Chapter 11

CHEMICAL EQUILIBRIUM

1. INTRODUCTION

Equilibrium represents the state of a process in which the proprties like temperature, pressure, concentration of the system do not show any change with the passage of time.

If the opposing processes involve only physical changes, the equilibrium is called **physical equilibrium**. If the opposing processes involve chemical changes, i.e., the opposing processes are chemical reactions, the equilibrium is called **chemical equilibrium**.

2. TYPES OF EQUILIBRIUM

Equilibrium is classified into 4 types:

(i) Physical Equilibrium

(ii) Chemical Equilibrium

(iii) Thermal Equilibrium

(iv) Mechanical Equilibrium

Here we will study about physical and chemical equilibrium.

2.1 Physical Equilibrium

The equilibrium estabilised during physical state transformation is called physical equilibrium.

2.1.1 Solid - Liquid Equilibrium:

For any substance the equilibrium estabilised at 1 atm pressure and its normal melting or freezing point is called solid-liquid equilibrium.

Rate of melting of soild = rate of freezing of liquid.

For example equilibrium estabilised between ice and water at 1 atm pressure and $0^{\circ}\mathrm{C}$ temperature.

2.1.2 Liquid -Vapour Equilibrium

For any substance the equilibrium estabilised at 1 atm pressure and its normal boiling point is called liquid-vapour equilibrium.

Rate of evaporation of liquid = rate of condensation of vapours.

For example equilibrium estabilised between water and steam at 1 atm pressure and $100^{\circ}\mathrm{C}$ temperature.

2.1.3 Soild -Vapour Equilibrium

The equilibrium estabilised when a solid is converted into its vapours directly, for example when dry ice changes into CO_2 gas.

Rate of sublimation of solid = rate of desublimation of vapours.

2.1.4 Equilibrium Involving Saturated Solutions:

In a saturated solution, an equilibrium exits between the solute molecules in the solid state and in the solution:

$$\text{Sugar (solution)} \rightleftharpoons \text{Sugar (solid)}$$

Rate of dissolution of sugar = rate of crystallisation of sugar.

Same type of equilibrium exists when a gas dissolves in of liquid.

2.1.5 Characteristics of Physical Equilibrium:

(i) Physical equilibrium is possible only in a closed system and at constant temperature.

(ii) Both forward and reverse processes occur at the same rate and there is a dynamic but stable condition.

(iii) All measurable properties of the system remain constant.

(iv) The magnitude of physical quantities like concentration, melting point etc. at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

3. TYPES OF REACTIONS

3.1 Reversible Reactions

A reaction in which not only the reactants react to form the products under certain conditions but also the products react to form reactants under the same conditions is called a **reversible reaction**.

In other words a reaction which takes place not only in the forward direction but also in the backward direction under the same conditions is called a reversible reaction.

Example :

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

3.2 Irreversible Reactions

If a reaction cannot take place in the reverse direction, i.e., the products formed do not react to give back the reactants under the same conditions, it is called an **irreversible reaction**.

$$A + B \longrightarrow C + D$$

Types of Reactions

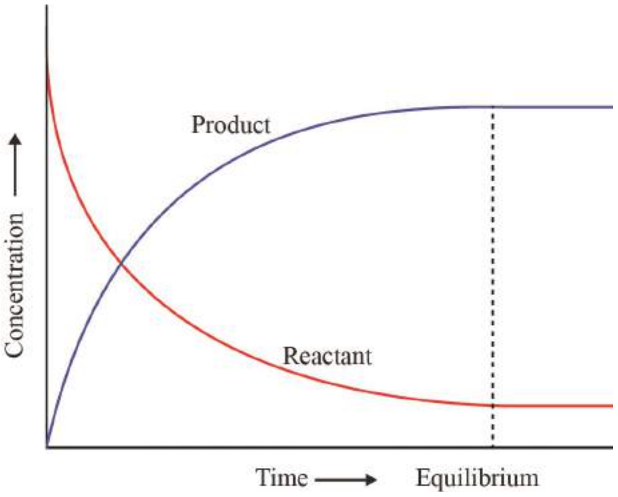
Irreversible reaction	Reversible reaction
Reaction which proceeds in forward direction only	Reaction which proceeds in forward as well as backward direction
Reactants are nearly completely converted in to products	Reactants are never completely converted in to products
Do not attain equilibrium state	Attain the equilibrium state and never go to completion

4. CHEMICAL EQUILIBRIUM

Just like physical equilibrium in physical processes, we have chemical equilibrium in reversible chemical reactions.

When the rates of the forward and reverse reactions become equal and the concentrations of the reactants and the products become constant, this state is called **chemical equilibrium**.

Chemical equilibrium is dynamic in nature because it consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

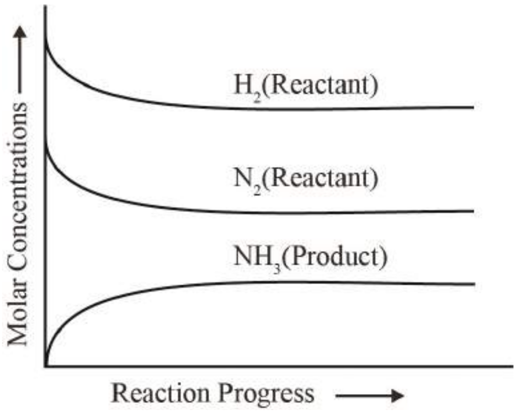


Attainment of chemical equilibrium

- Rate of forward reaction = Rate of backward reaction
- This equilibrium is dynamic and stable in nature

Example of Chemical Equilibrium

In the Haber's process, starting with definite amounts of N_2 and H_2 and carrying out the reaction at a particular temperature, when equilibrium is attained, the concentrations of N_2, H_2 and NH_3 become constant. If the experiment is repeated by taking deuterium (D_2) in place of H_2 but with the same amounts and exactly similar conditions as before, equilibrium is attained containing D_2 and ND_3 in place of H_2 and NH_3 but in the same amounts. Now, if the two reaction mixtures are mixed, then after some time, it is found that the concentrations of ammonia and hydrogen are same except that now all forms of ammonia (i.e., NH_3, NH_2D, NHD_2, ND_3) and all forms of hydrogen (i.e., H_2, HD, D_2) are present. This shows that at equilibrium, the reaction is still going on, i.e., equilibrium is dynamic in nature.



Equilibrium in manufacture of NH_3

4.1 Characteristics of Chemical Equilibrium

(i) At equilibrium, the concentration of each of the reactants and the products becomes constant.

(ii) At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and hence the equilibrium is dynamic in nature.

(iii) A chemical equilibrium can be established only if none of the products is allowed to escape out or separate out as a solid.

e.g. if CO_2 gas escapes out in case of decomposition of $CaCO_3$, the reaction will no longer remain reversible.

Similarly, the reaction is irreversible if one of the products separates out as solid,

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

(iv) Chemical equilibrium can be attained from either direction, i.e., from the direction of the reactants as well as from the direction of the products.

5. HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

5.1 Homogeneous Equilibria

Equilibrium estabilish in reactions with all reactants and products in the same phase is called **homogenous equilibrium**.

For example: $2NO_2(g) \rightleftharpoons N_2O_4(g)$

Here, reactant and product both are gases.

5.2 Heterogeneous Equilibria

Equilibrium established in reaction where various phases/states exist is termed as heterogeneous equilibrium.

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

This example there is the gas as well as solid phase.

In heterogeneous equilibria involving a pure liquid or pure solid, the molar concentration of pure solid or liquid is taken as constant.

On the other end molar concentration of gaseous and solutes in aqueous solution varies during the reaction.

6. LAW OF MASS ACTION

"The rate of a reaction is proportional to the product of the active masses of the reactants, each raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation". This is called **law of mass action**.

$$aA + bB + cC + \ldots\ldots \longrightarrow \text{Products}$$

$$\text{Rate of reaction} \propto [A]^a [B]^b [C]^c \ldots\ldots$$

Law of chemical equilibrium is a result obtained by applying the law of mass action to a reversible reaction in equilibrium.

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

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

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

6.1 Equilibrium Constant

At equilibrium,

Rate of forward reaction = Rate of backward reaction

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

At constant temperature, as k_f and k_b are constant, therefore, $\frac{k_f}{k_b} = K$ is also constant at constant temperature and is called **'equilibrium constant'.**

The product of the molar concentrations of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar concentrations of the reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temperature and is called equilibrium constant.

6.2 Equilibrium Constant in Gaseous Systems

Equilibrium constant of the reactions are expressed in terms of molar concentration of the reactants and products, and represented as K_c. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressures.

From ideal gas equation, we know that

$$pV = nRT$$

$$p = \frac{n}{V}RT$$

Here, $\frac{n}{V}$ is molar concentration of the reactant or product.

For a gaseous reaction

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

Equilibrium constant can be given as

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}; \quad K_p = \frac{\left(p_C^c\right)\left(p_D^d\right)}{\left(p_A^a\right)\left(p_B^b\right)}$$

6.3 Relationship between K_p and K_c

K_p and K_c of a gaseous reactions can be related as follows:

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

$$p = C.RT$$

$$K_p = \frac{\left(p_C^c\right)\left(p_D^d\right)}{\left(p_A^a\right)\left(p_B^b\right)} = \frac{[C]^c[D]^d(RT)^{(c+d)}}{[A]^a[B]^b(RT)^{(a+b)}}$$

$$K_p = \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{\Delta n} = K_c(RT)^{\Delta n}$$

where Δn = (number of moles of gaseous products) – (number of moles of gaseous reactants) in the balanced chemical equation.

Gaseous reaction can be of three types based on change in number of gaseous mode.

(i) Those reactions where gaseous moles increase ($\Delta n = +ve$)

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

(ii) Those reactions where gaseous moles remain the same ($\Delta n = 0$), In this case $K_p = K_c$

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

(iii) Those reactions where gaseous moles decrease ($\Delta n = -ve$)

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

6.4 Equilibrium Constant in Terms of Mole Fractions ($K\chi$)

Just like molar concentration mole fraction can also be used to represent equilibrium constant.

Considering a simple reaction;

$aA \rightarrow cC$

The equilibrium constant for the reaction is as

$$K_\chi = \frac{\chi_C^c}{\chi_A^a}$$

K_χ can be related to K_p as follows:

$$K_p = \frac{P_C^c \chi_C^c}{P_A^a \chi_A^a} = \frac{\chi_C^c}{\chi_A^a} \times (P_T)^{b-a}$$

$$K_p = K_\chi \times (P_T)^{b-a}$$

$$K_\chi = K_p \times (P_T)^{b-a}$$

$$K_\chi = K_p (P_T)^{-\Delta n}$$

Here, K_χ and K_p are the equilibrium constant in terms of molar fraction and pressure respectively and P_T represents the partial pressure of the reactants and products and Δn represents the no. of moles of the reactants minus the no.of moles of the products.

6.5 Units of Equilibrium Constant

The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same.

For the reactions, $H_2(g) + I_2(g) \rightleftharpoons 2HI$, K_p and K_c have no unit. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, K_c has unit mol/L and Kp has unit bar. Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified.

7. CHARACTERISTICS OF EQUILIBRIUM CONSTANT

(i) The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start or the direction from which the equilibrium is approached.

(ii) If the reaction is reversed, the value of the equilibrium constant in inversed.

for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \text{as, } K_c = \frac{[HI]^2}{[H_2][I_2]} = x$$

The equilibrium constant for the reverse reaction,

$2HI(g)\ H_2(g) + I_2(g)$, at the same temperature is,

$$K_c' = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{x}$$

Thus, $K_c' = 1/K_c$

(iii) If the equation (having equilibrium constant K) is divided by 2, the equilibrium constant for the new equation is the square root of K (i.e., $\sqrt{K}$).

For example, if the reaction is written as,

$$½H_2(g) + ½I_2(g) \rightleftharpoons HI(g)$$

the equilibrium constant for the above reaction is given by

$$K_c' = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} = K_c^{1/2}$$

(iv) If the equation (having equilibrium constant K) is multiplied by 2, the equilibrium constant for the new equation is the square of K (i.e., K^2)

For example, if the reaction is written as,

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

the equilibrium constant for the above reaction is given by

$$K_c'' = \frac{[HI]^4}{[H_2]^2[I_2]^2} = K_c^{\,2}$$

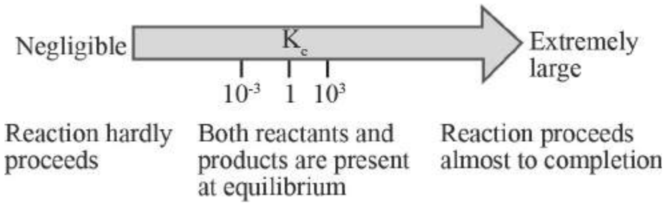
8. APPLICATIONS OF EQUIIBRIUM CONSTANTS

8.1 Predicting the Extent of a Reaction

High value of K_c **($K_c > 10^3$)** → At equilibrium reaction is forward dominant

Low value of K_c **($K_c < 10^{-3}$)** → At equilibrium reaction is backward dominant

Moderate value of K_c **(between 10^3 and 10^{-3})** → At equilibrium neither direction dominates



Dependence of extent of reaction on K_c

8.2 Predicting the Direction of a Reaction

The equilibrium constant helps in predicting the direction of a reaction in which it will proceed at any stage. For this purpose, we calculate the reaction quotient Q.

The reaction quotient, Q is defined in the same way as the equilibrium constant K except that the concentrations in Q are not necessarily equilibrium values.

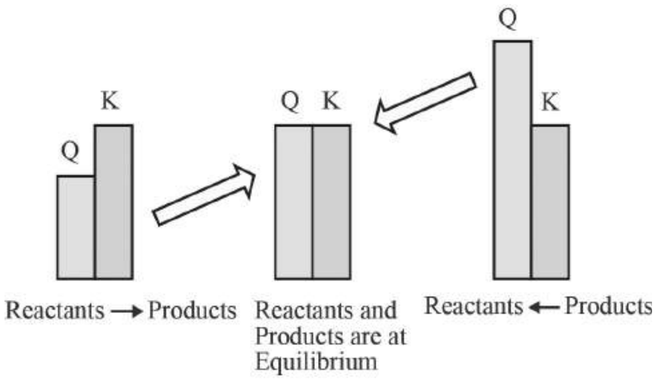
$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Q > K : Reaction will tend towards backward direction

Q < K : Reaction will tend towards forward direction

Q = K : Reaction will be at equilibrium



Predicting the direction of the reaction

NOTE

Q is a variable which always approaches K which is a constant.

8.3 Calculating Equilibrium Concentrations

Suppose we are given the following data :

1. The balanced reaction and value of K_c
2. The initial concentration of the reactants, or the initial moles
3. Volume of the container

We need to find the final equilibrium concentration of the reactants and products. Then we can follow the following steps :

Step-1: Write down the balanced chemical equation for the reaction.

Step-2: Under every reactant and product, write down the initial moles/concentration.

Step-3: Subtract the amount reacting and add the amount produced in terms of a variable x and note down the equilibrium concentration in terms of x. If we are dealing in moles then we will need to divide the moles by volume to obtain concentrations.

Step-4: Substitute the equilibrium concentration in the expression of K_c and equate it to the value of K_c.

Step-5: Solve the above equation and calculate the value of x and in case of multiple solutions select the value which is sensible from reaction point of view. Then back substitute the value of x in the equilibrium concentration expression and obtain the actual value of the same.

Example: 3.00 mol of PCl_5 kept in 1L closed reaction vessel was allowed to attain equilibrium at 380K. Calculate composition of the mixture at equilibrium. $K_c = 1.80$

Sol.

$$\begin{array}{lccc} & PCl_5 & \rightleftharpoons PCl_3 & + Cl_2 \\ \text{Initial conc.} & 3.0 & 0 & 0 \\ \text{At equilibrium:} & (3-x) & x & x \end{array}$$

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

$$1.8 = \frac{x^2}{(3-x)}$$

$$x^2 + 1.8x - 5.4 = 0$$

On solving quadratic equation

$x = 1.59$

$[PCl_5] = 3.0 - x = 3 - 1.59 = 1.41\ M$

$[PCl_3] = [Cl_2] = x = 1.59\ M$

9. DEGREE OF DISSOCIATION (α)

If the dissociation of a substance is a reversible reaction, then some amount of the substance will remain undissociated at the equilibrium.

Degree of dissociation is basically the amount of reactant dissociated at equilibrium, if we start with one mole of the reactant.

$$\text{Degree of dissociation}\,(\alpha) = \frac{\text{Number of moles dissociated at equilibriumm}}{\text{Initial number of moles taken}}$$

Percentage dissociation = $\alpha \times 100$

Example - Suppose 5 moles of PCl_5 is taken and if 2 moles of PCl_5 dissociated then-

	$PCl_5(g)$	$\rightleftharpoons PCl_3(g)$	$+\ Cl_2(g)$
Initial	5mole	0	0
At equilibrium	$5 - 2 = 3$mole	2mole	2mole

$$\alpha = \frac{2}{5} = 0.4$$

9.1 Equilibrium Constant in Terms of α

Since equilibrium constant is independent of the amount of substance taken initially, we can assume that we are starting with one mole of the substance. (if the initial amount is not given)

	$PCl_5(g)$	$\rightleftharpoons PCl_3(g)$	$+\ Cl_2(g)$
Initial	1	0	0
at equilibrium	$1-\alpha$	α	α

Total moles at equilibrium = $1 + \alpha$

Partial pressures of reaction components can be given as

$$P_{PCl_5} = \frac{(1-\alpha)}{(1+\alpha)}P\ ;\quad P_{PCl_3} = \frac{\alpha}{(1+\alpha)}P;\quad P_{Cl_2} = \frac{\alpha}{(1+\alpha)}P$$

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

9.2 Observed Molar Mass at Equilibrium

For a dissociating substance, at equilibrium, both the substance and the dissociated products are present. Thus, the molar mass of the equilibrium mixture will be the average of the molar mass of all the substances present in the equilibrium mixture. It is also known as observed molar mass.

