**2.5 Phase and Phase Equilibrium ---**

In each of the equilibria the system consists of two distinct parts; solid, liquid, solution or vapor. Each of these parts is called a phase. A phase is defined as a homogenous part of a system which has uniform composition and properties throughout. A phase is not the same as physical state. A mixture of two solids, even when powdered finely is a two phase system, because particles of the two solids have different chemical compositions and physical properties. The gaseous mixture constitute only one phase each. All the cases of physical equilibrium are in fact the systems in which different phases are in equilibrium; only if they contain, at least one common component. A dynamic exchange of the common component between two phases takes place.

**2.5.1 Equilibrium in Homogeneous and Heterogeneous Systems --**

Homogeneous system is one which has one phase. It has the same chemical composition and uniform properties throughout. It is formed by particles of molecular size only. Pure solids, liquids, gases and solutions are the examples of homogeneous systems. A system consisting of only one phase is called a homogeneous system

Heterogeneous system has at least two phases – a mixture of solids or immiscible liquids constitutes a heterogeneous system. Any system consisting of two or more phases is called heterogeneous system

**Homogeneous and Heterogeneous Equilibrium Systems**

Since all physical equilibria involve at least two phases, therefore these are all examples of heterogeneous equilibrium. But chemical equilibrium can be homogeneous or heterogeneous in nature. It is homogeneous if both the reactants and products are present only in one phase gas or liquid and heterogeneous if present in more than one phase.

**2.5.2 Homogeneous Chemical Equilibrium System --**

1. **Gas – Phase homogeneous systems**---

Such systems contain only gaseous reactants and products. Since all gaseous mixtures are homogeneous in nature they constitute only one phase.

(i) N2 (g) + 3H2 (g) ⇌2NH3 (g)

(ii) 2N2O5 (g) ⇌ 4NO2 (g) + O2 (g)

1. **Liquid – Phase homogeneous systems**------

Such systems containboth the reactants and products are present in only one liquid phase as a solution.

(i) CH3 COOH (l) + C2H5OH (l) ⇌CH3COOC2H5 (l) + H2O

(ii) KCN (aq) + H2O (l) ⇌ HCN (aq) + KOH (aq)

**2.5.3 Heterogeneous Chemical Equilibrium Systems -----**

Such systems containreactants and products are present in more than one phase.

(i) Formation of ferric oxide.

Fe (s) + 4H2O (g) ⇌Fe3O4 (s) + 4H2 (g)

(ii)Decompositionof calcium carbonate. (Limestone)

CaCO3 (s) ⇌CaO (s) + CO2 (g)

**2.6 Law of Equilibrium and Concentration Equilibrium Constant-**

Consider the equilibrium reaction

H2 (g) + I2(g)⇌ 2HI (g)

At equilibrium the concentrations of H2, I2 and HI become constant. It has been found experimentally that irrespective of the starting concentrations of H2 and I2 ratio of concentration terms always remains constant.

KC = [HI] 2/ [H2] [I2]

[HI] represent the equilibrium molar concentrations of H2, I2 and HI respectively and KC is called the concentration equilibrium constant.

In general, for reversible reaction,

aA + bB⇌cC + dDat equilibrium, the following ratio of concentration terms always remains constant at a given temperature.

KC = [c]c [D]d/ [A]a [B]b

The above relation is known as the law of equilibrium. All the concentrations values in the law of equilibrium are the equilibrium concentrations of reactants and products. The numerator of the law of equilibrium is the product of equilibrium molar concentrations of products, each term being raised to the power equal to its stoichiometric coefficient in the chemical equation and the denominator contains products of similar concentration terms of reactants.

**2.6.1 Pressure Equilibrium Constant --- (Kp)**

In case of gases their partial pressures can be used in place of molar concentrations in the law of equilibrium. The new equilibrium constant, Kp , is called the pressure equilibrium constant. For the reaction between H2 and I2 ,Kpis given by

Kp = P2HI / PH2 x PI2

Here PH2, PI2 and PHIare the equilibrium partial pressures of H2 , I2 and HI respectively.

