पुणा International School

Shree Swaminarayan Gurukul, Zundal

Grade – XII Chemistry Study material (Ch-1,2,3) Year 21-22

1 Marks Questions

1. What are fluids? Give examples.

Ans. Substances which flow are fluids e.g. liquids and gases.

2. Solids are rigid why?

Ans. Rigidity in solids is due to fixed positions of the constituent particles and their oscillations about their mean positions

3. How are solids classified?

Ans. Solids may be classified into two categories – crystalline and amorphous.

4. Why do crystalline solids are anisotropic nature and amorphous solid are isotropic in nature.

Ans. Anisotropy in crystals is due to different arrangement of particles along different directions. Isotropic in amorphous solid is due to its long range order in them and arrangement is irregular along all the directions.

5. Define the term: Crystal lattice

Ans. A regular three dimensional arrangement of points in space is called crystal lattice.

6. What is a unit cell?

Ans. The smallest portion of a crystal lattice which, when, repeated in different directions, generates the entire lattice, is called its unit cell.

7. What are the axial angles and edge length in a cubic crystal system?

Ans. Axial angles, $\alpha = \beta = \gamma = 90^0$ and edge lengths a = b = c.

8. Give one example of each – Tetragonal and hexagonal crystal system.

Ans. Tetragonal crystal system – white tin, SnO_2 .

Hexagonal crystal system – Graphite, ZnO.

10. Give an example which shows both frenkel and Schottky defect.

Ans. AgBr.

11. What is the difference between ferromagnetic and paramagnetic substances?

Ans. A ferromagnetic substance has permanent magnetic behaviour whereas a paramagnetic substance acts as a magnet only in the presence of an external magnetic field.

12. State Henry's Law.

Ans. Henry's Law states that at a constant temperature the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

13. State Raoult's Law.

Ans. Raoult's Law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

14. What are the factors on which vapour pressure depends?

Ans. The factors on which vapour pressure depends are –

1) Temperature of the liquid. 2) Nature of the liquid.

15. How is osmotic pressure of a solution related to its concentration?

Ans. Osmotic pressure, $\pi = CRT$

C = concentration ,R = gas constant.

T= temperature

16. Give some uses of electrochemical cells?

Ans. Electrochemical cells are used for determining the

a) pH of solutions

b) solubility product and equilibrium constant

c) in potentiometric titrations

2 Marks Questions

1. The window panes of the old buildings are thick at the bottom. Why?

Ans. Glass panes of old buildings are thicker at the bottom than at the top as from is an amorphous solid and flows down very slowly and makes the bottom portion thicker.

2. The stability of a crystal is reflected in the magnitude of its melting point. Explain

Ans. Melting point of a solid gives an idea about the intermolecular forces acting between particles. When these forces are strong, the melting point is higher and when these forces are weak, low melting point is observed. Higher is the melting point, more stable the solid is.

3. Graphite is soft and good conductor of electricity. Explain.

Ans. Graphite is soft and good conductor due to its typical structure here carbon atoms are arranged in different layers and each atom a covalently bonded to three of its neighbouring atoms in the same layer. The fourth electron of each atom is free to move about due to which it conducts electricity. Different layers can slide over the other which makes it a soft solid.

4. Ionic solids are good conductors in molten state and in aqueous solutions but not in solid state. Why?

Ans. In the solid state, the ions in the ionic solids are not free to move about due to their rigid structure & strong electrostatic forces. Therefore they cannot conduct electricity whereas in molten state and aqueous solution, the ions become free to move about and they conduct electricity.

5. Name three types of cubic unit cells?

Ans. (a) Simple cubic

(b) Face – centred cubic

(c) Body centred cubic

6. How many atoms are there in a unit cell of a metal crystallizing in a:

(a) FCC structure

(b) BCC structure

Ans. (a) FCC = 4 (b) BCC = 2

7. What is the contribution of an atom per unit cell if the atom is:

(a) At the corner of the cube.

(b) On the face of the cube.

(c) In the centre of the cube.