	$A_n(g)$	$\rightleftharpoons nA(g)$
Initial	1	0
At equilibrium	$1-\alpha$	$n\alpha$

Total moles at equilibrium $= 1 + (n-1)\alpha$

We know that, moles $= \dfrac{\text{Mass}}{\text{Molar Mass}}$

Thus, molar mass of equilibrium mixture

$$= \frac{\text{Mass of the equilibrium mixture}}{\text{Total moles at equilibrium}}$$

Since mass remains conserved during a chemical process,

mass of equilibrium mixture = initial mass

$= 1 \times$ Molar mass of $A_n = M_{actual}$

Thus, molar mass of equilibrium mixture $= \dfrac{M_{actual}}{1+(n-1)\alpha}$

Observed molar mass of a dissociating substance can be thus calculated using the formula -

$$M_{Observed} = \frac{M_{actual}}{1+(n-1)\alpha}$$

9.3 Vapour Density of an Equilibrium Mixture

Vapour density is the ratio of density of the gas divided by density of hydrogen under same temperature & pressure.

Vapour density $= \dfrac{\text{Molar Mass}}{2}$

If the vapour density of a substance without dissociation

$$= D = \frac{M_{actual}}{2}$$

And, the vapour density of equilibrium mixture $= d = \dfrac{M_{observed}}{2}$

Then, $2d = \dfrac{2D}{1+(n-1)\alpha}$

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

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

On rearranging, we get $\alpha = \frac{(D-d)}{(n-1)\times d}$

10. FACTORS AFFECTING EQUILIBRIA- LE CHATELIER'S PRINCIPLE

If a distrubance is introduced in any factor determining equilibrium condition of the system, then equilibrium mixture behave so as to undo the distrubance and re-establish the equilibrium.

10.1 Effect of Change in Temperature

Exothermic reactions are favoured by low temperature whereas endothermic reations are favoured by high temperature.

This can be explained by Van't Hoff equation.

$$\ln\left(\frac{K_2}{K_1}\right) = \left(\frac{\Delta H}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or}$$

$$\log\left(\frac{K_2}{K_1}\right) = \left(\frac{\Delta H}{2.303R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

For exothermic reactions, ΔH is negative.

On increasing the temperature the equilibrium constant will decrease i.e. The reaction will become more backward dominant.

For endothermic reactions, ΔH is positive.

On increasing the temperature the equilibrium constant will increase. The reaction will become more forward dominant.

For example dimerisation of NO_2 gas to give N_2O_4 is an exothermic reaction.

$$2NO_2(g) \rightleftharpoons N_2O_4(g); \ \Delta H = -57.2\,\text{kJ mol}^{-1}$$

This reaction moves in forward direction on decreasing the temperature while on increasing the temperature it proceeds in reverse direction.

10.2 Effect of Change of Concentration

If in a reaction in equilibrium, the concentration of any reactant is increased, the equilibrium shifts in the forward direction. On the other hand, if the concentration of any product is increased, the equilibrium shifts in the backward direction. The reverse happens if the concentrations are decreased.

For example to get more ammonia from Haber's process, constant addition of nitrogen and hydrogen gases and constant removal of ammonia is requred.

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

10.3 Effect of Change of Pressure

Low pressure favours those reactions which are accompanied by increase in total number of moles of gases and high pressure favours those reactions which take place with decrease in total number of moles of gases.

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

High pressure favours the formation of ammonia while low pressure favours decomposition of ammonia.

However, pressure has no effect on an equilibrium of a reaction which proceeds with no change in total number of moles of gases.

For example $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

Reactants and products have 2 moles each of gases therefore on changing pressure of reaction equilibrium remains unchanged.

10.4 Effect of Change in Volume

The effect of decrease of volume is equivalent to the effect of increase of pressure.

Hence the effect of decrease in volume will be to shift the equilibrium in the direction in which the number of gaseous moles decreases.

An increase in volume will shift the equilibrium in the direction in which the number of gaseous moles also increases.

For example $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$.

If volume of the reaction container is increased to double of original volume then the reaction will shift in backward direction and more decomposition of SO_3 will take place.

10.5 Effect of Addition of Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

In Haber's process iron is used as catalyst, which means it significantly increases the rate of formation of ammonia at optimum temperature and pressure but it can also increase the rate of decomposition ammonia if temperature and pressure favours the backward reaction.

10.6 Effect of Adding an Inert Gas

10.6.1 At Constant Volume

If the reaction takes place at constant volume addition of an inert gas will not change the molar concentrations of the reactants and products. Hence, the state of equilibrium will remain unaffected. Addition of any inert gas in any gaseous reaction like

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

will not cause any change in equilibrium state.

10.6.2 At Constant Pressure

If the reaction takes place at constant pressure, addition of inert gas must accompany in increase in the total volume to keep pressure constant. Thus, reaction shifts towards larger number of gaseous moles.

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

On adding an inert gas this reaction will shift it backward.

11. RELATIONSHIP OF K_{eq} AND ΔG

For any reaction :

$\Delta G = \Delta G^o + RT\ lnQ$ Where Q is the reaction quotient.

At equilibrium $\Delta G = 0$ and $Q = K_{eq}$

$\Delta G^o = -RT\ lnK_{eq} = -2.303RT\ \log K_{eq}$

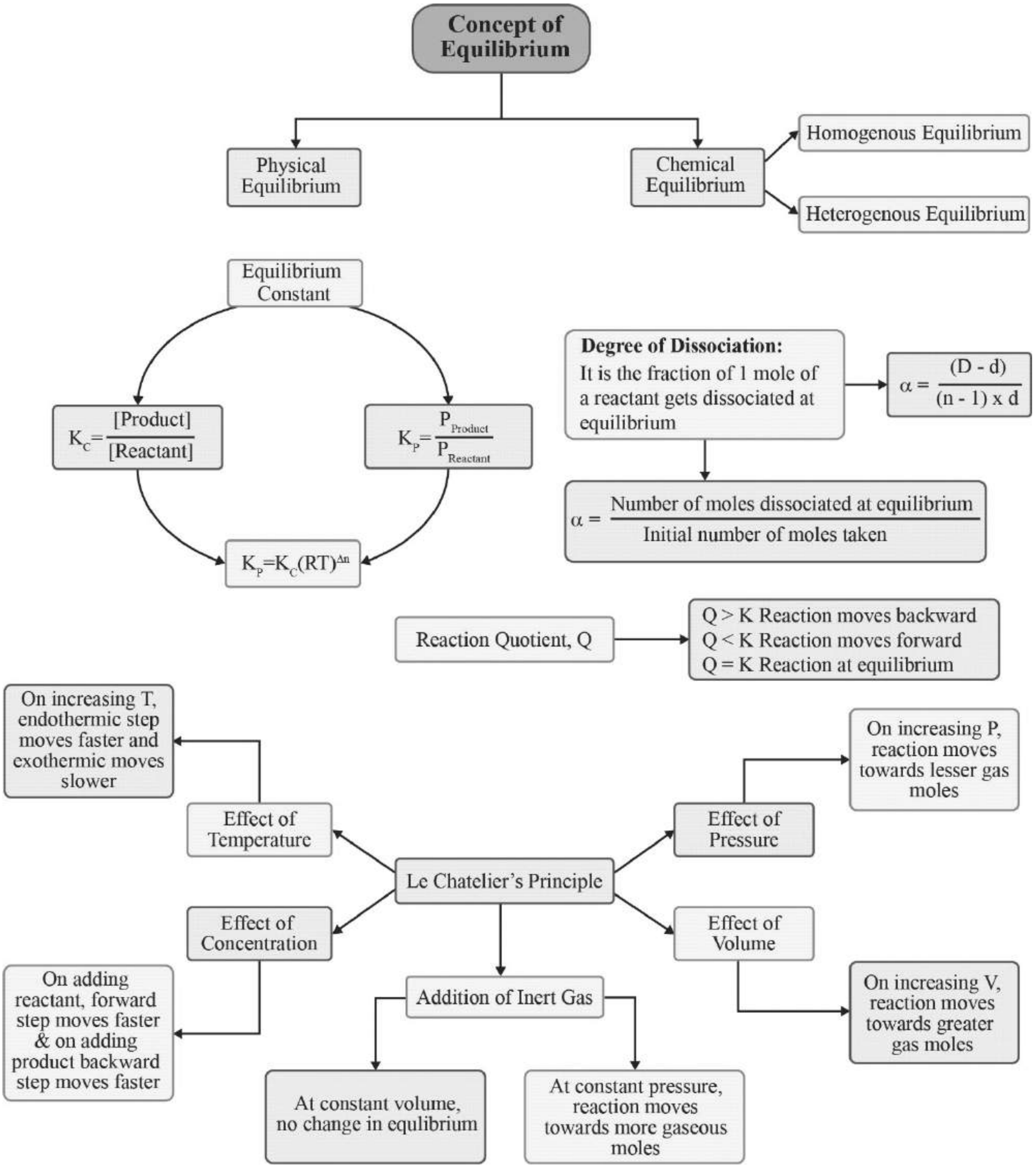
where K_{eq} is generally taken as K_p. It depends on the definition of standard values to define ΔG^o.

If the standard active masses are taken as 1 M each then we will take $K_{eq} = K_c$ and if they are taken as 1 atm each then we will take $K_{eq} = K_p$.

If $\Delta G^o < 0$, then $-\Delta G^o/RT$ is positive, and $e^{-\Delta G^o/RT} > 1$, making K >1, which indicates a spontaneous reaction.

If $\Delta G^o > 0$, then $-\Delta G^o/RT$ is negative, and $e^{-\Delta G^o/RT} < 1$, that is, K < 1, which indicates a non-spontaneous reaction.

SUMMARY



Concept of Equilibrium

Physical Equilibrium

Chemical Equilibrium

Homogenous Equilibrium

Heterogenous Equilibrium

Equilibrium Constant

$K_C = \frac{[\text{Product}]}{[\text{Reactant}]}$

$K_P = \frac{P_{\text{Product}}}{P_{\text{Reactant}}}$

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

Degree of Dissociation: It is the fraction of 1 mole of a reactant gets dissociated at equilibrium

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

$\alpha = \frac{\text{Number of moles dissociated at equilibrium}}{\text{Initial number of moles taken}}$

Reaction Quotient, Q

Q > K Reaction moves backward

Q < K Reaction moves forward

Q = K Reaction at equilibrium

Le Chatelier's Principle

Effect of Temperature

On increasing T, endothermic step moves faster and exothermic moves slower

Effect of Concentration

On adding reactant, forward step moves faster & on adding product backward step moves faster

Effect of Pressure

On increasing P, reaction moves towards lesser gas moles

Effect of Volume

On increasing V, reaction moves towards greater gas moles

Addition of Inert Gas

At constant volume, no change in equlibrium

At constant pressure, reaction moves towards more gaseous moles

SOLVED EXAMPLES

Example - 1

The following reaction has attained equilibrium

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g), \Delta H^\circ = -92.0 \text{kJ mol}^{-1}$$

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?

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

(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 $Q_c = K_c$.

(ii) $$Q_P = \frac{P_{CH_3OH}}{P_{CO}} \times \frac{1}{(2P_{H_2})^2} = \frac{1}{4}K_p$$

Again $Q_p < K_p$, equilibrium will shift in the forward direction to make $Q_p = K_p$.

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

Example - 2

A sample of HI (g) is placed in a flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI (g) is 0.04 atm. What is K_p for the given equilibrium?

Sol.

	$2HI(g) \rightleftharpoons$	$H_2(g)$	$+ I_2(g)$
Initial pressure	0.2 atm	0	0
At equilibrium	0.2 - 2x	x	x

$0.2 - 2x = 0.04$

$x = 0.08$ atm

(Decrease in the pressure of HI = 0.2–0.04=0.16 atm.)

$$\therefore K_P = \frac{P_{H_2} \times P_{I_2}}{P_{HI}^2} = \frac{0.08\text{atm} \times 0.08\text{atm}}{(0.04\text{atm})^2} = 4.0.$$

Example - 3

One mole of H_2O and one mole of CO are taken in a 10 litre vessel and heated at 725 K. At equilibrium, 40% of water (by mass) reacts with CO according to the equation:

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

Calculate the equilibrium constant for the reaction.

Sol.

	$H_2O(g)$	$+ CO(g) \rightleftharpoons$	$H_2(g)$	$+ CO_2(g)$
Initial conc.	$\frac{1}{10}M$	$\frac{1}{10}M$	0	0
At equilibrium	$\frac{1-0.4}{10}M$	$\frac{1-0.4}{10}M$	$\frac{0.4}{10}M$	$\frac{0.4}{10}M$
	$= 0.06$ M	$= 0.06$ M	$= 0.04$ M	$= 0.04$ M

At equilibrium, $[H_2O] = \dfrac{1-0.40}{10} \text{mol L}^{-1} = 0.06 \text{ mol L}^{-1}$,

$[CO] = 0.06 \text{ mol L}^{-1}$.

$$[H_2] = \frac{0.4}{10} \text{mol L}^{-1} = 0.04 \text{mol L}^{-1},$$

$[CO_2] = 0.04 \text{ mol L}^{-1}$,

$$K_C = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{0.04 \times 0.04}{0.06 \times 0.06} = 0.444$$

Example - 4

At 700 K, equilibrium constant for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.8. If 0.5 mol L^{-1} of HI (g) is present at equilibrium at 700K, what are the concentrations of H_2(g) and I_2(g) assuming that we initially started with HI (g) and allowed it to reach equilibrium at 700 K.

Sol. $H_2(g)+I_2(g) \rightleftharpoons 2HI(g), K = 54.8$

$$2HI(g) \rightleftharpoons H_2(g)+I_2(g), K' = \frac{1}{54.8}$$

At equilibrium [HI]= 0.5 mol L^{-1},

$[H_2] = [I_2] = x \text{ mol } L^{-1}$

$$\therefore K = \frac{[H_2][I_2]}{[HI]^2} = \frac{x \times x}{(0.5)^2} = \frac{1}{54.8}$$

This gives $x = 0.068$. *i.e.*, $[H_2] = [I_2] = 0.068 \text{ mol } L^{-1}$

Example - 5

What is the equilibrium concentration of each of substances in the equilibrium when the initial concentration of ICl was 0.78 M?

$$2ICl(g) \rightleftharpoons I_2(g)+Cl_2(g), K_c = 0.14$$

Sol. Suppose at equilibrium, $[I_2] = [Cl_2] = x \text{ mol } L^{-1}$. Then

	$2ICl \rightleftharpoons$	$I_2(g)$ +	$Cl_2(g)$
Initial conc.	0.78 M	0	0
At equilibrium	0.78 - 2x	x	x

$$K_c = \frac{[I_2][Cl_2]}{[ICl]^2} \quad \therefore \quad 0.14 = \frac{x \times x}{(0.78-2x)^2}$$

$$\text{or } x^2 = 0.14(0.78-2x)^2 \text{ or } \frac{x}{0.78-2x} = \sqrt{0.14} = 0.374$$

$$\text{or } x = 0.292 - 0.748x \text{ or } 1.748x = 0.292 \text{ or } x = 0.167$$

Hence, at equilibrium,

$[I_2] = [Cl_2] = 0.167M, [ICl]$
$= 0.78 - 2 \times 0.167M = 0.446M$

Example - 6

Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium represented as:

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

(i) Write the concentration ratio (reaction quotient), Q_c for this reaction (Note: water is not in excess and is not a solvent in this reaction)

(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after some time. Has equilibrium been reached?

Sol. (i) $Q_c = \dfrac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$

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

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial moles	1.00 mol	0.180 mol		
At eqm.	1–0.171 = 0.829 mol	0.180–0.171 = 0.009 mol	0.171 mol	0.171 mol
Molar concs	0.829/V	0.009/V	0.171/V	0.171/V

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{(0.171/V)(0.171/V)}{(0.829/V)(0.009/V)} = 3.92$$

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

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial moles	1.0 mol	0.5 mol		
After time t	= 1–0.214 = 0.786 mol	0.500–0.214 = 0.286 mol	0.214 mol	0.214 mol

$$\text{Reaction quotient } (Q_c) = \frac{(0.214/V)(0.214/V)}{(0.786/V)(0.286/V)} = 0.204$$

As $Q_c \neq K_c$, equilibrium has not been attained

Example - 7

A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

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

At eqm 0.5×10^{-1} M x M x M (suppose)

$$\therefore\ K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x^2}{0.5\times10^{-1}} = 8.3\times10^{-3}\text{(Given)}$$

or $x^2 = (8.3\times10^{-3})(0.5\times10^{-1}) = 4.15\times10^{-4}$

or $x = \sqrt{4.15\times10^{-4}} = 2.04\times10^{-2}M = 0.02M$

Hence, $[PCl_3]_{eq} = [Cl_2]_{eq} = 0.02M$

Example - 8

Equilibrium constant, K_c for the reaction, $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 K is 0.061. At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not, in which direction does the reaction tend to proceed to reach equilibrium?