**2.6.2 Relation between K p and Kc----**

For a general gas phase reaction at equilibrium

a A (g) + b B (g) ⇌c C (g) + d D (g)

The pressure and concentration equilibrium constants Kp and Kc are

Kp = PcC x PdD /PaAxPbB and

KC = [c]c [D]d / [A]a [B]b

For a gaseous substance i, the ideal gas equation is

PiV = niRT

where pi and ni are its partial pressure and amount in a gaseous mixture and V and T are its volume and temperature and R is the gas constant. The relation may be written as,

Pi  =ni/ V RT = ciRT

Where c Chemical dynamics i is the molar concentration or molarity of ‘i’ expressed in moles per litre. This relation can be used for replacing the partial pressure terms in the expression for Kp.

**2.6.3 LeChatelier Principles----**

It states that when a system in equilibrium is disturbed by a change in concentration, pressure or temperature, a 'net' change occurs in it in a direction that tends to decrease the disturbing factor

**Change in Concentration------**

Consider the state of equilibrium for the formation of ammonia from nitrogen and hydrogen.

N2(g) + 3H2(g) ⇌2NH3(g), ΔH = –92.4 kJ/mol

The concentration of nitrogen, hydrogen and ammonia become constant at the point of equilibrium. Now if any amount of reactants or ammonia is added or removed their concentration will change and the equilibrium will get disturbed.

**(i) Increase concentration of reactant:** When the concentration of either nitrogen or hydrogen is increased; a net forward reaction will take place which consumes the added reactant.

**(ii)Increase in the concentration of any product:** If the concentration of product ammonia is increased, a net backward reaction would take place to utilize the added ammonia.

**2.6.4 Change in Pressure----**

Change in pressure affects equilibrium involving gaseous phase either in a homogeneous or hetrogeneons system. Le Chatelierprinciple for systems involving gases can be studied as follows:

1. When the number of moles of products is more than the total number of moles of reactants as in the following system

N2O4(g) ⇌2NO2(g)

Increase in total pressure keeping the temperature constant, will cause a decrease in volume. This means that the number of moles per unit volume will increase. A net change will take place in the equilibrium in the direction where the number of moles decreasesi.e. backward direction.

1. When the number of moles of products is less than reactants.

As in the following case N2(g) + 3H2(g) ⇌2NH3(g)

According to Le Chatelier's principle increase in total pressure will bring a net change to the equilibrium in the direction where the total number of moles is decreasing i.e. to the product side as Δng = 2. Decrease in total pressure will bring the net change to equilibrium in the direction where the total number of moles is increasing i.e. backward direction.

1. When there is no change in the total number of moles of reactant and product as in the following state of equilibrium.

H2(g) + I2(g) ⇌2HI

There is no net change in equilibrium state when pressure is changed.

**2.6.5 Change of Temperature ----**

According to Le Chatelierprinciple when the temperature is changed (increased or decreased) the equilibrium system reacts to nullify the change in heat content. However, the net change in equilibrium is directed by the exothermic or endothermic nature of reaction.

**(i)Exothermic Equilibrium:**

For the following system of equilibrium of exothermic nature:

N2(g) + 3H2(g) ⇌2NH3(g); ΔH = – 92.4 kJ/mol According to Le Chatelierprinciple increase in temperature brings a net change in the equilibrium state in that direction where this extra heat is consumed. The net change is in the backward direction and some ammonia will decompose producing nitrogen and hydrogen. Similarly if the temperature is decreased the equilibrium shifts to the forward direction.

**(ii)Endothermic Equilibrium:**

N2(g) + O2(g)⇌ 2NO(g); ΔH = + 180.7 kJ/mol–1 If the temperature is increased the added heat will be absorbed by the reactant and the net change takes place to the equilibrium in the forward direction. If the temperature in decreased it will bring a 'net' change to equilibrium in the backward direction i.e. direction in which it is exothermic.

**2.7 Perfect gas equilibria** ----

When A and B are perfect gases we can use equation,

(µ = µ0 + RT ln p, with p interpreted as p/p0) to write

∆r G = µB − µA = (µB0 + RT lnPB) − (µA0 + RT lnPA)

= ∆r G + RT lnPB/PA.

 If we denote the ratio of partial pressure by Q, we obtain

∆rG = ∆r G0 + RT lnQ Q = PB /PA

The ratio Q is an example of a reaction quotient. It ranges from 0 when PB= 0 (corresponding to pure A) to infinity when PA = 0 (corresponding to pure B). The standard reaction Gibbs energy, ∆r G0, is defined (like the standard reaction enthalpy) as the difference in the standard molar Gibbs energies of the reactants and products.