Ans. (a) When atom is at the corner of the cube, the contribution is $\frac{1}{8}$ atom.

(b) When the atom is on the face of the cube, its contribution is $\frac{1}{2}$ atom.

(c) If the atom is in the centre of the cube, its contribution is 1 atom.

8. A compound formed by A & B crystallizes in the cubic structure where 'A' are at the corners of the cube and B are at the face centre. What is the formula of the compound?

Ans. Contribution of atom A per unit cell = $\frac{1}{8} \times 8 = 1$ atom

Contribution of atom B per unit cell = $\frac{1}{2} \times 6 = 3$ atom

Ratio of A & B = 1:3 Formula = AB_3 .

9. Calculate the no. of atoms in a cubic based unit – cell having one atom on each corner and two atoms on each body diagonal.

Ans. No. of atoms contributed by 8 corners per unit cell = $\frac{1}{8} \times 8 = 1$ atom.

No. of atoms contributed by one diagonal = 2

No. of diagonal = 4

$\therefore$ Total contribution by diagonal = 4$\times$ 2 = 8

$\therefore$ Total no. of atoms = 8 + 1 = 9 atoms

10. What is the no. of octahedral and tetrahedral voids present in a lattice?

Ans. No. of octahedral voids present in a lattice is equal to the no. of close packed particles and the number of tetrahedral voids is twice the no. of close packed particles.

11. Give the relationship between density and edge length of a cubic crystal.

Ans. Density, d of a cubic cell is given by –

$$d = \frac{ZM}{a^3 N_A}$$

Where Z = no. of atoms per unit cell

M = molar mass

N_A = Avogadro number

a = edge length

12. Copper which crystallizes as a face – centred cubic lattice has a density of $8.93\ g/cm^3$ at $20^0 C$. calculate the length of the unit cell.

Ans. 63.1 u

13. An element crystallizes in BCC structure. The edge of its unit cell is 288 pm. If the density is $7.2\ g/cm^3$, calculate the atomic mass of the element.

Ans. 52 g/ mol

14. The compound CuCl has ZnS structure and the edge length of the unit cell in 500 pm. Calculate the density. (Atomic masses: Cu = 63, Cl = 35.5, Avogadro no = $6.02\times10^{23} mol^{-1}$)

Ans. $5.22\ g/cm^3$

15. Calculate the volume of water which could be added to 20 ml of 0.65 m HCl to dilute the solution to 0.2 m?

Ans.For dilution –

$M_1V_1 = M_2V_2$

$V_2 = \frac{M_1V_1}{M_2} = \frac{0.65M \times 20\ \text{ml}}{0.2M}$ = 65 ml

Vol of water to be added to 20 ml = $V_2 - V_1$ = 65ml – 20ml = 45 ml.

16. A solution is prepared by dissolving 11g glucose in $200\ cm^3$ water at $30^0 C$. What is the mass Percentage of glucose in solution? The density of water

$30^0 C$ is $0.996\ g/cm^3$?

Ans.Density = $\frac{mass}{volume}$ = 0.996 g/cm^3

0.996 = $\frac{mass}{200cm^3}$

$Mass = 0.996\times200$ = 199.2 g

Mass% of glucose =

$= \frac{11}{199.2 + 11} 100 = 5.23\ \%$

17. What are the factors on which conductivity of an electrolyte depend?

Ans. The conductivity of an electrolyte depends upon

i) The nature of electrolyte

ii) Size of the ions produced

iii) Nature of solvent and its viscosity.

iv) Concentration of electrolyte.

v) Temperature

18. How is molar conductance related to conductivity of an electrolyte ?

Ans. Molar conductance, Ω m is related to conductively by the relation.

Ω m = $\frac{k}{c}$

Where κ = conductivity in s/m.

C = concentration in mol / m^3

19. Write an expression relating cell constant and conductivity?

Ans. Cell constant and conductivity are related by the expression-

$\kappa = \frac{G}{R}$ where G = Cell constant

κ = conductivity

R = Resistance.

