right) & & \left(505.8-1.8\right) & & 1.80 \qquad 1.80 \end{array}$$

$$K_p = \frac{p_{C_3H_5I}\times p_{HI}}{p_{I_2}\times p_{C_3H_6}} = \frac{1.8\times 1.8}{22.1\times 504} = 2.9\times 10^{-4}$$

Similarly, solve for second experiment.

Sol 14: We know that, $\log\frac{K_2}{K_1} = \frac{\Delta H}{2.303\,R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

$$\log\frac{0.144}{1.64} = \frac{\Delta H}{2.303\times 1.987\times 10^{-3}}\left(\frac{1}{673}-\frac{1}{773}\right)$$

$\Delta H = -25.14$ kcal for 2 mole

= -12.57 kcal mol^{-1}

Sol 15: $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

Moles of $NH_4HS = \frac{3.06}{51} = 0.06$

Degree of dissociation = 0.3

At equilibrium,

$$\left[NH_3(g)\right] = \frac{0.3\times 0.06}{2};\ \left[H_2S(g)\right] = \frac{0.3}{2}\times 0.06$$

$$K_c = \left[NH_3(g)\right]\left[H_2S(g)\right] = \frac{0.3 \times 0.06 \times 0.3 \times 0.06}{2 \times 2}$$

$$= 8.1 \times 10^{-5}$$

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.

Sol 16:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$\text{At equilibrium (mole)} \quad (0.1 - x) \qquad x \qquad x$$

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 $\quad x = 0.08$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x^2}{(0.1 - x) \times 8}$$

$$= \frac{0.08 \times 0.08}{(0.1 - 0.08)8} = 4 \times 10^{-2} \text{ mol L}^{-1}$$

$$K_p = K_c (RT)^{\Delta n} = K_c RT (\Delta n = +1)$$

$$= 4 \times 10^{-2} \times 0.082 \times 540 = 1.77 \text{ atm}$$

Sol 17: 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

$$x = \frac{D - d}{(n - 1)d} = \frac{46 - 29}{29} = 0.586$$

$$\begin{array}{llll} & N_2O_4 \rightleftharpoons & 2NO_2 & \\ t = 0 & 1 & 0 & \\ t_{eq.} & 1 - x & 2x & (\text{Total moles = 1 + x}) \end{array}$$

$$p_{N_2O_4} = \frac{1 - x}{1 + x} \times P; \; p_{NO_2} = \frac{2x}{1 + x} \times P$$

$$K_p = \frac{4x^2P}{1 - x^2} = \frac{4 \times (0.586)^2 \times 1}{1 - (0.586)^2} = 2.09 \text{ atm}$$

Sol 18:

$$\begin{array}{lll} 2NOBr \longrightarrow & 2NO \quad + & Br_2 \\ 2\text{-}2a & 2a & a \end{array}$$

P = 0.28 atm; a = 0.33

$$K_p = \frac{\left(\frac{2a}{2 + a} 0.28\right)^2 \left(\frac{a}{2 + a} 0.28\right)}{\left(\frac{2.2a}{2 + a} 0.28\right)^2}$$

Sol 19: Partial pressure $= \dfrac{\text{no. of moles}}{\text{total moles}} \times \text{eq}^m$ pressure

Sol 20: Let calculate no. of moles & 0.92 atm is the total equilibrium pressure.

$$k_p = \frac{(P_{H_2})^2 (P_{CS_2})}{(P_{CH_4})(P_{H_2S})^2}$$

$$k_p = (\text{no. of moles}) \times \left(\frac{RT}{v}\right)^{\Delta n}$$

Sol 21:

$$Cl_2(g) \longrightarrow 2Cl(g)$$

$$\frac{(\text{effusion rate})_{Cl_2}}{(\text{effusion rate})_{k_r}} = \sqrt{\frac{Mk_r}{M_{Cl_2}}} = \sqrt{\frac{n_{Cl_2}}{n_{k_r}}}$$

$$\frac{1.16 kr}{kr} = \sqrt{\frac{83.1}{71}} = \sqrt{\frac{n_{Cl_2}}{n_{k_r}}}$$

$$\frac{(1.16)^2 \times n_{k_r}}{83.7} = 71 \, n_{Cl_2}; \quad 0.01607 n_{k_r} = 71 \, n_{Cl_2}$$

$$n_{k_r} = \frac{71 \times 1}{0.01607} = 4418.17$$

Sol 22: $\underset{(g)}{SO_3} \longrightarrow \underset{(g)}{SO_2} + \frac{1}{2} \underset{(g)}{O_2}$

