NCERT Solutions for Class 12 Chemistry Chemistry Part 1 Chapter 1

The Solid State Class 12

The Solid State Class 12
Chapter 1 The Solid State Exercise Solutions
In text: Solutions of Questions on Page Number: 4 Q1:
Why are solids rigid?
Answer:
The intermolecular forces of attraction that are present in solids are very strong. The constituent particles of solids cannot move from their positions i.e., they have fixed positions. However, they can oscillate about their mean positions. This is the reason solids are rigid.
Q2:
Why do solids have a definite volume?
Answer:
The intermolecular forces of attraction that are present in solids are very strong. The constituent particles of solids have fixed positions i.e., they are rigid. Hence, solids have a definite volume.
Q3:
Classify the following as amorphous or crystalline solids:
Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.
Answer:
Amorphous solids
Polyurethane, teflon, cellophane, polyvinyl chloride, fibre glass
Crystalline solids
Naphthalene, benzoic acid, potassium nitrate, copper
Q4:
Why is glass considered a super cooled liquid?
Answer:

Similar to liquids, glass has a tendency to flow, though very slowly. Therefore, glass is considered as a super cooled liquid. This is the reason that glass windows and doors are slightly thicker at the bottom than at the top.

Q5:

Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property?

Answer:

An isotropic solid has the same value of physical properties when measured along different directions. Therefore, the given solid, having the same value of refractive index along all directions, is isotropic in nature. Hence, the solid is an amorphous solid.

When an amorphous solid is cut with a sharp edged tool, it cuts into two pieces with irregular surfaces.

Q6:

Classify the following solids in different categories based on the nature of intermolecular forces operating in them:

Potassium sulphate, tin, benzene, urea, ammonia, water, zinc sulphide, graphite, rubidium, argon, silicon carbide.

Answer:

Potassium sulphate \rightarrow Ionic solid

Tin → Metallic solid

Benzene → Molecular (non-polar) solid

Urea → Polar molecular solid

Ammonia → Polar molecular solid

Water → Hydrogen bonded molecular solid

Zinc sulphide \rightarrow Ionic solid

Graphite → Covalent or network solid

Rubidium → Metallic solid

Argon → Non-polar molecular solid

Silicon carbide → Covalent or network solid

Q7:

Solid A is a very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?
Answer:
The given properties are the properties of a covalent or network solid. Therefore, the given solid is a covalent or network solid. Examples of such solids include diamond (C) and quartz (SiO ₂).
Q8:
lonic solids conduct electricity in molten state but not in solid state. Explain.
Answer:
In ionic compounds, electricity is conducted by ions. In solid state, ions are held together by strong electrostatic forces and are not free to move about within the solid. Hence, ionic solids do not conduct electricity in solid state. However, in molten state or in solution form, the ions are free to move and can conduct electricity.
Q9:
Whattype of solids are electrical conductors, malleable and ductile?
Answer:
Metallic solids are electrical conductors, malleable, and ductile.
Q10:
Give the significance of a 'lattice point'.
Answer:
The significance of a lattice point is that each lattice point represents one constituent particle of a solid which may be an atom, a molecule (group of atom), or an ion.
Q11:
Name the parameters that characterize a unit cell.
Answer:

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The six parameters that characterise a unit cell are as follows.

(i) Its dimensions along the three edges, a, b, and c

These edges may or may not be equal.

(ii) Angles between the edges

These are the angle \propto (between edges b and c), $\tilde{A}\check{Z}\hat{A}^2$ (between edges a and c), and $\tilde{A}\check{Z}\hat{A}^3$ (between edges a and b).

Q12:

Distinguish between

- (i)Hexagonal and monoclinic unit cells
- (ii) Face-centred and end-centred unit cells.

Answer:

(i) Hexagonal unit cell

For a hexagonal unit cell,

$$a = b \neq c$$

and $\alpha = \beta = 90^{\circ}$
 $\gamma = 120^{\circ}$

Monoclinic unit cell

For a monoclinic cell,

$$a \neq b \neq c$$

and $\alpha = \gamma = 90^{\circ}$
 $\beta \neq 90^{\circ}$

(ii) Face-centred unit cell

In a face-centred unit cell, the constituent particles are present at the corners and one at the centre of each face.

End-centred unit cell

Anend-centred unit cell contains particles at the corners and one at the centre of any two opposite faces.

Q13:

Explain how much portion of an atom located at (i)corner and (ii)body-centre of a cubic unit cell is part of its neighbouring unit cell.

Answer:

(i) An atom located at the corner of a cubic unit cell is shared by eight adjacent unit cells.

$$\frac{1}{8}$$
th portion of the atom is shared by one unit cell.

(ii) An atom located at the body centre of a cubic unit cell is not shared by its neighbouring unit cell. Therefore, the atom belongs only to the unit cell in which it is present i.e., its contribution to the unit cell is 1.

Q14:

What is the two dimensional coordination number of a molecule in square close packed layer?

Answer:

In square close-packed layer, a molecule is in contact with four of its neighbours. Therefore, the two-dimensional coordination number of a molecule in square close-packed layer is 4.

Q15:

A compound forms *hexagonal close-packed* structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

Answer:

Number of close-packed particles = $0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$

Therefore, number of octahedral voids = 3.011×10^{23}

And, number of tetrahedral voids = $2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$

Therefore, total number of voids = $3.011 \times 10^{23} + 6.022 \times 10^{23} = 9.033 \times 10^{23}$

Q16:

A compound is formed by two elements M and N. The element N forms *ccp* and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

Answer:

The *ccp*lattice is formed by the atoms of the element N.

Here, the number of tetrahedral voids generated is equal to twice the number of atoms of the element N.

According to the question, the atoms of element M occupy $\frac{1}{3}^{\rm rd}$ of the tetrahedral voids.

Therefore, the number of atoms of M is equal to $2 \times \frac{1}{3} = \frac{2}{3}$ of the number of atoms of N.

$$=\frac{2}{3}:$$
 Therefore, ratio of the number of atoms of M to that of N is M: N

= 2:3

Thus, the formula of the compound is M₂N₃.

Q17:

Which of the following lattices has the highest packing efficiency (i) simple cubic (ii) body-centred cubic and (iii) hexagonal close-packed lattice?

Answer:

Hexagonal close-packed lattice has the highest packing efficiency of 74%. The packing efficiencies of simple cubic and body-centred cubic lattices are 52.4% and 68% respectively.

Q18:

An element with molar mass 2.7 x 10⁻²kg mol⁻¹forms a cubic unit cell with edge length 405 pm. If its density is 2.7 x 10³ kg m⁻³, what is the nature of the cubic unit cell?

Answer:

It is given that density of the element, $d=2.7 \times 10^3$ kg m⁻³

Molar mass, $M = 2.7 \times 10^{-2} \text{kg mol}^{-1}$

Edge length, $a = 405 \text{ pm} = 405 \times 10^{-12} \text{m}$

$$= 4.05 \times 10^{-10} \text{m}$$

It is known that, Avogadro's number, N_A= 6.022 ×1023 mol⁻¹

Applying the relation,

$$d = \frac{z, M}{a^{3} \cdot N_{A}}$$

$$z = \frac{d \cdot a^{3} N_{A}}{M}$$

$$= \frac{2.7 \times 10^{3} \text{ kg m}^{-3} \times (4.05 \times 10^{-10} \text{ m})^{3} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{2.7 \times 10^{-2} \text{ kg mol}^{-1}}$$

$$= 4.004$$

$$= 4$$

This implies that four atoms of the element are present per unit cell. Hence, the unit cell is face-centred cubic (*fcc*) or cubic close-packed (*ccp*).

Q19:

What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?

Answer:

When a solid is heated, vacancy defect can arise. A solid crystal is said to have vacancy defect when some of the lattice sites are vacant.

Vacancy defect leads to a decrease in the density of the solid.

Q20:

What type of stoichiometric defect is shown by:

(i) ZnS (ii) AgBr

Answer:

- (i) ZnS shows Frenkel defect.
- (ii) AgBr shows Frenkel defect as well as Schottky defect.

Q21:

Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.

Answer:

When a cation of higher valence is added to an ionic solid as an impurity to it, the cation of higher valence replaces more than one cation of lower valence so as to keep the crystal electrically neutral. As a result, some sites become vacant. For example, when Sr²+is added to NaCl, each Sr²+ ion replaces two Na+ ions. However, one Sr²+ ion occupies the site of one Na+ion and the other site remains vacant. Hence, vacancies are introduced.

Q22:

lonic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.

Answer:

The colour develops because of the presence of electrons in the anionic sites. These electrons absorb energy from the visible part of radiation and get excited.

For example, when crystals of NaCl are heated in an atmosphere of sodium vapours, the sodium atoms get deposited on the surface of the crystal and the chloride ions from the crystal diffuse to the surface to form NaCl with the deposited Na atoms. During this process, the Na atoms on the surface lose electrons to form Na⁺ions and the

released electrons diffuse into the crystal to occupy the vacant anionic sites. These electrons get excited by absorbing energy from the visible light and impart yellow colour to the crystals.

Q23:

A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

Answer:

An *n*-type semiconductor conducts because of the presence of extra electrons. Therefore, a group 14 element can be converted to *n*-type semiconductor by doping it with a group 15 element.

Q24:

What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer.

Answer:

Ferromagnetic substances would make better permanent magnets.

In solid state, the metal ions of ferromagnetic substances are grouped together into small regions. These regions are called domains and each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance, the domains are randomly oriented. As a result, the magnetic moments of the domains get cancelled. However, when the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced.

The ordering of the domains persists even after the removal of the magnetic field. Thus, the ferromagnetic substance becomes a permanent magnet.

Next Chapter 2 : Solutions >>

Exercise: Solutions of Questions on Page Number: 30

Q1:

Define the term 'amorphous'. Give a few examples of amorphous solids.

Answer:

Amorphous solids are the solids whose constituent particles are of irregular shapes and have short range order. These solids are isotropic in nature and melt over a range of temperature. Therefore, amorphous solids are sometimes called pseudo solids or super cooled liquids. They do not have definite heat of fusion. When cut with a sharp-edged tool, they cut into two pieces with irregular surfaces. Examples of amorphous solids include glass, rubber, and plastic.

Q2:

What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

Answer:

The arrangement of the constituent particles makes glass different from quartz. In glass, the constituent particles have short range order, but in quartz, the constituent particles have both long range and short range orders.

Quartz can be converted into glass by heating and then cooling it rapidly.

Q3:

Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.

- (i) Tetra phosphorus decoxide (P₄O₁₀) (vii) Graphite
- (ii) Ammonium phosphate (NH₄)₃PO₄ (viii) Brass
- (iii) SiC (ix) Rb
- (iv) I₂ (x) LiBr
- (v) P4 (xi) Si

Answer:

Ionic → (ii)Ammonium phosphate (NH₄)₃PO₄, (x) LiBr

Metallic → (viii)Brass, (ix)Rb

 $Molecular \rightarrow \textbf{(i)} \; Tetra \; phosphorus \; decoxide \; (P_4O_{10}), \; \textbf{(iv)} \; I_2, \; (v) \; P_4.$

Covalent (network) \rightarrow (iii) SiC, (vii)Graphite, (xi) Si

Amorphous \rightarrow (vi)Plastic

Q4:

- (i) What is meant by the term 'coordination number'?
- (ii) What is the coordination number of atoms:
- (a) in a cubic close-packed structure?
- (b) in a body-centred cubic structure?

Answer:

(i) The number of nearest neighbours of any constituent particle present in the crystal lattice is called its coordination number.

- (ii) The coordination number of atoms
- (a)in a cubic close-packed structure is 12, and
- (b) in a body-centred cubic structure is 8

Q5:

How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain.

Answer:

By knowing the density of an unknown metal and the dimension of its unit cell, the atomic mass of the metal can be determined

Let 'a' be the edge length of a unit cell of a crystal, 'd' be the density of the metal, 'm' be the mass of one atom of the metal and 'z' be the number of atoms in the unit cell.

Now, density of the unit cell $= \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$

 $\Rightarrow d = \frac{z m}{a^3}$ (i)

[Since mass of the unit cell = Number of atoms in the unit cell x mass of one atom]

[Volume of the unit cell = (Edge length of the cubic unit cell)³]

From equation (i), we have:

$$m = \frac{d a^3}{7} \qquad (ii)$$

 $= \frac{\text{Atomic mass (M)}}{\text{Avogadro's number (N}_{A})}$

Now, mass of one atom of metal (m)

 $M = \frac{d a^3 N_A}{z} \quad (iii)$

Therefore,

If the edge lengths are different (say a, b and c), then equation (ii) becomes:

$$M = d(abc)NA$$

Q6:

'Stability of a crystal is reflected in themagnitude of its melting point'. Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

Answer:

Higher the melting point, greater is the intermolecular force of attraction and greater is the stability. A substance with higher melting point is more stable than a substance with lower melting point.

The melting points of the given substances are:

Solid water → 273 K

Ethyl alcohol → 158.8 K

Diethyl ether → 156.85 K

Methane → 89.34 K

Now, on observing the values of the melting points, it can be said that among the given substances, the intermolecular force in solid water is the strongest and that in methane is the weakest.

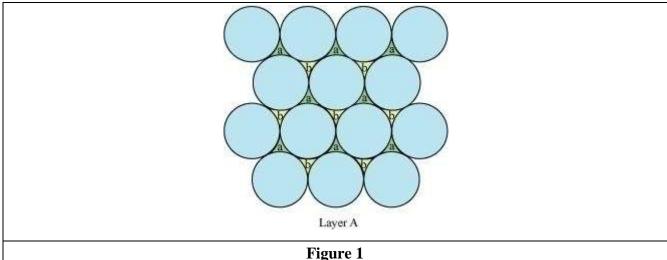
Q7:

How will you distinguish between the following pairs of terms:

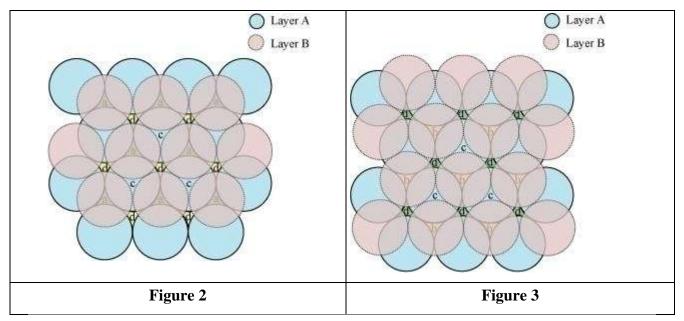
- (i) Hexagonal close-packing and cubic close-packing?
- (ii) Crystal lattice and unit cell?
- (iii) Tetrahedral void and octahedral void?

Answer:

i. A 2-D hexagonal close-packing contains two types of triangular voids (a and b) as shown in figure 1. Let us call this 2-D structure as layer A. Now, particles are kept in the voids present in layer A (it can be easily observed from figures 2 and 3 that only one of the voids will be occupied in the process, i.e., either a or b). Let us call the particles or spheres present in the voids of layer A as layer B. Now, two types of voids are present in layer B (c and d). Unlike the voids present in layer A, the two types of voids present in layer B are not similar. Void c is surrounded by 4 spheres and is called the tetrahedral void. Void d is surrounded by 6 spheres and is called the octahedral void.



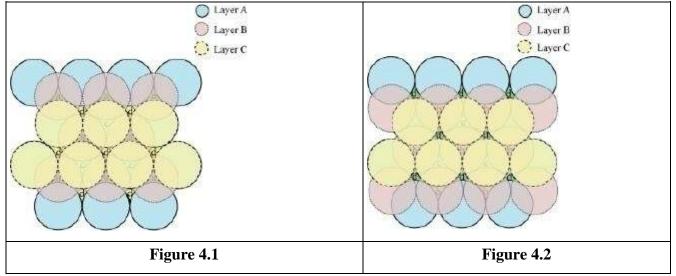
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Now, the next layer can be placed over layer B in 2 ways.

Case 1: When the third layer (layer C) is placed over the second one (layer B) in such a manner that the spheres of layer C occupy the tetrahedral voids c.

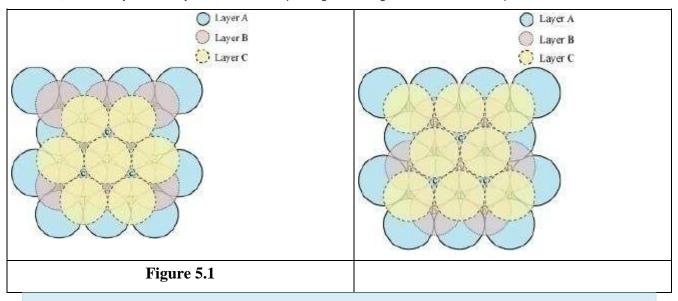
In this case we get hexagonal close-packing. This is shown in figure 4. In figure 4.1, layer B is present over the voids a and layer C is present over the voids c. In figure 4.2, layer B is present over the voids b and layer C is present over the voids c. It can be observed from the figure that in this arrangement, the spheres present in layer C are present directly above the spheres of layer A. Hence, we can say that the layers in hexagonal close-packing are arranged in an ABAB..... pattern.



Case 2: When the third layer (layer C) is placed over layer B in such a manner that the spheres of layer C occupy the octahedral voids d.

In this case we get cubic close-packing. In figure 5.1, layer B is present over the voids a and layer C is present over the voids d. In figure 5.2, layer B is present over the voids b and layer C is present over the voids d. It can be observed from the figure that the arrangement of particles in layer C is completely different from that in layers A or B.

When the fourth layer is kept over the third layer, the arrangement of particles in this layer is similar to that in layer A. Hence, we can say that the layers in cubic close-packing are arranged in an ABCABC..... pattern.



Q8:

How many lattice points are there in one unit cell of each of the following lattice?

- (i) Face-centred cubic
- (ii) Face-centred tetragonal
- (iii) Body-centred

Answer:

- (i) There are 14 (8 from the corners + 6 from the faces) lattice points in face-centred cubic.
- (ii) There are 14 (8 from the corners + 6 from the faces) lattice points in face-centred tetragonal.
- (iii) There are 9 (1 from the centre + 8 from the corners) lattice points in body-centred cubic.

Q9:

Explain

- (i) The basis of similarities and differences between metallic and ionic crystals.
- (ii) lonic solids are hard and brittle.

Answer:

(i) The basis of similarities between metallic and ionic crystals is that both these crystal types are held by the electrostatic force of attraction. In metallic crystals, the electrostatic force acts between the positive ions and the electrons. In ionic crystals, it acts between the oppositely-charged ions. Hence, both have high melting points.

The basis of differences between metallic and ionic crystals is that in metallic crystals, the electrons are free to move and so, metallic crystals can conduct electricity. However, in ionic crystals, the ions are not free to move. As a result, they cannot conduct electricity. However, in molten state or in aqueous solution, they do conduct electricity.

(ii) The constituent particles of ionic crystals are ions. These ions are held together in three-dimensional arrangements by the electrostatic force of attraction. Since the electrostatic force of attraction is very strong, the charged ions are held in fixed positions. This is the reason why ionic crystals are hard and brittle.

Q10:

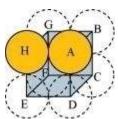
Calculate the efficiency of packing in case of a metal crystal for

- (i) simple cubic
- (ii) body-centred cubic
- (iii) face-centred cubic (with the assumptions that atoms are touching each other).

Answer:

(i) Simple cubic

In a simple cubic lattice, the particles are located only at the corners of the cube and touch each other along the edge.



Let the edge length of the cube be 'a' and the radius of each particle be r.