20. The conductivity of an aqueous solution of NaCl in a cell is $92\Omega^{-1}\ cm^{-1}$ the resistance offered by this cell is 247.8Ω. Calculate the cell constant?

Ans. Specific conductivity = $\frac{\text{cell constant}}{\text{Resistance}}$

Or cell constant = $conductivity \times Resistance$

$= 92\ \Omega^{-1}\ cm^{-1} \times 247.8\ \Omega$

$= 22797.6\ \Omega^{-1}$

3 Marks Questions

1. How are crystalline solids classified on the basis of nature of bonding? Explain with examples.

Ans. Classification of crystalline solids.

1. Molecular solids: The forces operating between molecules are dispersion or London forces, dipole – dipole interactions, hydrogen bounding e.g. CCl_4, HCl, ice etc.

2. Ionic solids:The intermolecular forces are coulomibic or electrostatic forces, e.g. NaCl, MgO etc.

3. Metallic solids: The forces operating is metallic bonding e.g. Fe, Cu, Ag etc.

4. Covalent or network solids: The attractive forces are covalent bonding e.g. Diamond, Quartz etc.

2. In crystalline solid, anions C are arranged in cubic close – packing, cations A occupy 50% of tetrahedral voids & cations B occupy 50% of octahedral voids. What is the formula of solid?

Ans. Suppose no. of anions, C = 100

Suppose no. of cations, A = $\frac{50}{100}\times$ no. of tetrahedral voids

$= \frac{1}{2}(2\times C)$

No. of cations, B = $\frac{50}{100}\times$ no. of octahedral voids

$= \frac{1}{2}\times(C)$

$= \frac{1}{2}\times 100 = 50$

Ratio of ions A : B : C = 100 : 50 : 100

= 2 : 1 : 2

Formula = A_2BC_2

3. Which type of ionic substances show?

(a) Schottky defect

(b) Frenkel defect

Ans. (a) Schottky defect – ionic substances in which the cation and anion are of almost similar sizes eg. NaCl, KCl, CrCl.

(b) Feenkel Defect – Ionic substances in which there is large difference in size of ions eg. ZnS, AgCl, AgBr.

4. Silver crystallizes in fcc lattice. If edge length of the cell is $4.07\times10^{-8} cm$ and density is 10.5 g cm^{-3}, calculate the atomic mass of silver.

Ans. It is given that the edge length, $a = 4.077\times10^{-8} cm$

Density, $d = 10.5 g\, cm^{-3}$

As the lattice is fcc type, the number of atoms per unit cell, z= 4

We also know that, $NA = 6.022\times1023 mol^{-1}$

Using the relation:

$d = zMa^3NA$

$M = da^3NAz = 10.5 g\, cm^3 \times \left(4.077\times10^{-8} cm\right)\times6.022\times1023\, mol^{-14}$

$= 107.13\, g\, mol^{-1}$

5. Copper crystallises into a fcc lattice with edge length $3.61\times10^{-8} cm$. Show that the calculated density is in agreement with its measured value of 8.92 g cm^3.

Ans. Edge length, $a = 3.61\times10^{-8} cm$

As the lattice is fcc type, the number of atoms per unit cell, z= 4

Atomic mass, M = 63.5 g mol^{-1}

We also know that, $NA = 6.022\times1023 mol^{-1}$

Applying the relation:

$d = zMa^3NA$

$= 4 \times 63.5 g\, mol^{-1} (3.61 \times 10^{-8} cm) 3 \times 6.022 \times 1023 mol^{-1}$

$8.97\, g\, cm^{-3}$

The measured value of density is given as $8.92\, g\, cm^{-3}$. Hence, the calculated density $8.97\, g\, cm^{-3}$ is in agreement with its measured value.

6. Calculate the % composition in terms of mass of a solution obtained by mixing 300g of a 25% & 400 g of a 40% solution by mass?