Sol. $$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$$

As $Q_c \neq K_c$, reaction is not in equilibrium

As $Q_c < K_c$, reaction will proceed in the forward direction.

Example - 9

The equilibrium constant for the reaction $H_2(g)+Br_2(g) \rightleftharpoons 2HBr(g)$ at 1024 K is 1.6×10^5. Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

Sol. $$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g).\ K = \frac{1}{(1.6\times10^5)}$$

Initial	10 bar	0	0
At eqm.	10–p	p/2	p/2

$$K_p = \frac{(p/2)(p/2)}{(10-p)^2} = \frac{1}{1.6\times10^5} = \frac{p^2}{4(10-p)^2} = \frac{1}{1.6\times10^5}$$

Taking square root of both sides, we get

$$\frac{p}{2(10-p)} = \frac{1}{4\times10^2}\ \text{or}\ \left(4\times10^2\right)p = 2(10-p)$$

or $402p = 20$ or $p = \frac{20}{402} = 4.98\times10^{-2}$ bar

Hence, at equilibrium, $p_{H_2} = p_{Br_2}$

$= p/2 = 2.5\times10^{-2}$ bar, $p_{HBr} = 10 - p \approx 10$ bar

Example - 10

Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

$CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$. If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? $K_p = 0.1$ at 400°C.

Sol. Suppose the partial pressure of H_2 at equilibrium= p bar

	$CO(g)$	$+\ H_2O(g) \rightleftharpoons$	$CO_2(g)\ +$	$H_2(g)$
Initial pressure	4.0 bar	4.0 bar		
At eqm	(4–p)	(4–p)	p	p

$$K_p = \frac{p^2}{(4-p)^2} = 0.1\text{(given)}\ \therefore \frac{p}{4-p} = \sqrt{0.1} = 0.316$$

$p = 1.264 - 0.316p$ or $1.316p = 1.264$ or $p = 0.96$ bar.

Hence, $(p_{H_2})_{eq} = 0.96$ bar

Example - 11

Predict which of the following reaction will have appreciable concentration of reactants and products:

(a) $Cl_2(g) \rightleftharpoons 2Cl(g), K_c = 5\times10^{-39}$

(b) $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g), K_c = 3.7\times10^8$

(c) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g), K_c = 1.8$

Sol. For reaction (c), as K_c is neither very high nor very low, reactants and products will be present in comparable amounts.

Example - 12

The value of K_c for reaction, $3O_2(g) \rightleftharpoons 2O_3$ (g), is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3?

Sol. $$K_c = \frac{[O_3]^2}{[O_2]^3} \therefore 2.0\times10^{-50} = \frac{[O_3]^2}{\left(1.6\times10^{-2}\right)^3}$$

or $[O_3]^2 = (2.0 \times 10^{-50})(1.6\times10^{-2})^3 = 8.192\times10^{-56}$

or $[O_3] = 2.86\times10^{-28}$ M

Example - 13

The reaction, $CO(g)+3H_2(g) \rightleftharpoons CH_4(g) + H_2O$ (g), is at equilibrium at 1300 K in a 1 L flask. It also contains 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant K_C, for the reaction at the given temperature is 3.90.

Sol. $$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

$$\therefore\ 3.90 = \frac{[CH_4](0.02)}{(0.30)(0.10)^3}$$

(molar conc= No. of moles because volume of flask = 1L)

or $[CH_4] = 0.0585$ M $= 5.85\times10^{-2}$ M

Example - 14

At temperature T, a compound $AB_2(g)$ dissociates according to the reaction

$$2AB_2 \rightleftharpoons 2AB(g) + B_2(g)$$

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.

Sol. $$2AB_2 \rightleftharpoons 2AB(g) + B_2(g)$$

Initial moles	1 mole	0	0
At equilibrium	$1 - x$	2 x	x

Total number of moles at equilibrium = $1 - x + 2x + x = 1 + 2x$

Partial pressure = mole fraction × P_{Total}

$$p_{AB_2} = \frac{1-x}{1+2x}\times P,\ p_{AB} = \frac{2x}{1+2x}\times P, p_{B_2} = \frac{x}{1+2x}\times P$$

$$\therefore\ K_p = \frac{p^2_{AB}\times p_{B_2}}{p^2_{AB_2}} = \left(\frac{2x\times P}{1+2x}\right)^2 \times \left(\frac{x\times P}{1+2x}\right) \times \left(\frac{1+2x}{(1-x)p}\right)^2$$

$$\text{or } K_p = \frac{4x^3P}{(1-x)(1+2x)}$$

Neglecting x in comparison to unity,

$$K_p = 4x^3P \text{ or } x = \left(\frac{K_p}{4P}\right)^{1/3}$$

Example - 15

Prove that the pressure necessary to obtain 50% dissociation of PCl_5 at 500 K is numerically equal to three times the value of the equilibrium constant, K_p.

Sol. $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial moles	1	0	0
Moles at eqm.	1–0.5=0.5	0.5	0.5

Total=1.5 moles

If P is the total required pressure, then

$$p_{PCl_5} = \frac{0.5}{1.5}\times P = \frac{P}{3}, p_{PCl_3} = \frac{0.5}{1.5}\times P = \frac{P}{3}$$

$$p_{Cl_2} = \frac{0.5}{1.5}\times P = \frac{P}{3}$$

$$\therefore K_p = \frac{p_{PCl_3}\times p_{Cl_2}}{p_{PCl_5}} = \frac{(P/3)(P/3)}{(P/3)} = \frac{P}{3} \text{ or } P = 3K_p.$$

Example - 16

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

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

Sol. 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 - 17

The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Assuming ideal behaviour of all the gases, calculate the density of the equilibrium mixture at 400 K and 1.0 atmosphere. (Atomic mass of P = 31.0 and Cl = 35.5)

Sol.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2
Initial	1 mole	0	0
At eqm.	0.6	0.4	0.4 moles

Average molecular mass of mixture

$$= \frac{0.6(31+5\times35.5)+0.4(31+3\times35.5)+0.4(2\times35.5)}{0.6+0.4+0.4}$$

$$= \frac{125.1+55+28.4}{1.4} = 148.92$$

For ideal gases,

$$PV = nRT = \frac{w}{M}RT \text{ or } PM = \frac{w}{V}RT = d\,RT$$

$$\therefore d = \frac{PM}{RT} = \frac{1\times148.92}{0.082\times400} = 4.540\,g\,L^{-1}$$

Example - 18

At 540 K, 0.10 mol of PCl_5 are heated in a 8.0 L flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.

Sol.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2
Initial	0.1 mol		
At eqm.	0.1 – x	x	x

Total no. of moles at eqm. = 0.1 + x

$$PV = nRT, \text{i.e.}, n = \frac{PV}{RT} = \frac{1\times8}{0.0821\times540} = 0.18$$

$$\therefore 0.1 + x = 0.18 \text{ or } x = 0.08$$

$$\therefore K_c = \frac{(0.08/8)(0.08/8)}{(0.02/8)} = 0.04$$

$$K_p = K_c(RT)^{\Delta n} = 0.04(0.0821\times540)^1 = 1.77$$

Example - 19

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.

$$K_c = \frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]} = \frac{0.2\times0.6}{0.4\times0.3} = 1$$

Step 2. To calculate extra CO_2 to be added

Suppose extra CO_2 to be added = x mole. Then writing the reverse reaction, we have

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

	CO_2	$+ H_2$	$\rightleftharpoons$ CO	+ H_2O
initial moles after addition	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	0.6	(0.3+0.2) = 0.5

(V=1L) (given)

$$K_c' = \frac{1}{K_c} = \frac{0.6\times0.5}{x\times0.4} = 1 \quad \text{or} \quad x = 0.75\,\text{moles}$$

Example - 20

The degree of dissociation of N_2O_4 into NO_2 at one atmospheric pressure and 313 K is 0.310. Calculate K_p of the dissociation reaction at this temperature. What will be the degree of dissociation at 10 atmospheric pressure at the same temperature?

Sol. For the dissociation reaction

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

Initial moles $\quad 1 \qquad\qquad 0$

Moles at eqm. $1 - 0.310 \qquad 2 \times 0.310 \ (\alpha = 0.310, \text{Given})$

$\qquad\qquad = 0.69 \qquad\qquad = 0.62$

Total $= 0.69 + 0.62 = 1.31$ moles

At one atmospheric pressure,

$$p_{N_2O_4} = \frac{0.69}{1.31} \times 1 \text{ atm}, \quad p_{NO_2} = \frac{0.62}{1.31} \times 1 \text{atm}$$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{(0.62/1.31 \text{atm})^2}{(0.69/1.31 \text{atm})} = 0.425 \text{atm}$$

At 10 atmoshperic pressure, suppose degree of dissociation $= \alpha$. Then

$$N_2O_4 \rightleftharpoons 2NO_2$$

Initial moles $\quad 1 \qquad\qquad 0$

Moles at eqm $\quad 1 - \alpha \qquad 2\alpha, \qquad$ Total $= 1 + \alpha$

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times 10 \text{atm}, p_{NO_2} = \frac{2\alpha}{1+\alpha} \times 10 \text{atm}$$

$$K_p = \frac{[20\alpha/(1+\alpha)]^2}{[10(1-\alpha)/(1+\alpha)]} = \frac{40\alpha^2}{1-\alpha(1+\alpha)} = \frac{40\alpha^2}{1-\alpha^2}$$

$$\therefore \quad \frac{40\alpha^2}{1-\alpha^2} = 0.425$$

Neglecting α^2 in comparison to 1, $40\,\alpha^2 = 0.425$

or $\alpha = 0.103 = 10.3\,\%$

Example - 21

When $\alpha - D$ glucose is dissolved in water, it undergoes mutarotation to form an equilibrium mixture of $\alpha - D$ glucose and $\beta - D$ glucose containing 63.6% of the latter. Calculate K_c for the mutarotation.

Sol. $\qquad \alpha\text{-D glucose} \rightleftharpoons \beta\text{ - D glucose}$

At equilibrium $\quad 36.4\% \qquad 63.6\%$

$$K_C = \frac{[\beta - D \text{ glucose}]}{[\alpha - D \text{ glucose}]} = \frac{63.6}{36.4} = 1.747$$

Example - 22

At 77°C and one atmoshpheric pressure, N_2O_4 is 70% dissociated into NO_2. What will be the volume occupied by the mixture under these conditions if we start with 10g of N_2O_4?

Sol. $\qquad N_2O_4 \rightleftharpoons 2NO_2$

Initial moles $\quad \frac{10}{92} \qquad\qquad 0$

After dissociation $\quad \frac{10}{92} - \frac{70}{100} \times \frac{10}{92} \qquad 2 \times 0.076$

$\qquad = 0.109 - 0.076 \qquad = 0.152$

$\qquad = 0.033$

Molar mass of N_2O_4

$= 28 + 64 = 92 \text{g mol}^{-1}$

Total moles after dissociation $= 0.033 + 0.152 = 0.185$

$T = 77°C = 77 + 273\text{ K} = 350\text{ K}$

$$PV = nRT \text{ or } V = \frac{nRT}{P}$$

$$V = \frac{0.185 \text{ mole} \times 0.0821 \text{L atm K}^{-1} \text{mol}^{-1} \times 350\text{K}}{1 \text{ atm}}$$

$V = 5.32\text{ L}$

Example - 23

0.1 mole of N_2O_4 (g) was sealed in a tube under atmospheric condition at 25ºC. Calculate the number of moles of NO_2(g) present if the equilibrium N_2O_4(g) is reached after some time ($K_p = 0.14$).

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

Initial amount 0.1 mole 0

At equilibrium (0.1–x) 2x

Total = 0.1 + x moles

As P=1 atm, $p_{N_2O_4} = \dfrac{0.1-x}{0.1+x}, p_{NO_2} = \dfrac{2x}{0.1+x}$ atm

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{(2x/(0.1+x))^2}{(0.1-x)/(0.1+x)}$$

$$= \frac{4x^2}{(0.1-x)(0.1+x)} = \frac{4x^2}{0.01-x^2}$$

$$\therefore \quad \frac{4x^2}{0.01-x^2} = 0.14$$

or $4.14x^2 = 0.0014$ or $x = 0.018$

$\therefore$ No. of moles of NO_2 at equilibrium

$= 2x = 2 \times 0.018 = 0.036$ mole

Example -24

What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2]$= 0.60 M, $[O_2]$ = 0.82 M and $[SO_3]$ = 1.90 M ?

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

Sol. Equilibrium constant (K_c) which is the ratio of concentration of product to reactant when each raise to the power of its stoichiometric constant.It can be expressed as:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$= \frac{(1.90)^2 M^2}{(0.60)^2 (0.82)M^3}$$

$$= 12.23\,M^{-1}$$

Hence, the value of equilibrium constant is 12.23 M^{-1}.

Example - 25

For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000 K

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c, for the reverse reaction?

Sol. $K_c = 6.3 \times 10^{14}$ at 1000 K

K'_c for the reverse reaction will be $= \dfrac{1}{K_c}$

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Introduction to Equilibrium & Law of Mass Action

1. In chemical reaction $A \rightleftharpoons B$, the system will be known in equilibrium when

(a) A completely changes to B

(b) 50% of A changes to B

(c) The rate of change of A to B and B to A on both the sides are same

(d) Only 10% of A changes to B

2. According to law of mass action, rate of a chemical reaction is proportional to

(a) Concentration of reactants

(b) Molar concentration of reactants

(c) Concentration of products

(d) Molar concentration of products

3. The rate constant for forward and backward reactions of hydrolysis of ester are 1.1×10^{-2} and 1.5×10^{-3} per minute respectively. Equilibrium constant for the reaction is

$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$

(a) 4.33 (b) 5.33

(c) 6.33 (d) 7.33

Equilibrium Constants (K_p and K_c) and Their Properties

4. For the system $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant is

(a) $\frac{[3A][2B]}{C}$ (b) $\frac{[C]}{[3A][2B]}$

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

5. On a given condition, the equilibrium concentration of HI, H_2 and I_2 are 0.80, 0.10 and 0.10 mole/litre. The equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ will be

(a) 64 (b) 12

(c) 8 (d) 0.8

6. For the system $A(g) + 2B(g) \rightleftharpoons C(g)$, the equilibrium concentrations are A = 0.06 mol/litre, B = 0.12 mol/litre, C = 0.216 mole/litre. The K_{eq} for the reaction is

(a) 250 (b) 416

(c) 4×10^{-3} (d) 125

7. For the reaction $A + 2B \rightleftharpoons C$, the expression for equilibrium constant is

(a) $\frac{[A][B]^2}{[C]}$ (b) $\frac{[A][B]}{[C]}$

(c) $\frac{[C]}{[A][B]^2}$ (d) $\frac{[C]}{2[B][A]}$

8. Unit of equilibrium constant for the reversible reaction $H_2 + I_2 \rightleftharpoons 2HI$ is

(a) mol^{-1} litre (b) mol^{-2} litre

(c) mol $litre^{-1}$ (d) None of these

9. In a reaction $A + B \rightleftharpoons C + D$, the concentrations of A, B, C and D (in moles/litre) are 0.5, 0.8, 0.4 and 1.0 respectively. The equilibrium constant is

(a) 0.1 (b) 1.0

(c) 10 (d) ∞

10. The suitable expression for the equilibrium constant of the reaction $2NO\,(g) + Cl_2(g) \rightleftharpoons 2NOCl\,(g)$ is

(a) $K_c = \frac{[2NOCl]}{[2NO][Cl_2]}$ (b) $K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$

(c) $K_c = \frac{[NOCl]^2}{[NO][Cl_2]^2}$ (d) $K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]^2}$

11. For the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the units of K_c are

(a) litre/mol (b) mol/litre

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

12. The equilibrium concentration of X, Y and YX_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) 6.25 (d) 0.00625

13. In a 500 ml capacity vessel, CO and Cl_2 are mixed to form $COCl_2$. At equilibrium, it contains 0.2 moles of $COCl_2$ and 0.1 mole of each of CO and Cl_2. The equilibrium constant K_c for the reaction $CO + Cl_2 \rightleftharpoons COCl_2$ is

(a) 5

(b) 10

(c) 15

(d) 20

14. An equilibrium mixture of the reaction

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

had 0.5 mole H_2S, 0.10 mole H_2 and 0.4 mole S_2 in one litre vessel. The value of equilibrium constant (K) in mole litre^{-1} is

(a) 0.004

(b) 0.008

(c) 0.016

(d) 0.160

15. For the reaction 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 litre^{-1} respectively. The value of K_c for the reaction is

(a) 3.3×10^2 mole litre^{-1}

(b) 3×10^1 mol litre^{-1}

(c) 3×10^{-3} mol litre^{-1}

(d) 3×10^3 mol litre^{-1}

16. In the reaction, $H_2 + I_2 \rightleftharpoons 2HI$. In a 2 litre flask, 0.4 moles of each H_2 and I_2 are taken. At equilibrium 0.5 moles of HI are formed. What will be the value of equilibrium constant, K_c?