So, we can write:

Now, volume of the cubic unit cell = a^3

$$= (2r)^3$$

$$= 8r^3$$

We know that the number of particles per unit cell is 1.

$$= \frac{4}{3}\pi r^3$$

Therefore, volume of the occupied unit cell

$$\frac{\text{Volume of one particle}}{\text{Volume of cubic unit cell}} \times 100\%$$

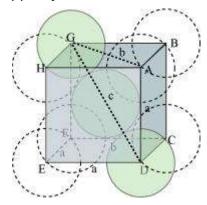
$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100\%$$

$$= \frac{1}{6}\pi \times 100\%$$

$$= \frac{1}{6} \times \frac{22}{7} \times 100\%$$

$$= 52.4\%$$

(ii) Body-centred cubic



Itcan be observed from the above figure that the atom at the centre is in contact with the other two atoms diagonally arranged.

From Δ FED, we have:

$$b^{2} = a^{2} + a^{2}$$
$$\Rightarrow b^{2} = 2a^{2}$$
$$\Rightarrow b = \sqrt{2}a$$

Again, from $\triangle AFD$, we have:

$$c^2 = a^2 + b^2$$

 $\Rightarrow c^2 = a^2 + 2a^2$ (Since $b^2 = 2a^2$)
 $\Rightarrow c^2 = 3a^2$
 $\Rightarrow c = \sqrt{3}a$

Let the radius of the atom be r.

Length of the body diagonal, $c=4\pi$

$$\Rightarrow \sqrt{3}a = 4r$$

$$\Rightarrow a = \frac{4r}{\sqrt{3}}$$

$$r = \frac{\sqrt{3}a}{4}$$

$$a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$$

Volume of the cube,

A body-centred cubic lattice contains 2 atoms.

$$=2\pi\frac{4}{3} r^3$$

So, volume of the occupied cubic lattice

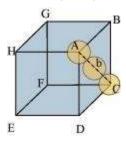
$$=\frac{8}{3}\pi r^3$$

 $\therefore \text{ Packing efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100\%$

$$= \frac{\frac{8}{3}\pi r^3}{\left(\frac{4}{\sqrt{3}}r\right)^3} \times 100\%$$
$$= \frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}}r^3} \times 100\%$$
$$= 68\%$$

(iii) Face-centred cubic

Let the edge length of the unit cell be 'a' and the length of the face diagonal AC be b.



From $\triangle ABC$, we have:

$$AC^2 = BC^2 + AB^2$$

$$\Rightarrow b^2 = a^2 + a^2$$

$$\Rightarrow b^2 = 2a^2$$

$$\Rightarrow b = \sqrt{2a}$$

Q11:

Silver crystallises in fcc lattice. If edge length of the cell is 4.07 x 10°cm and density is 10.5 g cm³, calculate the atomic mass of silver.

Answer:

It is given that the edge length, $a=4.077 \times 10^{-8}$ cm

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

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

We also know that, $N_A = 6.022 \times 10^{23} \text{mol}^{-1}$

Using the relation:

$$d = \frac{z \,\mathrm{M}}{a^{3} \,\mathrm{N_{A}}}$$

$$\Rightarrow \mathrm{M} = \frac{d \,a^{3} \,\mathrm{N_{A}}}{z}$$

$$= \frac{10.5 \,\mathrm{gcm^{-3}} \times (4.077 \times 10^{-8} \,\mathrm{cm})^{3} \times 6.022 \times 10^{23} \,\mathrm{mol^{-1}}}{4}$$

= 107.13 gmol⁻¹

Therefore, atomic mass of silver = 107.13 u

Q12:

A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q?

Answer:

It is given that the atoms of Q are present at the corners of the cube.

$$= 8 \times \frac{1}{8} = 1$$

Therefore, number of atoms of Q in one unit cell

It is also given that the atoms of P are present at the body-centre.

Therefore, number of atoms of P in one unit cell = 1

This means that the ratio of the number of P atoms to the number of Q atoms, P:Q = 1:1

Hence, the formula of the compound is PQ.

The coordination number of both P and Q is 8.

Q13:

Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm⁻³, calculate atomic radius of niobium using its atomic mass 93 u.

Answer:

It is given that the density of niobium, $d=8.55 \text{ g cm}^{-3}$

Atomic mass, M = 93 gmol⁻¹

As the lattice is bcc type, the number of atoms per unit cell, z=2

We also know that, $N_A = 6.022 \times 10^{23} \text{mol}^{-1}$

Applying the relation:

$$d = \frac{z M}{a^{3} N_{A}}$$

$$\Rightarrow a^{3} = \frac{z M}{d N_{A}}$$

$$= \frac{2 \times 93 \text{ gmol}^{-1}}{8.55 \text{ gcm}^{-3} \times 6.022 \times 10^{23} \text{mol}^{-1}}$$

 $= 3.612 \times 10^{-23} \text{cm}^3$

So, $a = 3.306 \times 10^{-8}$ cm

For body-centred cubic unit cell:

$$r = \frac{\sqrt{3}}{4}a$$
$$= \frac{\sqrt{3}}{4} \times 3.306 \times 10^{-8} \text{ cm}$$

 $= 1.432 \times 10^{-8} \text{cm}$

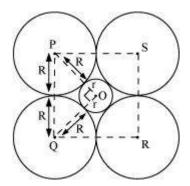
 $= 14.32 \times 10^{-9} \text{cm}$

= 14.32 nm

Q14:

If the radius of the octachedral void is r and radius of the atoms in close packing is R, derive relation between r and R.

Answer:



A sphere with centre O, is fitted into the octahedral void as shown in the above figure. It can be observed from the figure that Δ POQ is right-angled

Now, applying Pythagoras theorem, we can write:

$$PQ^{2} = PO^{2} + OQ^{2}$$

$$\Rightarrow (2R)^{2} = (R + r)^{2} + (R + r)^{2}$$

$$\Rightarrow (2R)^{2} = 2(R + r)^{2}$$

$$\Rightarrow 2R^{2} = (R + r)^{2}$$

$$\Rightarrow \sqrt{2}R = R + r$$

$$\Rightarrow r = \sqrt{2}R - R$$

$$\Rightarrow r = (\sqrt{2} - 1)R$$

$$\Rightarrow r = 0.414R$$

Q15:

Copper crystallises into a fcc lattice with edge length 3.61 x 10° cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm⁻³.

Answer:

Edge length, $a=3.61 \times 10^{-8}$ 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, N_A = 6.022 × 10²³mol⁻¹

Applying the relation:

$$d = \frac{z \,\mathrm{M}}{a^3 \,\mathrm{N_A}}$$

$$= \frac{4 \times 63.5 \,\mathrm{g \, mol^{-1}}}{\left(3.61 \times 10^{-8} \,\mathrm{cm}\right)^3 \times 6.022 \times 10^{23} \mathrm{mol^{-1}}}$$

 $= 8.97 \text{ g cm}^{-3}$

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.

Q16:

Analysis shows that nickel oxide has the formula Ni_{0.98}O_{1.00}. What fractions of nickel exist as Ni²⁺and Ni³⁺ions?

Answer:

The formula of nickel oxide is Ni_{0.98}O_{1.00}.

Therefore, the ratio of the number of Ni atoms to the number of O atoms,

Ni : O = 0.98 : 1.00 = 98 : 100

Now, total charge on 100 O^{2} ions = 100 \times (- 2)

= - 200

Let the number of $Ni^{2+}ions$ be x.

So, the number of $Ni^{3+}ions$ is 98 - x.

Now, total charge on Ni²⁺ions = x(+2)

= +2x

And, total charge on Ni³⁺ions = (98 - x)(+3)

= 294 - 3x

Since, the compound is neutral, we can write:

$$2x + (294 - 3x) + (-200) = 0$$

$$\Rightarrow$$
 - x + 94 = 0

$$\Rightarrow x = 94$$

= 0.959

Therefore, number of Ni²⁺ions = 94

And, number of $Ni^{3+}ions = 98 - 94 = 4$

Hence, fraction of nickel that exists as
$$Ni^{2+}$$

richee, macheri of moder that exists as in

$$Ni^{3+} = \frac{4}{99}$$

And, fraction of nickel that exists as

= 0.041

Alternatively, fraction of nickel that exists as Ni3+= 1 - 0.959

= 0.041

Q17:

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

Answer:

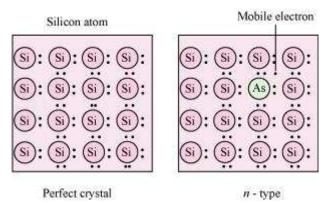
Semiconductors are substances having conductance in the intermediate range of 10⁻⁶to 10⁻⁴ohm⁻¹m⁻¹.

The two main types of semiconductors are:

- (i) *n*-type semiconductor
- (ii) p-type semiconductor

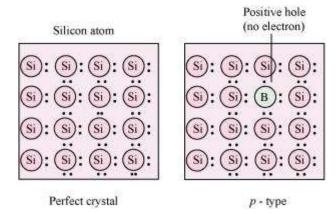
*n***-type semiconductor:** The semiconductor whose increased conductivity is a result of negatively-charged electrons is called an *n*-type semiconductor. When the crystal of a group 14 element such as Si or Ge is doped with a group 15 element such as P or As, an *n*-type semiconductor is generated.

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 Ge is 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 neighbouring 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.



Q18:

Non-stoichiometric cuprous oxide, Cu₂O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a *p*-type semiconductor?

Answer:

In the cuprous oxide (Cu₂O) prepared in the laboratory, copper to oxygen ratio is slightly less than 2:1. This means that the number of Cu⁺ions is slightly less than twice the number of O²-ions. This is because some Cu⁺ions have been replaced by Cu²+ions. Every Cu²+ion replaces two Cu⁺ions, thereby creating holes. As a result, the substance conducts electricity with the help of these positive holes. Hence, the substance is a *p*-type semiconductor.

Q19:

Ferric oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

Answer:

Let the number of oxide (O^{2}) ions be x.

So, number of octahedral voids = x

It is given that two out of every three octahedral holes are occupied by ferric ions.

So, number of ferric (Fe³⁺) ions $= \frac{2}{3}x$

Therefore, ratio of the number of Fe³⁺ions to the number of O²⁻ions,

Fe³⁺: O² =
$$\frac{2}{3}x$$
: x

Hence, the formula of the ferric oxide is Fe₂O₃.

Q20:

Classify each of the following as being either a p-type or an n-type semiconductor:

(i) Ge doped with In (ii) B doped with Si.

Answer:

- (i) Ge (a group 14 element) is doped with In (a group 13 element). Therefore, a hole will be created and the semiconductor generated will be a *p*-type semiconductor.
- (ii) B (a group 13 element) is doped with Si (a group 14 element). Thus, a hole will be created and the semiconductor generated will be a *p*-type semiconductor.

Q21:

Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell?

Answer:

For a face-centred unit cell:

$$a = 2\sqrt{2}r$$

It is given that the atomic radius, *r*= 0.144 nm

So.
$$a = 2\sqrt{2} \times 0.144 \text{ nm}$$

= 0.407 nm

Hence, length of a side of the cell = 0.407 nm

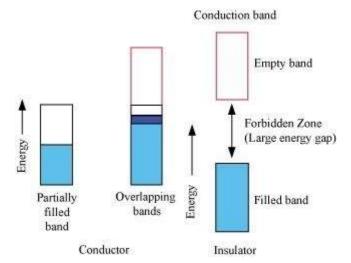
Q22:

In terms of band theory, what is the difference

- (i) Between a conductor and an insulator
- (ii) Between a conductor and a semiconductor

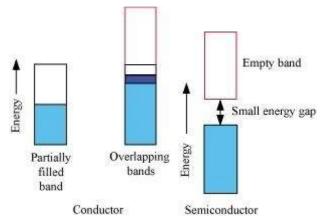
Answer:

(i) The valence band of a conductor is partially-filled or it overlaps with a higher energy, unoccupied conduction band.



On the other hand, in the case of an insulator, the valence band is fully-filled and there is a large gap between the valence band and the conduction band.

(ii) In the case of a conductor, the valence band is partially-filled or it overlaps with a higher energy, unoccupied conduction band. So, the electrons can flow easily under an applied electric field.



On the other hand, the valence band of a semiconductor is filled and there is a small gap between the valence band and the next higher conduction band. Therefore, some electrons can jump from the valence band to the conduction band and conduct electricity.

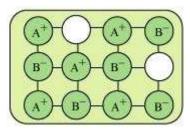
Q23:

Explain the following terms with suitable examples:

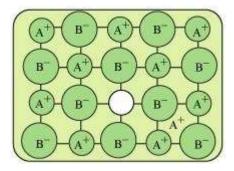
- (i) Schottky defect
- (ii) Frenkel defect
- (iii) Interstitials and
- (iv) F-centres

Answer:

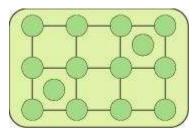
(i) Schottky defect: Schottky defect is basically a vacancy defect shown by ionic solids. In this defect, an equal number of cations and anions are missing to maintain electrical neutrality. It decreases the density of a substance. Significant number of Schottky defects is present in ionic solids. For example, in NaCl, there are approximately 10°Schottky 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.



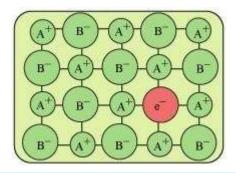
(ii) Frenkel defect: Ionic solids containing large differences in the sizes of ions show this type of defect. When the smaller ion (usually cation) is dislocated from its normal site to an interstitial site, Frenkel defect is created. It creates a vacancy defect as well as an interstitial defect. Frenkel 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 NaCl are 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.



Q24:

Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.

- (i) What is the length of the side of the unit cell?
- (ii) How many unit cells are there in 1.00 cm³of aluminium?

Answer:

(i) For cubic close-packed structure:

$$a = 2\sqrt{2}r$$

$$=2\sqrt{2}\times125 \text{ pm}$$

- = 353.55 pm
- = 354 pm (approximately)
- (ii) Volume of one unit cell = (354 pm)³

$$= 4.4 \times 10^7 \text{pm}^3$$

$$= 4.4 \times 10^7 \times 10^{-30} \text{cm}^3$$

$$= 4.4 \times 10^{-23} \text{cm}^3$$

Therefore, number of unit cells in 1.00 cm³= $\overline{4.4\times10^{-23}~cm^3}$

$$= 2.27 \times 10^{22}$$

Q25:

If NaCl is doped with 10³mol % of SrCl₂, what is the concentration of cation vacancies?

Answer:

It is given that NaCl is doped with 10⁻³mol% of SrCl₂.

This means that 100 mol of NaCl is doped with 10⁻³mol of SrCl₂.

$$10^{-3}$$

Therefore, 1 mol of NaCl is doped with 100 mol of SrCl₂

= 10⁻⁵mol of SrCl₂

Cation vacancies produced by one Sr2+ion = 1

... Concentration of the cation vacancies

produced by
$$10^{-5}$$
 mol of Sr^{2+} ions = $10^{-5} \times 6.022 \times 10^{23}$
= 6.022×10^{18} mol⁻¹

Hence, the concentration of cation vacancies created by SrCl₂is 6.022 x 10⁸per mol of NaCl.

Q26:

Explain the following with suitable examples:

- (i) Ferromagnetism
- (ii)Paramagnetism
- (iii)Ferrimagnetism
- (iv)Antiferromagnetism
- (v)12-16 and 13-15 group compounds.

Answer:

(i) Ferromagnetism: The substances that are strongly attracted by a magnetic field are called ferromagnetic substances. Ferromagnetic substances can be permanently magnetised even in the absence of a magnetic field. Some examples of ferromagnetic substances are iron, cobalt, nickel, gadolinium, and CrO₂.

In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains and each domain acts as a tiny magnet. In an un-magnetised piece of a ferromagnetic substance, the domains are randomly-oriented and so, their magnetic moments get cancelled. However, when the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field. As a result, a strong magnetic effect is produced. This ordering of domains persists even after the removal of the magnetic field. Thus, the ferromagnetic substance becomes a permanent magnet.



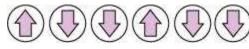
Schematic alignment of magnetic moments in ferromagnetic substances

(ii) Paramagnetism: The substances that are attracted by a magnetic field are called paramagnetic substances. Some examples of paramagnetic substances are O_2 , Cu^{2t} , Fe^{3t} , and Cr^{3t} .

Paramagnetic substances get magnetised in a magnetic field in the same direction, but lose magnetism when the magnetic field is removed. To undergo paramagnetism, a substance must have one or more unpaired electrons. This is because the unpaired electrons are attracted by a magnetic field, thereby causing paramagnetism.

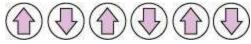
(iii) Ferrimagnetism: The substances in which the magnetic moments of the domains are aligned in parallel and anti-parallel directions, in unequal numbers, are said to have ferrimagnetism. Examples include Fe_3O_4 (magnetite), ferrites such as $MgFe_2O_4$ and $ZnFe_2O_4$.

Ferrimagnetic substances are weakly attracted by a magnetic field as compared to ferromagnetic substances. On heating, these substances become paramagnetic.



Schematic alignment of magnetic moments in ferrimagnetic substances

(iv) Antiferromagnetism: Antiferromagnetic substanceshave domain structures similar to ferromagnetic substances, but are oppositely-oriented. The oppositely-oriented domains cancel out each other's magnetic moments.



Schematic alignment of magnetic moments in antiferromagnetic substances

(v) 12-16 and 13-15 group compounds: The 12-16 group compounds are prepared by combining group 12 and group 16 elements and the 13-15 group compounds are prepared by combining group 13 and group15 elements. These compounds are prepared to stimulate average valence of four as in Ge or Si. Indium (III) antimonide (IrSb), aluminium phosphide (AIP), and gallium arsenide (GaAS) are typical compounds of groups 13-15. GaAs semiconductors have a very fast response time and have revolutionised the designing of semiconductor devices. Examples of group 12-16 compounds include zinc sulphide (ZnS), cadmium sulphide (CdS), cadmium selenide (CdSe), and mercury (II) telluride (HgTe). The bonds in these compounds are not perfectly covalent. The ionic character of the bonds depends on the electronegativities of the two elements.

NCERT Solutions for Class 12 Chemistry Part 1 Chapter 2

Solutions Class 12

Chapter 2 Solutions Exercise Solutions

In text: Solutions of Questions on Page Number: 37

Calculate the mass percentage of benzene (C₀H₀) and carbon tetrachloride (CCI₄) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

Answer:

$$= \frac{\text{Mass of C}_6 \text{H}_6}{\text{Total mass of the solution}} \times 100\%$$
ass percentage of C₆H₆

Mass percentage of C_6H_6

$$= \frac{\text{Mass of C}_6\text{H}_6}{\text{Mass of CCl}_4} \times 100\%$$

$$=\frac{22}{22+122}\times100\%$$

$$=15.28\%$$

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

$$= \frac{\text{Mass of CCl}_4}{\text{Mass of C}_6\text{H}_6 + \text{Mass of CCl}_4} \times 100\%$$

$$=\frac{122}{22+122}\times100\%$$

$$= 84.72\%$$

Alternatively,

Mass percentage of CCI₄= (100 - 15.28)%

= 84.72%

Q2:

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

Answer:

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

$$= 70 g$$

Molar mass of benzene (C_6H_6) = (6 x 12 + 6 x 1) g mol⁻¹

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

$$C_6H_6 = \frac{30}{78}$$
 mol

∴Number of moles of

= 0.3846 mol

Molar mass of carbon tetrachloride (CCI₄) = 1 \times 12 + 4 \times 355

= 154 g mol⁻¹

$$∴ Number of moles of CCI4 = \frac{70}{154} mol$$

= 0.4545 mol

Thus, the mole fraction of C₆H₆is given as:

Number of moles of C₆H₆ + Number of moles of CCl₄

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

= 0.458

Q3:

Calculate the molarity of each of the following solutions: (a)30 g of $Co(NO_3)_2$. $6H_2O$ in 4.3 L of solution (b)30 mL of 0.5 M H_2SO_4 diluted to 500 mL.