Ans. mass of solute in 400g of 40% = $\frac{40}{100} \times 400 = 160g$

Total mass of solute = 160+75 = 235g

Total mass of solution = 400+300 = 700g

Mass% of solute = $\frac{\text{mass of solute}}{\text{Total mass of solution}} \times 100$

= $\frac{235}{700} \times 100 = 33.57\%$

Mass % of solvent = 100 – 33.57 = 66.43%

7. One litre of sea water weight 1030g and contains about $6 \times 10^{-3} g$ of dissolved O_2 . Calculate the concentration of dissolved oxygen in ppm?

Ans. mass of $O_2 = 6 \times 10^{-3} g$

ppm of O_2 in 1030 g sea water = $\frac{\text{mass of } o_2}{\text{mass of sea water}} \times 10^6$ = $\frac{6 \times 10^{-3}}{1030} \times 10^6 = 5.8$ ppm.

8. The density of 85% phosphoric acid is $1.70\, g / cm^3$. What is the volume of a solution that contains 17g of phosphoric acid?

Ans. 85g phosphoric acid is present in 100g of solution.

17g of phosphoric acid is present in $\frac{100}{85} \times 17 = 20\text{g of soution}$

Volume of 17g of 85% acid = $\frac{mass}{density}$

$= \frac{20g}{1.70 g/cm^3} = 11.8\ cm^3$

9. How much electricity in terms of Faraday is required to produce

(i) 20.0 g of Ca from molten $CaCl_2$.

(ii) 40.0 g of Al from molten Al_2O_3.

Ans.(i) According to the question,

$Ca^{2+} + 2e^{-1} \rightarrow \underset{40g}{Ca}$

Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium = $\frac{2 \times 20}{40}F$

= 1 F

(ii) According to the question,

$Al^{3+} + 3e^{-1} \rightarrow \underset{27g}{Al}$

Electricity required to produce 27 g of Al = 3 F

Therefore, electricity required to produce 40 g of Al = $\frac{3 \times 40}{27}F$

= 4.44 F

10. How much electricity is required in coulomb for the oxidation of

(i) 1 mol of H_2O to O_2.

(ii) 1 mol of FeO to Fe_2O_3.

Ans.(i) According to the question,

$H_2O \rightarrow H_2 + \frac{1}{2}O_2$

Now, we can write:

$$O^{2} \rightarrow \frac{1}{2}O_2 + 2e^-$$

Electricity required for the oxidation of 1 mol of H_2O to O_2 = 2 F

= 2×96487 C

= 192974 C

(ii) According to the question,

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$$

Electricity required for the oxidation of 1 mol of FeO to Fe_2O_3 = 1 F

= 96487 C

11. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Ans.Given,

Current = 5A

Time = 20×60 = 1200 s

Therefore, $\text{Charge} = \text{current} \times \text{time}$

$= 5 \times 1200$

= 6000 C

According to the reaction,

$$Ni^{2+}_{(aq)} + 2e^- \rightarrow \underset{58.7g}{Ni_{(s)}}$$

Nickel deposited by 2×96487 C = 58.71 g

Therefore, nickel deposited by 6000 C $= \frac{58.71 \times 6000}{2 \times 96487}$ g

= 1.825 g

Hence, 1.825 g of nickel will be deposited at the cathode.

12. A weak electrolyte AB in 5% dissociated in aqueous solution? What is the freezing point of a 0.10 molar aqueous solution of AB? Kf = 1.86 deg/molal?

Ans. Degree of dissociation $\times$ of AB = $\frac{5}{100} = 0.05$.

AB $\rightarrow$ A+ + B-

M 0 0

No. of moles dissolved

No. of moles after dissociations m(1-α) mα mα

0.1 (1 – 0.05) 0.1×0.05 0.1×0.0

Total moles = [0.1(1- 0.05)] + (0.1×0.05) + $(.1 \times 0.05)$

= 0.095 + 0.005 + 0.005 = 0.105m

$\Delta T_f = K_f$ .m

$= 1.86 \times 0.105$

= 0.1953 deg.