Note that in the definition of ∆r G0, the ∆r has its normal meaning as a difference whereas in the definition of ∆r G the ∆r signifies a derivative.

∆r G0 = G0B,m– G0A,m = µ B0 − µA0

The difference in standard molar Gibbs energies of the products and reactants is equal to the difference in their standard Gibbs energies of formation, so in practice we calculate ∆r G0 from

∆r G0 = ∆Fg0 (B) − ∆fG0 (A)

At equilibrium ∆r G = 0. The ratio of partial pressures at equilibrium is denoted K,

 0 = ∆r G0 + RT ln K

This expression rearranges to RT ln K =−∆r G0

 K = (PB /PA)equilibrium

This relation is a special case of one of the most important equations in chemical thermodynamicsand the chemically important equilibrium constant, K.

when ∆r G0> 0, the equilibrium constant K < 1. Therefore, at equilibrium the partial pressure of A exceeds that of B, which means that the reactant A is favored in the equilibrium. When ∆r G0< 0, the equilibrium constant K > 1, so at equilibrium the partial pressure of B exceeds that of A. Now the product B is favored in the equilibrium.

**2.8Van’t Hoff equation-Temperature Effect on Equilibrium**

**Van’t Hoff equation**connectingchemical equilibriumconstant and temperature bythermodynamicsrelation of Gibbs-Helmholtzfree energyequation. The standard chemical equilibrium constant of the endothermic and**exothermic reaction**depends on the temperature. When the temperature of the system in equilibrium increases, the equilibrium of the chemical reaction shifted in the direction that absorbs heat. The extent of reactioncan be easily derived by Van’t Hoff equation relation.

If the equilibrium shifted in the forward direction or the concentration of the productmoleculeincreases then more of the reactant molecule is converted into a product. Hence the increases in the extent of reaction lead to increases in the equilibrium constant in physicalchemistrywhich is related mathematically by Van’t Hoff equation.



## Derivation of Van’t Hoff Equation---

At a given temperature according to Vant Hoff, the equilibrium constant of the chemical reaction remains unaltered, but the value varies considerably when the temperature is changed. The quantitative relation, known Van’t Hoff equation connecting equilibrium constant and temperature can be derived thermodynamically starting from Gibbs – Helmholtz freeenergyequation.

**Van’t Hoff Equation:**

Gibbs Helmholtz equation

ΔG° =ΔH° + T [$\frac{d(ΔG°)}{dT}]$P

Separating and integrating the slandered values,

-$\frac{ΔH°}{T2}$ = -$\frac{ΔG°}{T2}$ + $\frac{1}{T}$ [$\frac{d(ΔG°)}{dT}$]p = [$\frac{d }{dT}(\frac{ΔG°}{T})$]p ------(1)

Again from Van’t Hoff isotherm

-R[$\frac{dlnKp}{dT}$]p = [$\frac{d }{dT}(\frac{ΔG°}{T})$]p -------------------(2)

Comparing the above two equation, we get,

$$\frac{dlnKp}{dT}= \frac{ΔH°}{RT2}$$

The above relation is the differential forms of the Van’t Hoff equation but the greater the value of ΔH0, the faster the equilibrium constant changes with temperature.

**Integration form of Van’t Hoff Equation**

The integration of Van’t Hoff isotherm enables us to calculate numerically the shift of equilibrium constant with temperature. Integration of the above equation given, ln kp= – (ΔH0/RT) + c, where c = integration constant. The integration constant can be calculated from the thermodynamicentropyrelation, ΔG0= ΔH0– TΔS0.

The equation becomes,

 ln kp= – (ΔH0/RT) + (ΔS0/R).

Hence the integrated form of the Van’t Hoff equation at two temperatures

log$\frac{kp1}{kp2}$ = $\frac{ΔH◦}{R}(\frac{T1-T2}{T1T2})$

Where KP1and KP2are the equilibrium constants of the Van’t Hoff equation at two different temperatures T1and T2respectively. The determination of KP1and KP2at two temperatures helps to calculate the value of change of enthalpy of the chemical reaction. The above relation is called Van’t Hoff reaction isobar sincepressureremains constant during the change of temperature.