Answer:

Molarity is given by:

$$Molarity = \frac{Moles \text{ of solute}}{Volume \text{ of solution in litre}}$$

- (a) Molar mass of Co $(NO_3)_2.6H_2O = 59 + 2(14 + 3 \times 16) + 6 \times 18$
- = 291 g mol⁻¹

∴Moles of Co (NO₃)₂.6H₂O =
$$\frac{30}{291}$$
 mol

= 0.103 mol

Therefore, molarity
$$= \frac{0.103 \text{ mol}}{4.3 \text{ L}}$$

= 0.023 M

(b) Number of moles present in 1000 mL of 0.5 M H₂SO₄= 0.5 mol

∴Number of moles present in 30 mL of 0.5 M H₂SO₄ =
$$\frac{0.5 \times 30}{1000}$$
 mo

= 0.015 mol

$$\frac{0.015}{\text{Therefore, molarity}} = \frac{0.015}{0.5 \text{ L}} \text{mol}$$

= 0.03 M

Q4:

Calculate the mass of urea (NH₂CONH₂) required in making 2.5 kg of 0.25 molal aqueous solution.

Answer:

Molar mass of urea $(NH_2CONH_2) = 2(1 \times 14 + 2 \times 1) + 1 \times 12 + 1 \times 16$

 $= 60 \text{ g mol}^{-1}$

0.25 molar aqueous solution of urea means:

1000 g of water contains 0.25 mol = (0.25×60) g of urea

= 15 g of urea

That is,

(1000 + 15) g of solution contains 15 g of urea

$$= \frac{15 \times 2500}{1000 + 15}$$
 Therefore, 2.5 kg (2500 g) of solution contains

= 36.95 g

= 37 g of urea (approximately)

Hence, mass of urea required = 37 g

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q5:

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.

Answer:

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

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

$$= \frac{\text{Moles of KI}}{\text{Mass of water in kg}}$$

Therefore, molality of the solution

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

= 1.506 m

= 1.51 m (approximately)

(b) It is given that the density of the solution = 1.202 g mL⁻¹

$$=\frac{\text{Mass}}{\text{Density}}$$

::Volume of 100 g solution

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

 $= 83.19 \, mL$

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

$$= \frac{\frac{20}{166} \text{mol}}{83.19 \times 10^{-3} \,\text{L}}$$

Therefore, molarity of the solution

= 1.45 M

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

 $=\frac{80}{18} = 4.44 \text{ mol}$

$$= \frac{\text{Moles of KI}}{\text{Moles of KI + Moles of water}}$$

Therefore, mole fraction of KI

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

= 0.0263

Q6:

H₂S, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H₂S in water at STP is 0.195 m, calculate Henry's law constant.

Answer:

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.

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

= 55.56 mol

$$= \frac{\text{Moles of H}_2S}{\text{Moles of H}_2S + \text{Moles of water}}$$

$$\therefore \text{Mole fraction of H}_2S, x$$

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

= 0.0035

At STP, pressure (p) = 0.987 bar

According to Henry's law:

 $p = K_H x$

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

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

= 282 bar

Q7:

Henry's law constant for CO_2 in water is 1.67 x 10 8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

Answer:

It is given that:

 $K_{H} = 1.67 \times 10^{8} Pa$

$$p_{\text{CO}_2} = 2.5 \text{ atm} = 2.5 \times 1.01325 \times 10^5 \text{Pa}$$

= 2.533125 x 10⁵Pa

According to Henry's law:

$$p_{\text{CO}_2} = K_{\text{H}} x$$

$$\Rightarrow x = \frac{p_{\text{CO}_2}}{K_{\text{H}}}$$

$$=\frac{2.533125\times10^5}{1.67\times10^8}$$

= 0.00152

$$x = \frac{n_{\rm CO_2}}{n_{\rm CO_2} + n_{\rm H_2O}} \approx \frac{n_{\rm CO_2}}{n_{\rm H_2O}}$$

We can write,

[Since, $n_{\mathrm{CO_2}}$ is negligible as compared to $n_{\mathrm{H_2O}}$]

In 500 mL of soda water, the volume of water = 500 mL

[Neglecting the amount of soda present]

We can write:

500 mL of water = 500 g of water

$$=\frac{500}{18}$$
 mol of water

= 27.78 mol of water

$$\frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}}} = x$$
Now

$$\frac{n_{\text{CO}_2}}{27.78} = 0.00152$$

$$n_{\rm CO_2} = 0.042 \text{ mol}$$

Hence, quantity of CO₂in 500 mL of soda water = (0.042 x 44)g

= 1.848 g

Q8:

The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

Answer:

It is given that:

$$p_{\rm A}^0$$
 = 450 mm of Hg

$$p_{\rm B\,=\,700}^{\rm 0}$$
 mm of Hg

 p_{total} = 600 mm of Hg

From Raoult's law, we have:

$$\begin{aligned} p_{\mathrm{A}} &= p_{\mathrm{A}}^{0} x_{\mathrm{A}} \\ p_{\mathrm{B}} &= p_{\mathrm{B}}^{0} x_{\mathrm{B}} = p_{\mathrm{B}}^{0} \left(1 - x_{\mathrm{A}} \right) \quad \text{Therefore, total pressure,} \quad p_{\mathrm{total}} = p_{\mathrm{A}} + p_{\mathrm{B}} \\ &\Rightarrow p_{\mathrm{total}} = p_{\mathrm{A}}^{0} x_{\mathrm{A}} + p_{\mathrm{B}}^{0} \left(1 - x_{\mathrm{A}} \right) \\ &\Rightarrow p_{\mathrm{total}} = p_{\mathrm{A}}^{0} x_{\mathrm{A}} + p_{\mathrm{B}}^{0} - p_{\mathrm{B}}^{0} x_{\mathrm{A}} \\ &\Rightarrow p_{\mathrm{total}} = \left(p_{\mathrm{A}}^{0} - p_{\mathrm{B}}^{0} \right) x_{\mathrm{A}} + p_{\mathrm{B}}^{0} \\ &\Rightarrow 600 = \left(450 - 700 \right) x_{\mathrm{A}} + 700 \\ &\Rightarrow -100 = -250 x_{\mathrm{A}} \\ &\Rightarrow x_{\mathrm{A}} = 0.4 \end{aligned}$$

Therefore,
$$x_{\rm B} = 1 - x_{\rm A}$$

Now,
$$p_A = p_A^0 x_A$$

$$= 450 \times 0.4$$

= 180 mm of Hg

$$p_{\rm B} = p_{\rm B}^0 x_{\rm B}$$

$$= 700 \times 0.6$$

Now, in the vapour phase:

$$\label{eq:Mole fraction of liquid A} = \frac{p_{\rm A}}{p_{\rm A}\,+\,p_{\rm B}}$$
 Mole fraction of liquid A

$$= \frac{180}{180 + 420}$$
$$= \frac{180}{180 + 420}$$

$$= 0.30$$

And, mole fraction of liquid B = 1 - 0.30

= 0.70

Q9:

Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea (NH₂CONH₂) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

Answer:

It is given that vapour pressure of water, $p_1^0 = 23.8 \text{ mm}$ of Hg

Weight of water taken, $w_1 = 850 \text{ g}$

Weight of urea taken, w_2 = 50 g

Molecular weight of water, M_1 = 18 g mol⁻¹

Molecular weight of urea, M_2 = 60 g mol⁻¹

Now, we have to calculate vapour pressure of water in the solution. We take vapour pressure as p_1 .

Now, from Raoult's law, we have:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

$$\Rightarrow \frac{p_1^0 - p_1}{p_1^0} = \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1} + \frac{w_2}{M_2}}$$

$$\Rightarrow \frac{23.8 - p_1}{23.8} = \frac{\frac{50}{60}}{\frac{850}{18} + \frac{50}{60}}$$

$$\Rightarrow \frac{23.8 - p_1}{23.8} = \frac{0.83}{47.22 + 0.83}$$

$$\Rightarrow \frac{23.8 - p_1}{23.8} = 0.0173$$

$$\Rightarrow p_1 = 23.4 \text{ mm of Hg}$$

Hence, the vapour pressure of water in the given solution is 23.4 mm of Hg and its relative lowering is 0.0173.

Q10:

Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C.Molal elevation constant for water is 0.52 K kg mol⁻¹.

Answer:

Here, elevation of boiling point $\Delta T_b = (100 + 273) - (99.63 + 273)$

= 0.37 K

Mass of water, $w_i = 500 \text{ g}$

Molar mass of sucrose ($C_{12}H_{22}O_{11}$), M_2 = 11 × 12 + 22 × 1 + 11 × 16

= 342 g mol-1

Molal elevation constant, K_b= 0.52 K kg mol⁻¹

We know that:

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$\Rightarrow w_2 = \frac{\Delta T_b \times M_2 \times w_1}{K_b \times 1000}$$

$$=\frac{0.37\times342\times500}{0.52\times1000}$$

= 121.67 g (approximately)

Hence, 121.67 g of sucrose is to be added.

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q11:

Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. K_7 = 3.9 K kg mol⁻¹.

Answer:

Mass of acetic acid, $w_1 = 75 \text{ g}$

Molar mass of ascorbic acid ($C_6H_8O_6$), $M_2=6 \times 12 + 8 \times 1 + 6 \times 16$

 $= 176 \text{ g mol}^{-1}$

Lowering of melting point, $\Delta T = 1.5 \text{ K}$

We know that:

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

$$\Rightarrow w_2 = \frac{\Delta T_f \times M_2 \times w_1}{K_f \times 1000}$$
$$= \frac{1.5 \times 176 \times 75}{3.9 \times 1000}$$

= 5.08 g (approx)

Hence, 5.08 g of ascorbic acid is needed to be dissolved.

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q12:

Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

Answer:

It is given that:

Volume of water, V=450 mL = 0.45 L

Temperature, T = (37 + 273)K = 310 K

$$n = \frac{1}{185000}$$
 mol

Number of moles of the polymer,

We know that:

Osmotic pressure,
$$\pi = \frac{n}{V} RT$$

$$= \frac{1}{185000}\, mol \times \frac{1}{0.45\;L} \times \; 8.314 \times 10^3\; Pa\;L\;K^{-1} mol^{-1} \times 310\;K$$

= 30.98 Pa

= 31 Pa (approximately)

<< Previous Chapter 1 : The Solid StateNext Chapter 3 : Electrochemistry >>

Exercise: Solutions of Questions on Page Number: 59

Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.

Answer:

Homogeneous mixtures of two or more than two components are known as solutions.

There are three types of solutions.

(i) Gaseous solution:

The solution in which the solvent is a gas is called a gaseous solution. In these solutions, the solute may be liquid, solid, or gas. For example, a mixture of oxygen and nitrogen gas is a gaseous solution.

(ii) Liquid solution:

The solution in which the solvent is a liquid is known as a liquid solution. The solute in these solutions may be gas, liquid, or solid.

For example, a solution of ethanol in water is a liquid solution.

(iii) Solid solution:

The solution in which the solvent is a solid is known as a solid solution. The solute may be gas, liquid or solid. For example, a solution of copper in gold is a solid solution.

Q2:

Give an example of solid solution in which the solute is a gas.

Answer:

In case a solid solution is formed between two substances (one having very large particles and the other having very small particles), an interstitial solid solution will be formed. For example, a solution of hydrogen in palladium is a solid solution in which the solute is a gas.

Q3:

Define the following terms:

- (i) Mole fraction
- (ii) Molality
- (iii) Molarity
- (iv) Mass percentage.

Answer:

(i) Mole fraction:

The mole fraction of a component in a mixture is defined as the ratio of the number of moles of the component to the total number of moles of all the components in the mixture.

i.e.,

= Number of moles of the component

Total number of moles of all components

Mole fraction of a component

Mole fraction is denoted by 'x'.

If in a binary solution, the number of moles of the solute and the solvent are n_A and n_B respectively, then the mole fraction of the solute in the solution is given by,

$$x_A = \frac{n_A}{n_A + n_B}$$

Similarly, the mole fraction of the solvent in the solution is given as:

$$x_B = \frac{n_B}{n_A + n_B}$$

(ii) Molality

Molality (m) is defined as the number of moles of the solute per kilogram of the solvent. It is expressed as:

$$\frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

(iii) Molarity

Molarity (M) is defined as the number of moles of the solute dissolved in one Litre of the solution.

It is expressed as:

$$_{\text{Molarity (M)}} = \frac{\text{Moles of solute}}{\text{Volume of solution in Litre}}$$

(iv) Mass percentage:

The mass percentage of a component of a solution is defined as the mass of the solute in grams present in 100 g of the solution. It is expressed as:

$$= \frac{\text{Mass of component in solution}}{\text{Total mass of solution}} \times 100$$

Q4:

Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL⁻¹?

Answer:

Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in an aqueous solution. This means that 68 g of nitric acid is dissolved in 100 g of the solution.

Molar mass of nitric acid (HNO₃) = $1 \times 1 + 1 \times 14 + 3 \times 16 = 63$ g mol⁻¹

$$=\frac{68}{63} \text{ mol}$$

Then, number of moles of HNO₃

$$=1.079 \text{ mol}$$

Given,

Density of solution = 1.504 g mL⁻¹

$$\therefore \text{Volume of 100 g solution} = \frac{100}{1.504} \text{ mL}$$
= 66.49 mJ

$$=66.49 \text{ mL}$$

$$=66.49\times10^{-3} L$$

$$\text{Molarity of solution} = \frac{1.079 \, \text{mol}}{66.49 \times 10^{-3} \, \text{L}}$$

=16.23 M

Q5:

A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is 1.2 g mL1, then what shall be the molarity of the solution?

Answer:

10% w/w solution of glucose in water means that 10 g of glucose in present in 100 g of the solution i.e., 10 g of glucose is present in (100 - 10) g = 90 g of water.

Molar mass of glucose $(C_6H_{12}O_6) = 6 \times 12 + 12 \times 1 + 6 \times 16 = 180 \text{ g mol}^{-1}$

 $=\frac{10}{180}$ mol Then, number of moles of glucose

= 0.056 mol

$$\frac{0.056 \text{ mol}}{0.09 \text{ kg}} = 0.62 \text{ m}$$

$$0.62 \text{ m}$$

$$=\frac{90 \,\mathrm{g}}{18 \,\mathrm{g \, mol^{-1}}}$$

Number of moles of water

= 5 mol

$$(x_{\rm g}) = \frac{0.056}{0.056 + 5}$$
$$= 0.011$$

⇒ Mole fraction of glucose

And, mole fraction of water
$$x_{\rm w} = 1 - x_{\rm g}$$

$$= 0.989$$

If the density of the solution is 1.2 g mL⁻¹, then the volume of the 100 g solution can be given as:

$$= \frac{100 \text{ g}}{1.2 \text{ g mL}^{-1}}$$
$$= 83.33 \text{ mL}$$
$$= 83.33 \times 10^{-3} \text{ L}$$

$$\therefore \text{Molarity of the solution} = \frac{0.056 \text{mol}}{83.33 \times 10^{-3} \text{L}}$$

= 0.67 M

Q6:

How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na₂CO₃ and NaHCO₃containing equimolar amounts of both?

Answer:

Let the amount of Na_2CO_3 in the mixture be x g.

Then, the amount of NaHCO₃ in the mixture is (1 - x) g.

Molar mass of Na₂CO₃ = $2 \times 23 + 1 \times 12 + 3 \times 16$

 $= 106 \text{ g mol}^{-1}$

$$\therefore \text{ Number of moles Na}_2\text{CO}_3 = \frac{x}{106} \text{ mol}$$

Molar mass of NaHCO₃ = $1 \times 23 + 1 \times 1 \times 12 + 3 \times 16$

 $= 84 \text{ g mol}^{-1}$

$$\therefore \text{Number of moles of NaHCO}_3 = \frac{1-x}{84} \text{ mol}$$

According to the question,

$$\frac{x}{106} = \frac{1-x}{84}$$

$$\Rightarrow 84x = 106 - 106x$$

$$\Rightarrow 190x = 106$$

$$\Rightarrow x = 0.5579$$

Therefore, number of moles of Na₂CO₃
$$=\frac{0.5579}{106}$$
 mo

= 0.0053 mol

$$=\frac{1-0.5579}{84}$$

And, number of moles of NaHCO3

= 0.0053 mol

HCl reacts with Na₂CO₃ and NaHCO₃ according to the following equation.

$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2$$

2 mol 1 mol

$$\mbox{HCl} \ + \ \mbox{NaHCO}_3 \longrightarrow \mbox{NaCl} \ + \ \mbox{H}_2\mbox{O} \ + \ \mbox{CO}_2$$

1 mol 1 mol

1 mol of Na₂CO₃ reacts with 2 mol of HCl.

Therefore, 0.0053 mol of Na₂CO₃ reacts with 2×0.0053 mol = 0.0106 mol.

Similarly, 1 mol of NaHCO₃ reacts with 1 mol of HCl.

Therefore, 0.0053 mol of NaHCO₃ reacts with 0.0053 mol of HCl.

Total moles of HCl required = (0.0106 + 0.0053) mol

= 0.0159 mol

In 0.1 M of HCI,

0.1 mol of HCl is preset in 1000 mL of the solution.

$$\frac{1000 \times 0.0159}{0.1}$$
 mol

Therefore, 0.0159 mol of HCl is present in

= 159 mL of the solution

Hence, 159 mL of 0.1 M of HCl is required to react completely with 1 g mixture of Na₂CO₃ and NaHCO₃, containing equimolar amounts of both.

Q7:

A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

Answer:

Total amount of solute present in the mixture is given by,

$$300 \times \frac{25}{100} + 400 \times \frac{40}{100}$$

$$= 75 + 160$$

$$= 235 g$$

Total amount of solution = 300 + 400 = 700 g

$$=\frac{235}{700}\times100\%$$

Therefore, mass percentage (w/w) of the solute in the resulting solution,

= 33.57%

And, mass percentage (w/w) of the solvent in the resulting solution,

$$= (100 - 33.57)\%$$

= 66.43%

Q8:

An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL⁻¹, then what shall be the molarity of the solution?

Answer:

Molar mass of ethylene glycol $\left[C_2H_4\left(OH\right)_2\right]_{=2\times12+6\times1+2\times16}$

= 62 gmol⁻¹

Number of moles of ethylene glycol $= \frac{222.6 \,\mathrm{g}}{62 \,\mathrm{gmol}^{-1}}$

= 3.59 mol

 $= \frac{3.59 \text{ mol}}{0.200 \text{ kg}}$

Therefore, molality of the solution

= 17.95 m

Total mass of the solution = (222.6 + 200) g

= 422.6 g

Given,

Density of the solution = 1.072 g mL⁻¹

$$\frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}}$$

= 394.22 mL

 $= 0.3942 \times 10^{-3} L$

$$\Rightarrow \frac{3.59 \text{ mol}}{0.39422 \times 10^{-3} \text{ L}}$$

= 9.11 M

Q9:

A sample of drinking water was found to be severely contaminated with chloroform (CHCI₃) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass):

- (i) express this in percent by mass
- (ii) determine the molality of chloroform in the water sample.