$T_f = 0^0 C - 0.1953 = 0.1953^0 C$

13. Henry's law constant for the molality of methane in benzene at 298 K is $4.27 \times 105 \, \text{mm Hg}$. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

Ans. Here,

p = 760 mm Hg

$k_H = 4.27 \times 105 \, \text{mm Hg}$

According to Henry's law,

$p = k_H x$

$$x = \frac{p}{k_H}$$

$$= \frac{760 \text{ mm Hg}}{4.27 \times 10^5 \text{ mm Hg}}$$

$= 177.99 \times 10^{-5}$

$= 178 \times 10^{-5}$ (approximately)

Hence, the mole fraction of methane in benzene is 178×10^{-5}.

14. Nalorphene $C_{19}H_{21}NO_3$, similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of 1.5×10^{-3} m aqueous solution required for the above dose.

Ans. The molar mass of nalorphene $C_{19}H_{21}NO_3$ is given as:

$19 \times 12 + 21 \times 1 + 1 \times 14 + 3 \times 16 = 311 \text{ g mol}^{-1}$

In 1.5×10^{-3} m aqueous solution of nalorphene,

1 kg (1000 g) of water contains 1.5×10^{-3} mol = $1.5 \times 10^{-3} \times 311$ g

= 0.4665 g

Therefore, total mass of the solution = (1000 + 0.4665) g

= 1000.4665 g

This implies that the mass of the solution containing 0.4665 g of nalorphene is 1000.4665 g.

Therefore, mass of the solution containing 1.5 mg of nalorphene is:

$$\frac{1000.4665 \times 1.5 \times 10^{-3}}{0.4665} \text{ g}$$

= 3.22 g

Hence, the mass of aqueous solution required is 3.22 g.

15. Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol.

Ans. 0.15 M solution of benzoic acid in methanol means,

1000 mL of solution contains 0.15 mol of benzoic acid

Therefore, 250 mL of solution contains = $\frac{0.15 \times 250}{1000}$ mol of benzoic acid

= 0.0375 mol of benzoic acid

Molar mass of benzoic acid $(C_6H_5COOH) = 7 \times 12 + 6 \times 1 + 2 \times 16$

= 122 g mol^{-1}

Hence, required benzoic acid = $0.0375 \text{ mol} \times 122 \text{ g mol}^{-1}$

= 4.575 g

16. If the solubility product of CuS is 6×10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

Ans. Solubility product of CuS, $K_sp = 6 \times 10^{-16}$

Let s be the solubility of CuS in $mol\ L^{-1}$.

$$\underset{}{CuS} \leftrightarrow \underset{s}{Cu^{2+}} + \underset{s}{S^{2+}}$$

Now, $K_sp = [Cu^{2+}][S^{2-}]$

$= \underset{}{\overset{s \times s}{}} = s^2$

Then, we have, $K_sp = s^2 = 6 \times 10^{-16}$

$s = \sqrt{6 \times 10^{-16}}$

= 2.45 × 10 - 8 mol L^{-1}

Hence, the maximum molarity of CuS in an aqueous solution is $2.45 \times 10^{-8} \text{mol L}^{-1}$.

5 Marks Questions

1. What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism.

Ans. Semiconductors are substances having conductance in the intermediate range of 10^–6to10^4ohm^–1m^–1.

The two main types of semiconductors are:

(i) n-type semiconductor

(ii) p-type semiconductor

n-type semiconductor: The semiconductor whose increased conductivity is a result of negatively-charged electrons is called an n-type semiconductor. When the crystal of a group 14 element such as Si or Ge is doped with a group 15 element such as P or As, an n-type semiconductor is generated.

Si and Ge have four valence electrons each. In their crystals, each atom forms four covalent bonds. On the other hand, P and As contain five valence electrons each. When Si or Ge is doped with P or As, the latter occupies some of the lattice sites in the crystal. Four out of five electrons are used in the formation of four covalent bonds with four neighbouring Si or Ge atoms. The remaining fifth electron becomes delocalised and increases the conductivity of the doped Si or Ge.

p-type semiconductor: The semiconductor whose increased in conductivity is a result of electron hole is called a p-type semiconductor. When a crystal of group 14 elements such as Si or Geis doped with a group 13 element such as B, Al, or Ga (which contains only three valence electrons), a p-type of semiconductor is generated.