(a) 20.2

(b) 25.4

(c) 0.284

(d) 11.1

17. Equilibrium constants K_1 and K_2 for the following equilibria

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

$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ are related as

(a) $K_2 = \frac{1}{K_1}$

(b) $K_2 = K_1^2$

(c) $K_2 = \frac{K_1}{2}$

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

18. Two gaseous equilibria

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

$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ have equilibrium constants K_1 and K_2 respectively at 298 K. Which of the following relationships between K_1 and K_2 is correct?

(a) $K_1 = K_2$

(b) $K_2 = K_1^2$

(c) $K_2 = 1/K_1^2$

(d) $K_2 = 1/K_1$

19. At a given temperature, the equilibrium constant for reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 2.4×10^{-3}. At the same temperature, the equilibrium constant for reaction.

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

(a) 2.4×10^{-3}

(b) -2.4×10^{-3}

(c) 4.2×10^2

(d) 4.8×10^{-2}

20. In which of the following reaction, the value of K_p will be equal to K_c ?

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

(b) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

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

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

21. For $N_2 + 3H_2 \rightleftharpoons 2NH_3$ + heat

(a) $K_p = K_c(RT)$

(b) $K_c = K_p(RT)$

(c) $K_p = K_c(RT)^{-2}$

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

22. In which of the following equilibria, the value of K_p is less than K_c?

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

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

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

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

23. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 721K the value of equilibrium constant (K_c) is 50. When the equilibrium concentration of both is 0.5M, the value of K_p under the same conditions will be?

(a) 0.002

(b) 0.2

(c) 50.0

(d) $50/RT$

24. 4 moles of A are mixed with 4 moles of B. At equilibrium for the reaction $A + B \rightleftharpoons C + D$, 2 moles of C and D are formed. The equilibrium constant for the reaction will be

(a) $\frac{1}{4}$

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

(c) 1

(d) 4

25. For which of the following reactions does the equilibrium constant depend on the units of concentration?

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

(b) $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$

(c) $C_2H_5OH(l) + CH_3COOH \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$
(Reaction carried in an inert solvent)

(d) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

26. $A + B \rightleftharpoons C + D$. If initially the concentration of A and B are both equal but at equilibrium, concentration of D will be twice of that of A then what will be the equilibrium constant of reaction?

(a) 4 / 9 (b) 9 / 4

(c) 1 / 9 (d) 4

27. 4.5 moles each of hydrogen and iodine heated in a sealed ten litre vessel. At equilibrium, 3 moles of HI were found. The equilibrium constant for $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ is

(a) 1 (b) 10

(c) 5 (d) 0.33

28. For the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$, K_c at 1000K is 2.37×10^{-3} If at equilibrium $[N_2] = 2M$, $[H_2] = 3M$, the concentration of NH_3 is

(a) 0.00358 M (b) 0.0358 M

(c) 0.358 M (d) 3.58 M

29. Two moles of NH_3 when put into a previously evacuated vessel (one litre), partially dissociate into N_2 and H_2. If at equilibrium one mole of NH_3 is present, the equilibrium constant is

(a) 3/4 mol^2 litre^{-2} (b) 27/64 mol^2 litre^{-2}

(c) 27/32 mol^2 litre^{-2} (d) 27/16 mol^2 litre^{-2}

30. The equilibrium constant for the reaction

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction

$NO\,(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2\,(g)$ at the same temperature is

(a) 4×10^{-4} (b) 50

(c) 2.5×10^2 (d) 0.02

31. 2 mol of N_2 is mixed with 6 mol of H_2 in a closed vessel of one litre capacity. If 50% of N_2 is converted into NH_3 at equilibrium, the value of K_c for the reaction .

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

(a) 4/27 (b) 27/4

(c) 1/27 (d) 24

32. The reaction between N_2 and H_2 to form ammonia has $K_c = 6 \times 10^{-2}$ at the temperature 500°C. The numerical value of K_p for this reaction is

(a) 1.5×10^{-5} (b) 1.5×10^{5}

(c) 1.5×10^{-6} (d) 1.5×10^{6}

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

34. A mixture of 0.3 mole of H_2 and 0.3 mole of I_2 is allowed to react in a 10 litre 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 I_2 at equilibrium is

(a) 0.15 mole (b) 0.06 mole

(c) 0.03 mole (d) 0.2 mole

35. XY_2 dissociates as :

$XY_2 \rightleftharpoons XY + Y$

Initial pressure of XY_2 is 600 mm Hg. The total pressure at equilibrium is 800 mm Hg. Assuming volume of system to remain constant, the value of K_p is

(a) 50 (b) 100

(c) 200 (d) 400

36. 15 mol of H_2 and 5.2 moles of I_2 are mixed and allowed to attain equilibrium at 500°C. At equilibrium, the concentration of HI is found to be 10 mol. The equilibrium constant for the formation of HI is.

(a) 50 (b) 25

(c) 200 (d) 15

37. For the equilibrium $AB\,(g) \rightleftharpoons A(g) + B(g)$. K_p is equal to four times the total pressure. Calculate the number moles of A formed if one mol of AB is taken initially.

(a) 0.45 (b) 0.30

(c) 0.60 (d) 0.90

38. $I_2 + I^- \rightleftharpoons I_3^-$

This reaction is set-up in aqueous medium. We start with 1 mol of I_2 and 0.5 mol of I^- in 1L flask. After equilibrium is reached, excess of $AgNO_3$ gave 0.25 mol of yellow precipitate. Equilibrium constant is

(a) 1.33 (b) 2.66

(c) 2.00 (d) 3.00

39. At a certain temp. $2HI \rightleftharpoons H_2 + I_2$ Only 50% HI is dissociated at equilibrium. The equilibrium constant is

(a) 0.25 (b) 1.0

(c) 3.0 (d) 0.50

40. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm. pressure. Ammonium 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 NH_4HS decomposition at this temperature is

(a) 0.30 (b) 0.18

(c) 0.17 (d) 0.11

Applications of Equilibrium Constant

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

(a) $K = 10^3$ (b) $K = 10^{-2}$

(c) $K = 10$ (d) $K = 1$

42. $\Delta G^\circ(HI; g) \cong +1.7$ kJ. What is the equilibrium constant at 25ºC for $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$?

(a) 24.0 (b) 3.9

(c) 2.0 (d) 0.5

43. Calculate ΔG° for conversion of oxygen to ozone

$\frac{3}{2} O_2(g) \rightarrow O_3(g)$ at 298 K, if K_p for this conversion is 2.47×10^{-29}

(a) $163\ kJ\ mol^{-1}$ (b) $2.4 \times 10^2\ kJ\ mol^{-1}$

(c) $1.63\ kJ\ mol^{-1}$ (d) $2.38 \times 10^6\ kJ\ mol^{-1}$

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

(a) 20 litres ammonia, 25 litres nitrogen, 15 litres hydrogen

(b) 20 litres ammonia, 20 litres nitrogen, 20 litres hydrogen

(c) 10 litres ammonia, 25 litres nitrogen, 15 litres hydrogen

(d) 20 litres ammonia, 10 litres nitrogen, 30 litres hydrogen

45. A 1 M solution of glucose reaches dissociation equilibrium according to equation given below $6HCHO \rightleftharpoons C_6H_{12}O_6$. What is the concentration of HCHO at equilibrium if equilibrium constant is 6×10^{22}?

(a) 1.6×10^{-8} M (b) 3.2×10^{-6} M

(c) 3.2×10^{-4} M (d) 1.6×10^{-4} M

46. 0.6 mole of NH_3 in a reaction vessel of $2 dm^3$ capacity was brought to equilibrium. The vessel was then found to contain 0.15 mole of H_2 formed by the reaction.

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

which of the following statements is true?

(a) 0.15 mole of the original NH_3 had dissociated at equilibrium.

(b) 0.55 mole of ammonia is left the vessel

(c) At equilibrium the vessel contained 0.45 mole of N_2

(d) The concentration of NH_3 at equilibrium is 0.25 mole per dm^3

47. 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) 10.0 (b) 8.5

(c) 10.5 (d) 3.9

48. The equilibrium $P_4(s) + 6\,Cl_2(g) \rightleftharpoons 4\,PCl_3(g)$ is attained by mixing equal moles of P_4 and Cl_2 in an evacuated vessel. Then at equilibrium

(a) $[Cl_2] > [PCl_3]$ (b) $[Cl_2] > [P_4]$

(c) $[P_4] > [Cl_2]$ (d) $[PCl_3] > [P_4]$

49. 40% of a mixture of 0.2 mol of N_2 and 0.6 mol of H_2 reacts to give NH_3 according to the equation :

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

at constant temperature and pressure. Then the ratio of the final volume to the initial volume of gases are

(a) 4 : 5 (b) 5 : 4

(c) 7 : 10 (d) 8 : 5

50. Calculate the partial pressure of carbon monoxide from the following

$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2\uparrow;\ K_p = 8 \times 10^{-2}$

$CO_2(g) + C(s) \rightarrow 2CO(g);\ K_p = 2$

(a) 0.2 (b) 0.4

(c) 1.6 (d) 4

Degree of Dissociation

51. 3.2 moles of hydrogen iodide 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 iodide present at equilibrium are

(a) 2.496 (b) 1.87

(c) 2 (d) 4

52. One mole of $N_2O_4(g)$ at 100 K is kept in a closed container at 1.0 atm pressure. It is heated to 400 K, where 30% by mass of $N_2O_4(g)$ decomposes of $NO_2(g)$. The resultant pressure will be

(a) 4.2 (b) 5.2

(c) 3.2 (d) 6.2

53. The vapour density of completely dissociated NH_4Cl is

(a) Double than that of NH_4Cl

(b) Half than that of NH_4Cl

(c) Same as that of NH_4Cl

(d) Determined by the amount of solid NH_4Cl taken

54. The equilibrium constant (K_p) for the decomposition of gaseous H_2O

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$$

is related to degree of dissociation (α) at a total pressure p, given by

(a) $K_p = \dfrac{\alpha^3 p^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$ (b) $K_p = \dfrac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(c) $K_p = \dfrac{\alpha^{3/2} p^2}{(1-\alpha)(2+\alpha)^{1/2}}$ (d) $K_p = \dfrac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

55. At the equilibrium of the reaction,

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

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

(a) 10% (b) 15%

(c) 20% (d) 18%

Le Chatelier's Principle

56. Pure ammonia is placed in a vessel at temperature where its dissociation (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

57. Change in volume of the system does not alter the number of moles in which of the following equilibrium

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

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

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

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

58. 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) 32 (b) 64

(c) 16 (d) 4

59. 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 followinng statement held 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

60. What is the effect of halving the pressure by doubling the volume on the following system at 500°C?

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

(a) Shift to product side

(b) Shift to product formation

(c) Liquefaction of HI

(d) No effect

61. In equilibrium $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H^+$

The equilibrium constant may change when

(a) CH_3COO^- are added (b) CH_3COOH is added

(c) Catalyst is added (d) Mixture is heated

62. Which of the following statements regarding a chemical equilibrium is wrong?

(a) An equilibrium can be shifted by altering the temperature or pressure

(b) An equilibrium is dynamic

(c) The same state of equilibrium is reached whether one starts with the reactants or the products

(d) The forward reaction is favoured by the addition of a catalyst

63. The formation of SO_3 takes place according to the following reaction,

$2SO_2 + O_2 \rightleftharpoons 2SO_3$; $\Delta H = -45.2$ kcal

The formation of SO_3 is favoured by

(a) Increasing in temperature

(b) Removal of oxygen

(c) Increase of volume

(d) Increasing of pressure

64. $N_2 + O_2 \rightleftharpoons 2NO$ - Q cals

In the above reaction which is the essential condition for the higher production of NO?

(a) High temperature (b) High pressure

(c) Low temperature (d) Low pressure

65. Which of the following reactions proceed at low pressure?

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (b) $H_2 + I_2 \rightleftharpoons 2HI$

(c) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (d) $N_2 + O_2 \rightleftharpoons 2NO$

66. The reaction A + B $\rightleftharpoons$ C + D +Heat has reached equilibrium. The reaction may be made to proceed forward by

(a) Adding more C

(b) Adding more D

(c) Decreasing the temperature

(d) Increasing the temperature

67. According to Le-chatelier principle, if heat is given to solid-liquid system, then

(a) Quantity of solid will reduce

(b) Quantity of liquid will reduce

(c) Increase in temperature

(d) Decrease in temperature

68. Following gaseous reaction is undergoing in a vessel $C_2H_4 + H_2 \rightleftharpoons C_2H_6$; $\Delta H = -32.7$ Kcal

Which will increase the equilibrium concentration of C_2H_6?

(a) Increase of temperature

(b) By reducing temperature

(c) By removing some hydrogen

(d) By adding some C_2H_6

69. The effect of increasing the pressure on the equilibrium

$2A(g) + 3B(g) \rightleftharpoons 3A(g) + 2B(g)$ is

(a) Forward reaction is favoured

(b) Backward reaction is favoured

(c) No effect

(d) None of the above

70. The exothermic formation of ClF_3 is represented by the equation

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

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

(a) Increasing the temperature

(b) Removing Cl_2

(c) Increasing the volume of the container

(d) Adding F_2

71. In which of the following system, doubling the volume of the container cause a shift to the right?

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

(b) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

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

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

72. Which of the following information can be obtained on the basis of Le-chatelier's principle?

(a) Entropy change in a reaction

(b) Dissociation constant of a weak acid

(c) Equilibrium constant of a chemical reaction

(d) Shift in equilibrium position on changing value of a constant

73. 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?

(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 change

74. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)\ \Delta H = +q$ cal, then formation of HI

(a) Is favoured by lowering the temperature

(b) Is favoured by increasing the pressure

(c) Is unaffected by change in pressure

(d) Is unaffected by change in temperature

75. The formation of nitric oxide by contact process $N_2 + O_2 \rightleftharpoons 2NO, \Delta H = 43.200$ kcal is favoured by

(a) Low temperature and low pressure

(b) Low temperature and high pressure

(c) High temperature and high pressure

(d) High temperature and excess reactants concentration

76. The following two equilibria exist simultaneously in a closed vessel :

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

$COCl_2\ (g) \rightleftharpoons CO\ (g) + Cl_2\ (g)$

If some CO is added into the vessel, then after the equilibrium is attained again, concentration of

(a) PCl_5 will increase

(b) PCl_5 will decrease

(c) PCl_5 will remain unaffected

(d) Cl_2 will increase

77. In the reaction, $A_2(g) + 4\ B_2(g) \rightleftharpoons 2AB_4(g)$

$\Delta H < 0$ the formation of AB_4 is will be favoured at

(a) Low temperature, high pressure

(b) High temperature, low pressure

(c) Low temperature, low pressure

(d) High temperature, high pressure

78. In the following reversible reaction

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

Most suitable condition for the higher production of SO_3 is

(a) High temperature and high pressure

(b) High temperature and low pressure

(c) Low temperature and high pressure

(d) Low temperature and low pressure

79. In the reaction $A(g) + 2B(g) \rightleftharpoons C(g) + Q$ kJ, greater product will be obtained or the forward reaction is favoured by

(a) At high temperature and high pressure

(b) At high temperature and low pressure

(c) At low temperature and high pressure

(d) At low temperature and low pressure

80. The yield of product in the reaction

$A_2(g) + 2B(g) \rightleftharpoons C(g) - Q$.kJ. would be high at

(a) High temperature and high pressure

(b) High temperature and low pressure

(c) Low temperature and high pressure

(d) Low temperature and low pressure

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTIONS

Objective Questions I [Only one correct option]

1. For the reaction **(2002)**

$$CO\,(g) + \frac{1}{2}O_2\,(g) \rightleftharpoons CO_2\,(g), K_p/K_c \text{ is}$$

(a) RT

(b) $(RT)^{-1}$

(c) $(RT)^{-1/2}$

(d) $(RT)^{1/2}$

2. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equilibrium? **(2002)**

(a) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

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

(c) $H_{2(g)} + 1/2O_{2(g)} \rightleftharpoons H_2O_{(g)}$

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

3. For the reaction 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 the reaction is **(2003)**

(a) 3×10^3 mol L^{-1}

(b) 3.3×10^2 mol L^{-1}

(c) 3×10^{-1} mol L^{-1}

(d) 3×10^{-3} mol L^{-1}

4. The conditions favourable for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)};\quad \Delta H^o = -198 \text{ kJ}$$

are **(2003)**

(a) Low temperature, high pressure

(b) Any value of T and P

(c) Low temperature and low pressure

(d) High temperature and high pressure

5. What is the equilibrium expression for the reaction **(2004)**

$$P_4(s) + 5O_2\,(g) \rightleftharpoons P_4O_{10}\,(s)\,?$$

(a) $K_c = \dfrac{[P_4O_{10}]}{[P_4][O_2]^5}$

(b) $K_c = \dfrac{1}{[O_2]^5}$

(c) $K_c = [O_2]^5$

(d) $K_c = \dfrac{[P_4O_{10}]}{5[P_4][O_2]}$

6. For the reaction **(2004)**

$$CO(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g), \text{ the } \frac{K_p}{K_c} \text{ is equal to}$$

(a) $\dfrac{1}{RT}$

(b) 1.0

(c) $\sqrt{RT}$

(d) RT

7. The equilibrium constant for the reaction

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

at temperature, T is 4×10^{-4}. The value of K_c for the reaction

$$NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$

at the same temperature is **(2004)**

(a) 2.5×10^2

(b) 0.02

(c) 4×10^{-4}

(d) 50

8. A small amount of NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium 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 NH_4HS decomposition at this temperature is **(2005)**

(a) 0.30

(b) 0.18

(c) 0.17

(d) 0.11

9. For the reaction

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

$(K_c = 1.8 \times 10^{-6}$ at 184°C) $[R = 0.0831$ kJ/(mol.K)]

When K_p and K_c are compared at 184°C it is found that **(2005)**

(a) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure

(b) $K_p = K_c$

(c) K_p is greater than K_c

(d) K_p is greater than K_c

10. Phosphorus pentachloride dissociates 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 PCl_5 is x, the partial pressure of PCl_3 will be **(2006)**

(a) $\left(\frac{x}{x+1}\right)P$ (b) $\left(\frac{2x}{1-x}\right)P$

(c) $\left(\frac{x}{x-1}\right)P$ (d) $\left(\frac{x}{1-x}\right)P$

11. 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

$2SO_2 + O_2(g) \rightleftharpoons 2SO_3(g)$ will be **(2006)**

(a) 416 (b) 2.40×10^{-3}

(c) 9.8×10^{-2} (d) 4.9×10^{-2}

12. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressure at these equilibria is **(2008)**

(a) 1 : 36 (b) 1 : 1

(c) 1 : 3 (d) 1 : 9

13. For the following three reactions 1, 2 and 3 equilibrium constants are given

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

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

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

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

(a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$

(c) $K_3 = K_1K_2$ (d) $K_3 \,.\, K_2^3K_1^2$

14. A vessel at 1000 K contains CO with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_p is **(2011)**

(a) 1.8 atm (b) 3 atm

(c) 0.3 atm (d) 0.18 atm

15. 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) -1/2 (b) 1/2

(c) 1 (d) –1

16. At a certain temperature, only 50% HI is dissociated into H_2 and I_2 at equilibrium. The equilibrium constant is: **(Online 2014 Set-1)**

(a) 1.0 (b) 3.0

(c) 0.5 (d) 0.25

17. What happens when an inert gas is added to an equilibrium keeping volume unchanged? **(Online 2014 Set-3)**

(a) More reactant will form

(b) More product will form

(c) Equilibrium will remain unchanged

(d) Less product will form

18. For the decomposition of the compound represented as

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

The $K_p = 2.9 \times 10^{-5}$ atm³.

