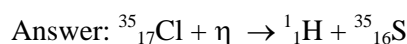


Model Answer: B.Sc-VIth Semester-CBT-602

AR-7781 (Physical Chemistry)

One Mark Questions:

1. Write a nuclear reaction for following Bethe's notation? $^{35}\text{Cl}(n, p)^{35}\text{S}$



2. What are the characteristics of α radiation?

Answer: The particle is a helium nucleus ^4_2He with a discrete energy. The penetrating power of α particle is less compared to β and γ radiations. They deflected towards a negative plate in the presence of electric field.

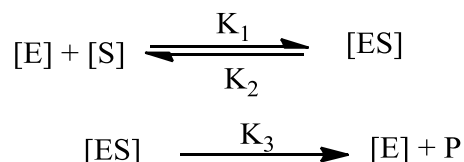
3. Structure of Cesium Chloride?

In CsCl, each Cl^- is surrounded by 8 Cs^+ ions and each Cs^+ is surrounded by 8 Cl^- ions. The structure is body centered cubic.

4. Define Lattice energy.

Lattice energy is the amount of energy required to break solid into its ions or the amount of energy released when one mole of a crystal is formed from its constituent ions.

5. Michalies constant?



In enzymatic catalysis, steady state approximation is applicable. Michalies constant is

$$K_m = K_2 + K_3 / K_1$$

6. What is van't Hoff "k" in adsorption?

The temperature dependence of the equilibrium constant K, if it is expressed as a equilibrium constant, it follows,

$$d \ln K/dT = \Delta U^\circ/RT^2$$

ΔU° is the standard molar internal energy change in the adsorption process.

7. Define partial molar quantity.

Partial Molar Quantity is defined as the increase in the thermodynamic quantity of an infinite amount of solution when one mol of component *i* is added. Partial molar quantity: it is defined as the increase in an extensive property on account of addition

of one mole of its respective constituent, at constant temperature and pressure, to such a large amount of a system that there is no appreciable change in the concentration.

8. What is activity and activity coefficient?

The chemical potential of an ideal solution is $\mu = \mu^\circ + RT \ln x_i$, where x_i is the mole fraction

For every solution; $\mu = \mu^\circ + RT \ln a_i$ where a_i replaces the mole fraction, known as activity.

For ideal solutions: $a_i = x_i$

For non ideal solutions $a_i = \gamma_i x_i$ where γ is known as activity coefficient. $\gamma_i = a_i/x_i$. The activity coefficient measures the degree of departure from ideal behaviour.

9. What is the expression for relationship between electrode potential and ionic concentration of the electrolyte solutions?

From Nernst equation $E = E^\circ - \frac{2.303RT}{nf} \log \frac{[P]}{[R]}$

(Or)

$$\log \gamma_{\pm} = -(Z_+ Z_-) A \sqrt{I}$$

10. Saturated solution of KNO_3 is used to make salt bridge because to avoid liquid junction potential.

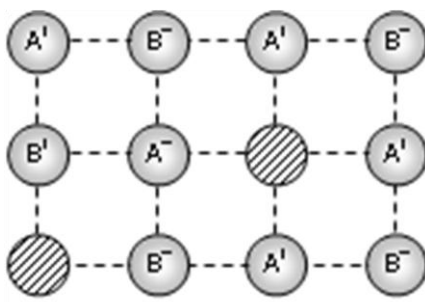
Section-B

2. What is a defective crystal? Explain Schottky and Frenkel defects.

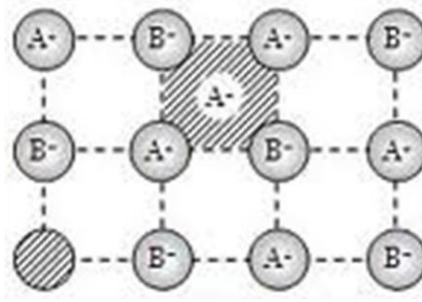
Any departure from crystal symmetry caused by free surfaces, disorder, impurities, and vacancies is known as a defective crystal.