When a crystal of Si is doped with B, the three electrons of B are used in the formation of three covalent bonds and an electron hole is created. An electron from the neighboring atom can come and fill this electron hole, but in doing so, it would leave an electron hole at its original position. The process appears as if the electron hole has moved in the direction opposite to that of the electron that filled it. Therefore, when an electric field is applied, electrons will move toward the positively-charged plate through electron holes. However, it will appear as if the electron holes are positively-charged and are moving toward the negatively- charged plate.

2. Explain the following terms with suitable examples:

(i) Schottky defect

(ii) Frenkel defect

(iii) Interstitials and

(iv) F-centres

Ans. (i) Schottky defect: Schottky defect is basically a vacancy defect shown by ionic solids. In this defect, an equal number of cations and anions are missing to maintain electrical neutrality. It decreases the density of a substance. Significant number of Schottky defects is present in ionic solids. For example, in NaCl, there are approximately 106Schottky pairs per cm3at room temperature. Ionic substances containing similar-sized cations and anions show this type of defect. For example: NaCl, KCl, CsCl, AgBr, etc.

(ii) Frenkel defect: Ionic solids containing large differences in the sizes of ions show this type of defect. When the smaller ion (usually cation) is dislocated from its normal site to an interstitial site, Frenkel defect is created. It creates a vacancy defect as well as an interstitial defect. Frenkel defect is also known as dislocation defect. Ionic solids such as AgCl, AgBr, AgI, and ZnS show this type of defect.

(iii) Interstitials: Interstitial defect is shown by non-ionic solids. This type of defect is created when some constituent particles (atoms or molecules) occupy an interstitial site of the crystal. The density of a substance increases because of this defect.

(iv) F-centres:When the anionic sites of a crystal are occupied by unpaired electrons, the ionic sites are called F-centres. These unpaired electrons impart colour to the crystals. For example, when crystals of NaClare heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl ions diffuse from the crystal to its surface and combine with Na atoms, forming NaCl. During this process, the Na atoms on the surface of the crystal lose electrons. These released electrons diffuse into the crystal and occupy the vacant anionic sites, creating F-centres.

3. Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

Ans. Mass percentage of $C_6H_6 = \frac{\text{Mass of } C_6H_6}{\text{Total mass of the solution}} \times 100\%$

$$= \frac{\text{Mass of } C_6H_6}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4} \times 100\%$$

$$= \frac{22}{22+122} \times 100\%$$

= 15.28%

Mass percentage of $CCl_4 = \frac{\text{Mass of } CCl_4}{\text{Total mass of the solution}} \times 100\%$

$$= \frac{\text{Mass of } CCl_4}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4}$$

$$= \frac{122}{22+122} \times 100\%$$

=84.72%

Alternatively,

Mass percentage of CCl_4 = (100 - 15.28)%

= 84.72%

4. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

Ans. Let the total mass of the solution be 100 g and the mass of benzene be 30 g.

∴ Mass of carbon tetrachloride = (100 - 30)g

= 70 g

Molar mass of benzene (C_6H_6) = (6 $\times$ 12 + 6 $\times$) $g\ mol^{-1}$

= 78 $g\ mol^{-1}$

∴ Number of moles of $C_6H_6 = \frac{30}{78} mol$

= 0.3846 mol

Molar mass of carbon tetrachloride (CCl_4) = 1 $\times$ 12 + 4 $\times$ 355

= 154 $g\ mol^{-1}$

∴ Number of moles of $CCl_4 = \frac{70}{154} mol$

= 0.4545 mol

Thus, the mole fraction of C_6H_6 is given as:

$$\frac{\text{Number of moles of } C_6H_6}{\text{Number of moles of } C_6H_6 + \text{Number of moles of } CCl_4}$$

$$= \frac{0.3846}{0.3846 + 0.4545}$$

= 0.458

5. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Ans. In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,

Electrons released at the anodic spot move through the metallic object and go to another spot of the object.