If the reaction is started with 1 mol of the compound, the total pressure at equilibrium would be : **(Online 2014 Set-4)**

(a) 5.82×10^{-2} atm (b) 7.66×10^{-2} atm

(c) 38.8×10^{-2} atm (d) 1.94×10^{-2} atm

19. 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 : **(2015)**

[R = 8.314 J/K/mol, e = 2.718]

(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 $Q > K_C$

20. The increase of pressure on ice $\rightleftharpoons$ water system at constant temperature will lead to : **(Online 2015 Set-1)**

(a) a decrease in the entropy of the system

(b) an increase in the Gibbs energy of the system

(c) no effects on the equilibrium

(d) a shift of the equilibrium in the forward direction

21. For the equilibrium, $A(g) \rightleftharpoons B(g)$, ΔH is –40 kJ/mol. If the ratio of the activation energies of the forward (E_f) and reverse (E_b) reactions is $\frac{2}{3}$ then : **(Online 2015 Set- 1)**

(a) $E_f = 80$ kJ/mol; $E_b = 120$ kJ/mol

(b) $E_f = 60$ kJ/mol; $E_b = 100$ kJ/mol

(c) $E_f = 30$ kJ/mol; $E_b = 70$ kJ/mol

(d) $E_f = 70$ kJ/mol; $E_b = 30$ kJ/mol

22. The equilibrium constant at 298 K for reaction $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1M each, then equilibrium concentration of D (in mol L^{-1}) will be: **(2016)**

(a) 0.818 (b) 1.818

(c) 1.182 (d) 0.182

23. A solid XY kept in an evacuated sealed container undergoes decomposition to form a mixture of gases X and Y at temperature T. The equilibrium pressure is 10 bar in this vessel. K_p for this reaction is : **(Online 2016 Set-2)**

(a) 5 (b) 10

(c) 25 (d) 100

24. The following reaction occurs in the Blast Furnace where iron ore is reduced to iron metal :

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(l) + 3CO_2(g)$$

Using the Le Chatelier's principle, predict which one of the following will not disturb the equilibrium ?

(Online 2017 Set-2)

(a) Removal of CO (b) Removal of CO_2

(c) Addition of CO_2 (d) Addition of Fe_2O_3

25. In which of the following reactions, an increase in the volume of the container will favour the formation of products ? **(Online 2018 Set-1)**

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

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

(c) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l)$

(d) $3O_2(g) \rightleftharpoons 2O_2(g)$

26. At a certain temperature in a 5L vessel, 2 moles of carbon monoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction,

$$CO + Cl_2 \rightleftharpoons COCl_2$$

At equilibrium, if one mole of CO is present then equilibrium constant (K_c) for the reaction is : **(Online 2018 Set-2)**

(a) 2 (b) 2.5

(c) 3 (d) 4

27. The gas phase reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ is an exothermic reaction. The decomposition of N_2O_4, in equilibrium mixture of $NO_2(g)$ and $N_2O_4(g)$, can be increased by : **(Online 2018 Set-3)**

(a) lowering the temperature.

(b) increasing the pressure.

(c) addition of an inert gas at constant volume.

(d) addition of an inert gas at constant pressure.

28. Consider the following reversible chemical reactions

$$A_2(g) + B_2(g) \overset{K_1}{\rightleftharpoons} 2AB(g) \quad .....(1)$$

$$6AB(g) \overset{K_2}{\rightleftharpoons} 3A_2(g) + 3B_2(g) \quad ....(2)$$

The relation between K_1 and K_2 is: **(09-01-2019 Shift-2)**

(a) $K_1K_2 = \frac{1}{3}$ (b) $K_2 = K_1^3$

(c) $K_2 = K_1^{-3}$ (d) $K_1K_2 = 3$

29. The value of K_p/K_c for the following reactions at 300 K are, respectively: (At 300 K, RT = 24.62 dm^3 atm mol^{-1})

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(10-01-2019 Shift-1)

(a) 1, 24.62 dm^3 atm^2 mol, 606.0 dm^6 atm^2 mol

(b) 1, 24.62 dm^3 atm mol^{-1}, 1.65 x 10^{-3} dm^{-6} atm^{-3} mol^2

(c) 1, 4.1 × 10^{-2} dm atm mol, 606 dm^6 atm^2 mol

(d) 24.62 dm^3 atm mol, 606 dm^6 atm^2 mol, 1.65 × 10^{-3} dm atm mol^2

30. 5.1g NH_4SH is introduced in 3.0 L evacuated flask at 327°C, 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327°C is (R = 0.082 L atm mol^{-1} K^{-1}, molar mass of S = 32 g mol^{-1}, molar mass of N = 14 g mol^{-1}) **(10-01-2019 Shift-2)**

(a) 0.242×10^{-4} atm^2 (b) 1×10^{-4} atm^2

(c) 4.9×10^{-3} atm^2 (d) 0.242 atm^2

31. Consider the reaction $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$

The equilibrium constant of the above reaction is K_p. If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $P_{NH_3} << P_{Total}$ at equilibrium) **(11-01-2019 Shift-1)**

(a) $\frac{3^{\frac{3}{2}}K_p^{\frac{1}{2}}P^2}{16}$ (b) $\frac{K_p^{\frac{1}{2}}P^2}{16}$

(c) $\frac{K_p^{\frac{1}{2}}P^2}{4}$ (d) $\frac{3^{\frac{3}{2}}K_p^{\frac{1}{2}}P^2}{4}$

32. Two solids dissociate as follows

$$A(s) \rightarrow B(g)+C(g); K_{P_1} = z atm^2, D(s) \rightarrow$$

$$C(g)+E(g); K_{P_2} = y atm^2$$

The total pressure when both the solids dissociate simultaneously is. **(12-01-2019 Shift-1)**

(a) $\sqrt{x+y} atm$ (b) $2\left(\sqrt{x+y}\right) atm$

(c) $(x+y) atm$ (d) $x^2+y^2 atm$

33. In a chemical reaction, $A+2B \overset{K}{\rightleftharpoons} 2C+D$, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is: **(12-01-2019 Shift-1)**

(a) 4 (b) 16

(c) $\frac{1}{4}$ (d) 1

34. For the following reactions, equilibrium constants are given,

$$S(s)+O_2(g) \rightleftharpoons SO_2(g); K_1 = 10^{52}$$
$$2S(s)+3O_2(g) \rightleftharpoons 2SO_3(g); K_2 = 10^{129}$$

The equilibrium constant for the reaction, is

$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$ **(08-04-2019 Shift-2)**

(a) 10^{154} (b) 10^{181}

(c) 10^{25} (d) 10^{77}

35. For the reaction,

$$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$$
$$\Delta H = -57.2 \text{ kJ mol}^{-1} \text{ and } K_c = 1.7 \times 10^{16}$$

Which of the following statement is INCORRECT? **(10-04-2019 Shift-2)**

(a) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.

(b) The equilibrium will shift in forward direction as the pressure increases.

(c) The equilibrium constant decreases as the temperature increases.

(d) The addition of inert gas at constant volume will not affect the equilibrium constant.

36. In which one of the following equilibria, $K_P \neq K_C$? **(12-04-2019 Shift-2)**

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

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

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

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

37. For the reaction,

$2H_2(g)+2NO(g) \rightleftharpoons N_2(g)+2H_2O(g)$

The observed rate expression is, rate $= k_f [NO]^2 [H_2]$.

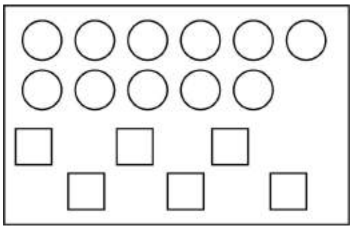
The rate expression for the reverse reaction is: **(07-01-2020 Shift-2)**

(a) $k_b [N_2][H_2O]^2$ (b) $k_b [N_2][H_2O]$

(c) $k_b [N_2][H_2O]^2/[H_2]$ (d) $k_b [N_2][H_2O]^2/[H_2]$

38. In the figure shown below reactant A (represented by the square) is in equilibrium with product B (represented by circle). The equilibrium constant is:

(09-01-2020 Shift-2)



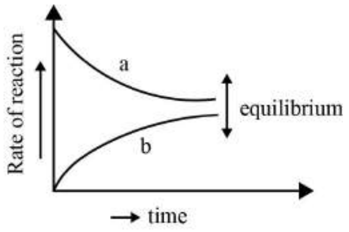
(a) 1 (b) 2

(c) 8 (d) 4

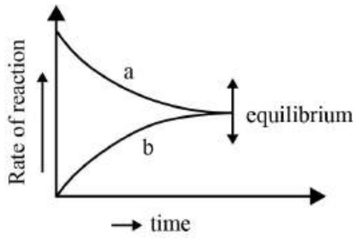
39. For the equilibrium A $\rightleftharpoons$ B the variation of the rate of the forward (a) and reverse (b) reaction with time is given by:

(09-01-2020 Shift-1)

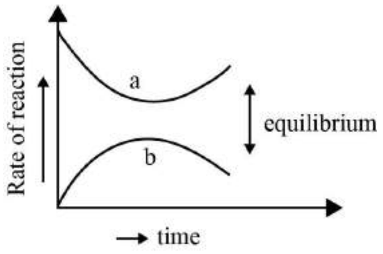
(a)



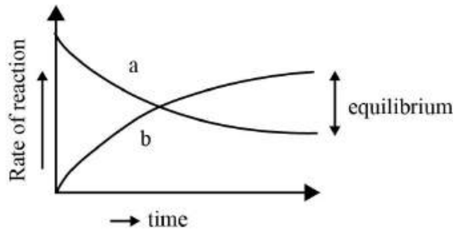
(b)



(c)



(d)



40. If the equilibrium constant for A $\rightleftharpoons$ B + C is $K_{eq}^{(1)}$ and that of B + C $\rightleftharpoons$ P is $K_{eq}^{(2)}$, the equilibrium constant for A $\rightleftharpoons$ P is: **(04-09-2020 Shift-2)**

(a) $K_{eq}^{(1)}K_{eq}^{(2)}$ (b) $K_{eq}^{(2)} - K_{eq}^{(1)}$

(c) $K_{eq}^{(1)} + K_{eq}^{(2)}$ (d) $K_{eq}^{(1)} / K_{eq}^{(2)}$

41. Consider the following reaction:

$N_2O_4(g) \rightleftharpoons 2NO_2(g);\ = +58\ kJ$

For each of the following cases (A, B), the direction in which the equilibrium shifts is:

(A) Temperature is decreased

(B) Pressure is increased by adding N_2 at constant T.

(05-09-2020 Shift-1)

(a) (A) towards reactant, (B) towards product

(b) (A) towards reactant, (B) no change

(c) (A) towards product, (B) towards reactant

(d) (A) towards product, (B) no change

42. For the reaction **(06-09-2020 Shift-1)**

$$Fe_2N(s) + \frac{3}{2}H_2(g) \rightleftharpoons 2Fe(s) + NH_3(g)$$

(a) $K_c = K_p(RT)^{1/2}$ (b) $K_c = K_p(RT)^{-1/2}$

(c) $K_c = K_p(RT)^{\frac{3}{2}}$ (d) $K_c = K_p(RT)$

43. The variation of equilibrium constant with temperature is given below:

Temp., Equilibrium Constant

$T_1 = 25°C, K_1 = 10$

$T_2 = 100°C, K_2 = 100$

The value of $\Delta H°, \Delta G°$ at T_1 and $\Delta H°, \Delta G°$ at T_2(in $kJmol^{-1}$) respectively, are close to

[use $R = 8.314\ JK^{-1}\ mol^{-1}$] **(06-09-2020 Shift-1)**

(a) 28.4, –7.14 and –5.71 (b) 0.64. –7.41 and –5.71

(c) 28.4, –5.71 and –14.29 (d) 0.64, –5.71 and –14.29

44. The value of K_C is 64 at 800 K for the reaction $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ The value of K_C for the following reaction is:

$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)$ **(06-09-2020 Shift-2)**

(a) 1/4
(b) 8
(c) 1/8
(d) 1/64

Numerical Value Type Questions

45. For a reaction $X+Y \rightleftharpoons 2Z$, 1.0 mol of X, 1.5 mol of Y and 0.5 mol of Z were taken in a 1 L vessel and allowed to react. The equilibrium, the concentration of Z was 1.0 mol L^{-1}. The equilibrium constant of reaction is...... $\frac{x}{15}$. The value of x is. **(05-09-2020 Shift-2)**

46. For the reaction $A_{(g)} \rightarrow B_{(g)}$, the value of the equilibrium constant at 300 K and 1 atm is equal to 100.0. The value of $\Delta_r G°$ for the reaction at 300 K and 1 atm in J mol^{-1} is -xR, where x is_____. (Rounded off to the nearest integer) $[R = 8.31]\ mol^{-1}\ K^{-1}$ and $\ln 10 = 2.3)$

(24-02-2021 Shift-1)

47. At 1990 K and 1 atm pressure, there are equal number of Cl_2 molecules and Cl atoms in the reaction mixture. The value of K_P for the reaction $Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$ under the above conditions is $x \times 10^{-1}$. The value of x is _____. (Rounded off to the nearest integer)

(24-02-2021 Shift-1)

48. Assuming ideal behaviour, the magnitude of log K for the following reaction at 25°C is $x \times 10^{-1}$. The value of x is _____ (integer answer)

$3HC \equiv CH_{(g)} \rightleftharpoons C_6H_{6(l)}$

[Given: $\Delta_f G°(HC \equiv CH) = -2.04 \times 10^5 Jmol^{-1}$;

$\Delta_f G°(C_6H_6) = -1.24 \times 10^5 Jmol^{-1}; R = 8.314 JK^{-1}mol^{-1}$]

(24-02-2021 Shift-2)

49. A homogeneous ideal gaseous reaction $AB_{2(g)} \rightleftharpoons A_{(g)} + 2B_{(g)}$ is carried out in a 25 litre flask at 27°C. The initial amount of AB_2 was 1 mole an the equilibrium pressure was 1.9 atm. The value of K_P is $x \times 10^{-2}$. The value of x is ___. (Integer answer) **(26-02-2021 Shift-1)**

50. For the reaction $A(g) \rightleftharpoons B(g)$ at 495 K, $\Delta_r G° = -9.478$ kJ mol^{-1}. If we start the reaction in a closed container at 495 K with 22 millimoles of A, the amount of B in the equilibrium mixture is_____ millimole. [Round off to the Nearest integer). $[R = 8.314 J\ mol^{-1}K^{-1}; \ln 10 = 2.303]$ **(16-03-2021 Shift-1)**

51. Consider the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. The temperature at which $K_C = 20.4$ and $K_P = 600.1$, is ..... K. (Round off to the Nearest integer). [Assume all gases are ideal and $R = 0.0831\ L\ bar\ K^{-1}\ mol^{-1}$]

(17-03-2021 Shift-2)