The simplest type of a defect in a crystal is due to vacancy. If an atom or ion is removed from its normal position in the lattice and is placed at an interstitial site, is known as interstitial defect. Some defects are due to misplaced atom. Many crystals show combination of defects, *i.e* one type of defect is associated with an equivalent number of defects of another type. Such a combination of defects is important in ionic crystals for maintaining overall charge neutrality of the crystal. Two such defects are Frenkel and Schottky defects.

When an atom or ion is removed from its normal site and placed in an interstitial site, the crystal has simultaneously a vacancy and one interstitial. The combination is known as Frenkel defect. In a crystal, when a cation vacancy exists with an equivalent number of anion vacancies necessary for its charge neutrality, the combination is known as a Schottky defect. The formation of Schottky defect is accompanied by the creation of equivalent number of new lattice sites or removal of ions to the gas phase from the lattice.



Schottky defect



Frenkel defect

3. Describe the rate expression for bimolecular surface reaction.

The isotherm for two substances A and B adsorbed on the same surface is of importance with the kinetics of surface reactions involving two reactants. Suppose that the fraction of surface covered by molecules of type A is θ_A and that fraction covered by B is θ_B . The bare fraction is $1 - \theta_A - \theta_B$.

The rate of adsorption of A and B are

$$r_a^A = K_a^A [A] (1 - \theta_A - \theta_B)$$

$$r_a^B = K_a^B [A] (1 - \theta_A - \theta_B)$$

The rates of desorption are

$$r_d^A = K_d^A \theta_A$$

$$r_d^B = K_d^B \theta_B$$

At equilibrium, rate of adsorption is equal to rate of desorption,

$$\text{Therefore, } K_a^A[A](1-\theta_A-\theta_B) = K_d^A\theta_A$$

$$\theta_A/1-\theta_A-\theta_B = K_A[A]; K_A \text{ is equilibrium constant; i.e } K_A \text{ is } k_a^A/k_d^A$$

Similarly, $\theta_B/1-\theta_A-\theta_B = K_B[B]$ where K_B is k_a^B/k_d^B

From above these two equations, fractions covered by A and B are,

$$\theta_A = K_A[A]/1 + K_A[A] + K_B[B] \text{ and } \theta_B = K_B[B]/1 + K_A[A] + K_B[B]$$

The rate of reaction is therefore, $R = k\theta_A\theta_B$

$$R = kK_AK_B[A][B]/(1 + K_A[A] + K_B[B])^2$$

Examples for heterogeneous catalyzed reaction are

- (i) Synthesis of ammonia using Haber's process
- (ii) Hydrogenation of olefins on Nickel surface.

4. Solution to numerical given:

The volume of this solution will be $V = n_1V_1 + n_2V_2$

$$V = (0.53\text{mol})(74.17 \text{ cm}^3/\text{mol}) + (0.47 \text{ mol})(80.24 \text{ cm}^3/\text{mol})$$

$$39.31 \text{ cm}^3 + 37.71 \text{ cm}^3 = 77.02 \text{ cm}^3$$

The mass of the solution will be $m = n_1M_1 + n_2M_2$

$$= (0.53 \text{ mol})(58 \text{ g/mol}) + (0.47)(119.5 \text{ g/mol}) = 86.91 \text{ g}$$

The density of solution will be $m/v = 86.91 \text{ g}/77.02 \text{ cm}^3 = 1.128 \text{ g/cm}^3$

5. (i) In general, fugacity of a real gas is related to its pressure by an equation $f/p=\gamma$.

Where γ is known as the fugacity coefficient and is a measure of deviations of a real gas from the ideal gas behaviour. Since all gases approach ideality in the limit of zero pressure, it is obvious that $f/p=\gamma=1$.

(ii) Chemical potential of an ideal gas at a given temperature is related to its pressure p through the equation $\mu=\mu^\circ+RT \ln(p/p^\circ)$

Where μ° is the standard chemical potential: when the pressure of gas is p° . Chemical potential depends upon both T and p and whereas μ° depends only on T .