Answer:

(i) 15 ppm (by mass) means 15 parts per million (106) of the solution.

$$= \frac{15}{10^6} \times 100\%$$
 Therefore, percent by mass

 $= 1.5 \times 10^{-3} \%$

(ii) Molar mass of chloroform (CHCl₃) = $1 \times 12 + 1 \times 1 + 3 \times 35.5$

 $= 119.5 \text{ g mol}^{-1}$

Now, according to the question,

15 g of chloroform is present in 10° g of the solution.

i.e., 15 g of chloroform is present in (10⁶ - 15) â‰Ë† 10⁶ g of water.

$$= \frac{\frac{15}{119.5} \text{ mol}}{10^6 \times 10^{-3} \text{ kg}}$$

· Molality of the solution

 $= 1.26 \times 10^{-4} \text{ m}$

Q10:

What role does the molecular interaction play in a solution of alcohol and water?

Answer:

In pure alcohol and water, the molecules are held tightly by a strong hydrogen bonding. The interaction between the molecules of alcohol and water is weaker than alcohol-alcohol and water-water interactions. As a result, when alcohol and water are mixed, the intermolecular interactions become weaker and the molecules can easily escape. This increases the vapour pressure of the solution, which in turn lowers the boiling point of the resulting solution.

Q11:

Why do gases always tend to be less soluble in liquids as the temperature is raised?

Answer:

Solubility of gases in liquids decreases with an increase in temperature. This is because dissolution of gases in liquids is an exothermic process.

Therefore, when the temperature is increased, heat is supplied and the equilibrium shifts backwards, thereby decreasing the solubility of gases.

Q12:

State Henry's law and mention some important applications?

Answer:

Henry's law states that partial pressure of a gas in the vapour phase is proportional to the mole fraction of the gas in the solution. If p is the partial pressure of the gas in the vapour phase and x is the mole fraction of the gas, then Henry's law can be expressed as:

$$p = K_H x$$

Where,

K_H is Henry's law constant

Some important applications of Henry's law are mentioned below.

- (i) Bottles are sealed under high pressure to increase the solubility of CO2 in soft drinks and soda water.
- (ii) Henry's law states that the solubility of gases increases with an increase in pressure. Therefore, when a scuba diver dives deep into the sea, the increased sea pressure causes the nitrogen present in air to dissolve in his blood in great amounts. As a result, when he comes back to the surface, the solubility of nitrogen again decreases and the dissolved gas is released, leading to the formation of nitrogen bubbles in the blood. This results in the blockage of capillaries and leads to a medical condition known as 'bends' or 'decompression sickness'.

Hence, the oxygen tanks used by scuba divers are filled with air and diluted with helium to avoid bends.

(iii) The concentration of oxygen is low in the blood and tissues of people living at high altitudes such as climbers. This is because at high altitudes, partial pressure of oxygen is less than that at ground level. Low-blood oxygen causes climbers to become weak and disables them from thinking clearly. These are symptoms of anoxia.

Q13:

The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?

Answer:

Molar mass of ethane $(C_2H_6) = 2 \times 12 + 6 \times 1$

 $= 30 \text{ g mol}^{-1}$

$$\therefore \text{ Number of moles present in } 6.56 \times 10^{-3} \text{ g of ethane} = \frac{6.56 \times 10^{-3}}{30}$$

 $= 2.187 \times 10^{-4} \text{ mol}$

Let the number of moles of the solvent be x.

According to Henry's law,

$$p = K_{+}x$$

$$\Rightarrow 1 bar = K_{H} \cdot \frac{2.187 \times 10^{-4}}{2.187 \times 10^{-4} + x}$$

$$\Rightarrow 1 bar = K_{H} \cdot \frac{2.187 \times 10^{-4} + x}{x} \quad (Since \ x > > 2.187 \times 10^{-4})$$

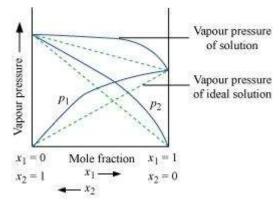
$$\Rightarrow K_{H} = \frac{x}{2.187 \times 10^{-4}} bar$$

Q14:

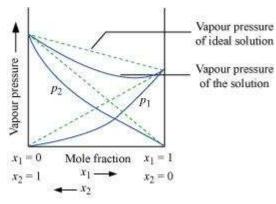
What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{sol}H$ related to positive and negative deviations from Raoult's law?

Answer:

According to Raoult's law, the partial vapour pressure of each volatile component in any solution is directly proportional to its mole fraction. The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. The solutions that do not obey Raoult's law (non-ideal solutions) have vapour pressures either higher or lower than that predicted by Raoult's law. If the vapour pressure is higher, then the solution is said to exhibit positive deviation, and if it is lower, then the solution is said to exhibit negative deviation from Raoult's law.



Vapour pressure of a two-component solution showing positive deviation from Raoult's law



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Vapour pressure of a two-component solution showing negative deviation from Raoult's law

In the case of an ideal solution, the enthalpy of the mixing of the pure components for forming the solution is zero.

 $\Delta_{sol}H=0$

In the case of solutions showing positive deviations, absorption of heat takes place.

 $::\Delta_{sol}H=$ Positive

In the case of solutions showing negative deviations, evolution of heat takes place.

 $∴\Delta_{sol}H=$ Negative

Q15:

An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

Answer:

Here,

Vapour pressure of the solution at normal boiling point $(p_1) = 1.004$ bar

Vapour pressure of pure water at normal boiling point $(p_1^0) = 1.013$ bar

Mass of solute, $(w_2) = 2 g$

Mass of solvent (water), $(w_1) = 98 g$

Molar mass of solvent (water), $(M_1) = 18 \text{ g mol}^{-1}$

According to Raoult's law,

$$\begin{split} &\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \\ &\Rightarrow \frac{1.013 - 1.004}{1.013} = \frac{2 \times 18}{M_2 \times 98} \\ &\Rightarrow \frac{0.009}{1.013} = \frac{2 \times 18}{M_2 \times 98} \\ &\Rightarrow M_2 = \frac{1.013 \times 2 \times 18}{0.009 \times 98} \end{split}$$

 $= 41.35 \text{ g mol}^{-1}$

Hence, the molar mass of the solute is 41.35 g mol⁻¹.

Q16:

Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?

Answer:

Vapour pressure of heptane $(p_1^0) = 105.2 \text{ kPa}$

Vapour pressure of octane $\left(p_2^0\right)_{\text{= 46.8 kPa}}$

We know that,

Molar mass of heptane $(C_7H_{16}) = 7 \times 12 + 16 \times 1$

 $= 100 \text{ g mol}^{-1}$

· Number of moles of heptane

= 0.26 mol

Molar mass of octane $(C_8H_{18}) = 8 \times 12 + 18 \times 1$

= 114 g mol⁻¹

 $\therefore \text{Number of moles of octane} = \frac{35}{114} \text{ mol}$

= 0.31 mol

 $x_1 = \frac{0.26}{0.26 + 0.31}$ Mole fraction of heptane,

= 0.456

And, mole fraction of octane, $x_2 = 1 - 0.456$

= 0.544

Now, partial pressure of heptane, $p_1 = x_1 p_1^0$

 $= 0.456 \times 105.2$

= 47.97 kPa

Partial pressure of octane, $p_2 = x_2 p_2^0$

 $= 0.544 \times 46.8$

= 25.46 kPa

Hence, vapour pressure of solution, $p_{total} = p_1 + p_2$

=47.97 + 25.46

= 73.43 kPa

Q17:

The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a nonvolatile solute in it.

Answer:

1 molal solution means 1 mol of the solute is present in 1000 g of the solvent (water).

Molar mass of water = 18 g mol⁻¹

$$\therefore \text{ Number of moles present in 1000 g of water} = \frac{1000}{18}$$

= 55.56 mol

Therefore, mole fraction of the solute in the solution is

$$x_2 = \frac{1}{1 + 55.56} = 0.0177$$

It is given that,

Vapour pressure of water, $p_1^0 = 12.3 \text{ kPa}$

$$\frac{p_1^0 - p_1}{p_1^0} = x_2$$

Applying the relation,

$$\Rightarrow \frac{12.3 - p_1}{12.3} = 0.0177$$

$$\Rightarrow$$
 12.3 - p_1 = 0.2177

$$\Rightarrow p_1 = 12.0823$$

Hence, the vapour pressure of the solution is 12.08 kPa.

Q18:

Calculate the mass of a non-volatile solute (molar mass 40 g mol⁻¹) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

Answer:

Let the vapour pressure of pure octane be $p_1^{\rm v}$.

Then, the vapour pressure of the octane after dissolving the non-volatile solute is
$$\frac{80}{100}p_1^0=0.8p_1^0$$
. Molar mass of solute, $M_2=40$ g mol⁻¹

Molar mass of solute, $M_2 = 40 \text{ g mol}^{-1}$

Mass of octane, $w_1 = 114 \text{ g}$

Molar mass of octane, (C_8H_{18}), $M_1 = 8 \times 12 + 18 \times 1$

 $= 114 \text{ g mol}^{-1}$

Applying the relation,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

$$\Rightarrow \frac{p_1^0 - 0.8 p_1^0}{p_1^0} = \frac{w_2 \times 114}{40 \times 114}$$

$$\Rightarrow \frac{0.2 p_1^0}{p_1^0} = \frac{w_2}{40}$$

$$\Rightarrow 0.2 = \frac{w_2}{40}$$

$$\Rightarrow w_2 = 8 \text{ g}$$

Hence, the required mass of the solute is 8 g.

Q19:

A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate:

- i. molar mass of the solute
- ii. vapour pressure of water at 298 K.

Answer:

(i) Let, the molar mass of the solute be M g mol⁻¹

 $n_1 = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ mol}$ Now, the no. of moles of solvent (water),

 $n_2 = \frac{30 \text{ g}}{\text{M mol}^{-1}} = \frac{30}{\text{M}} \text{mol}$

And, the no, of moles of solute.

$$p_1 = 2.8 \,\text{kPa}$$

Applying the relation:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

$$\Rightarrow \frac{p_1^0 - 2.8}{p_1^0} = \frac{\frac{30}{M}}{5 + \frac{30}{M}}$$

$$\Rightarrow 1 - \frac{2.8}{p_1^0} = \frac{\frac{30}{M}}{\frac{5M + 30}{M}}$$

$$\Rightarrow 1 - \frac{2.8}{p_1^0} = \frac{30}{5M + 30}$$

$$\Rightarrow \frac{2.8}{p_1^0} = 1 - \frac{30}{5M + 30}$$

$$\Rightarrow \frac{2.8}{p_1^0} = \frac{5M + 30 - 30}{5M + 30}$$

$$\Rightarrow \frac{2.8}{p_1^0} = \frac{5M}{5M + 30}$$

$$\Rightarrow \frac{p_1^0}{2.8} = \frac{5M + 30}{5M}$$
 (i)

After the addition of 18 g of water:

$$n_1 = \frac{90 + 18g}{18} = 6 \text{ mol}$$

$$p_1 = 2.9 \,\text{kPa}$$

Again, applying the relation:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

$$\Rightarrow \frac{p_1^0 - 2.9}{p_1^0} = \frac{\frac{30}{M}}{6 + \frac{30}{M}}$$

$$\Rightarrow 1 - \frac{2.9}{p_1^0} = \frac{\frac{30}{M}}{\frac{6M + 30}{M}}$$

$$\Rightarrow 1 - \frac{2.9}{p_1^0} = \frac{30}{6M + 30}$$

$$\Rightarrow \frac{2.9}{p_1^0} = 1 - \frac{30}{6M + 30}$$

$$\Rightarrow \frac{2.9}{p_1^0} = \frac{6M + 30 - 30}{6M + 30}$$

$$\Rightarrow \frac{2.9}{p_1^0} = \frac{6M}{6M + 30}$$

$$\Rightarrow \frac{p_1^0}{2.9} = \frac{6M + 30}{6M}$$
 (ii)

Dividing equation (i) by (ii), we have:

$$\frac{2.9}{2.8} = \frac{\frac{5M + 30}{5M}}{\frac{6M + 30}{6M}}$$

$$\Rightarrow \frac{2.9}{2.8} \times \frac{6M + 30}{6} = \frac{5M + 30}{5}$$

$$\Rightarrow$$
 2.9 × 5 × (6M + 30) = 2.8 × 6 × (5M + 30)

$$\Rightarrow$$
 87 M + 435 = 84 M + 504

$$\Rightarrow$$
 3 M = 69

$$\Rightarrow$$
 M = 23 u

Therefore, the molar mass of the solute is 23 g mol⁻¹.

(ii) Putting the value of 'M' in equation (i), we have:

$$\frac{p_1^0}{2.8} = \frac{5 \times 23 + 30}{5 \times 23}$$

$$\Rightarrow \frac{p_1^0}{2.8} = \frac{145}{115}$$

$$\Rightarrow p_1^0 = 3.53$$

Hence, the vapour pressure of water at 298 K is 3.53 kPa.

Q20:

A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.

Answer:

Here, $\Delta T_f = (273.15 - 271) \text{ K}$

= 2.15 K

Molar mass of sugar $(C_{12}H_{22}O_{11}) = 12 \times 12 + 22 \times 1 + 11 \times 16$

= 342 g mol⁻¹

5% solution (by mass) of cane sugar in water means 5 g of cane sugar is present in (100 - 5)g = 95 g of water.

$$= \frac{5}{342} \text{ mol}$$

Now, number of moles of cane sugar

= 0.0146 mol

$$m = \frac{0.0146 \text{ mol}}{0.095 \text{ kg}}$$

Therefore, molality of the solution,

 $= 0.1537 \text{ mol kg}^{-1}$

Applying the relation,

 $\Delta T_f = K_f \times m$

$$\Rightarrow K_f = \frac{\Delta T_f}{m}$$

$$= \frac{2.15 \text{ K}}{0.1537 \text{ mol kg}^{-1}}$$

= 13.99 K kg mol⁻¹

Molar of glucose $(C_6H_{12}O_6) = 6 \times 12 + 12 \times 1 + 6 \times 16$

= 180 g mol⁻¹

5% glucose in water means 5 g of glucose is present in (100 - 5) g = 95 g of water.

$$\therefore \text{ Number of moles of glucose} = \frac{5}{180} \text{ mol}$$

= 0.0278 mol

$$m = \frac{0.0278 \text{ mol}}{0.095 \text{ kg}}$$

Therefore, molality of the solution,

 $= 0.2926 \text{ mol kg}^{-1}$

Applying the relation,

$$\Delta T_f = K_f \times m$$

= $13.99 \text{ K kg mol}^{-1} \times 0.2926 \text{ mol kg}^{-1}$

= 4.09 K (approximately)

Hence, the freezing point of 5% glucose solution is (273.15 - 4.09) K= 269.06 K.

Q21:

Two elements A and B form compounds having formula AB_2 and AB_4 . When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 Kwhereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is 5.1 Kkg mol⁻¹. Calculate atomic masses of A and B.

Answer:

We know that,

$$M_2 = \frac{1000 \times w_2 \times k_f}{\Delta T_f \times w_1}$$

$$M_{\mathrm{AB_2}} = \frac{1000 \times 1 \times 5.1}{2.3 \times 20}$$
 Then,

= 110.87 g mol⁻¹

$$M_{AB_4} = \frac{1000 \times 1 \times 5.1}{1.3 \times 20}$$

 $= 196.15 \text{ g mol}^{-1}$

Now, we have the molar masses of AB₂ and AB₄ as 110.87 g mol ¹ and 196.15 g mol ¹ respectively.

Let the atomic masses of A and B be x and y respectively.

Now, we can write:

$$x + 2y = 110.87$$
 (i)

$$x + 4y = 196.15$$
 (ii)

Subtracting equation (i) from (ii), we have

$$2y = 85.28$$

$$\Rightarrow$$
 $y = 42.64$

Putting the value of 'y' in equation (1), we have

$$x + 2 \times 42.64 = 110.87$$

$$\Rightarrow x = 25.59$$

Hence, the atomic masses of A and B are 25.59 u and 42.64 u respectively.

Q22:

At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?

Answer:

Here.

T = 300 K

 $\pi = 1.52 \text{ bar}$

 $R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}$

Applying the relation,

 $\pi = CRT$

$$\Rightarrow C = \frac{\pi}{RT}$$

$$= \frac{1.52 \text{ bar}}{0.083 \text{ bar L K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$

= 0.061 mol

Since the volume of the solution is 1 L, the concentration of the solution would be 0.061 M.

Q23:

Suggest the most important type of intermolecular attractive interaction in the following pairs.

- (i) n-hexane and n-octane
- (ii) I2 and CCI4
- (iii) NaClO₄ and water
- (iv) methanol and acetone
- (v) acetonitrile (CH₃CN) and acetone (C₃H₀O).

Answer:

- (i) Van der Wall's forces of attraction.
- (ii) Van der Wall's forces of attraction.
- (iii) Ion-diople interaction.
- (iv) Dipole-dipole interaction.
- (v) Dipole-dipole interaction.

Q24:

Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCI, CH₃OH, CH₃CN.

Answer:

n-octane is a non-polar solvent. Therefore, the solubility of a non-polar solute is more than that of a polar solute in the *n*-octane.

The order of increasing polarity is:

Cyclohexane < CH₃CN < CH₃OH < KCI

Therefore, the order of increasing solubility is:

KCI < CH₃OH < CH₃CN < Cyclohexane

Q25:

Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?

(i) phenol (ii) toluene (iii) formic acid

(iv) ethylene glycol (v) chloroform (vi) pentanol.

Answer:

(i) Phenol (C₆H₅OH) has the polar group -OH and non-polar group -C₆H₅. Thus, phenol is partially soluble in water.

(ii) Toluene (C₆H₅-CH₃) has no polar groups. Thus, toluene is insoluble in water.

(iii) Formic acid (HCOOH) has the polar group -OH and can form H-bond with water. Thus, formic acid is highly soluble in water.

(iv) Ethylene glycol has polar -OH group and can form H-bond. Thus, it is highly soluble in water.

(v) Chloroform is insoluble in water.

(vi) Pentanol ($C_5H_{11}OH$) has polar -OH group, but it also contains a very bulky non-polar - C_5H_{11} group. Thus, pentanol is partially soluble in water.

Q26:

If the density of some lake water is 1.25 g mL⁻¹ and contains 92 g of Na⁺ ions per kg of water, calculate the molality of Na⁺ ions in the lake.

Answer:

Number of moles present in 92 g of Na⁺ ions = $\frac{92~g}{23~g~mol^{-1}}$

= 4 mol

 $= \frac{4 \ mol}{1 \ kg}$ Therefore, molality of Na $^{\scriptscriptstyle +}$ ions in the lake

=4 m

Q27:

If the solubility product of CuS is 6 x 10⁻¹⁶, calculate the maximum molarity of CuS in aqueous solution.

Answer:

Solubility product of CuS, $K_{sp} = 6 \times 10^{-16}$

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

$$\begin{array}{cccc} CuS & \longleftrightarrow & Cu^{2^+} + & S^{2^-} \\ & s & & s \end{array}$$

Now,
$$K_{sp} = \left[Cu^{2+} \right] \left[S^{2-} \right]$$

 $= s \times s$

 $= S^2$

Then, we have, $K_{\rm sp}=~s^2=6\times 10^{-16}$

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

 $= 2.45 \times 10^{-8} \text{ mol L}^{-1}$

Hence, the maximum molarity of CuS in an aqueous solution is 2.45×10^{-8} mol L⁻¹.

Q28:

Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN .

Answer:

6.5~g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN .

Then, total mass of the solution = (6.5 + 450) g

= 456.5 g

Therefore, mass percentage of $C_0H_0O_4$ = $\frac{6.5}{456.5} \times 100\%$

= 1.424%

Q29:

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 x 10^3 m aqueous solution required for the above dose.