There, in the presence of ions, the electrons reduce oxygen. This spot behaves as the cathode. These H+ ions come either from , which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.

The reaction corresponding at the cathode is given by,

The overall reaction is:

Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide i.e., rust.

Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.

6. The molar conductivity of 0.025 mol L-1 methanoic acid is 46.1 S $cm^2\ mol^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda°H^+$ = 349.6 S $cm^2\ mol^{-1}$ and $\lambda°(HCOO-) = 54.6\,S\,cm^2\,mol$

Ans. C = 0.025 $mol\,L^{-1}$

$$\Lambda_m = 46.1\,S\,cm^2\,mol^{-1}$$
$$\lambda°(H^+) = 349.6\,S\,cm^2\,mol^{-1}$$
$$\lambda°(HCOO^-) = 54.6\,S\,cm^2\,mol^{-1}$$

$$\Lambda_m^{\circ}(HCOOH) = \lambda°(H^+) + \lambda°(HCOO^-)$$

= 349.6 + 54.6 = $404.2\,S\,cm^2\,mol^{-1}$

Now, degree of dissociation:

$$\alpha = \frac{\Lambda_m(HCOOH)}{\Lambda_m^0(HCOOH)}$$

$$= \frac{46.1}{404.2}$$

= 0.114 (approximately)

Thus, dissociation constant:

$$K = \frac{c\alpha^2}{(1-\alpha)}$$

$$= \frac{(0.025\,mol\,L^{-1})(0.114)^2}{(1-0.114)}$$

$$= 3.67 \times 10^{-4}\,mol\,L^{-1}$$

7. Write the Nernst equation and emf of the following cells at 298 K:

(i) $Mg_{(s)} \mid Mg^{2+} + (0.001M) \parallel Cu^{2+}(0.0001M)$

(ii) $Fe_{(s)} \mid Fe^{2+}(0.001M) \parallel H^{+}(1M) \mid H_{2(g)}(1bar) \mid Pt_{(s)}$

(iii) $Sn_{(s)} \mid Sn^{2+}(0.050M) \parallel H^{+}(0.020M) \mid H^{2}_{(g)}(1bar) \mid Pt_{(s)}$

(iv) $Pt_{(s)} \mid Br^{2}(l) \mid Br^{-}(0.010M) \parallel H^{+}(0.030M) \mid H^{2}_{(g)}(1bar) \mid Pt_{(s)}$

Ans. (i) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$= \{0.34-(-236)\} - \frac{0.0591}{2}\log\frac{.001}{.0001}$$

$$= 2.7 - \frac{0.0591}{2}\log 10$$

= 2.7 – 0.02955

= 2.67 V (approximately)

(ii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{[Fe^{2+}]}{[H^{+}]^{2}}$$

$$= \{0-(-0.44)\} - \frac{0.0591}{2}\log\frac{0.001}{1^{2}}$$

= 0.44–0.02955(–3)

= 0.52865 V

= 0.53 V (approximately)

(iii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{[Sn^{2+}]}{[H^{+}]^{2}}$$

$$= \{0-(-0.14)\} - \frac{0.0591}{2}\log\frac{0.050}{(0.020)^{2}}$$

$$= 0.14 - 0.0295 \times \log 125$$

= 0.14–0.062

= 0.078 V

= 0.08 V (approximately)

(iv) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{1}{[Br^{-}]^{2}[H^{+}]^{2}}$$

$$= (0-1.09) - \frac{0.0591}{2}\log\frac{1}{(0.010)^{2}(0.030)^{2}}$$

$$= -1.09 - 0.02955 \times \log\frac{1}{0.00000009}$$

$$= -1.09 - 0.02955 \times \log\frac{1}{9\times10^{-8}}$$

$= -1.09 - 0.02955 \times \log\left(1.11 \times 10^{7}\right)$

= –1.09–0.02955(0.0453+7)