Variation of K with temperature as given by Vant’s Hoff equation can be written as –

log K1 / K2 = - ΔH / 2.303 [ 1 / T2 – 1 / T1]

or

log K2 / K1= ΔH / 2.303 [ 1 / T1 – 1 / T2]

or

log K2 / K1 = - ΔH / 2.303 [T2–T1 /T1T2]

Here, K1 and K2 are the values of the equilibrium constants at temperatures

T1and T2. ΔH is the enthalpy change for the reaction.

**Multiple Choice Questions**

**1.On increasing the concentration of reactants in a reversible reaction, then equilibrium constant will**

(a) Depend on the concentration(b) increase

 (c) Unchanged(d) decrease

**2.** When the system A + B⇌C + D is at equilibrium,

(a) the sum of the concentrations of A and B must equal the sum of the concentrations of C and D.

(b) the forward reaction has stopped.

(c) both the forward and the reverse reactions have stopped.

(d) neither the forward nor the reverse reaction has stopped.

**3. For which of the following conditions a reaction will be spontaneous at all the temperature?**

(a) ΔH < 0 and ΔS < 0(b) ΔH < 0 and ΔS = 0

(c) ΔH < 0 and ΔS > 0(d) both (b) and (c)

**4. Which of the following are the correct criteria for a spontaneous process?**

(a) ΔSsystem– ΔSsurroundings> 0(b) ΔSsurroundings> 0 only

(c) ΔSsystem+ ΔSsurroundings> 0(d) ΔSsystem> 0 only

**5.For a spontaneous reaction**

(a) ΔS must be negative(b) (ΔH – TΔS) must be negative

(c) ΔH must be negative(d) (ΔH + TΔS) must be negative

**6.Which of the following is correct for the net entropy change in an irreversible process?**

(a) It is positive (b) It is negative(c) It is zero (d) All of the above

**7.**Find out whether the following reaction is spontaneous or not at 127 degrees centigrade? N2(g) + 3H2(g)⇌2NH3(g); ΔH = 92.22 kJ/mol and ΔS = -198.75 J/K-mol.

(a) it is spontaneous(b) it is not spontaneous

(c) it may be spontaneous (d) cannot predict

**8.**The melting of ice into liquid water is an example of tube \_\_\_\_\_reaction.

 (a) endergonic (b) exergonic (c) exothermic (d) endothermic

**9.** Which of the following is not a type of exergonic reaction?

 (a) formation of table salt from Sodium and chlorine

 (b) combustion reaction (c) chemiluminescence(d) photosynthesis

**10.**The Gibbs free energy is positive when a change in enthalpy and change

 in entropy are positive at \_\_\_\_\_\_

 (a) high temperatures(b) low temperature

 (c) all temperatures(d) only at 0 Kelvin

**11.** In the equation, ΔG = – 2.303 RT logK, what is K?

 (a) change in temperature (b) Kelvin

 (c) equilibrium constant(d) change in enthalpy

**12.On increasing the concentration of reactants in a reversible reaction, then equilibrium constant will**
(a) depend on the concentration(b) increase
(c) unchanged(d) decrease

**13.**In equilibrium constant expression, the concentration of products is taken in/on the

1. right side (b) left side(c) numerator (d) denominator

**14.**The rate at which the reaction proceeds is directly proportional to the product of the active masses of

1. products(b) reactants (c) catalysts (d) none of above

**15.**What does the dotted curve in the diagram given below represent?



(a) concentration of reactants (b) equilibrium constant

(c) concentration of products (d) concentration of catalyst

**16.**At dynamic equilibrium the concentration of both the reactants and products are \_\_\_\_\_\_\_\_

 (a) equal(b) not equal (c) cannot predict

 (d) sometimes equal sometimes not equal

**17.** Dynamic equilibrium mainly concerns about \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 (a) spontaneous reactions (b) nonspontaneous reactions

 (c) reversible reactions (d) Irreversible reactions

**18.** At which of the following temperatures water is a dynamic equilibrium with ice?

 (a) 0 Kelvin(b) zero degree centigrade

 (c) zero degree Fahrenheit (d) 100 Kelvin

**19.**At equilibrium the total Gibb’s free energy for all phases is

(a) Minimum (b) Maximum (c) Infinity (d) Zero

**20.**The chemical potential of a species is:

 (a) Different in all phases at chemical equilibrium

 (b) Same in all phases at chemical equilibrium

 (c) Different in all phases at physical equilibrium

(d) Same In all phases at equilibrium

**21.**What is the phase equilibrium ratio?

 (a) Ratio of heat of species in two phases at equilibrium

 (b) Ratio of temperature of species in two phases at equilibrium

(c) Ratio of mole fractions of species in two phases at equilibrium

(d) Ratio of equilibrium concentration of species in two phases at equilibrium.