52. The gas phase reaction $2A_{(g)} \rightleftharpoons A_2(g)$ at 400 K has $\Delta G° = +25.2\ kJ\ mol^{-1}$ the equilibrium constant K_C for this reaction is ... x 10^{-2}. (Round off to the Nearest integer).
[Use: $R = 8.3 J\ mol^{-1}\ K^{-1}$, $\ln 10 = 2.3$, $\log_{10} 2 = 0.30$, 1 atm = 1 bar] [antilog (–0.3) = 0.501] **(18-03-2021 Shift-2)**

53. $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$

In an equilibrium mixture, the partial pressures are $P_{SO_3} = 43 kPa; P_{O_2} = 530 Pa$ and $P_{SO_2} = 45 kPa$. The equilibrium constant $K_P =$ _____$\times 10^{-2}(kPa)^{-1}$ (nearest integer) **(20-07-2021 Shift-1)**

54. Value of K_p for the equilibrium reaction $N_2O_{4(g)} \rightleftharpoons 2NO_2(g)$ at 288 K is 47.9. The K_c for this reaction at same temperature is _____. (Nearest integer). ($R = 0.083\ L\ bar\ K^{-1}\ mol^{-1}$) **(20-07-2021 Shift-2)**

55. For the reaction $A+B \rightleftharpoons 2C$ the value of equilibrium constant is 100 at 298 K. If the initial concentration of all the three species is 1 M each, then the equilibrium concentration of C is $x \times 10^{-1} M$. The value of x is _____. (Nearest integer)

(25-07-2021 Shift-1)

56. Equilibrium constant for the reaction

$$A(s) \rightleftharpoons M(s) + \frac{1}{2}O_2(g)$$

is $K_p = 4$. At equilibrium, the partial pressure of O_2 is _____ atm. (Round off to the nearest integer)

(27-07-2021 Shift-2)

57. $PCl_5 \rightleftharpoons PCl_3 + Cl_2; K_c = 1.844$

3.0 moles of PCl_5 is introduced in a 1 L vessel. The number of moles of PCl_5 at equilibrium is _____ x 10^{-3}. (Round off to the Nearest integer) **(27-07-2021 Shift-1)**

58. The equilibrium constant K_c at 298 K for the reaction $A + B \rightleftharpoons C + D$ is 100. Starting with an equimolar solution with concentrations of A, B, C and D all equal to 1 M, the equilibrium concentration of D is….. x 10^{-2} M. (Nearest integer) **(26-08-2021 Shift-2)**

59. The reaction rate for the reaction

$$[PtCl_4]^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3]^{-} + Cl^{-}$$

was measured as a function of concentrations of different species, it was observed that

$$\frac{-d\left[[PtCl_4]^{2-}\right]}{dt} = 4.8\times10^{-5}\left[[PtCl_4]^{2-}\right] - 2.4\times10^{-3}$$

$$\left[[Pt(H_2O)Cl_3]^{-}\right]\left[Cl^{-}\right]$$

where square brackets are used to denote molar concentrations. The equilibrium constant, K_c = _____

(26-08-2021 Shift-2)

60. When 5.1 g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 20% of the solid decomposes into gaseous ammonia and hydrogen sulphide. The K_p for the reaction at 27°C is $x \times 10^{-2}$. The value of x is _____. (integer answer)[Given $R = 0.082$ L atm K^{-1} mol^{-1}]

(26-08-2021 Shift-1)

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

Objective Questions I [Only one correct option]

1. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted to CO on addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :

(a) 0.18 atm (b) 1.8 atm

(c) 3 atm (d) 0.3 atm

2. The equilibrium reaction : $2AB(aq) \rightleftharpoons 2A(aq) + B_2(g)$ has an equilibrium constant equal to 1.28. If the concentrations of AB and A are 5 mol/L and 4 mol/L respectively, what is $[B_2]$?

(a) 0.50 M (b) 1.60 M

(c) 2.00 M (d) 2.84 M

3. For a reversible reaction : $A + B \rightleftharpoons C$

$$\left(\frac{dx}{dt}\right) = 2.0 \times 10^3\ \text{L mol}^{-1}\ \text{s}^{-1}\ [A]\ [B] - 1.0 \times 10^2\ \text{s}^{-1}\ [C]$$

where x is the amount of 'A' dissociated. The value of equilibrium constant (K_{eq}) is :

(a) 10 (b) 0.05

(c) 20 (d) Can't be calculated

4. Equilibrium constant K_c for the following reaction at 800K is, 4.

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

The value of K_P for the following reaction will be :

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

(a) $\left(\frac{800R}{4}\right)^{-2}$ (b) $16 \times (800R)^2$

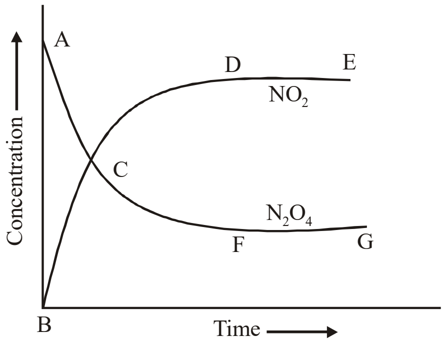
(c) $\left[\frac{1}{4 \times 800R}\right]^2$ (d) $(800R)^{1/2} 4$

5. $N_2O_4 \rightleftharpoons 2NO_2$, $K_c = 4$. This reversible reaction is studied graphically as shown in the given figure. Select the correct statement out of I, II and III.

I : Reaction quotient has maximum value at point A

II : Reaction proceeds left to right at a point when $[N_2O_4] = [NO_2] = 0.1$ M

III : $K_c = Q$ when point D or F is reached.



(a) I, II (b) II, III

(c) II (d) I, II, III

6. $I_2 + I^- \rightleftharpoons I_3^-$

This reaction is set-up in aqueous medium. We start with 1 mol of I_2 and 0.5 mol of I^- in 1L flask. After equilibrium is reached, excess of $AgNO_3$ gave 0.25 mol of yellow ppt. Equilibrium constant is : [Given : $AgNO_3$ gives yellow ppt with I^-]

(a) 1.33 (b) 2.66

(c) 2.00 (d) 3.00

7. Equilibrium constant for two complexes are :

A : $K_4[Fe(CN)_6]$ $K = 2.6 \times 10^{37}$ (for dissociation)

B : $K_3[Fe(CN)_6]$ $K = 1.9 \times 10^{17}$ (for dissociation)

(a) A and B are equally stable

(b) A is more stable than B

(c) B is more stable than A

(d) the predictable stability

8. Consider the reaction

$$NaBr(aq)+H_2SO_4(aq) \rightleftharpoons NaHSO_4(aq)+HBr(aq).$$

The equilibrium constant is 8.3×10^{-2}. If the equilibrium concentrations of NaBr, H_2SO_4 and $NaHSO_4$ are 6.0 M, 9.0 M and 3.0 M respectively, what is the molarity of HBr ?

(a) 1.8×10^{-2} M (b) 6.7×10^{-1} M

(c) 1.5×10^{0} M (d) 3.6×10^{1} M

9. For the all gas reaction at 1000 K : $2HI \rightleftharpoons H_2 + I_2$, K = 0.0344. If you were to begin with 8.0 M of HI in a fixed volume container, what would be the equilibrium concentration of H_2 ?

(a) 1.10 M (b) 0.48 M

(c) 5.8 M (d) 2.92 M

10. If for the heterogeneous equilibrium

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; K = 1 at 1 atm,

the temperature is given by :

(a) $T = \frac{\Delta S^o}{\Delta H^o}$ (b) $T = \frac{\Delta H^o}{\Delta S^o}$

(c) $T = \frac{\Delta G^o}{R}$ (d) $T = \frac{\Delta G^o}{\Delta H^o}$

11. The free energy of formation of NO is 78 kJ mol^{-1} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at this reaction at 1000 K ?

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

(a) 8.4×10^{-5} (b) 7.1×10^{-9}

(c) 4.2×10^{-10} (d) 1.7×10^{-19}

12. Volume of the flask in which the following equilibria are separately established are transferred to a flask that is double the size of the earlier flask. In which of the following cases, equilibrium constants are affected ?

(a) $N_{2(g)} + H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, exothermic

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

(c) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$, endothermic

(d) none of these

13. During thermal dissociation, the observed vapour density of N_2O_4 (g) is 26.0. The extent of dissociation of N_2O_4 (g) is :

(a) 50% (b) 87%

(c) 77% (d) 23%

14. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the value of K_p is 1.7 $\times 10^3$ at 500 K and 1.78×10^4 at 600 K. Which of the following is correct ?

I. The proportion of NO_2 in the equilibrium mixture is increased by decreasing the pressure

II. The standard enthalpy change for the forward reaction is negative

III. units of K_p are atm

IV. At 500 K, the degree of dissociation N_2O_4 decreases by 50% by increasing the pressure by 100%.

The correct choice is :

(a) I, III (b) I

(c) II, IV (d) III

15. Consider the equilibrium, $CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$

The equilibrium constant K is given by (when $\alpha <<< 1$) :

(a) $K = \frac{\alpha^{3/2}}{\sqrt{2}}$ (b) $K = \frac{\alpha^3}{2}$

(c) $K = \frac{\alpha^{3/2}}{2}$ (d) $K = \frac{\alpha^{3/2}}{\sqrt{3}}$

16. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; if percentage dissociation of N_2O_4 are 25%, 50%, 75% and 100%, then the sequence of observed vapour densities will be :

(a) $d_1 > d_2 > d_3 > d_4$ (b) $d_4 > d_3 > d_2 > d_1$

(c) $d_1 = d_2 = d_3 = d_4$ (d) $(d_1 = d_2) > (d_3 = d_4)$

17. In the preparation of CaO from $CaCO_3$ using the equilibrium,

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, (At 1 atm)

K_p is expressed as $\log K_p = 7.282 - \frac{8500}{T}$.

For complete decomposition of $CaCO_3$ the temperature in celsius to be used is :

(a) 1167 (b) 894

(c) 8500 (d) 850

18. To the system $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

in equilibrium, some N_2 gas was added at constant volume. Then,

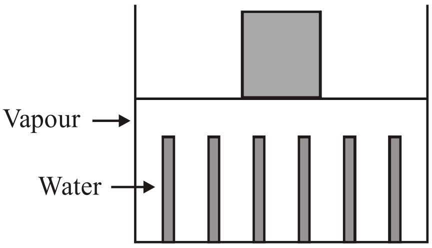
(a) K_p will remain constant and K_c will change

(b) K_c will remain constant and K_p will change

(c) Both K_p and K_c will remain constant

(d) Both K_p and K_c will change

19. Some quantity of water is contained in a container as shown in figure below. As neon is added to this system at constant pressure, the amount of liquid water in the vessel:



(a) increases (b) decrease

(c) remains same (d) change unpredictably

20. Solubility of a substance which dissolves with a decrease in volume and absorption of heat will be favoured by

(a) high p and high T (b) low p and low T

(c) high p and Low T (d) low p and high T

21. When a liquid in equilibrium with its vapour is heated

(a) the rate of the reaction, vapour $\rightleftharpoons$ liquid, is increased

(b) the same equilibrium mixture is re-established

(c) a new equilibrium mixture with a higher vapour pressure is established

(d) a new equilibrium mixture is established in which the rate of evaporation is greater than the rate of condensation

22. Given the following reactions and associated equilibrium constants, select the correct expression for the third equilibrium constant in terms of the first two.

$$(A)\, 2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g); K_{c_1}$$

$$(B)\, H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g); K_{c_2}$$

$$(C)\, CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_{c_3}$$

(a) $K_{c_3} = \dfrac{K_{c_1}}{K_{c_2}}$ (b) $K_{c_3} = \dfrac{(K_{c_1})^{1/2}}{K_{c_2}}$

(c) $K_{c_3} = K_{c_1} \times (K_{c_2})^{1/2}$ (d) $K_{c_3} = (K_{c_1})^{1/2} \times (K_{c_2})^{1/2}$

23. In the reaction : $A + B \rightleftharpoons 2C + D$. The initial concentration of A and B are 1M each. The value of K_c is 10^8. What is the equilibrium concentration of A ?

(a) 2×10^{-4} M (b) 2×10^4 M

(c) 0.005 M (d) 0.0025 M

24. For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$, the equilibrium constant K_c at 25°C is 4×10^{-19} ; then Ag^+ concentration in a solution which has 0.1 M KCN and 0.03M $AgNO_3$ is :

(a) 7.5×10^{18} (b) 7.5×10^{-18}

(c) 7.5×10^{19} (d) 7.5×10^{-19}

25. In reversible reaction $A \rightleftharpoons B$, the initial concentration of A and B are a and b in moles per litre and the equilibrium concentration are (a – x) and (b – x) respectively ; express x in terms of k_1, k_2, a and b.

(a) $\dfrac{k_1a - k_2b}{k_1 + k_2}$ (b) $\dfrac{k_1a - k_2b}{k_1 - k_2}$

(c) $\dfrac{k_1a - k_2b}{k_1k_2}$ (d) $\dfrac{k_1a + k_2b}{k_1 + k_2}$

26. In each of the following, total pressure set-up at equilibrium is assumed to be equal and is one atm with equilibrium constants K_P given :

I : $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g), K_1$

II : $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g), K_2$

III : $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g), K_3$

In the increasing order :

(a) $K_1 = K_2 = K_3$ (b) $K_1 < K_2 < K_3$

(c) $K_3 < K_2 < K_1$ (d) None of these

27. The equilibrium constant for the decomposition of water,

$$\left[H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)\right]$$

is given by :

(a) $K = \dfrac{\alpha^3 p^{1/2}}{(1-\alpha)(2-\alpha)^{1/2}}$ (b) $K = \dfrac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(c) $K = \dfrac{\alpha^3 p^{1/2}}{\sqrt{2}}$ (d) $K = \dfrac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

28. In a 1.0 L aqueous solution when the reaction

$$2\,Ag^{+}_{(aq)} + Cu_{(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2\,Ag_{(s)}$$

reaches equilibrium, $[Cu^{2+}] = x$ M and $[Ag^{+}] = y$ M.

If the volume of solution is doubled by adding water, then at equilibrium :

(a) $[Cu^{2+}] = \frac{x}{2}M, [Ag^{+}] = \frac{y}{2}M$

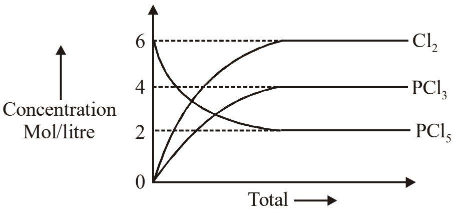
(b) $[Cu^{2+}] > \frac{x}{2}M, [Ag^{+}] > \frac{y}{2}M$

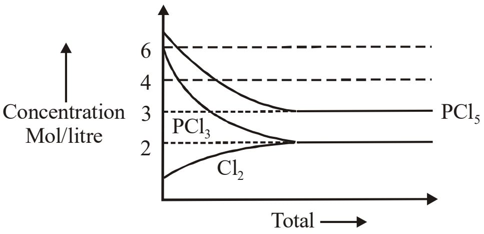
(c) $[Cu^{2+}] < \frac{x}{2}M, [Ag^{+}] > \frac{y}{2}M$

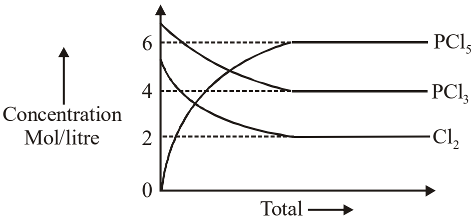
(d) $[Cu^{2+}] < \frac{x}{2}M, [Ag^{+}] < \frac{y}{2}M$

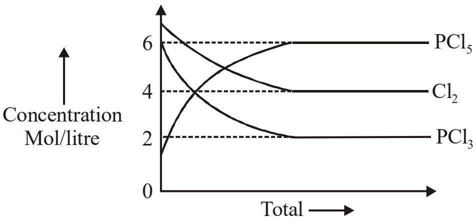
29. For the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

Which of the following sketch may represent above equilibrium ? Assume equilibrium can be achieved from either side and by taking any one or more components initially. (Given K_C for the reaction < 2) ?

(a)


(b)


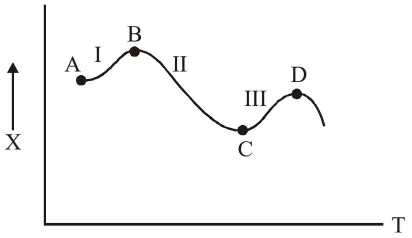
(c)


(d)


30. For the following reaction through stages I, II and III

$$A \xrightarrow{I} B \xrightarrow{II} C \xrightarrow{III} D$$

quantity of the product formed (x) varies with temperature (T) as given. Select correct statement :



(a) Stages I and III are endothermic but II is exothermic

(b) Stages I and III are exothermic but II is endothermic

(c) Stages II and III are exothermic but I is endothermic

(d) Stage I is exothermic but stages II and III are endothermic

31. 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) has no effect

(d) increase the reaction rate

32. A solution is transferred to a 1 L flask, some pure ice is added and a stopper is inserted to close the flask. After the system has reached constant temperature, there are still a few cubes of ice left in the flask, but no other solid. Which of the following statements is false relative to this system at equilibrium ?

(a) The system is a heterogeneous one.

(b) There are four phases present in the system, not including the container and stopper.

(c) The vapour pressure is constant.