= –1.09–0.208

= –1.298 V

8. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Ans. Conductivity of a solution is defined as the conductance of a solution of 1 cm in length and area of cross-section 1 sq. cm. The inverse of resistivity is called conductivity or specific conductance. It is represented by the symbol K. If ρ is resistivity, then we can write: $K = \frac{1}{\rho}$

The conductivity of a solution at any given concentration is the conductance (G) of one unit volume of solution kept between two platinum electrodes with the unit area of cross-section and at a distance of unit length.

i.e., $G = K\frac{a}{l} = k.1 = k$

(Since a = 1, l = 1)

Conductivity always decreases with a decrease in concentration, both for weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases with a decrease in concentration.

Molar conductivity:

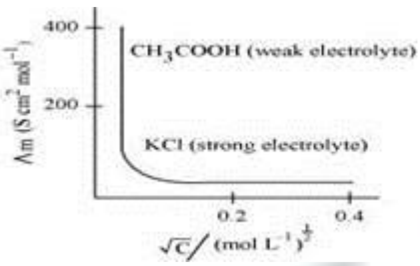
Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing 1 mole of the electrolyte kept between two electrodes with the area of cross-section A and distance of unit length. $\Lambda_m = K\frac{A}{l}$

Now, l = 1 and A = V (volume containing 1 mole of the electrolyte).

Therefore, $\Lambda_m = \kappa V$

Molar conductivity increases with a decrease in concentration. This is because the total volume V of the solution containing one mole of the electrolyte increases on dilution.

The variation of Λ_m with $\sqrt{c}$ for strong and weak electrolytes is shown in the following plot:



9. Calculate (a)molality (b)molarity and (c)mole fraction of KI if the density of 20% (mass/mass) aqueous KI is $1.202\ g\ ml^{-1}$.

Ans. (a) Molar mass of KI = 39 + 127 = 166 $g\ mol^{-1}$

20% (mass/mass) aqueous solution of KI means 20 g of KI is present in 100 g of solution.

That is,

20 g of KI is present in (100 - 20) g of water = 80 g of water

Therefore, molality of the solution = $\frac{\text{Moles of KI}}{\text{Mass of water in kg}}$

$$\frac{\frac{20}{166}}{0.08} m$$

= 1.506 m

= 1.51 m (approximately)

(b) It is given that the density of the solution = $1.202\ g\ ml^{-1}$

Therefore, Volume of 100 g solution = $\frac{\text{Mass}}{\text{Density}}$

$= \frac{100 g}{1.202\ g\ ml^{-1}}$

= 83.19 mL

$= 83.19 \times 10^{-3} L$

Therefore, molarity of the solution = $\frac{\frac{20}{166} mol}{83.19 \times 10^{-3} L}$

= 1.45 M

(c) Moles of KI = $\frac{20}{166} = 0.12 \text{mol}$

Moles of water = $\frac{80}{18} = 4.44 \text{mol}$

Therefore, mole fraction of KI = $\frac{\text{Moles of KI}}{\text{Moles of KI} + \text{Moles of water}}$

= $\frac{0.12}{0.12 + 4.44}$

= 0.0263

10. H_2S, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

Ans. It is given that the solubility of H_2S in water at STP is 0.195 m, i.e., 0.195 mol of H_2S is dissolved in 1000 g of water.

Moles of water = $\frac{1000 \text{g}}{18 \text{g mol}^{-1}}$

= 55.56 mol

∴ Mole fraction of H_2S, x = $\frac{\text{Moles of } H_2S}{\text{Moles of } H_2S + \text{Moles of wtaer}}$

= $\frac{0.195}{0.195 + 55.56}$

= 0.0035

At STP, pressure (p) = 0.987 bar

According to Henry's law:

p= KHx

$$K_H = \frac{p}{x}$$

$$= \frac{0.987}{0.0035}\,\text{bar}$$

= 282 bar