Answer:

The molar mass of nalorphene $\left(C_{19}H_{21}NO_{3}\right)$ 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 x 10 $^{\text{-3}}$ mol = 1.5 \times $10^{\text{-3}}$ \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:

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

$$= 3.22 g$$

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

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q30:

Calculate the amount of benzoic acid (C₀H₅COOH) required for preparing 250 mL of 0.15 M solution in methanol.

Answer:

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 = 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 mol x 122 g mol⁻¹

= 4.575 g

Q31:

The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

Answer:

Acetic acid Trichloroacetic acid Trifluoroacetic acid

Among H, Cl, and F, H is least electronegative while F is most electronegative. Then, F can withdraw electrons towards itself more than Cl and H. Thus, trifluoroacetic acid can easily lose H⁺ ions i.e., trifluoroacetic acid ionizes to the largest extent. Now, the more ions produced, the greater is the depression of the freezing point. Hence, the depression in the freezing point increases in the order:

Acetic acid < trichloroacetic acid < trifluoroacetic acid

Q32:

Calculate the depression in the freezing point of water when 10 g of CH₃CH₂CHCICOOH is added to 250 g of water. $K_a = 1.4 \times 10^3$, $K_f = 1.86$

K kg mol-1.

Answer:

Molar mass of $CH_3CH_2CHCICOOH = 15+14+13+35.5+12+16+16+1$

 $=122.5 \text{ g mol}^{-1}$

$$CH_3CH_2CHCICOOH = \frac{10 \text{ g}}{122.5 \text{ g mol}^{-1}}$$

:No. of moles present in 10 g of

 $= 0.0816 \, \text{mol}$

It is given that 10 g of ${
m CH_3CH_2CHCICOOH}$ is added to 250 g of water.

∴Molality of the solution,
$$= \frac{0.0186}{250} \times 1000$$

 $= 0.3264 \text{ mol kg}^{-1}$

Let α be the degree of dissociation of ${\rm CH_3CH_2CHCICOOH.}$

CH3CH2CHClCOOH

undergoes dissociation according to the following equation:

$$CH_3CH_2CHCICOOH \leftrightarrow CH_3CH_2CHCICOO^- + H^+$$
Initial conc. $C \text{ mol } L^{-1}$ 0 0
At equilibrium $C(1-\alpha)$ $C\alpha$ $C\alpha$

$$\therefore K_a = \frac{C\alpha . C\alpha}{C(1-\alpha)}$$
$$= \frac{C\alpha^2}{1-\alpha}$$

Since αis very small with respect to 1, 1 - α â‰Ë†1

Now,
$$K_a = \frac{C\alpha^2}{1}$$

$$\Rightarrow K_a = C\alpha^2$$

$$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$$

$$= \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} \quad (\because K_a = 1.4 \times 10^{-3})$$

$$= 0.0655$$

Again,

CH₃CH₂CHClCOOH ↔ CH₃CH₂CHClCOO⁻ + H⁺ 0

Initial moles

0

At equilibrium

 $1-\alpha$

α

Total moles of equilibrium = 1 - α + α + α

$$= 1 + \alpha$$

$$\therefore i = \frac{1+\alpha}{1}$$

$$=1+\alpha$$

$$=1+0.0655$$

$$=1.0655$$

Hence, the depression in the freezing point of water is given as:

$$\Delta T_f = i.K_f m$$

$$= 1.0655 \times 1.86 \, K \, kg \, mol^{-1} \times 0.3264 \, mol \, kg^{-1}$$

$$= 0.65 \text{ K}$$

Q33:

19.5 g of CH₂FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

Answer:

It is given that:

$$w_1 = 500 \text{ g}$$

$$w_2 = 19.5 \,\mathrm{g}$$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$\Delta T_f = 1 \text{ K}$$

We know that:

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$

$$= \frac{1.86 \, \text{K kg mol}^{-1} \times 19.5 \, \text{g} \times 1000 \, \text{g kg}^{-1}}{500 \, \text{g} \times 1 \, \text{K}}$$

$$=72.54 \,\mathrm{g}\,\mathrm{mol}^{-1}$$

Therefore, observed molar mass of CH_2FCOOH , $(M_2)_{obs} = 72.54 \, \mathrm{g} \, \mathrm{mol}$

The calculated molar mass of ${
m CH_2FCOOH}_{
m is:}$

$$(M_2)_{\text{cal}} = 14 + 19 + 12 + 16 + 16 + 1$$

= 78 g mol⁻¹

$$i = \frac{\left(M_2\right)_{\text{cal}}}{\left(M_2\right)_{\text{obs}}}$$

Therefore, van't Hoff factor,

$$= \frac{78 \,\mathrm{g \, mol^{-1}}}{72.54 \,\mathrm{g \, mol^{-1}}}$$

$$=1.0753$$

Let abe the degree of dissociation of $\ensuremath{\text{CH}_2\text{FCOOH}}$

C mol L⁻¹ 0 Initial conc.

0 $C(1-\alpha)$ $Total = C(1 + \alpha)$ $C\alpha$ At equilibrium $C\alpha$

$$\therefore i = \frac{C(1+\alpha)}{C}$$

$$\Rightarrow i = 1+\alpha$$

$$\Rightarrow \alpha = i-1$$

$$= 1.0753 - 1$$

$$= 0.0753$$

Now, the value of K_a is given as:

$$K_a = \frac{[\text{CH}_2\text{FCOO}^-][\text{H}^+]}{[\text{CH}_2\text{FCOOH}]}$$

$$=\frac{C\alpha.C\alpha}{C(1-\alpha)}$$

$$=\frac{C\alpha^2}{1-\alpha}$$

Taking the volume of the solution as 500 mL, we have the concentration:

$$C = \frac{\frac{19.5}{78}}{500} \times 1000 \,\mathrm{M}$$

$$= 0.5 M$$

$$K_a = \frac{C\alpha^2}{1 - \alpha}$$

Therefore,

$$=\frac{0.5\times\left(0.0753\right)^2}{1-0.0753}$$

$$=\frac{0.5\times0.00567}{0.9247}$$

$$=3.07 \times 10^{-3}$$

Q34:

Vapour pressure of water at 293 Kis 17.535 mm Hg. Calculate the vapour pressure of water at 293 Kwhen 25 g of glucose is dissolved in 450 g of water.

Answer:

Vapour pressure of water, $p_1^v = 17.535$ mm of Hg

Mass of glucose, $w_2 = 25 \text{ g}$

Mass of water, $w_1 = 450 \text{ g}$

We know that,

Molar mass of glucose ($C_6H_{12}O_6$), $M_2 = 6 \times 12 + 12 \times 1 + 6 \times 16$

 $= 180 \text{ g mol}^{-1}$

Molar mass of water, $M_1 = 18 \text{ g mol}^{-1}$

$$n_2 = \frac{25}{180 \text{ g mol}^{-1}}$$
 Then, number of moles of glucose,

= 0.139 mol

$$n_1 = \frac{450 \,\mathrm{g}}{18 \,\mathrm{g} \,\mathrm{mol}^{-1}}$$

And, number of moles of water,

= 25 mol

We know that,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_1}{n_2 + n_1}$$

$$\Rightarrow \frac{17.535 - p_1}{17.535} = \frac{0.139}{0.139 + 25}$$

$$\Rightarrow 17.535 - p_1 = \frac{0.139 \times 17.535}{25.139}$$

$$\Rightarrow$$
 17.535 - p_1 = 0.097

$$\Rightarrow p_1 = 17.44 \text{ mm of Hg}$$

Hence, the vapour pressure of water is 17.44 mm of Hg.

Q35:

Henry's law constant for the molality of methane in benzene at 298 Kis 4.27 x 10⁵ mm Hg. Calculate the solubility of methane in benzene at 298 Kunder 760 mm Hg.

Answer:

Here,

$$p = 760 \text{ mm Hg}$$

$$k_{H} = 4.27 \times 10^{5} \text{ mm Hg}$$

According to Henry's law,

$$p = k_H x$$

$$\Rightarrow x = \frac{p}{k_{\rm H}}$$
$$= \frac{760 \text{ mm Hg}}{4.27 \times 10^5 \text{ mm Hg}}$$

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

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

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

Q36:

100 g of liquid A (molar mass 140 g mol⁻¹) was dissolved in 1000 g of liquid B (molar mass 180 g mol⁻¹). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr.

Answer:

Number of moles of liquid A, $n_{\rm A} = \frac{100}{140} \; {\rm mol}$

= 0.714 mol

 $n_{\rm B} = \frac{1000}{180} \text{ mol}$

Number of moles of liquid B,

= 5.556 mol

 $x_{\rm A} = \frac{n_{\rm A}}{n_{\rm A} + n_{\rm B}} \label{eq:xA}$ Then, mole fraction of A,

$$=\frac{0.714}{0.714 + 5.556}$$

= 0.114

And, mole fraction of B, $x_B = 1 - 0.114$

= 0.886

Vapour pressure of pure liquid B, $p_{\rm B}^0 = 500 \ {\rm torr}$

Therefore, vapour pressure of liquid B in the solution,

$$p_{\rm B} = p_{\rm B}^0 x_{\rm B}$$

 $=500 \times 0.886$

= 443 torr

Total vapour pressure of the solution, $p_{total} = 475$ torr

· Vapour pressure of liquid A in the solution,

$$p_{A} = p_{total} - p_{B}$$

= 32 torr

Now,

$$p_{\rm A} = p_{\rm A}^0 x_{\rm A}$$

$$\Rightarrow p_{A}^{0} = \frac{p_{A}}{x_{A}}$$
$$= \frac{32}{0.114}$$

= 280.7 torr

Hence, the vapour pressure of pure liquid A is 280.7 torr.

Q37:

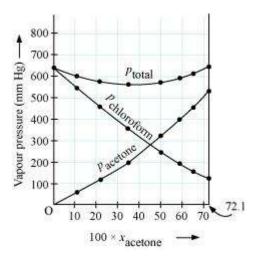
Vapour pressure of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total} $p_{chloroform}$ and $p_{acetone}$ as a function of $x_{acetone}$. The experimental data observed for different compositions of mixture is.

$100 imes x_{ ext{acctone}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{ ext{acctone}}$ /mm Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{ ext{ iny chloroform}}$ /mm Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

Answer:

From the question, we have the following data

$100 \times x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
p _{acetone} /mm Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
p _{chloroform} /mm Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
p _{tota} (mm Hg)	632.8	603.0	579.5	562.1	580.4	599.5	615.3	641.8



It can be observed from the graph that the plot for the p_{total} of the solution curves downwards. Therefore, the solution shows negative deviation from the ideal behaviour.

Q38:

Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of toluene.

Answer:

Molar mass of benzene $\left(C_6H_6\right) = 6 \times 12 + 6 \times 1$

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

Molar mass of toluene $(C_6H_5CH_3) = 7 \times 12 + 8 \times 1$

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

Now, no. of moles present in 80 g of benzene $= \frac{80}{78} \text{ mol} = 1.026 \text{ mol}$

And, no. of moles present in 100 g of toluene $= \frac{100}{92} \text{mol} = 1.087 \text{ mol}$

∴Mole fraction of benzene, $x_b = \frac{1.026}{1.026 + 1.087} = 0.486$

And, mole fraction of toluene, $x_t = 1 - 0.486 = 0.514$

It is given that vapour pressure of pure benzene, $p_b^0 = 50.71 \text{ mm Hg}$

And, vapour pressure of pure toluene, $p_t^0 = 32.06 \text{ mm Hg}$

Therefore, partial vapour pressure of benzene, $\, p_{\scriptscriptstyle b} = x_{\scriptscriptstyle b} \times p_{\scriptscriptstyle b} \,$

$$=0.486 \times 50.71$$

$$= 24.645 \text{ mm Hg}$$

And, partial vapour pressure of toluene, $p_{\scriptscriptstyle t} = x_{\scriptscriptstyle t} \times p_{\scriptscriptstyle t}$

$$=0.514 \times 32.06$$

$$=16.479 \text{ mm Hg}$$

Hence, mole fraction of benzene in vapour phase is given by:

$$\frac{p_b}{p_b + p_t}$$

$$=\frac{24.645}{24.645 + 16.479}$$

$$=\frac{24.645}{41.124}$$

$$=0.599$$

$$= 0.6$$

Q39:

The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298

K. The water is in equilibrium with air at a pressure of 10 atm. At 298 Kif the

Henry's law constants for oxygen and nitrogen are 3.30 x 10⁷ mm and 6.51 x 10⁷mm respectively, calculate the composition of these gases in water.

Answer:

Percentage of oxygen (O2) in air = 20 %

Percentage of nitrogen (N_2) in air = 79%

Also, it is given that water is in equilibrium with air at a total pressure of 10 atm, that is, (10×760) mm Hg = 7600 mm Hg

Therefore,

$$p_{\text{O}_2} = \frac{20}{100} \times 7600 \,\text{mm}\,\text{Hg}$$

Partial pressure of oxygen,

$$p_{N_2} = \frac{79}{100} \times 7600 \,\text{mmHg}$$

Partial pressure of nitrogen,

= 6004 mmHg

Now, according to Henry's law:

$$p = K_H.x$$

For oxygen:

$$p_{O_2} = K_H \cdot x_{O_2}$$

 $\Rightarrow x_{O_2} = \frac{p_{O_2}}{K_H}$
 $= \frac{1520 \text{ mm Hg}}{3.30 \times 10^7 \text{ mm Hg}}$ (Given $K_H = 3.30 \times 10^7 \text{ mm Hg}$)
 $= 4.61 \times 10^{-5}$

For nitrogen:

$$\begin{aligned} p_{\rm N_2} &= K_{\rm H} \cdot x_{\rm N_2} \\ \Rightarrow x_{\rm N_2} &= \frac{p_{\rm N_2}}{K_{\rm H}} \\ &= \frac{6004 \, \rm mm \, Hg}{6.51 \times 10^7 \, \rm mm \, Hg} \\ &= 9.22 \times 10^{-5} \end{aligned}$$

Hence, the mole fractions of oxygen and nitrogen in water are 4.61 ×10⁻⁵ and 9.22 × 10⁻⁵ respectively.

Q40:

Determine the amount of CaCl2 (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27°C.

Answer:

We know that,

$$\pi = i \frac{n}{V} RT$$

$$\Rightarrow \pi = i \frac{w}{MV} RT$$

$$\Rightarrow w = \frac{\pi MV}{iRT}$$

$$\pi = 0.75 \text{ atm}$$
 $V = 2.5 \text{ L}$
 $i = 2.47$
 $T = (27 + 273) \text{ K} = 300 \text{ K}$

Here,

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

 $M = 1 \times 40 + 2 \times 35.5$

= 111g mol⁻¹

Therefore, w =
$$\frac{0.75 \times 111 \times 2.5}{2.47 \times 0.0821 \times 300}$$

= 3.42 g

Hence, the required amount of CaCl₂ is 3.42 g.

Q41:

Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 liter of water at 25° C, assuming that it is completely dissociated.

Answer:

When K_2SO_4 is dissolved in water, $\begin{array}{c} K^+ \ and \ SO_4^{2-} \\ \end{array}$ ions are produced.

$$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$$

Total number of ions produced = 3

i = 3

Given,

w = 25 mg = 0.025 g

V = 2 L

$$T = 25^{\circ}\text{C} = (25 + 273) \text{ K} = 298 \text{ K}$$

Also, we know that:

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

$$M = (2 \times 39) + (1 \times 32) + (4 \times 16) = 174 \text{ g mol}^{-1}$$

Appling the following relation,

$$\pi = i \frac{n}{v} RT$$

$$= i \frac{w}{M} \frac{1}{v} RT$$

$$= 3 \times \frac{0.025}{174} \times \frac{1}{2} \times 0.0821 \times 298$$

$$= 5.27 \times 10^{-3} \text{ atm}$$

NCERT Solutions for Class 12 Chemistry Part 1 Chapter 3

Electrochemistry Class 12

Chapter 3 Electrochemistry Exercise Solutions

In text: Solutions of Questions on Page Number: 68

Q1:

How would you determine the standard electrode potential of the systemMg²⁺| Mg?

Answer:

The standard electrode potential of $Mg^{2+}|Mg$ can be measured with respect to the standard hydrogen electrode, represented by $Pt_{(s)}$, $H_{2(g)}(1 \text{ atm}) \mid H^+_{(aq)}(1 \text{ M})$.

A cell, consisting of Mg | MgSO₄(aq 1 M) as the anode and the standard hydrogen electrode as the cathode, is set up.

$$Mg|Mg^{2+}(aq, 1M)||H^{+}(aq, 1M)|H_{2}(g, 1 bar), Pt_{(s)}$$

Then, the emf of the cell is measured and this measured emf is the standard electrode potential of the magnesium electrode.

$$E^{\ominus} = E_R^{\ominus} - E_L^{\ominus}$$

Here, $E_{\it R}^{\scriptscriptstyle \ominus}$ for the standard hydrogen electrode is zero.

$$E^{\ominus} = 0 - E_L^{\ominus}$$

$$= -E_L^{\oplus}$$

Q2:

Can you store copper sulphate solutions in a zinc pot?

Answer:

Zinc is more reactive than copper. Therefore, zinc can displace copper from its salt solution. If copper sulphate solution is stored in a zinc pot, then zinc will displace copper from the copper sulphate solution.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

Hence, copper sulphate solution cannot be stored in a zinc pot.

Q3:

Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

Answer:

Substances that are stronger oxidising agents than ferrous ions can oxidise ferrous ions.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-1}$$
; $E^{\Theta} = -0.77 \vee$

This implies that the substances having higher reduction potentials than

+0.77 V can oxidise ferrous ions to ferric ions. Three substances that can do so are F2, Cl2, and O2.

Q4:

Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Answer:

For hydrogen electrode,
$$H^+ + e^- \longrightarrow \frac{1}{2} \ H_2$$
 , it is given that pH = 10

∴[H⁺] = 10⁻¹⁰M

Now, using Nernst equation:

$$\begin{split} &\mathbf{H}_{\left(\mathbf{H}^{+}/\frac{1}{2}\mathbf{H}_{2}\right)_{=}}E_{\left(\mathbf{H}^{+}/\frac{1}{2}\mathbf{H}_{2}\right)}^{\Theta}-\frac{\mathbf{R}T}{n\mathbf{F}}\ln\frac{1}{\left[\mathbf{H}^{+}\right]}\\ &=E_{\left(\mathbf{H}^{+}/\frac{1}{2}\mathbf{H}_{2}\right)}^{\Theta}-\frac{0.0591}{1}\log\frac{1}{\left[\mathbf{H}^{+}\right]}\\ &=0-\frac{0.0591}{1}\log\frac{1}{\left[10^{-10}\right]} \end{split}$$

$$= -0.0591 \log 10^{10}$$

$$= -0.591 \text{ V}$$

Q5:

Calculate the emf of the cell in which the following reaction takes place:

$$Ni_{(s)} + 2Ag^{+}(0.002 \text{ M}) \rightarrow Ni^{2+}(0.160 \text{ M}) + 2Ag_{(s)}$$

Given that
$$E_{(\text{cell})}^{\ominus}$$
 = 1.05 V

Answer:

Applying Nernst equation we have:

$$E_{\text{(cell)}} = E_{\text{(cell)}}^{\ominus} - \frac{0.0591}{n} \log \frac{\left[\text{Ni}^{2+}\right]}{\left[\text{Ag}^{+}\right]^{2}}$$

$$=1.05 - \frac{0.0591}{2} \log \frac{\left(0.160\right)}{\left(0.002\right)^2}$$

$$=1.05-0.02955 \log \frac{0.16}{0.000004}$$

- $= 1.05 0.02955 \log 4 \times 10^4$
- = 1.05 0.02955 (log 10000 + log 4)
- = 1.05 0.02955 (4 + 0.6021)
- = 0.914 V

Q6:

The cell in which the following reactions occurs:

$$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$$

has
$$E_{\text{cell}}^{0}$$
 = 0.236 V at 298 K.

Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Answer:

Here,
$$n = 2$$
, $E_{\text{cell}}^{\Theta} = 0.236 \text{ V}$, $T = 298 \text{ K}$

We know that:

$$\Delta_r G^{\ominus} = -nFE_{cell}^{\ominus}$$

- $= -2 \times 96487 \times 0.236$
- = 45541.864 J mol -1
- = 45.54 kJ mol⁻¹

$${\rm Again,} \ \ \Delta_r G^{\rm \Theta} = -2.303 {\rm R} \, {\rm Tlog} \, \, {\rm \textit{K}_{\rm c}}$$

$$\Rightarrow \log K_{c} = -\frac{\Delta_{r}G^{\circ}}{2.303 \text{ R}T}$$

$$= -\frac{-45.54 \times 10^{3}}{2.303 \times 8.314 \times 298}$$

= 7.981

∴ K_c= Antilog (7.981)

 $= 9.57 \times 10^7$

Q7:

Why does the conductivity of a solution decrease with dilution?

Answer:

The conductivity of a solution is the conductance of ions present in a unit volume of the solution. The number of ions (responsible for carrying current) decreases when the solution is diluted. As a result, the conductivity of a solution decreases with dilution.

Q8:

Suggest a way to determine the $\Lambda_{\it m}^0$ value of water.

Answer:

Applying Kohlrausch's law of independent migration of ions, the Λ_m^0 value of water can be determined as follows:

$$\begin{split} \Lambda^{0}_{m(\mathrm{H}_{2}\mathrm{O})} &= \lambda^{0}_{\mathrm{H}^{+}} + \lambda^{0}_{\mathrm{OH}^{-}} \\ &= \left(\lambda^{0}_{\mathrm{H}^{+}} + \lambda^{0}_{\mathrm{Cl}^{-}}\right) + \left(\lambda^{0}_{\mathrm{Na}^{+}} + \lambda^{0}_{\mathrm{OH}^{-}}\right) - \left(\lambda^{0}_{\mathrm{Na}^{+}} + \lambda^{0}_{\mathrm{Cl}^{-}}\right) \\ \Lambda^{0}_{m(\mathrm{HCl})} &+ \Lambda^{0}_{m(\mathrm{NaOH})} - \Lambda^{0}_{m(\mathrm{NaCl})} \end{split}$$

Hence, by knowing the Λ_m^0 values of HCI, NaOH, and NaCI, the Λ_m^0 value of water can be determined.

Q9:

The molar conductivity of 0.025 mol L-1 methanoic acid is

46.1 S cm2 mol⁻¹.

Calculate its degree of dissociation and dissociation constant. Given λ (H+)

= 349.6 S cm² mol⁻¹ and $\tilde{A}\tilde{Z}\hat{A}$ » (HCOO-) = 54.6 S cm² mol

Answer:

C = 0.025 mol L⁻¹

$$\Lambda_{m} = 46.1 \text{ S cm}^{2} \text{ mol}^{-1}$$

$$\lambda^{0} (\text{H}^{+}) = 349.6 \text{ S cm}^{2} \text{ mol}^{-1}$$

$$\lambda^{0} (\text{HCOO}^{-}) = 54.6 \text{ S cm}^{2} \text{ mol}^{-1}$$

$$\Lambda_{m}^{0} (\text{HCOOH}) = \lambda^{0} (\text{H}^{+}) + \lambda^{0} (\text{HCOO}^{-})$$

$$= 349.6 + 54.6$$

$$= 404.2 \text{ S cm}^{2} \text{ mol}^{-1}$$

Now, degree of dissociation:

$$\alpha = \frac{\Lambda_m (\text{HCOOH})}{\Lambda_m^0 (\text{HCOOH})}$$
$$= \frac{46.1}{404.2}$$
$$= 0.114 (\text{approximately})$$

Thus, dissociation constant:

$$K = \frac{c \, \infty^2}{\left(1 - \infty\right)}$$

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

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

Q10:

If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

Answer:

$$I = 0.5 \text{ A}$$

 $t = 2 \text{ hours} = 2 \times 60 \times 60 \text{ s} = 7200 \text{ s}$
Thus, $Q = It$
= 0.5 A × 7200 s

= 3600 C

We know that $96487\,C = 6.023 \times 10^{23}$ number of electrons.

Then,

$$3600 \text{ C} = \frac{6.023 \times 10^{23} \times 3600}{96487} \text{ number of electrons}$$
$$= 2.25 \times 10^{22} \text{ number of electrons}$$

Hence, 2.25×10^{22} number of electrons will flow through the wire.

Q11:

Suggest a list of metals that are extracted electrolytically.

Answer:

Metals that are on the top of the reactivity series such as sodium, potassium, calcium, lithium, magnesium, aluminium are extracted electrolytically.

Q12:

What is the quantity of electricity in coulombs needed to reduce 1 mol of

$$Cr_{\!_{2}}O_{\scriptscriptstyle{7}}^{^{2-}}$$
 ? Consider the reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 8H_2O$$

Answer:

The given reaction is as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Therefore, to reduce 1 mole of $Cr_2O_7^{2-}$, the required quantity of electricity will be:

=6 F

 $= 6 \times 96487 C$

= 578922 C

Q13:

Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

Answer:

A lead storage battery consists of a lead anode, a grid of lead packed with lead oxide (PbO_2) as the cathode, and a 38% solution of sulphuric acid (H_2SO_4) as an electrolyte.

When the battery is in use, the following cell reactions take place:

At anode:
$$Pb_{(s)} + SO_{4(aq)}^{2-} \longrightarrow PbSO_{4(s)} + 2e^{-}$$

At cathode:
$$PbO_{2(s)} + SO_{4(aq)}^{2-} + 4H_{(aq)}^{+} + 2e^{-} \longrightarrow PbSO_{4(s)} + 2H_{2}O_{(l)}$$

The overall cell reaction is given by,

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

When a battery is charged, the reverse of all these reactions takes place.

Hence, on charging, PbSO_{$$4(s)$$} present at the anode and cathode is converted into $Pb_{(s)}$ and $PbO_{2(s)}$ respectively.

Q14:

Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Answer:

Methane and methanol can be used as fuels in fuel cells.

Q15:

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

Answer:

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,

$$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^{-}$$

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

There, in the presence of H^+ ions, the electrons reduce oxygen. This spot behaves as the cathode. These H^+ ions come either from H_2CO_3 , 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,

$$O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \longrightarrow 2H_{2}O_{(l)}$$

The overall reaction is:

$$2Fe_{(s)} + O_{2(g)} + 4H^{+}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + 2H_{2}O_{(l)}$$

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 (Fe_2O_3, xH_2O) i.e., rust.

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

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Exercise: Solutions of Questions on Page Number: 92

Q1:

Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn

Answer:

The following is the order in which the given metals displace each other from the solution of their salts.

Mg, Al, Zn, Fe, Cu

Q2:

Given the standard electrode potentials,

 $K^{+}/K = -2.93V$, $Ag^{+}/Ag = 0.80V$,

 $Hg^{2+}/Hg = 0.79V$

 $Mg^{2+}/Mg = -2.37 \text{ V}, Cr^{3+}/Cr = -0.74 \text{V}$

Arrange these metals in their increasing order of reducing power.

Answer:

The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of $K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag$.

Hence, the reducing power of the given metals increases in the following order:

Ag < Hg < Cr < Mg < K

Q3:

Depict the galvanic cell in which the reaction Zn(s) + 2Ag⁺(aq) → Zn²⁺(aq) + 2Ag(s) takes place. Further show:

(i) Which of the electrode is negatively charged?

- (ii) The carriers of the current in the cell.
- (iii) Individual reaction at each electrode.

Answer:

The galvanic cell in which the given reaction takes place is depicted as:

$$Zn_{(s)} |Zn^{2+}_{(aq)}| |Ag^{+}_{(aq)}| Ag_{(s)}$$

- (i) Zn electrode (anode) is negatively charged.
- (ii) lons are carriers of current in the cell and in the external circuit, current will flow from silver to zinc.
- (iii) The reaction taking place at the anode is given by,

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

The reaction taking place at the cathode is given by,

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$

Q4:

Calculate the standard cell potentials of galvanic cells in which the following reactions take place:

(i)
$$2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$$

(ii)
$$Fe^{2*}(aq) + Ag^{*}(aq) \rightarrow Fe^{3*}(aq) + Ag(s)$$

Calculate the $\Delta_r G^{\lambda \dot{z} \dot{A}_r}$ and equilibrium constant of the reactions.

Answer:

(i)
$$E_{Cr^{3+}/Cr}^{\ominus} = 0.74 \text{ V}$$

$$E^{\oplus}_{Cd^{2+}/Cd} = -0.40 \text{ V}$$

The galvanic cell of the given reaction is depicted as:

$$\operatorname{Cr}_{(s)} \left| \operatorname{Cr}^{3+}_{(aq)} \right| \left| \operatorname{Cd}^{2+}_{(aq)} \left| \operatorname{Cd}_{(s)} \right|$$

Now, the standard cell potential is

$$E_{\text{cell}}^{\Theta} = E_{\text{R}}^{\Theta} - E_{\text{L}}^{\Theta}$$

$$= -0.40 - (-0.74)$$

$$= +0.34 \text{ V}$$

$$\Delta_{\epsilon}G^{\Theta} = -nFE_{\text{cell}}^{\Theta}$$

In the given equation,

$$n = 6$$

F = 96487 C mol⁻¹

$$E_{\rm cell}^{\scriptscriptstyle \ominus} = +0.34 \, \rm V$$

Then,
$$^{\Delta_{\rm r}G^{\Theta}}$$
 = -6 × 96487 C mol $^{\text{-1}}$ × 0.34 V

= - 196833.48 CV mol⁻¹

= - 196833.48 J mol -1

= - 196.83 kJ mol⁻¹

Again,

$$\Delta_{\rm r}G^{\scriptscriptstyle \Theta}$$
 = -R $T \ln K$

$$\Rightarrow \Delta_{\rm r} G^{\scriptscriptstyle \ominus} = -2.303 \; {
m R} T \ln K$$

$$\Rightarrow \log K = -\frac{\Delta_{r}G}{2.303 \text{ R}T}$$
$$= \frac{-196.83 \times 10^{3}}{2.303 \times 8.314 \times 298}$$

$$= 3.13 \times 10^{34}$$

(ii)
$$E_{Fe^{3+}/Fe^{2+}}^{\ominus} = 0.77 \text{ V}$$

$$E_{Ag^{+}/Ag}^{\Theta} = 0.80 \text{ V}$$

The galvanic cell of the given reaction is depicted as:

$$Fe^{2+}_{(aq)} | Fe^{3+}_{(aq)} | Ag^{+}_{(aq)} | Ag_{(s)}$$

Now, the standard cell potential is

$$E_{\text{cell}}^{\ominus} = E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus}$$
$$= 0.80 - 0.77$$
$$= 0.03 \text{ V}$$

Here, n = 1.

Then,
$$\Delta_{r}G^{\ominus} = -nFE_{cell}^{\ominus}$$

$$= -1 \times 96487 \text{ C mol}^{-1} \times 0.03 \text{ V}$$

Again,
$$\Delta_r G^{\oplus} = -2.303 \text{ R} T \ln K$$

$$\Rightarrow \log K = -\frac{\Delta_r G}{2.303 \text{ R} T}$$

$$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$$

= 0.5073

∴ K = antilog (0.5073)

= 3.2 (approximately)

Q5:

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

(i) Mg(s) | Mg²⁺(0.001M) || Cu²⁺(0.0001 M) | Cu(s)

(ii) Fe(s) | Fe²⁺(0.001M) || H⁺(1M)|H₂(g)(1bar) | Pt(s)

(iii) $Sn(s) | Sn^{2+}(0.050 \text{ M}) || H^{+}(0.020 \text{ M}) | H_{2}(g) (1 \text{ bar}) | Pt(s)$

(iv) $Pt(s) | Br_2(I) | Br'(0.010 M) | H^+(0.030 M) | H_2(g) (1 bar) | Pt(s).$

Answer:

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

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{\left[\text{Mg}^{2+}\right]}{\left[\text{Cu}^{2+}\right]}$$
$$= \left\{0.34 - \left(-2.36\right)\right\} - \frac{0.0591}{2} \log \frac{.001}{.0001}$$
$$= 2.7 - \frac{0.0591}{2} \log 10$$

= 2.7 - 0.02955

= 2.67 V (approximately)

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

$$\begin{split} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{\left[\text{Fe}^{2^{+}} \right]}{\left[\text{H}^{+} \right]^{2}} \\ &= \left\{ 0 - \left(-0.44 \right) \right\} - \frac{0.0591}{2} \log \frac{0.001}{1^{2}} \\ &= 0.44 - 0.02955 \left(-3 \right) \end{split}$$

= 0.52865 V

= 0.53 V (approximately)

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

$$\begin{split} E_{\text{cell}} &= E_{\text{cell}}^{\oplus} - \frac{0.0591}{n} \log \frac{\left[\text{Sn}^{2+}\right]}{\left[\text{H}^{+}\right]^{2}} \\ &= \left\{0 - \left(-0.14\right)\right\} - \frac{0.0591}{2} \log \frac{0.050}{\left(0.020\right)^{2}} \end{split}$$

- $= 0.14 0.0295 \times \log 125$
- = 0.14 0.062
- = 0.078 V
- = 0.08 V (approximately)
- (iv) For the given reaction, the Nernst equation can be given as:

$$\begin{split} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{1}{\left[\text{Br}^{-}\right]^{2} \left[\text{H}^{+}\right]^{2}} \\ &= \left(0 - 1.09\right) - \frac{0.0591}{2} \log \frac{1}{\left(0.010\right)^{2} \left(0.030\right)^{2}} \\ &= -1.09 - 0.02955 \times \log \frac{1}{0.000000009} \\ &= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \\ &= -1.09 - 0.02955 \times \log \left(1.11 \times 10^{7}\right) \\ &= -1.09 - 0.02955 \left(0.0453 + 7\right) \\ &= -1.09 - 0.208 \\ &= -1.298 \text{ V} \end{split}$$

Q6:

In the button cells widely used in watches and other devices the following reaction takes place:

$$Zn(s) + Ag_2O(s) + H_2O(I) \tilde{A} \phi \hat{a} \in 'Zn^{2+}(aq) + 2Ag(s) + 2OH^{-}(aq)$$

Determine $^{\Delta_r G^{\odot}}$ and E^{\odot} for the reaction.

Answer:

$$Zn_{(s)} \longrightarrow Zn_{(aq)}^{2+} + 2e^{-}; E^{\Theta} = 0.76V$$

$$Ag_{2}O_{(s)} + H_{2}O_{(l)} + 2e^{-} \longrightarrow 2Ag_{(s)} + 2OH_{(aq)}^{-}; E^{\Theta} = 0.344 V$$

$$Zn_{(s)} + Ag_{2}O_{(s)} + H_{2}O_{(l)} \longrightarrow Zn_{(aq)}^{2+} + 2Ag_{(s)} + 2OH_{(aq)}^{-}; E^{\Theta} = 1.104 V$$

$$\therefore E^{\Theta} = 1.104 \text{ V}$$

We know that,

$$\Delta_r G^{\ominus} = -nFE^{\ominus}$$

 $= -2 \times 96487 \times 1.04$

= - 213043.296 J

= - 213.04 kJ

Q7:

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

Answer:

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 $\tilde{A}\tilde{Z}\hat{A}^{\circ}$. If $\tilde{A}\hat{A}$ is resistivity, then we can write:

$$\kappa = \frac{1}{\rho}$$

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.

$$G = \kappa \frac{a}{l} = \kappa \cdot 1 = \kappa$$
 i.e.,

(Since a = 1, I = 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.

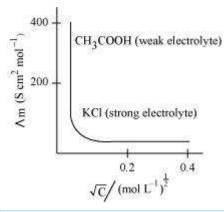
$$\Lambda_m = \kappa \frac{A}{l}$$

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

$$\Lambda_m = \kappa V$$

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:



Q8:

The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm⁻¹. Calculate its molar conductivity.

Answer:

Given,

 $\tilde{A}\tilde{Z}\hat{A}^{\circ} = 0.0248 \text{ S cm}^{-1}$

c = 0.20 M

$$\Lambda_m = \frac{\kappa \times 1000}{c}$$

$$\therefore \text{ Molar conductivity,}$$

0.0248×1000

0.2

= 124 Scm²mol⁻¹

Q9:

The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 $\tilde{A}\check{Z}\hat{A}\odot$. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146 x 10⁻³ S cm⁻¹.

Answer:

Given,

Conductivity, $\tilde{A}\tilde{Z}\hat{A}^{\circ} = 0.146 \times 10^{-3} \text{ S cm}^{-1}$

Resistance, R = 1500 Ω

 \cdot Cell constant = $\tilde{A}\tilde{Z}\hat{A}^{\circ} \times R$

 $= 0.146 \times 10^{-3} \times 1500$

 $= 0.219 \text{ cm}^{-1}$

Q10:

The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

Concentration/M 0.001 0.010 0.020 0.050 0.100

10° × ÃŽÂ°/S m⁻¹ 1.237 11.85 23.15 55.53 106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and c ½. Find the value of Λ_m^0 .

Answer:

Given,

$$\tilde{A}\tilde{Z}\hat{A}^{\circ} = 1.237 \times 10^{-2} \text{ S m}^{-1}, c = 0.001 \text{ M}$$

Then, $\tilde{A}\tilde{Z}\hat{A}^{\circ} = 1.237 \times 10^{-4} \text{ S cm}^{-1}$, c $\frac{1}{2} = 0.0316 \text{ M}^{\frac{1}{2}}$

$$\Lambda_{m} = \frac{\kappa}{c}$$

$$= \frac{1.237 \times 10^{-4} \text{ S cm}^{-1}}{0.001 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{3}}{L}$$

= 123.7 S cm² mol⁻¹

Given,

$$\tilde{A}\tilde{Z}\hat{A}^{\circ} = 11.85 \times 10^{-2} \text{ S m}^{-1}, c = 0.010 \text{M}$$

Then, $\tilde{A}\tilde{Z}\hat{A}^{\circ} = 11.85 \times 10^{-4} \text{ S cm}^{-1}$, c $\frac{1}{2} = 0.1 \text{ M}^{\frac{1}{2}}$

= 118.5 S cm² mol⁻¹

Given,

$$\tilde{A}\tilde{Z}\hat{A}^{\circ} = 23.15 \times 10^{-2} \text{ S m}^{-1}, c = 0.020 \text{ M}$$

Then, $\tilde{A}\tilde{Z}\hat{A}^{\circ} = 23.15 \times 10^{-4} \text{ S cm}^{-1}$, $c^{1/2} = 0.1414 \text{ M}^{1/2}$

$$\therefore \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{23.15 \times 10^{-4} \text{ S cm}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{L}$$

= 115.8 S cm² mol⁻¹

Given,

 $\tilde{A}\tilde{Z}\hat{A}^{\circ} = 55.53 \times 10^{-2} \text{ S m}^{-1}, c = 0.050 \text{ M}$

Then, $\tilde{A}\tilde{Z}\hat{A}^{\circ} = 55.53 \times 10^{-4} \text{ S cm}^{-1}$, $c^{1/2} = 0.2236 \text{ M}^{1/2}$

$$\kappa = \frac{\kappa}{c}$$

$$= \frac{55.53 \times 10^{-4} \text{ S cm}^{-1}}{0.050 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{L}$$

= 111.1 1 S cm² mol⁻¹

Given,

$$\tilde{A}\tilde{Z}\hat{A}^{\circ} = 106.74 \times 10^{-2} \text{ S m}^{-1}, c = 0.100 \text{ M}$$

Then, $\tilde{A}\tilde{Z}\hat{A}^{\circ} = 106.74 \times 10^{-4} \text{ S cm}^{-1}$, $c^{1/2} = 0.3162 \text{ M}^{1/2}$

$$\Lambda_m = \frac{\kappa}{c}$$

$$= \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{L}$$

= 106.74 S cm² mol⁻¹

Now, we have the following data:

$C^{1/2}/M^{1/2}$	0.0316	0.1	0.1414	0.2236	0.3162
$\Lambda_m \left(\text{S cm}^2 \text{ mol}^{-1} \right)$	123.7				

Q11:

Conductivity of 0.00241 M acetic acid is 7.896 × 10⁻⁵ S cm⁻¹. Calculate its molar conductivity and if Λ_m^0 for acetic acid is 390.5 S cm² mol⁻¹, what is its dissociation constant?