(iii) A large number of solids consist of positive and negative ions held together by the predominantly electrostatic attraction between the oppositely charged ions. Such solids are known as ionic solids and this type of force of attraction is called ionic bond. The electrostatic energy of attraction between them is given by $U= - Ne^2/ 4\pi\epsilon_0r_0$

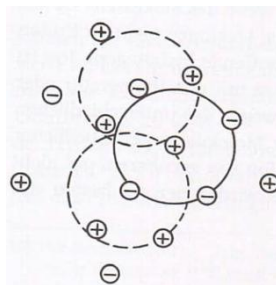
Examples are NaCl, CaF₂

(iv) Metallic bond: Some solids possess metallic bond. Their melting and boiling temperatures vary widely, for example, mercury is a liquid at room temperature and tungsten melts at 3000 °C. They are hard and ductile. They are good conductors of electricity because of the presence of free electrons.

6. Debye-Hückel-Onsager theory of electrolyte conductivity:

Electrostatic interactions: each ion attracts (repels) ions of opposite (same) charge

Thermal motion: causing random motion of anions/cations.



The ion cloud around a central ion in presence of an electric field: cations and anions accelerated into opposite directions. Distortion of ion cloud (rebuilding requires relaxation)

1. Ionophores are completely ionized at all concentrations for which the theory is valid.
2. The ions are point charges and are not subjected to distortions possessing a symmetrical coulombic field.
3. Inter-ionic attractions are only due to coulombic forces and no other inter-ionic forces are possible.
4. The electric potential energy is smaller than its thermal energy.
5. The bulk relative permittivity of the solvent controls the attraction between ions, and remains unchanged in the presence of solute.

At very low concentrations: $\log \gamma_{\pm} = -(Z_+Z_-)A\sqrt{I}$ where γ is known as activity coefficient

For ion, it is given by $\log \gamma_{\pm} = -Z_i^2A\sqrt{I}$, where $A = 0.59$ depends upon permittivity

I is the ionic strength.

When ionic strength of solution is too high for the limiting law to be valid, activity coefficient may be extended from Debye-Huckel law, extended.

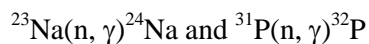
$\log \gamma_{\pm} = -(Z_+Z_-)A\sqrt{I} / (1+B\sqrt{I})$, where “B” is dimensionless constant.

Debye Huckel-Onsagar equation for strong electrolytes is $\log \gamma_{\pm} = \log \gamma_{\pm}^0 - (A+B\sqrt{I})\sqrt{C}$

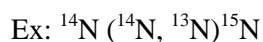
- 7 Types of nuclear reactions: One way of designating a nuclear reaction is merely by naming (a,b) on the target.
 - (a) Elastic Scattering: Here $a = b$ and both target and product nucleus are same.

The incoming particle strikes the target nucleus, loses a fraction of its kinetic energy in translating the later. The projectile particle gets its direction deflected by an angle θ as in the scattering of a billiard ball.
 - (b) Inelastic scattering: A process of scattering is considered to be inelastic if some of the kinetic energy of the particle is used up in raising the potential energy of the target in some way or other as in exciting it to a higher energy level. Here the kinetic energy of the system, as such is not conserved.

(c) Radiative Capture: Here the particle on capture leads to the emission of radiation in the form of one or more γ photons. i.e $b = \gamma$. The most common are (n, γ) reactions in which the product is an isotope of the target element one mass unit higher as in:



(d) Transformations: In this target, the projectile, the ejectile and the recoil residue are all isotopes of the same element.



8. Determination of molecular weight:

From elevation of boiling point and depression of freezing point, we know that $\Delta T_b = K_b m$ and $\Delta T_f = K_f m$. If we can determine ΔT_b or ΔT_f , molality, m and hence the molecular weight can be determined.

Molecular weight may also determine from colligative properties. From osmotic pressure, we know that

$$\Pi = CRT = (n/v) RT = (W/MV)RT \quad \text{where } \pi \text{ is the osmotic pressure.}$$

But by Raoult's law we know that,

$$\begin{aligned} (p_0 - p/p_0) &= X_2 = n_2/n_1 + n_2 ; \text{ where } n_1 \text{ and } n_2 \text{ are the number of moles} \\ &= (W_2/M_2)/(W_1/M_1) + (W_2/M_2) \end{aligned}$$

Molecular weight of polymer can be calculated as $M = (\text{Total Mass of the polymer sample}) / (\text{number of molecules present in the sample})$

$$M = (n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots) / n_1 + n_2 + n_3 + \dots$$

$$\sum n_i M_i / \sum n_i$$