(d) The temperature of the system is below 0ºC.

33. On heating a mixture of SO_2Cl_2 and CO, two equilibria are simultaneously established :

$$SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$$
$$CO(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$$

On adding more SO_2 at equilibrium what will happen ?

(a) Amount of CO will decrease

(b) Amount of SO_2Cl_2 and $COCl_2$ will increase

(c) Amount of CO will remain unaffected

(d) Amount of SO_2Cl_2 and CO will increase

Objective Questions II

[One or more than one correct option]

34. Which of the following statements about the reaction quotient, Q are correct ?

(a) the reaction quotient, Q and the equilibrium constant always have the same numerical value

(b) Q may be lesser than, equal to or greater than K_{eq}

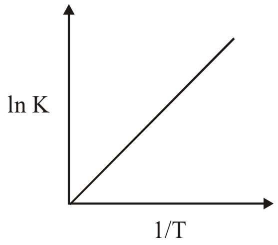
(c) Q (numerical value) varies as reaction proceeds

(d) $Q = 1$ at equilibrium

35. Variation of equilibrium constant K for the reaction

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

is plotted against absolute temperature T in figure as : ln K vs (1/T)



(a) the forward reaction is exothermic

(b) the forward reaction is endothermic

(c) the slope of line is proportional to ΔH

(d) adding 'A' favours forward reaction

36. Which is/are correct ?

(a) $2.303 \log K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$

(b) $\Delta G^o = -2.303\, RT \log K$

(c) $-2.303 \log K = -\frac{\Delta H^o}{RT^2} + \frac{\Delta S^o}{R}$

(d) $2.303 \log K = \frac{1}{RT}(\Delta H^o + \Delta S^o)$

37. The variation of equilibrium constant K with temperature is represented by :

(a) $\log_e K_2 - \log_e K_1 = -\frac{\Delta H}{R}\int_{T_1}^{T_2}\left(\frac{1}{T}\right)dT$

(b) $\left\{\frac{d \log_e K}{dT}\right\}_P = -\frac{\Delta H}{RT}$

(c) $\log_e K = \text{Constant} - \frac{RT}{\Delta H}$

(d) $\log_e K = \text{Constant} - \frac{\Delta H}{RT}$

38. An industrial fuel, 'water gas' which consists of a mixture of H_2 and CO can be made by passing steam over red-hot carbon. The reaction is

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g); \Delta H = +131 \text{ kJ}$$

The yield of CO and H_2 at equilibrium would be shifted to the product side by

(a) raising the relative pressure of steam

(b) adding hot carbon

(c) raising the temperature

(d) reducing the volume of the system

39. Yield of NH_3 in Haber's process

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}, \Delta H = -22 \text{ kcal};$$

can be increased by

(a) compressing the reaction system

(b) raising the temperature

(c) decreasing the temperature

(d) using the catalyst to lower down the activation energy

40. The volume of the reaction flask is reduced to half of its initial value, temperature being constant. In which of the following cases the position of the equilibrium would shift?

(a) $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(s)}$

(b) $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$

(c) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

(d) $I_{2(g)} \rightleftharpoons 2I_{(g)}$

41. $KNO_{3(s)}$ dissociates on heating as :

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

At equilibrium in a closed container

(a) addition of $NaNO_{3(s)}$ favours forward reaction

(b) addition of $KNO_{2(s)}$ favours reverse reaction

(c) increasing temperature favours forward reaction

(d) decreasing pressure favours forward reaction

42. The dissociation of phosgene, which occurs according to the reaction :

$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$

is an endothermic process. Which of the following factors will increase the degree of dissociation of $COCl_2$?

(a) Adding Cl_2 to the system

(b) Adding helium to the system at constant pressure

(c) Decreasing the temperature of the system

(d) Reducing the total pressure

43. For the following endothermic equilibrium established by dissociation of NH_4HS to its components,

$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

partial pressure of NH_3 will increase

(a) if NH_3 is added after equilibrium is established

(b) if H_2S is added after equilibrium is established

(c) temperature is increased

(d) volume of the flask is decreased

44. Volume of the flask in which the following equilibria are separately established are transferred to a flask that is double the size of the earlier flask. In which of the following cases, equilibrium concentrations are affected ?

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

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

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

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

45. For the reaction : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$,

The forward reaction at constant temperature is favoured by

(a) introducing an inert gas at constant volume

(b) introducing chlorine gas at constant volume

(c) introducing an inert gas at constant pressure

(d) increasing the volume of the container

46. Which of the following factors will favour the backward reaction ?

$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g) ; \Delta H = -ve$

(a) Addition of inert gas at constant pressure

(b) Addition of Cl_2 gas

(c) Increase in the temperature of reaction

(d) Increasing the volume of the container

47. For the reaction : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, The forward reaction at constant temperature is favoured by

(a) introducing an inert gas at constant volume

(b) introducing chlorine gas at constant volume

(c) introducing an inert gas at constant pressure

(d) increasing the volume of the container

48. The dissociation of ammonium carbamate may be represented by the equation

$NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$

$\Delta H°$ for the forward reaction is negative. The equilibrium will shift from right to left if there is

(a) a decrease in pressure

(b) an increase in temperature

(c) an increase in the concentration of ammonia

(d) an increase in the concentration of carbon dioxide

49. Which of the following factors will increase solubility of a well known weak base, $NH_{3(g)}$, in H_2O ?

$NH_{3(g)} + H_2O_{(aq)} \rightleftharpoons NH_4OH_{(aq)}$

(a) increase in pressure (b) addition of water

(c) addition of an acid to water

(d) addition of a base to water

50. For the gas phase reaction,

$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g) ; \Delta H° = -136.8 \text{ kJ mol}^{-1}$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by :

(a) increase in temperature (b) decrease in pressure

(c) removing some H_2 (d) adding some C_2H_6

Numerical Value Type Questions

51. Given the hypothetical reaction :

$2A(s) + nB(g) \rightleftharpoons 3C(g) \quad K_p = 0.0105$

and K_c = 0.45 at 250°C. What is the value of coefficient 'n' ?

52. For the equilibrium AB(g) $\rightleftharpoons$ A(g) + B(g), at a given temperature $\frac{1}{3}$rd of AB is dissociated, then $\frac{P}{K_p}$ will be numerically equal to _____.

53. SO_2Cl_2 and Cl_2 are introduced into a 3L vessel. Partial pressure of SO_2Cl_2 and Cl_2 at equilibrium are 1 atm and 2 atm respectively. The value of K_p for the following reaction

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is 10.

The total pressure in atm at equilibrium would be ____.

54. What weight of solid ammonium carbamate (NH_2COONH_4) when vaporised at 200°C will have a volume of 8.96 litre at 1 atm ? Assume that solid completely decomposes into CO_2 and NH_3 at 200°C and 1 atm.

55. Two equilibria are simultaneously existing in a vessel at 25°C

$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g); K_{p_1}$ (say)

$2NO_2(g) \rightleftharpoons N_2O_4(g);\ K_{p_2} = 8\ atm^{-1}$

If initially only NO and NO_2 are present in a 3 : 5 mole ratio and the total pressure at equilibrium is 5.5 atm with the pressure of NO_2 is 0.5 atm, calculate K_{p_1} (in 10^{-1})

56. 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 40 atm, and that over solid C only is 60 atm. Find the pressure over the solid mixture.

Assertion Reason

(A) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

(B) If both Assertion and Reason are true but 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.

57. **Assertion (A) :** Chemical equilibrium represents a state of a reversible reaction in which measurable properties of the system (pressure, concentration, colour etc.) become constant under the given set of conditions.

Reason (R) : The chemical equilibrium is an apparent state of rest in which two opposing reactions are proceeding at the same rate.

(a) A (b) B
(c) C (d) D

58. **Assertion (A) :** The reaction quotient, Q has the same form as the equilibrium constant K_{eq} and is evaluated using any given concentrations of the species involved in the reaction, and not necessarily equilibrium concentrations.

Reason (R) : If the numerical value of Q is not the same as the value of equilibrium constant, a reaction will proceed.

(a) A (b) B
(c) C (d) D

59. **Assertion (A) :** The active mass of pure solids and pure liquids is taken unity.

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

(a) A (b) B
(c) C (d) D

60. **Assertion (A) :** For a reaction at equilibrium, the free energy for the reaction is minimum.

Reason (R) : The free energy for both reactants and products decreases and become equal.

(a) A (b) B
(c) C (d) D

61. **Assertion (A) :** If some $PCl_5(g)$ containing labelled phosphorus ^{31}P is added to a system with following equilibrium, after sometime the system was found to contain radioactive PCl_3.

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

Reason (R) : Chemical equilibrium is dynamic in nature.

(a) A (b) B
(c) C (d) D

62. **Assertion (A) :** As a reversible system approaches equilibrium, entropy of the system increases.

Reason (R) : The state of equilibrium is the most disordered state of a reversible system.

(a) A (b) B
(c) C (d) D

63. **Assertion (A) :** The dissociation of $CaCO_3$ can be represented as, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. Some solid $CaCO_3$ is placed in an evacuated vessel enclosed by a piston and heated so that a portion of it is decomposed. If the piston is moved so that the volume of the vessel is doubled, while the temperature is held constant, the number of moles of CO_2 in the vessel increases.

Reason (R) : The pressure of CO_2 in the vessel will remain the same.

(a) A (b) B
(c) C (d) D

64. **Assertion (A) :** For the reaction

$$A(g) + B(g) \rightleftharpoons 2AB(g)$$

at the given temperature, there will be no effect by addition of inert gas either at constant pressure or at constant volume.

Reason (R) : For the reaction where $\Delta n = 0$, there is no effect of inert gas either at constant volume or at constant pressure because K_p becomes purely a number.

(a) A (b) B

(c) C (d) D

65. **Assertion (A) :** Addition of an inert gas at constant pressure equilibrium will support the dissociation of PCl_5 at the same temperature.

Reason (R) : The addition of an inert gas will tend to increase the total pressure.

(a) A (b) B

(c) C (d) D

66. **Assertion (A) :** The addition of an inert gas under constant volume condition cause the total pressure of the system to increase. This would thus lower the degree of dissociation of PCl_5.

Reason (R) : Addition of inert gas at equilibrium increase the kinetic energy of molecules.

(a) A (b) B

(c) C (d) D

Match the Following

Each question has two columns. Four options are given representing matching of elements from Column-I and Column-II. Only one of these four options corresponds to a correct matching. For each question, choose the option corresponding to the correct matching.

67. Match the Column-I with Column-II :

Column-I (Equations)	**Column-II** (Type of process)
(A) $K_p > Q$	(p) Non spontaneous
(B) $\Delta G^o < RT \log_e Q$	(q) Equilibrium
(C) $K_p = Q$	(r) Spontaneous and endothermic
(D) $T > \dfrac{\Delta H}{\Delta S}$	(s) Spontaneous

(a) A -s, B - p, C - q, D - r (b) A -p, B - q, C - s, D - r

(c) A -r, B - q, C - p, D - r (d) A -q, B - r, C - s, D - p

68. Match the Column-I with Column-II :

Column-I (Reaction)	**Column-II** (Effect on equilibrium)
(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$ $\Delta H = -ve$	(p) Forward shift by lowering of temperature
(B) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = +ve$	(q) Forward shift by rise in temperature
(C) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\Delta H = +ve$	(r) No effect of pressure change
(D) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -ve$	(s) Forward shift by rise in pressure

(a) A- p,s B- q,r C- q D- p,s (b) A- p,r B- q,r C- s D- p,s

(c) A- p,s B- q,r C- r D- p,s (d) A- p,r B- q,r C- r D- p,s

69. Match the conditions on the left column with states on the right column.

Column–I Equilibrium types	**Column–II** K_p/K_c relationship
(A) $A_2(g) \rightleftharpoons 2A(g); K_c = 1.$	(p) System is at Mixture of 1.0 mole of each equilibrium is prepared in a 1.0 L flask.
(B) $A(g) + 2B(g) \rightleftharpoons AB_2(g)$	(q) Goes to right $K_c = 2$. A mixture of 2.0 moles of each A, B and AB_2 is prepared in a 1.0 L flask.
(C) $A_2(g) \rightleftharpoons 2A(g)\,; K_p = 2$. At	(r) $n(A) > n(A_2)$ at equilibrium the total pressure equilibrium is 2.0 atm.
(D) $2A(g) \rightleftharpoons A_2(g) K_p = 2$. A	(s) $n(A) < n(A_2)$ at mixture, initially containing equilibrium both A and A_2 at 1.0 atm partial pressure is prepared.

(a) A-p, r; B-p,q; C-p,q,r; D-p,q,b

(b) A-p, s; B-p,q; C-p,q,s; D-p,q,b

(c) A-p, r; B-p,q; C-p,q,r; D-p,r,b

(d) A-p, r; B-p,q; C-p,s,r; D-p,r,b

70. Match the Column–I with Column–II

Column–I	**Column–II**
(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(p) No effect of inert gas addition at constant volume
(B) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	(q) Homogenous equilibria
(C) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	(r) $K_p > K_c$
(D) $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$	(s) K_p depends on partial pressures of products only.

(a) A - q; B - q, p; C - r, s; D - s, r

(b) A - r; B - q, s; C - s; D - s, r

(c) A - q; B - q, p; C - r; D - s, r

(d) A - q; B - r, p; C - s; D - s, r

Paragraph Type Questions

Use the following passage, to solve Q. 71 to Q. 73

Passage

Effect of temperature on the equilibrium process is analyzed by using the thermodynamics. From the thermodynamics relation.

$\Delta G^o = -2.303\ RT \log K$ ...(i)

ΔG^o : Standard free energy change

$\Delta G^o = \Delta H^o - T\Delta S^o$ ...(ii)

ΔH^o : Standard heat of the reaction

From (i) and (ii)

$-2.303\ RT \log K = \Delta H^o - T\Delta S^o$

ΔS^o : Standard entropy change

$$\Rightarrow \log K = -\frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R} \quad ...(iii)$$

If a plot of log K vs 1/T is made then it is a straight line having slope $= \dfrac{-\Delta H^o}{2.303R}$ and Y intercept $= \dfrac{\Delta S^o}{2.303R}$

If at temperature T_1, equilibrium constant be K_1 and at temperature T_2, equilibrium constant be K_2 then the above equation reduces to :

$$\Rightarrow \log K_1 = -\frac{\Delta H^o}{2.303RT_1} + \frac{\Delta S^o}{2.303R}$$

$$\Rightarrow \log K_2 = -\frac{\Delta H^o}{2.303RT_2} + \frac{\Delta S^o}{2.303R}$$

Substracting (iv) from (v) we get.

$$\Rightarrow \log \frac{K_2}{K_1} = \frac{\Delta H^o}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

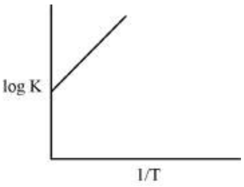
From the above relation we can conclude that the value of equilibrium constant increases with increase in temperature for an endothermic reaction and the same decreases with the increase in temperature for an exothermic reaction. Answer the following three questions based on the above information.

71. If standard heat of dissociation of PCl_5 is 230 cal, then slope of the graph of log K vs $\dfrac{1}{T}$ is

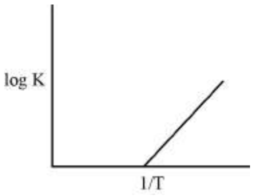
(a) +50
(b) –50
(c) 10
(d) None of these

72. For exothermic reaction if $\Delta S^o < 0$, then the sketch of log K vs 1/T may be

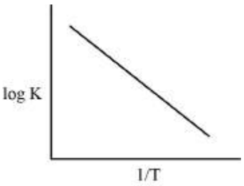
(a)



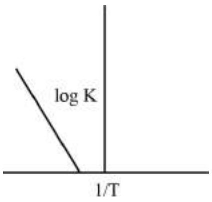
(b)



(c)



(d)



73. If for a particular reversible reaction : $K_c = 57$ at 355°C and $K_c^{'} = 69$ at 450°, then

(a) $\Delta H < 0$

(b) $\Delta H > 0$

(c) $\Delta H = 0$

(d) Sign of ΔH can't be determined

Use the following passage, to solve Q. 74 to Q. 76

Passage

These 3 questions deal with the following chemical reaction:

$$\underset{\text{(green solution)}}{Ni^{2+}(aq)} + 6NH_3(aq) \rightleftharpoons \underset{\text{(Blue Solution)}}{\left[Ni(NH_3)_6\right]^{2+}}(aq)$$

When H^+(aq) is added, the colour green is favoured. Use one or more of the following interpretations to answer the questions.

I. Some unreacted Ni^{2+} (aq) is present in the solution at equilibrium.

II. Some unreacted NH_3 (aq) is present in the solution at equilibrium.

III. The colour change indicates new equilibrium conditions with reduced $[Ni(NH_3)_6]^{2+}$(aq).

IV. The colour change indicates new equilibrium conditions with increased $[Ni(NH_3)_6]^{2+}$(aq).

74. The deepening colour on dissolving more $Ni(NO_3)_2$ supports interpretation(s)

(a) I only (b) I and IV only

(c) II and IV only (d) I and II only

75. The deepening colour on addition of more NH_3(aq) supports intepretation(s)

(a) I only (b) I and IV only

(c) I and II only (d) II and IV only

76. The disappearance of colour on addition of H^+ (aq). supports interpretation(s)

(a) I only (b) II and IV only

(c) I and II only (d) III only

Use the following passage, to solve Q. 77 to Q. 78

Passage

These 3 questions refer to the following experiment. Some $Fe(NO_3)_3$ solution is added to KSCN solution and a dark red colour appears. This colour is caused by $[Fe(SCN)]^{2+}$, which is formed by the reaction :

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

Experiments show this colour becomes deeper upon addition of more $Fe(NO_3)_3$ or KSCN. The colour disappears when Na_2HPO_4 is added. Use one or more of the interpretations below.