Total P = 1.642 atm

Density = 1.28 g/l

$\alpha = ?$

$$\text{V.D.} = \frac{PRT}{2P} = 1.28x$$

$\alpha = ?$

$$\text{V.D.} = \frac{PRT}{2P} = 1.28x$$

Sol 23: $\underset{(g)}{P} + \underset{(g)}{2Q} \rightleftharpoons \underset{(g)}{R}$

$$\text{eq}^m \quad \frac{3M}{v} \quad \frac{4M}{v} \quad \frac{x}{v} \quad k_c = \frac{3M}{v}$$

Exercise 2

Single Correct Choice Type

Sol 1: (A) It is an acid-base reaction;

Rest all occurs in reverse direction.

Sol 2: (D) Δn may be zero, positive or negative integers or fractional depending upon nature of reaction.

Sol 3: (A)

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

$\because \Delta n = -1$

$\therefore K_p = 26 \times (0.0821 \times 523)^{-1} = 0.61 \text{ atm}^{-1}$

Sol 4: (D) $K_p = K_c (RT)^{\Delta n}$; Δn for the given reaction is 2 – 4 = - 2

R = 0.082 L atm K^{-1} mol^{-1}

$$\text{Thus, } K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$$

Sol 5: (D) Addition of salt always lowers the vapour pressure. Also vapour pressure of a liquid is its characteristic pressure and depends only on temperature.

Sol 6: (C) An increase in volume for the equilibrium having,

$$K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{[\text{mole of } SO_2][\text{mole of } Cl_2]}{[\text{mole of } SO_2Cl_2] \times \text{volume}}$$

Will increase the mole of Cl_2 or SO_2 to maintain K_c values constant.

Sol 7: (C) Only CO_2 is gas at equilibrium and $K_p = P_{CO_2}$.

Sol 8: (B) Before attaining the equilibrium, the rate of forward reaction decreases due to decrease in concentration of reactants with time and the rate of backward reaction increases due to increase in concentration of products with time.

Sol 9: (C) Le Chatelier's principle is not valid for solid-solid equilibrium.

Sol 10: (B) 1 mole of N_2 reacts with 3 moles of H_2 thus, for

$$\begin{array}{llll} N_2 & + \; 3H_2 & \rightleftharpoons 2NH_3 \; ; & (a-x) > (a-3x) \\ a & a & & \\ (a-x) & (a-3x) & 2x & \end{array}$$

Sol 11: (A) Reversible reactions always attains equilibrium and never go for completion.

Sol 12: (C) Choices (A) and (D) involves precipitation of AgCl and PbI_2 respectively; In (B) H_2 is escaped out.

Sol 13: (D) $\Delta n = (a+b) - (a+b) = 0$

Sol 14: (B) Rest all occur in backward direction.

Sol 15: (A) Le Chatelier proposed a principle to explain the effect of P, T and C on system in equilibrium.

Sol 16: (A)

$$\begin{array}{lll} X & \rightleftharpoons & Y + Z \\ 1-\alpha & & \alpha \quad \alpha \end{array}$$

$$\text{For (i) } K_{p_1} = \frac{n_y . n_z}{n_x} \frac{P_1}{[\Sigma n]_1} = \frac{\alpha^2}{(1-\alpha)} . \frac{P_1}{(1+\alpha)}$$

$$\begin{array}{lll} A & \rightleftharpoons & 2B \\ 1-\alpha & & 2\alpha \end{array}$$

$$\text{For (ii) } K_{p_2} = \frac{(n_B)^2}{(n_A)} \times \frac{P_2}{[\Sigma n]_2} = \frac{4\alpha^2}{(1-\alpha)} . \frac{P_2}{(1+\alpha)}$$

$$\therefore \frac{K_{p_1}}{K_{p_2}} = \frac{\alpha^2 \times P_1}{(1-\alpha) \times (1+\alpha)} \times \frac{(1-\alpha)(1+\alpha)}{4\alpha^2 \times P_2}$$

$$\therefore\ \frac{P_1}{P_2} = \frac{4\times 9}{1} = \frac{36}{1}$$

Sol 17: (C) K_c is characteristic constant for a given reaction at a temperature.

Sol 18: (D) K_p remains constant with T. For the reaction,

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

$$K_c = \frac{4a^2\alpha^2}{(a - a\alpha).V}$$

Where, a is initial mole of N_2O_4 present in V L and α is its degree of dissociation.