**22**.**Le Chatelier’s principle is applicable to:**

(a)    Only homogeneous chemical reversible reactions

(b)    Only heterogeneous chemical reversible reactions

(c)    Only physical equilibria

(d)    All systems, chemical or physical, in equilibrium

 **23.In an exothermic reaction, a 10°C rise in temperature will:**

(a)    Decrease the value of equilibrium constant

(b)    Double the value of equilibrium constant

(c)    Not produce my change in equilibrium constant

(d)    Produce some increase in equilibrium constant

 **24.According to Le Chatelier’s principle, adding heat to a solid**

**and liquid in equilibrium will cause the:**

(a)Amount of solid to decrease(b)Amount of liquid to decrease

 (c)Temperature to rise (d)Temperature to fall

**25.For the reaction H2(g) + I2 (g) ƒ 2HI(g),**

**the equilibrium constant changes with:**

 (a)Total pressure (b)Catalyst

 (c)Concentration of H2 and I2 (d)Temperature

 **26.**When KOH is dissolved in water, heat is evolved. If the temperature

 is raised, the solubility of KOH.

1. Increases(b) Decreases(c) Remains the same(d) Cannot be predicted

**27.**For the liquefaction of gas, the favourable conditions are

 (a) Low T and high P(b) Low T and low P

(c) Low T and high P and a catalyst(d) Low T and catalyst

**28.**According to Le Chatlier’s principle adding heat to a solid and liquid

in equilibrium with endothermic nature will cause the

(a) Amount of solid to decrease(b) Amount of liquid to decrease

(c) Temperature to rise(d) Temperature to fall

**29.**In which of the following equilibrium, the value of KP is less than KC?

(a) N2O4⇌2NO2(b) N2+ O2⇌2NO

(c) N2+ 3H2 ⇌ 2NH3(d) 2SO2 + O2 ⇌  2SO3

**30.**In the reaction A2(g) + 4B2 (g) ⇌ 2AB4(g) , ΔH > 0. The decomposition

of AB4 (g) will be favoured at

1. low temperature and high pressure(b) high temperature and low pressure

(c)low temperature and low pressure(d) high temperature and high pressure

**31.**For the gaseous phase reaction, 2A ⇌ B + C,  ΔH° = –40 Kcal mol–1

 which statement is correct for

(a) K is independent of temperature(b) K increase as temperature decrease

(c) K increase as temperature increases(d) K varies with addition of A

**32.**The equilibrium between water and its vapour in an open vessel

(a) can be achieved(b) depends upon pressure

1. cannot be achieved (d)depends upon temperature

**33.**The chemical equilibrium of a reversible reaction is not influenced by

(a)temperature (b) pressure(c) catalyst (d) concentration

**34.**Le Chatelier Principle is applicable to

(a) heterogeneous reaction (b) homogeneous reaction

1. irreversible reaction(d) system in equilibrium

**35.**The reaction which can not occur spontaneously are

 (a)exothermic (b) endothermic (c)isothermic (d)thermodynamics

 **36.**Exothermic reactions have high

(a) entropy (b) enthalpy (c)pH (d) activation energy

**37.**Melting of ice cube is an example of

 (a) endothermic reaction(b) exothermic reaction

(c) chemical change (d) physical change

**Answers-**

**1. (c) 2. (d) 3. (d)4.(c) 5. (b) 6. (a) 7. (b)8.(a) 9.(d) 10. (b)**

 **11. (c) 12. (c)13.(c) 14. (b) 15. (c) 16. (b) 17. (d) 18. (b)**

 **19.(a) 20. (d) 21. (c) 22. (b) 23. (d) 24. (a) 25. (d) 26. (b)**

**27. (a)28.(a) 29. (a) 30. (c) 31. (c) 32.(c) 33. (c) 34.(d)**

**35. (b) 36. (a) 37. (a)**