(a) Unreacted Fe^{3+} (aq) is present in the original equilibrium mixture.

(b) Unreacted SCN^- (aq) is present in the original equilibrium mixture.

(c) Colour change indicates a new equilibrium ; $[Fe(SCN)^{2+}(aq)]$ has been reduced.

(d) Colour change indicates a new equilibrium ; $[Fe(SCN)^{2+}(aq)]$ has been increased.

77. The deepening of colour on addition of more $Fe(NO_3)_3$ supports

(a) A only (b) A and D only

(c) A and B only (d) B and D only

78. The disappearance of colour on addition of Na_2HPO_4 supports

(a) A only (b) A and D only

(c) A and B only (d) C only

Use the following passage, to solve Q. 79 to Q. 80

Passage

Le-Chatelier's principle : If a system at equilbrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way as to "Nullify" the effect of that change.

If a system in equilibrium consists of gases, then the concentrations of all components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionly. The total number of moles per unit volume will now be more and the equilibrium will shift in that direction in which there is decrease in number of moles i.e, towards the direction in which there is decrease in volume.

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

Solid (higher volume) $\rightleftharpoons$ liquid (lower volume)

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

Solids whose volume increase on melting e.g. Fe, Cu, Ag, Au, etc.

Solid (lower volume) $\rightleftharpoons$ liquid (higher volume)

In this case, the process of melting becomes difficult at high pressure ; thus melting point becomes high. Answer the following two questions based on the above information.

79. Au(s) $\rightleftharpoons$ Au(l)

Above equilibrium is favoured at

(a) high pressure, low temperature

(b) high pressure, high temperature

(c) low pressure, high temperature

(d) low pressure, low temperature

80. For the reaction : $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$

If pressure is increased by reducing the volume of the container, then

(a) total pressure at equilibrium will remain same

(b) concentration of all the components at equilibrium will change

(c) concentration of all the components at equilibrium will remain same

(d) equilibrium will shift in the forward direction

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTIONS

Objective Questions I [Only one correct option]

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

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ **(1984)**

(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 hydrogen is less than that of nitrogen

2. 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_2Cl_2 change

(b) More chlorine is formed

(c) Concentration of SO_2 is reduced

(d) All the above are incorrect

3. 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 of CO(g)

4. For the chemical reaction

$3X(g) + Y(g) \rightleftharpoons X_3Y(g)$

the amount of X_3Y at equilibrium is affected by **(1999)**

(a) temperature and pressure

(b) temperature only

(c) pressure only

(d) temperature, pressure and catalyst

5. 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 mole litre^{-1} is **(2000)**

(a) $\dfrac{1.44\times10^{-5}}{(0.082\times500)^{-2}}$ (b) $\dfrac{1.44\times10^{-5}}{(8.314\times773)^{-2}}$

(c) $\dfrac{1.44\times10^{-5}}{(0.082\times773)^{2}}$ (d) $\dfrac{1.44\times10^{-5}}{(0.082\times773)^{-2}}$

6. 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

7. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = (4x^2P) / (1 - x^2)$, where P = presssure, x = extent of decomposition. Which one of the following statements is true ? **(2001)**

(a) K_p increases with increase of P

(b) K_p increases with increase of x

(c) K_p increases with decrease of x

(d) K_p remains constant with change in P and x

8. Consider the following equilibrium in a closed container

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

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_p) and degree of dissociation (α) ? **(2008)**

(a) Neither K_p nor α changes

(b) Both K_p and α changes

(c) K_p changes but α does not change

(d) K_p does not change but α changes

9. $N_2 + 3H_3 \rightleftharpoons 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition ? **(2006)**

(a) The equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increase in the direction of spontaneous reaction

(b) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward directions to the same extent

(c) The catalyst will increase the rate of forward reaction by β

(d) Catalyst will not alter the rate of either of the reaction.

Objective Questions II [One or more than one correct option]

10. 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

11. 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 forward reaction

(d) increasing pressure favours reverse reaction

12. For the reaction, $PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

The forward reaction at constant temperature is favoured by **(1991)**

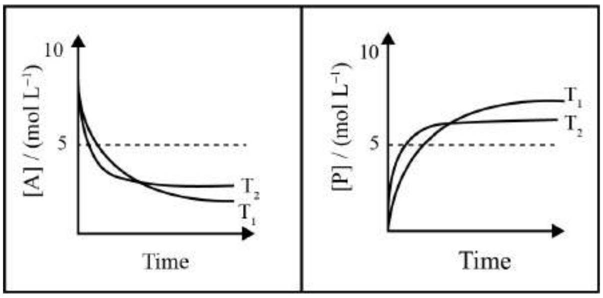
(a) introducing chlorine gas at constant volume

(b) introducing an inert gas at constant pressure

(c) increasing the volume of the container

(d) introducing PCl_5 at constant volume

13. For a reaction, $A \rightleftharpoons P$, the plots of [A] and [P] with time at temperatures T_1 and T_2 are given below. **(2018)**



If $T_2 > T_1$, the correct statement(s) is (are)

(Assume ΔH° and ΔS° are independent of temperature and ratio of lnK at T_1 to lnK at T_2 is greater than T_2/T_1. Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

(a) $\Delta H^\circ < 0, \Delta S^\circ < 0$

(b) $\Delta G^\circ < 0, \Delta H^\circ > 0$

(c) $\Delta G^\circ < 0, \Delta S^\circ < 0$

(d) $\Delta G^\circ < 0, \Delta S^\circ > 0$

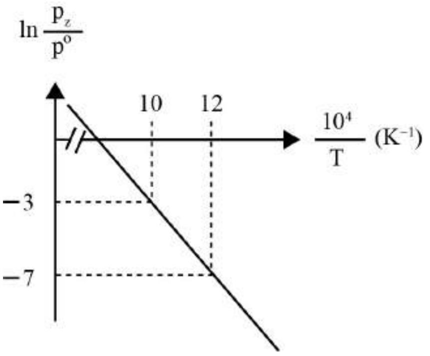
Numerical Value Type Questions

14. For the following reaction, equilibrium constant K_C at 298 is 1.6×10^{17}

$Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s)$

When equal volume of 0.06 M $Fe^{+2}(aq)$ and 0.2 M $S^{-2}(aq)$ solution are mixed, then equilibrium concentration of $Fe^{+2}(aq)$ is found to be $Y \times 10^{-17}$ M. The value of Y is_____. **(2019)**

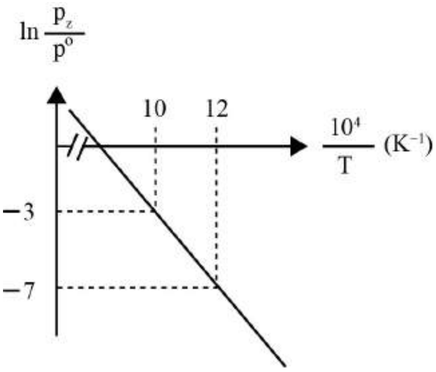
15. For the reaction, X(s) $\rightleftharpoons$ Y(s) + Z(g), the plot of ln $\frac{p_z}{p^\circ}$ versus $\frac{10^4}{T}$ is given below (in solid line), where p_z is the pressure (in bar) of the gas Z at temperature T and $p^\circ = 1$ bar.



(Given $\frac{d(\ln K)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ}{R}$, where the equilibrium constant, $K = \frac{p_z}{p^\circ}$ and the gas constant, $R = 8.314\ J\ K^{-1}\ mol^{-1}$)

The value of standard enthalpy, ΔH° (in kJ mol^{-1}) for the given reaction is______. **(2021)**

16. For the reaction, X(s) $\rightleftharpoons$ Y(s) + Z(g), the plot of ln $\frac{p_z}{p^\circ}$ versus $\frac{10^4}{T}$ is given below (in solid line), where p_z is the pressure (in bar) of the gas Z at temperature T and p°= 1 bar.



(Given $\frac{d(\ln K)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ}{R}$, where the equilibrium constant, $K = \frac{p_z}{p^\circ}$ and the gas constant, $R = 8.314\ J\ K^{-1}\ mol^{-1}$)

The value of ΔS° (in J K^{-1} mol^{-1}) for the given reaction, at 1000 K is_______. **(2021)**

Paragraph Type Questions

Use the following passage, to solve Q. 17 to Q. 18

Passage

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation :

$X_2(g) \rightleftharpoons 2X(g)$

The standard reaction Gibbs energy, $\Delta_r G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $\beta_{\text{equilibrium}}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given : $R = 0.083\ L\ bar\ K^{-1}\ mol^{-1}$)

17. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{\text{equilibrium}}$, is **(2016)**

(a) $\frac{8\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ (b) $\frac{8\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

(c) $\frac{4\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ (d) $\frac{4\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

18. 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) $\beta_{\text{equilibrium}} = 0.7$

(d) $K_C < 1$

Subjective Type Questions

19. One mole of nitrogen is mixed with three moles of hydrogen in a four litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, then calculate the equilibrium constant, K_c in concentration units. What will be the value of K_c for the following equilibrium ?

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$ **(1981)**

20. One mole of Cl_2 and 3 moles of PCl_5 are placed in a 100 litre vessel heated at 227°C. The equilibrium pressure is 2.05 atmosphere. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$ **(1984)**

21. Equilibrium constant of the reaction

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

at 100°C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2, how many mole of AB will be formed at 373°C ? **(1985)**

22. At a certain temperature, equilibrium constant K_c is 16 for the reaction

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

If we take one mole of each of all the four gases in a one litre container, what would be the equilibrium concentration of NO and NO_2 ? **(1987)**

23. $N_2O_4 \rightleftharpoons 2NO_2$ is 25% dissociated at 37 C ° and one atmosphere pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C ? **(1988)**

24. The equilibrium constant K_p of the reaction,

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

is 900 atm at 800 K. A mixture containing SO_3 and O_2 having initial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. **(1989)**

25. For the reaction, $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

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

26. 0.15 mole of CO taken in a 2.5 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place

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

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. **(1993)**

27. The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1.0 atm (relative atomic mass of P = 31.0 and Cl = 35.5) **(1998)**

28. When 3.06 g of solid NH_4SH is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_c and K_p for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4SH is introduced into the flask ? **(1999)**

Fill in the Blanks

29. For a given reversible reaction at a fixed temperature, equilibrium constant K_p and K_c are are related by .... **(1994)**

30. A ten-fold increase in pressure on the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium, results in .... in K_p. **(1996)**

31. For a gaseous reaction $2B \rightleftharpoons A$, the equilibrium constant K_p is .... to/than K_c. **(1998)**

True / False

32. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs. **(1984)**

33. If equilibrium constant for the reaction, $A_2 + B_2 \rightleftharpoons 2AB$, is K, then for the backward reaction $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$, the equilibrium constant is $\frac{1}{K}$. **(1984)**

34. Catalyst makes a reaction more exothermic. **(1987)**

35. The rate of an exothermic reaction increases with increasing temperature. **(1993)**

Answer Key

CHAPTER -11 | CHEMICAL EQUILIBRIUM

EXERCISE - 1 :
BASIC OBJECTIVE QUESTIONS

1.	(c)	**2.**	(b)	**3.**	(d)	**4.**	(d)	**5.**	(a)
6.	(a)	**7.**	(c)	**8.**	(d)	**9.**	(b)	**10.**	(b)
11.	(a)	**12.**	(b)	**13.**	(d)	**14.**	(c)	**15.**	(c)
16.	(d)	**17.**	(d)	**18.**	(c)	**19.**	(c)	**20.**	(a)
21.	(c)	**22.**	(b)	**23.**	(c)	**24.**	(c)	**25.**	(d)
26.	(d)	**27.**	(a)	**28.**	(c)	**29.**	(d)	**30.**	(b)
31.	(a)	**32.**	(a)	**33.**	(d)	**34.**	(b)	**35.**	(b)
36.	(a)	**37.**	(d)	**38.**	(a)	**39.**	(a)	**40.**	(d)
41.	(a)	**42.**	(d)	**43.**	(a)	**44.**	(c)	**45.**	(d)
46.	(d)	**47.**	(b)	**48.**	(c)	**49.**	(a)	**50.**	(b)
51.	(a)	**52.**	(b)	**53.**	(b)	**54.**	(d)	**55.**	(b)
56.	(a)	**57.**	(a)	**58.**	(c)	**59.**	(d)	**60.**	(d)
61.	(d)	**62.**	(d)	**63.**	(d)	**64.**	(a)	**65.**	(c)
66.	(c)	**67.**	(a)	**68.**	(b)	**69.**	(c)	**70.**	(d)
71.	(d)	**72.**	(d)	**73.**	(d)	**74.**	(c)	**75.**	(d)
76.	(b)	**77.**	(a)	**78.**	(c)	**79.**	(c)	**80.**	(a)

EXERCISE - 2 :
PREVIOUS YEAR JEE MAINS QUESTIONS

1.	(c)	**2.**	(d)	**3.**	(d)	**4.**	(a)	**5.**	(b)
6.	(a)	**7.**	(d)	**8.**	(d)	**9.**	(d)	**10.**	(a)
11.	(a)	**12.**	(a)	**13.**	(c)	**14.**	(a)	**15.**	(a)
16.	(d)	**17.**	(c)	**18.**	(a)	**19.**	(d)	**20.**	(d)
21.	(a)	**22.**	(b)	**23.**	(c)	**24.**	(d)	**25.**	(a)
26.	(b)	**27.**	(d)	**28.**	(c)	**29.**	(b)	**30.**	(d)
31.	(a)	**32.**	(b)	**33.**	(a)	**34.**	(c)	**35.**	(a)
36.	(a)	**37.**	(c)	**38.**	(b)	**39.**	(b)	**40.**	(a)
41.	(b)	**42.**	(a)	**43.**	(c)	**44.**	(c)		

45.	(16.00)	**46.**	(1380.00)
47.	(5.00)	**48.**	(855.00)
49.	(73.00)	**50.**	(20.00)
51.	(354.00)	**52.**	(2.00)
53.	(172.00)	**54.**	(2.00)
55.	(25.00)	**56.**	(16.00)
57.	(1396.00)	**58.**	(182.00)
59.	(0.02)	**60.**	(6.00)

CHAPTER -11 | CHEMICAL EQUILIBRIUM

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. (b) **2.** (c) **3.** (c) **4.** (c) **5.** (b)
6. (a) **7.** (c) **8.** (c) **9.** (a) **10.** (b)
11. (a) **12.** (d) **13.** (c) **14.** (a) **15.** (a)
16. (a) **17.** (b) **18.** (c) **19.** (b) **20.** (a)
21. (c) **22.** (b) **23.** (a) **24.** (b) **25.** (b)
26. (c) **27.** (b) **28.** (c) **29.** (c) **30.** (a)
31. (a) **32.** (b) **33.** (d) **34.** (b,c) **35.** (a,c)
36. (a,b) **37.** (a,d) **38.** (a,c)
39. (a,c) **40.** (a,b,d) **41.** (c,d)
42. (b,d) **43.** (a,c) **44.** (a,c)
45. (c,d) **46.** (a,c,d) **47.** (c,d)
48. (b,c,d) **49.** (a,b,c)
50. (a,b,c,d) **51.** (4.00)
52. (8.00) **53.** (8.00)
54. (6.00) **55.** (4.00)
56. (72.00) **57.** (a) **58.** (b) **59.** (a)
60. (c) **61.** (a) **62.** (c) **63.** (b) **64.** (a)
65. (a) **66.** (d) **67.** (a) **68.** (a) **69.** (a)
70. (a) **71.** (b) **72.** (a) **73.** (b) **74.** (c)
75. (b) **76.** (d) **77.** (d) **78.** (d) **79.** (c)
80. (b)

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTIONS

1. (a) **2.** (d) **3.** (d) **4.** (a) **5.** (d)
6. (d) **7.** (d) **8.** (d) **9.** (b)
10. (a,b,c,d) **11.** (c,d) **12.** (b, c,d)
13. (a, c) **14.** (8.93)
15. (166.28) **16.** (141.34)
17. (b) **18.** (c)
19. ($1.48 \times 10^{-5} L^2 mol^{-2}$, $3.84 \times 10^{-3} L\ mol^{-1}$)
20. (0.33 , 0.4) **21.** (1.86)
22. ($1.6\ mol\ L^{-1}$, $0.4\ mol\ L^{-1}$)
23. (0.266 atm, 63%)

24. (P_{O_2} =2.0118 atm, P_{SO_2} = 0.0236 atm,

P_{SO_3} = 0.9764 atm)

25. ($K_p = 0.11 atm^{-2}, K_c = 277.77 M^{-2}$)

27. (4.54 g/L)

28. (i) $8.1 \times 10^{-5}, 4.9 \times 10^{-2}$, (ii) No effect

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

30. no change **31.** smaller **32.** True
33. False **34.** False **35.** False