Also, $K_p = K(RT)^{\Delta n}$

On reducing the volume of container to $\frac{V}{2}$L, initial concentration of N_2O_4 becomes $\frac{2a}{V}$. An increase in concentration leads to more dissociation of N_2O_4 in order to have K_c constant, a characteristic constant for a given reaction at a temperature.

Sol 19: (D) K_p is a characteristic constant for a given reaction and changes only with temperature.

Sol 20: (A)

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left[1.2\times 10^{-2}\right]^2}{4.8\times 10^{-2}} = 3\times 10^{-3}\ \text{mol L}^{-1}$$

Sol 21: (A)

$$\begin{array}{cccc} A & + \ 2B & \rightleftharpoons & 2C \ + \ D \\ a & b & & 0 \quad 0 \\ (a-x) & (b-2x) & & 2x \quad x \end{array}$$

Given, 2x = 0.2, Also, a = 1.1

x = 0.1 b = 2.2

$$\therefore K_c = \frac{4x^3}{(a-x)(b-2x)^2}$$

$$= \frac{4\times(0.1)^3}{(1.1-0.1)(2.2-0.2)^2} = 0.001$$

Sol 22: (C) K_p is independent of initial concentration.

Sol 23: (A) $\Delta G^\circ = -2.303\ RT\ \log K_p$

$= -2.303\times 8.314\times 300 \log 10^{20}$

= -114.88 kJ

Sol 24: (A) $K_c = \frac{1}{[O_2]^5}$; note that the expression does not involve the concentration terms of solid species.

Sol 25: (D)

$$\begin{array}{lccc} & 2AB_3(g) & \rightleftharpoons A_2(g) + & 3B_2(g) \\ t=0 & 8 & 0 & 0 \\ \text{At equilibrium} & (8-a) & a/2 & \frac{3a}{2} \end{array}$$

Thus, $K_c = \frac{[A_2][B_2]^3}{[AB_3]^2}$; Also , $\frac{a}{2} = 2\ \therefore a = 4$

$$\therefore [AB_3] = \frac{4}{1}; [A_2] = \frac{2}{1}; [B_2] = \frac{6}{1}$$

Thus, $K_c = \frac{2\times 6^3}{4^2} = 27\ \text{mol}^2\text{L}^{-2}$

Sol 26: (B) K_p and K_c values do not change with catalyst.

Sol 27: (D)

$$\begin{array}{cccc} A & + \ 2B & \rightleftharpoons & 2C \ + \ D \\ a & \frac{3}{2}a & & 0 \quad 0 \\ (a-x) & \left(\frac{3}{2}a - 2x\right) & & 2x \quad x \end{array}$$

Given, a – x = 2x

$\therefore x = a/3$

Now, $K_c = \frac{[C]^2[D]}{[A][B]^2}$

Multiple Correct Choice Type

Sol 28: (A, B, C) According to Le – Chatlier's principle, the yield of product in the reaction

$$2A(g) + B(g) \rightleftharpoons 2C(g) + QkJ$$

Would be higher at high temperature and low pressure.

Sol 29:. (A, B, C, D) Le – Chatlier's principle.

Sol 30: (C, D) According to Le – Chatlier's principle, the forward reaction at constant temperature is favoured by introducing an inert gas at constant pressure and by introducing PCl_5 at constant volume.

Comprehension Type

Paragraph 1:

Sol 31: (A)

$$\begin{array}{llll} & 2NH_3 & \rightleftharpoons & N_2 + 3H_2 \\ \text{at 300 K} & 10 & 0 & 0 \\ \text{at 620 K} & (10-2x) & x & 3x \end{array}$$

Pressure increase due to increases in temperature as well as due to increase in moles.

Initially $P \propto T$

$15 \propto 300$

$P \propto 620$

$\therefore P = \frac{620}{300} \times 15 = 31$ atm of 10 moles of NH_3 at 620 K

Now, NH_3 is dissociated to attain 50 atm at 620 K.