Answer:

Given,
$$\tilde{A}\tilde{Z}\hat{A}^{\circ} = 7.896 \times 10^{-5} \text{ S m}^{-1}$$

 $c = 0.00241 \text{ mol } L^{-1}$

$$\Lambda_{\scriptscriptstyle m} = \frac{\kappa}{c}$$
 Then, molar conductivity,

$$= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1}}{0.00241 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{3}}{L}$$

= 32.76S cm² mol⁻¹

Again, $\Lambda_m^0 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}}$$

= 0.084

 $K_a = \frac{c\alpha^2}{\left(1 - \alpha\right)}$ \therefore Dissociation constant,

 $= \frac{\left(0.00241 \text{ mol } L^{-1}\right)\!\left(0.084\right)^2}{\left(1\!-\!0.084\right)}$

 $= 1.86 \times 10^{-5} \text{ mol L}^{-1}$

Q12:

How much charge is required for the following reductions:

- (i) 1 mol of Al3+ to Al.
- (ii) 1 mol of Cu2+ to Cu.
- (iii) 1 mol of $\begin{tabular}{ll} MnO_4^- \\ \hline \end{tabular}$ to Mn²+.

Answer:

(i)
$$Al^{3+} + 3e^{-} \longrightarrow Al$$

- · Required charge = 3 F
- $= 3 \times 96487 C$
- = 289461 C

(ii)
$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

- Required charge = 2 F
- $= 2 \times 96487 C$
- = 192974 C

(iii)
$$MnO_4^- \longrightarrow Mn^{2+}$$

$$_{\text{i.e.,}} \, Mn^{^{7+}} + 5e^- \quad \longrightarrow \quad Mn^{^{2+}}$$

· Required charge = 5 F

 $= 5 \times 96487 C$

= 482435 C

Q13:

How much electricity in terms of Faraday is required to produce

- (i) 20.0 g of Ca from molten CaCl₂.
- (ii) 40.0 g of Al from molten Al₂O₃.

Answer:

(i) According to the question,

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

Electricity required to produce 40 g of calcium = 2 F

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

= 1 F

(ii) According to the question,

$$Al^{3+} + 3e^{-} \longrightarrow Al$$
27 g

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

Q14:

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 Fe₂O₃.

Answer:

(i) According to the question,

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

Now, we can write:

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

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

- $= 2 \times 96487 C$
- = 192974 C
- (ii) According to the question,

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

Electricity required for the oxidation of 1 mol of FeO to Fe₂O₃ = 1 F

= 96487 C

Q15:

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?

Answer:

Given,

Current = 5A

Time = $20 \times 60 = 1200 \text{ s}$

- $= 5 \times 1200$
- = 6000 C

According to the reaction,

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

Nickel deposited by $2 \times 96487 C = 58.71 g$

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.

Q16:

Three electrolytic cells A,B,C containing solutions of ZnSO₄, AgNO₃ and CuSO₄, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Answer:

According to the reaction:

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$

108 g

i.e., 108 g of Ag is deposited by 96487 C.

Therefore, 1.45 g of Ag is deposited by =
$$\frac{96487 \times 1.45}{108} C$$

Given,

Current = 1.5 A

= 1295.43 C

$$\therefore \text{Time} = \frac{1295.43}{1.5} s$$

= 863.6 s

= 864 s

= 14.40 min

Again,

$$\operatorname{Cu^{2+}}_{(aq)} + 2e^{-} \longrightarrow \operatorname{Cu}_{(s)}$$
63.5 g

i.e., 2 x 96487 C of charge deposit = 63.5 g of Cu

Therefore, 1295.43 C of charge will deposit
$$= \frac{63.5 \times 1295.43}{2 \times 96487} g$$

= 0.426 g of Cu

$$\operatorname{Zn}^{2+}_{(aq)} + 2e^{-} \longrightarrow \operatorname{Zn}_{(s)}$$
65.4 g

i.e., 2×96487 C of charge deposit = 65.4 g of Zn

Therefore, 1295.43 C of charge will deposit
$$= \frac{65.4 \times 1295.43}{2 \times 96487}$$
 g = 0.439 g of Zn

Q17:

Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:

- (i) Fe3+(aq) and I-(aq)
- (ii) Ag+ (aq) and Cu(s)
- (iii) Fe3+ (aq) and Br- (aq)
- (iv) Ag(s) and Fe3+ (aq)
- (v) Br₂ (aq) and Fe²⁺ (aq).

Answer:

(i)
$$Fe^{3+}_{(aq)} + e^{-} \longrightarrow Fe^{2+}_{(aq)}$$
] $\times 2$; $E^{\circ} = +0.77 \text{ V}$

$$\frac{2I^{-}_{(aq)} \longrightarrow I_{2(s)} + 2e^{-};}{2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}}; E^{\circ} = +0.23 \text{ V}$$

Since E° for the overall reaction is positive, the reaction between Fe $^{\circ}$ and I $^{\circ}$ and I is feasible.

(ii)
$$Ag^{+}_{(\alpha q)} + e^{-} \longrightarrow Ag_{(s)}$$
] $\times 2$; $E^{\circ} = +0.80 \text{ V}$

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(\alpha q)} + 2e^{-}$$
; $E^{\circ} = -0.34 \text{ V}$

$$2Ag^{+}_{(\alpha q)} + Cu_{(s)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(\alpha q)}$$
; $E^{\circ} = +0.46 \text{ V}$

Since E° for the overall reaction is positive, the reaction between ${\sf Ag^{+}_{(aq)}}$ and ${\sf Cu_{(s)}}$ is feasible.

(iii)
$$Fe^{3+}_{(\alpha q)} + e^{-} \longrightarrow Fe^{2+}_{(\alpha q)}$$
] \times 2 ; $E^{\circ} = +0.77 \text{ V}$
 $\underbrace{2Br^{-}_{(\alpha q)}}_{(\alpha q)} \longrightarrow Br_{2(l)} + 2e^{-}$; $E^{\circ} = -1.09 \text{ V}$
 $\underbrace{2Fe^{3+}_{(\alpha q)}}_{(\alpha q)} + 2Br^{-}_{(\alpha q)} \longrightarrow 2Fe^{2+}_{(\alpha q)} \text{ and } Br_{2(l)}$; $E^{\circ} = -0.32 \text{ V}$

Since E° for the overall reaction is negative, the reaction between Fe $^{3+}_{(aq)}$ and Br $^{+}_{(aq)}$ is not feasible.

(iv)
$$Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + e^{-}$$
 ; $E^{\circ} = -0.80 \text{ V}$
 $Fe^{3+}_{(aq)} + e^{-} \longrightarrow Fe^{2+}_{(aq)}$; $E^{\circ} = +0.77 \text{ V}$
 $Ag_{(s)} + Fe^{3+}_{(aq)} \longrightarrow Ag^{+}_{(aq)} + Fe^{2+}_{(aq)}$; $E^{\circ} = -0.03 \text{ V}$

Since E^{o} E for the overall reaction is negative, the reaction between $Ag_{(s)}$ and $Fe^{3+}_{(aq)}$ is not feasible.

(iv)
$$Br_{2(\alpha q)} + 2e^{-} \longrightarrow 2Br_{(\alpha q)}^{-}$$
; $E^{\circ} = +1.09 \text{ V}$

$$\frac{Fe^{2+}_{(\alpha q)} \longrightarrow Fe^{3+}_{(\alpha q)} + e^{-}] \times 2 ; E^{\circ} = -0.77 \text{ V}}{Br_{2(\alpha q)} + 2Fe^{2+}_{(\alpha q)} \longrightarrow 2Br_{(\alpha q)}^{-} + 2Fe^{3+}_{(\alpha q)} ; E^{\circ} = +0.32 \text{ V}}$$

Since E° for the overall reaction is positive, the reaction between $\mathsf{Br}_{2(aq)}$ and $\mathsf{Fe}^{2^+}_{(aq)}$ is feasible.

Q18:

Predict the products of electrolysis in each of the following:

- (i) An aqueous solution of AgNO₃ with silver electrodes.
- (ii) An aqueous solution of AgNO₃with platinum electrodes.
- (iii) A dilute solution of H₂SO₄with platinum electrodes.
- (iv) An aqueous solution of CuCl₂ with platinum electrodes.

Answer:

(i) At cathode:

The following reduction reactions compete to take place at the cathode.

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$
; $E^{\circ} = 0.80V$

$$H^{+}_{(\alpha q)} + e^{-} \longrightarrow \frac{1}{2} H_{2(g)}; \quad E^{o} = 0.00 \text{ V}$$

The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

The Ag anode is attacked by NO_3^- ions. Therefore, the silver electrode at the anode dissolves in the solution to form Ag $^+$.

(ii) At cathode:

The following reduction reactions compete to take place at the cathode.

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$
; $E^{o} = 0.80V$

$$H^{+}_{(\alpha q)} + e^{-} \longrightarrow \frac{1}{2} H_{2(g)}; \quad E^{o} = 0.00 \text{ V}$$

The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

Since Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH $^+$ or NO_3^- ions can be oxidized at the anode. But OH $^+$ ions having a lower discharge potential and get preference and decompose to liberate O_2 .

$$OH^{-} \longrightarrow OH + e^{-}$$

 $4OH^{-} \longrightarrow 2H_{2}O + O_{3}$

(iii) At the cathode, the following reduction reaction occurs to produce H2 gas.

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$$

At the anode, the following processes are possible.

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-; E^o = +1.23V$$
 (i)
 $2SO_{4-(aq)}^{2-} \longrightarrow S_2O_{6-(aq)}^{2-} + 2e^-; E^o = +1.96 V$ (ii)

For dilute sulphuric acid, reaction (i) is preferred to produce O₂ gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At cathode:

The following reduction reactions compete to take place at the cathode.

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$$
; $E^{0} = 0.34V$
 $H^{+}_{(aq)} + e^{-} \longrightarrow \frac{1}{2} H_{2(g)}$; $E^{0} = 0.00 V$

The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of copper will take place at the cathode.

At anode:

The following oxidation reactions are possible at the anode.

$$CI^{-}_{(aq)} \longrightarrow \frac{1}{2}CI_{2(g)} + e^{-1} ; E^{\circ} = 1.36 \text{ V}$$

 $2H_{2}O_{(l)} \longrightarrow O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} ; E^{\circ} = +1.23\text{ V}$

At the anode, the reaction with a lower value of E° is preferred. But due to the over-potential of oxygen, Cl⁻gets oxidized at the anode to produce Cl₂ gas.

NCERT Solutions for Class 12 Chemistry Part 1 Chapter 4

Chemical Kinetics Class 12

Chapter 4 Chemical Kinetics Exercise Solutions

In text: Solutions of Questions on Page Number: 98

Q1

For the reaction R \rightarrow P, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Answer:

$$= -\frac{\Delta[R]}{\Delta t}$$

Average rate of reaction

$$=-\frac{\left[\mathbf{R}\right]_{2}-\left[\mathbf{R}\right]_{1}}{t_{2}-t_{1}}$$

$$= -\frac{0.02 - 0.03}{25} \text{ M min}^{-1}$$

$$=-\frac{-0.01}{25}$$
 M min⁻¹

$$= 4 \times 10^{-4} \text{ M min}^{-1}$$

$$= \frac{4 \times 10^{-4}}{60} \text{ M s}^{-1}$$

$$= 6.67 \times 10^{-6} \text{M s}^{-1}$$

Q2:

In a reaction, $2A \rightarrow Products$, the concentration of A decreases from 0.5 mol L-1 to 0.4 mol L-1 in 10 minutes. Calculate the rate during this interval?

Answer:

$$_{\text{Average rate}} = -\frac{1}{2} \frac{\Delta [A]}{\Delta t}$$

$$=-\frac{1}{2}\frac{\left[\mathbf{A}\right]_{2}-\left[\mathbf{A}\right]_{1}}{t_{2}-t_{1}}$$

$$=-\frac{1}{2}\frac{0.4-0.5}{10}$$

$$=-\frac{1}{2}\frac{-0.1}{10}$$

= 0.005 mol L⁻¹ min⁻¹

 $= 5 \times 10^{-3} \text{M min}^{-1}$

Q3:

For a reaction, A + B $\tilde{A} \notin \hat{a} \in \hat{P}$ roduct; the rate law is given by, $r = k \left[A \right]^{1/2} \left[B \right]^2$. What is the order of the reaction?

Answer:

 $= \frac{1}{2} + 2$ The order of the reaction

$$=2\frac{1}{2}$$

= 2.5

Q4:

The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

Answer:

The reaction $X \rightarrow Y$ follows second order kinetics.

Therefore, the rate equation for this reaction will be:

Rate = $k[X]^2$ (1)

Let $[X] = a \mod L^{-1}$, then equation (1) can be written as:

Rate₁ = $k \cdot (a)^2$

 $= ka^2$

If the concentration of X is increased to three times, then $[X] = 3a \text{ mol } L^{-1}$

Now, the rate equation will be:

Rate =
$$k (3a)^2$$

$$= 9(ka^2)$$

Hence, the rate of formation will increase by 9 times.

Q5:

A first order reaction has a rate constant 1.15 10⁻³s⁻¹. How long will 5 g of this reactant take to reduce to 3 g?

Answer:

From the question, we can write down the following information:

Initial amount = 5 g

Final concentration = 3 g

Rate constant = $1.15 \cdot 10^{-3} \text{s}^{-1}$

We know that for a 1st order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$=\frac{2.303}{1.15\times10^{-3}}\log\frac{5}{3}$$

$$=\frac{2.303}{1.15\times10^{-3}}\times0.2219$$

$$= 444.38 s$$

Q6:

Time required to decompose SO₂Cl₂to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Answer:

We know that for a 1storder reaction,

$$t_{1/2} = \frac{0.693}{k}$$

It is given that $t_{1/2}$ = 60 min

$$\therefore k = \frac{0.693}{t_{1/2}}$$

$$=\frac{0.693}{60}$$

$$= 0.01155 \text{ min}^{-1}$$

Or
$$k = 1.925 \times 10^{-4} \,\mathrm{s}^{-1}$$

Q7:

What will be the effect of temperature on rate constant?

Answer:

The rate constant of a reaction is nearly doubled with a 10° rise in temperature. However, the exact dependence of the rate of a chemical reaction on temperature is given by Arrhenius equation,

$$k = Ae^{-Ea/RT}$$

Where,

A is the Arrhenius factor or the frequency factor

Tis the temperature

Ris the gas constant

E_ais the activation energy

Q8:

The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a .

Answer:

It is given that $T_1 = 298 \text{ K}$

$$T_2 = (298 + 10) \text{ K}$$

$$= 308 K$$

We also know that the rate of the reaction doubles when temperature is increased by 10°.

Therefore, let us take the value of $k_1 = k$ and that of $k_2 = 2k$

Also, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Now, substituting these values in the equation:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

We get:

$$\log \frac{2k}{k} = \frac{E_{\rm a}}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$\Rightarrow \log 2 = \frac{E_{\text{a}}}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$\Rightarrow E_{\rm a} = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

= 52897.78 J mol-1

 $= 52.9 \text{ kJ mol}^{-1}$

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q9:

The activation energy for the reaction

$$2HI_{(g)} \rightarrow H_2 + I_{2(g)}$$

is 209.5 kJ mol⁻¹ at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Answer:

In the given case:

 $E_{\rm a} = 209.5 \text{ kJ mol}^{-1} = 209500 \text{ J mol}^{-1}$

T = 581 K

 $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as: x=e- $E_d/RT \Rightarrow In x=-E$

<< Previous Chapter 3 : ElectrochemistryNext Chapter 5 : Surface Chemistry >>

Exercise: Solutions of Questions on Page Number: 117

Q1:

From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(i) 3 NO(g) â†' N₂O(g) Rate = k[NO]²

(ii) H₂O₂ (aq) + 3 l⁻(aq) + 2 H⁺â†' 2 H₂O (l) +
$$I_3^-$$
 Rate = $k[H_2O_2][I^-]$

Answer:

(i) Given rate = $k [NO]^2$

Therefore, order of the reaction = 2

$$k = \frac{Rate}{\left[NO\right]^2}$$
 Dimension of

$$= \frac{mol \ L^{-1} \ s^{-1}}{\left(mol \ L^{-1}\right)^2}$$

$$= \frac{mol \ L^{-1} \ s^{-1}}{mol^2 \ L^{-2}}$$

$$= L \, mol^{-1} \, s^{-1}$$

(ii) Given rate = $k [H_2O_2] [I^-]$

Therefore, order of the reaction = 2

$$k = \frac{\text{Rate}}{\left[\text{H}_2\text{O}_2\right]\!\!\left[\text{I}^-\right]}$$
 Dimension of

$$= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\left(\text{mol } L^{-1}\right)\left(\text{mol } L^{-1}\right)}$$
$$= L \text{ mol}^{-1} \text{ s}^{-1}$$

(iii) Given rate = $k [CH_3CHO]^{3/2}$

Therefore, order of reaction = $\frac{1}{2}$

$$k = \frac{\text{Rate}}{\left[\text{CH}_3\text{CHO}\right]^{\frac{3}{2}}}$$

$$= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\left(\text{mol } L^{-1}\right)^{\frac{3}{2}}}$$

$$= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\text{mol}^{\frac{3}{2}} L^{-\frac{3}{2}}}$$

$$= L^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ s}^{-1}$$

(iv) Given rate = $k [C_2H_5CI]$

Therefore, order of the reaction = 1

$$k = \frac{\text{Rate}}{\left[\text{C}_2\text{H}_5\text{Cl}\right]}$$

Dimension of

$$= \frac{\text{mol } L^{-1} s^{-1}}{\text{mol } L^{-1}}$$
$$= s^{-1}$$

Q2:

For the reaction:

$$2A + B \rightarrow A_2B$$

the rate = $k[A][B]^2$ with $k= 2.0 \times 10^6$ mol²L²s¹. Calculate the initial rate of the reaction when [A] = 0.1 mol L¹, [B] = 0.2 mol L¹. Calculate the rate of reaction after [A] is reduced to 0.06 mol L¹.