Thus, $P \propto n$ or $10 \propto 31$

$10 + 2x \propto 31$

$\therefore 2x = 6.13$

$$\therefore \; \alpha = \frac{2x}{10} \times 100 = \frac{6.13 \times 100}{10} = 61.3\%$$

Sol 32: (D)

$$K_p = \frac{n_{N_2} \times (NH_2)^3}{(n_{NH_3})^2} \times \left[\frac{P}{\Sigma n}\right]^2$$

$$= \frac{\frac{6.13}{2} \times \left[\frac{6.13 \times 3}{2}\right]^3}{[10 - 6.13]^2} \times \left[\frac{50}{10 + 6.13}\right]^2 = 1.528 \times 10^3 \text{ atm}^2$$

Sol 33: (A) $PV = nRT$

$15 \times V = 10 \times 0.0821 \times 300$

$\therefore V = 16.42$ litre

Paragraph 2:

Sol 34: (B) Endothermic reactions are favoured with increase in temperature.

Sol 35: (A) Increase in temperature will favour the change showing absorption of heat.

Sol 36: (C) K_c remains constant and thus $\Delta G°$ is not changed.

Previous Years' Questions

Sol 1: (C) When $n_r > n_p$ then $K_P < K_C$

Where n_r = no. of moles of reactant

n_p = no. of moles of product.

Sol 2: (B) The reaction is exothermic so high temperature will favour backward reaction.

Sol 3: (B, C) According to Le-Chatelier's principle.

Sol 4: (A, B, C, D) $C_2H_4 + H_2 \rightleftharpoons C_2H_6 \quad \Delta H = -32.7$ kcal

The above reaction is exothermic, increasing temperature will favor backwawrd reaction, will increase the amount of C_2H_4. Decreasing pressure will favour reaction in direction containing more molecules (reactant side in the present case). Therefore, decreasing pressure will increase amount of C_2H_4.

Removing H_2. which is a reactant, will favour reaction in backward direction, more C_2H_4 will be formed.

Adding C_2H_6 will favour backward reaction and some of the C_2H_6 will be dehydrogenated to C_2H_4.

Sol 5: (D) $NaNO_3(s) \rightleftharpoons NaNO_2(s) + \frac{1}{2}O_2(g) \qquad \Delta H > 0$

$NaNO_3$ and $NaNO_2$ are in solid state, changing their amount has no effect on equilibrium. Increasing temperature will favour forward reaction due to endothermic nature of reaction. Also, increasing pressure will favour backward reaction in which some O_2 (g) will combine with $NaNO_2$(s) forming $NaNO_3$.

Sol 6: (A) Temperature and pressure both affects the concentration of X_3Y

Sol 7: (D) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

Adding inert gas at constant volume will not affect partial pressure of reactant or products, hence will not affect equilibrium amount of either reactant or products.

Sol 8: (A) Factors affecting equilibrium are pressure, temperature and concentration of product of reactant.

Sol 9: (D) As per Le-Chatelier's principle.

Sol 10: (D) At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

Sol 11: (A, B, D) ΔH is dependent on T

(B) K is independent of the initial amount of $CaCO_3$

(D) ΔH is independent of the catalyst, if any

Sol 12: (B)

$$\begin{array}{lcc} & X_{2(g)} \rightarrow & 2X_{(g)} \\ t = 0\ (\text{No. of moles}) & 1 & 0 \\ t = t & 1-\dfrac{\beta}{2} & \beta \\ t = t_{eq} & \left(1-\dfrac{\beta_{eq}}{2}\right) & \beta_{eq} \end{array}$$

$$P_x = 2\left(\frac{\beta_{eq}}{1+\dfrac{\beta_{eq}}{2}}\right) \qquad \text{nTotal} = 1-\frac{\beta_{eq}}{2}+\beta_{eq} = \left(1+\frac{\beta_{eq}}{2}\right)$$

$$Px_2 = 2\left(\frac{1-\beta_{eq/2}}{1+\beta_{eq/2}}\right)$$

$$K_P = \frac{(Px)^2}{Px_2} = \frac{\left[2\left(\dfrac{\beta_{eq}}{1+\beta_{eq}/2}\right)\right]^2}{\left[2\left(\dfrac{1-\beta_{eq}/2}{1+\beta_{eq}/2}\right)\right]^2} = \frac{2\beta_{eq}^2}{1-\dfrac{\beta_{eq}^2}{4}} = \frac{8\beta_{eq}^2}{4-\beta_{eq}^2}$$

Sol 13: (C) If $\beta_{eq} = 0.7$

$$K_p = \frac{8\times(0.7)^2}{4-(0.7)^2} = \frac{3.92}{3.51} > 1$$

Which can't be possible as $\Delta G^\circ > 0$ ($\Rightarrow K_p < 1$).

∴ Therefore, option (C) is incorrect.