Answer:

The initial rate of the reactionis

Rate = $k [A][B]^2$

= $(2.0 \times 10^{-6} \text{mol}^{-2} \text{L}^2 \text{s}^{-1})$ (0.1 mol L^{-1}) $(0.2 \text{ mol L}^{-1})^2$

 $= 8.0 \times 10^{-9} \text{mol}^{-2} \text{L}^2 \text{s}^{-1}$

When [A] is reduced from 0.1 mol L 1 to 0.06 mol 1, the concentration of A reacted = (0.1 - 0.06) mol L 1 = 0.04 mol L 1

 $= \frac{1}{2} \times 0.04 \text{ mol L}^{-1}$ Therefore, concentration of B reacted = 0.02 mol L⁻¹

Then, concentration of B available, [B] = (0.2 - 0.02) mol L⁻¹

 $= 0.18 \text{ mol } L^{-1}$

After [A] is reduced to 0.06 mol L⁻¹, the rate of the reaction is given by,

Rate = $k [A][B]^2$

= $(2.0 \times 10^{-6} \text{mol}^{-2} \text{L}^2 \text{s}^{-1}) (0.06 \text{ mol L}^{-1}) (0.18 \text{ mol L}^{-1})^2$

 $= 3.89 \text{ mol } L^{-1} s^{-1}$

Q3:

The decomposition of NH₃on platinum surface is zero order reaction. What are the rates of production of N₂and H₂if $k = 2.5 \times 10^4$ mol⁻¹L s⁻¹?

Answer:

The decomposition of NH₃on platinum surface is represented by the following equation.

$$2 \text{ NH}_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3 \text{ H}_{2(g)}$$

Therefore,

Rate =
$$-\frac{1}{2} \frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3} \frac{d[H_2]}{dt}$$

However, it is given that the reaction is of zero order.

Therefore,

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k$$
$$= 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$$

Therefore, the rate of production of N2is

$$\frac{d[N_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$$

And, the rate of production of H2is

$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$$

 $= 7.5 \times 10^{-4} \text{mol L}^{-1} \text{s}^{-1}$

Q4:

The decomposition of dimethyl ether leads to the formation of CH₄, H₂and CO and the reaction rate is given by

Rate = $k [CH_3OCH_3]^{3/2}$

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

Rate =
$$k \left(p_{\text{CH}_3\text{OCH}_3} \right)^{\frac{3}{2}}$$

If the pressure is measured in bar andtime in minutes, then what are the units of rate and rate constants?

Answer:

If pressure is measured in bar and time in minutes, then

Unit of rate = bar min⁻¹

Rate =
$$k \left(p_{\text{CH}_3\text{OCH}_3} \right)^{\frac{3}{2}}$$

$$\Rightarrow k = \frac{\text{Rate}}{\left(p_{\text{CH}_3\text{OCH}_3}\right)^{\frac{3}{2}}}$$

$$(k) = \frac{\text{bar min}^{-1}}{\text{bar}^{\frac{3}{2}}}$$

Therefore, unit of rate constants

$$= bar^{-1/2} min^{-1}$$

Q5:

Mention the factors that affect the rate of a chemical reaction.

Answer:

The factors that affect the rate of a reaction areas follows.

- (i) Concentration of reactants (pressure in case of gases)
- (ii) Temperature
- (iii) Presence of a catalyst

Q6:

A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled (ii) reduced to half?

Answer:

Let the concentration of the reactant be [A] = a

Rate of reaction, $R = k [A]^2$

$$= ka^2$$

(i) If the concentration of the reactant is doubled, i.e. [A] = 2a, then the rate of the reaction would be

$$R' = k \left(2a\right)^2$$

$$=4ka^2$$

$$= 4 R$$

Therefore, the rate of the reaction would increase by 4 times.

(ii) If the concentration of the reactant is reduced to half, i.e. $[A] = \frac{1}{2}a$, then the rate of the reaction would be

$$R' = k(\frac{1}{2}a)^{2}$$
$$= \frac{1}{4}ka^{2}$$
$$= \frac{1}{4}R$$

$$\frac{1}{4}$$

Therefore, the rate of the reaction would be reduced to '

Q7:

What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

Answer:

The rate constant is nearly doubled with a rise in temperature by 10° for a chemical reaction.

The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

where, kis the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

Tis the temperature, and

E_ais the energy of activation for the reaction

Q8:

In a pseudo first order hydrolysis of ester in water, the following results were obtained:

t/s	0	30	60	90
[Ester]mol L-1	0.55	0.31	0.17	0.085

- (i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
- (ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Answer:

(i) Average rate of reaction between the time interval, 30 to 60 seconds,

$$= \frac{0.31 - 0.17}{60 - 30}$$
$$= \frac{0.14}{30}$$

- $= 4.67 \times 10^{-3} \text{mol L}^{-1} \text{s}^{-1}$
- (ii) For a pseudo first order reaction,

$$k = \frac{2.303}{t} \log \frac{\left[R\right]_0}{\left[R\right]}$$

For
$$t = 30 \text{ s}$$
, $k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31}$

 $= 1.911 \times 10^{-2} \text{s}^{-1}$

For
$$t = 60 \text{ s}$$
, $k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17}$

 $= 1.957 \times 10^{-2} \text{s}^{-1}$

For
$$t = 90 \text{ s}$$
, $k_3 = \frac{2.303}{90} \log \frac{0.55}{0.085}$

 $= 2.075 \times 10^{-2} \text{s}^{-1}$

Then, average rate constant,
$$k = \frac{k_1 + k_2 + k_3}{3}$$

$$=\frac{\left(1.911\times10^{-2}\right)+\left(1.957\times10^{-2}\right)+\left(2.075\times10^{-2}\right)}{3}$$

$$=1.98\times10^{-2} \text{ s}^{-1}$$

Q9:

A reaction is first order in A and second order in B.

- (i) Write the differential rate equation.
- (ii) How is the rate affected on increasing the concentration of B three times?
- (iii) How is the rate affected when the concentrations of both A and B are doubled?

Answer:

(i) The differential rate equation will be

$$-\frac{d[R]}{dt} = k[A][B]^2$$

(ii) If the concentration of B is increased three times, then

$$-\frac{d[R]}{dt} = k[A][3B]^{2}$$
$$= 9 \cdot k[A][B]^{2}$$

Therefore, the rate of reaction will increase 9 times.

(iii) When the concentrations of both A and B are doubled,

$$-\frac{d[R]}{dt} = k[A][B]^{2}$$
$$= k[2A][2B]^{2}$$
$$= 8 \cdot k[A][B]^{2}$$

Therefore, the rate of reaction will increase 8 times.

Q10:

In a reaction between A and B, the initial rate of reaction (r₀) was measured for different initial concentrations of A and B as given below:

A/ mol L·1	0.20	0.20	0.40
B/ mol L-1	0.30	0.10	0.05
r ₀ / mol L ⁻¹ s ⁻¹	5.07 × 10 ⁻⁵	5.07 × 10 ⁻⁵	1.43 × 10 ⁻⁴

What is the order of the reaction with respect to A and B?

Answer:

Let the order of the reaction with respect to A be xand with respect to B be y.

Therefore,

$$r_{0} = k [A]^{x} [B]^{y}$$

$$5.07 \times 10^{-5} = k [0.20]^{x} [0.30]^{y}$$

$$5.07 \times 10^{-5} = k [0.20]^{x} [0.10]^{y}$$

$$1.43 \times 10^{-4} = k [0.40]^{x} [0.05]^{y}$$
(ii)

Dividing equation (i) by (ii), we obtain

$$\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k [0.20]^{x} [0.30]^{y}}{k [0.20]^{x} [0.10]^{y}}$$

$$\Rightarrow 1 = \frac{[0.30]^{y}}{[0.10]^{y}}$$

$$\Rightarrow \left(\frac{0.30}{0.10}\right)^{0} = \left(\frac{0.30}{0.10}\right)^{y}$$

$$\Rightarrow y = 0$$

Dividing equation (iii) by (ii), we obtain

$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k \left[0.40\right]^{x} \left[0.05\right]^{y}}{k \left[0.20\right]^{x} \left[0.30\right]^{y}}$$

$$\Rightarrow \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{\left[0.40\right]^{x}}{\left[0.20\right]^{x}} \qquad \begin{bmatrix} \text{Since } y = 0, \\ \left[0.05\right]^{y} = \left[0.30\right]^{y} = 1 \end{bmatrix}$$

$$\Rightarrow 2.821 = 2^{x}$$

$$\Rightarrow \log 2.821 = x \log 2 \qquad \text{(Taking log on both sides)}$$

$$\Rightarrow x = \frac{\log 2.821}{\log 2}$$

= 1.496

= 1.5 (approximately)

Hence, the order of the reaction with respect to A is 1.5 and with respect to B is zero.

Q11:

The following results have been obtained during the kinetic studies of the reaction:

2A + B â†' C + D

Experiment	A/ mol L-1	B/ mol L-1	Initial rate of formation of D/mol L-1 min-1
I	0.1	0.1	6.0×10^{-3}

II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

Answer:

Let the order of the reaction with respect to A be xand with respect to B be y.

Therefore, rate of the reaction is given by,

Rate =
$$k[A]^x[B]^y$$

According to the question,

$$6.0 \times 10^{-3} = k [0.1]^{x} [0.1]^{y}$$
 (i)

$$7.2 \times 10^{-2} = k [0.3]^x [0.2]^y$$
 (ii)

$$2.88 \times 10^{-1} = k [0.3]^{x} [0.4]^{y}$$
 (iii)

$$2.40 \times 10^{-2} = k [0.4]^x [0.1]^y$$
 (iv)

Dividing equation (iv) by (i), we obtain

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k \left[0.4\right]^x \left[0.1\right]^y}{k \left[0.1\right]^x \left[0.1\right]^y}$$

$$\Rightarrow 4 = \frac{\left[0.4\right]^x}{\left[0.1\right]^x}$$

$$\Rightarrow 4 = \left(\frac{0.4}{0.1}\right)^x$$

$$\Rightarrow (4)^1 = 4^x$$
$$\Rightarrow x = 1$$

Dividing equation (iii) by (ii), we obtain

Therefore, the rate law is

Rate = $k [A] [B]^2$

$$k = \frac{\text{Rate}}{[A][B]^2}$$

From experiment I, we obtain

$$k = \frac{6.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}}{\left(0.1 \text{ mol L}^{-1}\right) \left(0.1 \text{ mol L}^{-1}\right)^2}$$

= 6.0 L²mol⁻²min⁻¹

From experiment II, weobtain

$$k = \frac{7.2 \times 10^{-2} \text{ mol } L^{-1} \text{ min}^{-1}}{\left(0.3 \text{ mol } L^{-1}\right) \left(0.2 \text{ mol } L^{-1}\right)^2}$$

= 6.0 L²mol⁻²min⁻¹

From experiment III, we obtain

$$k = \frac{2.88 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1}}{\left(0.3 \text{ mol L}^{-1}\right) \left(0.4 \text{ mol L}^{-1}\right)^2}$$

 $= 6.0 L^2 mol^{-2} min^{-1}$

From experiment IV, we obtain

$$k = \frac{2.40 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{\left(0.4 \text{ mol L}^{-1}\right) \left(0.1 \text{ mol L}^{-1}\right)^2}$$

= 6.0 L²mol⁻²min⁻¹

Therefore, rate constant, $k = 6.0 \text{ L}^2\text{mol}^{-2}\text{min}^{-1}$

Q12:

The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	A/ mol L-1	B/ mol L-1	Initial rate/mol L-1 min-1
I	0.1	0.1	2.0 × 10 ⁻²
II		0.2	4.0 × 10-2
III	0.4	0.4	
IV		0.2	2.0×10^{-2}

Answer:

The given reaction is of the first order with respect to A and of zero order with respect to B.

Therefore, the rate of the reaction is given by,

Rate = $k [A]^{1}[B]^{0}$

 \Rightarrow Rate = k [A]

From experiment I, we obtain

2.0 x 10⁻²mol L⁻¹min⁻¹= k (0.1 mol L⁻¹)

 \Rightarrow $k=0.2 \text{ min}^{-1}$

From experiment II, we obtain

 $4.0 \times 10^{-2} \text{mol L}^{-1} \text{min}^{-1} = 0.2 \text{ min}^{-1} [A]$

 \Rightarrow [A] = 0.2 mol L⁻¹

From experiment III, we obtain

Rate = $0.2 \text{ min}^{-1} \times 0.4 \text{ mol L}^{-1}$

= 0.08 mol L-1min-1

From experiment IV, we obtain

 $2.0 \times 10^{-2} \text{mol L}^{-1} \text{min}^{-1} = 0.2 \text{ min}^{-1} [A]$

 \Rightarrow [A] = 0.1 mol L⁻¹

Q13:

Calculate the half-life of a first order reaction from their rate constants given below:

(i) 200 s⁻¹ (ii) 2 min⁻¹ (iii) 4 years⁻¹

Answer:

(i) Half life,
$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$=\frac{0.693}{200 \text{ s}^{-1}}$$

= 3.47×10^{-3} s (approximately)

(ii) Half life,
$$t_{1/2} = \frac{0.693}{k}$$

$$=\frac{0.693}{2 \, \text{min}^{-1}}$$

= 0.35 min (approximately)

(iii) Half life,
$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

= $\frac{0.693}{4 \text{ years}^{-1}}$

= 0.173 years (approximately)

Q14:

The half-life for radioactive decay of ¹⁴C is 5730 years. An archaeological artifact containing wood had only 80% of the ¹⁴C found in a living tree. Estimate the age of the sample.

Answer:

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$
Here,
$$= \frac{0.693}{5730} \text{ years}^{-1}$$

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$= \frac{2.303}{0.693} \log \frac{100}{80}$$

= 1845 years (approximately)

Hence, the age of the sample is 1845 years.

Q15:

The experimental data for decomposition of N_2O_5

$$\left[2N_2O_5 \longrightarrow 4NO_2 + O_2\right]$$

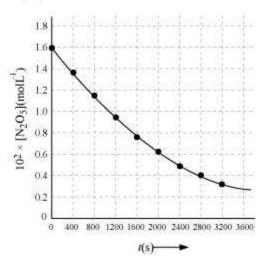
in gas phase at 318K are given below:

t(s)	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5] \text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot [N₂O₅] against t.

- (ii) Find the half-life period for the reaction.
- (iii) Draw a graph between log $[N_2O_5]$ and t.
- (iv) What is the rate law?
- (v)

Answer:



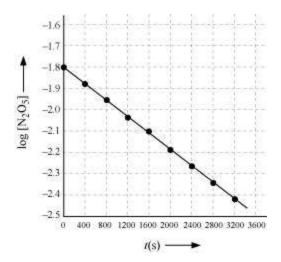
$$\frac{1.630 \times 10^2}{2} \, \text{mol} \, L^{-1} = 81.5 \, \text{mol} \, L^{-1},$$

(ii) Time corresponding to the concentration, the half life is obtained as 1450 s.

is the half life. From the graph,

(iii)

t(s)	$10^2 \times [N_2O_5]/ \text{mol L}^{-1}$	$log[N_2O_5]$
0	1.63	- 1.79
400	1.36	- 1.87
800	1.14	- 1.94
1200	0.93	- 2.03
1600	0.78	- 2.11
2000	0.64	- 2.19
2400	0.53	- 2.28
2800	0.43	- 2.37
3200	0.35	- 2.46



(iv) The given reaction is of the first order as the plot, $\log[N_2O_5]$ v/s t, is a straight line. Therefore, the rate law of the reaction is

Rate =
$$k[N_2O_5]$$

(v) From the plot, $\left. \log \left[N_2 O_5 \right] \right._{\text{v/s } \textit{t}, \text{ we obtain}}$

Slope =
$$\frac{-2.46 - (-1.79)}{3200 - 0}$$
$$= \frac{-0.67}{3200}$$

Again, slope of the line of the plot $\log \left[N_2 O_5 \right]_{\text{ v/s } \textit{t} \text{ is given by}}$

$$-\frac{k}{2.303}$$

Therefore, we obtain,

$$-\frac{k}{2.303} = -\frac{0.67}{3200}$$

Q16:

The rate constant for a first order reaction is 60 s⁻¹. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

Answer:

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{60 \text{ s}^{-1}} \log \frac{1}{\frac{1}{16}}$$

$$= \frac{2.303}{60 \text{ s}^{-1}} \log 16$$

$$= 4.6 \times 10^{-2} \text{ s (approximately)}$$

Hence, the required time is 4.6×10^{-2} s.

Q17:

During nuclear explosion, one of the products is ⁹⁰Sr with half-life of 28.1 years. If 1νg of ⁹⁰Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

Answer:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \text{ y}^{-1}$$

Here

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} (-\log[R])$$

$$\Rightarrow \log[R] = -\frac{10 \times 0.693}{2.303 \times 28.1}$$

$$\Rightarrow [R] = \text{antilog} (-0.1071)$$

$$= \text{antilog} (\overline{1}.8929)$$

$$= 0.7814 \mu g$$

Therefore, 0.7814 μg of 90Sr will remain after 10 years.

Again,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$\Rightarrow 60 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow \log[R] = -\frac{60 \times 0.693}{2.303 \times 28.1}$$

$$\Rightarrow [R] = \operatorname{antilog}(-0.6425)$$

$$= \operatorname{antilog}(\overline{1}.3575)$$

$$= 0.2278 \mu g$$

Therefore, 0.2278 μg of 90Sr will remain after 60 years.

Q18:

For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Answer:

For a first order reaction, the time required for 99% completionis

$$t_1 = \frac{2.303}{k} \log \frac{100}{100 - 99}$$
$$= \frac{2.303}{k} \log 100$$
$$= 2 \times \frac{2.303}{k}$$

For a first order reaction, the time required for 90% completion is

$$t_2 = \frac{2.303}{k} \log \frac{100}{100 - 90}$$
$$= \frac{2.303}{k} \log 10$$
$$= \frac{2.303}{k}$$

Therefore, $t_1 = 2t_2$

Hence, the time required for 99% completion of a first order reaction is twice the time required for the completion of 90% of the reaction.

Q19:

A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Answer:

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$k = \frac{2.303}{40 \text{ min}} \log \frac{100}{100 - 30}$$
$$= \frac{2.303}{40 \text{ min}} \log \frac{10}{7}$$
$$= 8.918 \times 10^{-3} \text{ min}^{-1}$$

Therefore, $t_{1/2}$ of the decomposition reaction is

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$
$$= \frac{0.693}{8.918 \times 10^{-3}} \min$$

= 77.7 min (approximately)

Q20:

For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

Answer:

The decomposition of azoisopropane to hexane and nitrogen at 543 K is represented by the following equation.

$$(CH3)2 CHN=NCH(CH3)2(g) \longrightarrow N2(g) + C6H14(g)$$
At $t = 0$ P₀ 0 0
At $t = t$ P₀ - p p

After time,
$$t$$
, total pressure, $P_t = (P_0 - p) + p + p$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

Therefore, $P_o - p = P_o - (P_t - P_o)$

$$= 2P_0 - P_t$$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - p}$$
$$= \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

When
$$t = 360 \text{ s}$$
, $k = \frac{2.303}{360 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 54.0}$

$$= 2.175 \times 10^{-3} \text{ s}^{-1}$$

When
$$t = 720 \text{ s}$$
, $k = \frac{2.303}{720 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 63.0}$

$$= 2.235 \times 10^{-3} \text{ s}^{-1}$$

Hence, the average value of rate constant is

$$k = \frac{\left(2.175 \times 10^{-3}\right) + \left(2.235 \times 10^{-3}\right)}{2} s^{-1}$$

$$= 2.21 \times 10^{-3} \, \text{s}^{-1}$$

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q21:

The following data were obtained during the first order thermal decomposition of SO₂Cl₂at a constant volume.

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

Experiment	Time/s ⁻¹	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Answer:

The thermal decomposition of SO₂Cl₂at a constant volume is represented by the following equation.

After time, t, total pressure, $P_t = (P_0 - p) + p + p$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

Therefore,
$$P_o - p = P_o - (P_t - P_o)$$

$$= 2 P_0 - P_t$$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - p}$$
$$= \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

When
$$t = 100 \text{ s}$$
, $k = \frac{2.303}{100 \text{ s}} \log \frac{0.5}{2 \times 0.5 - 0.6}$

 $= 2.231 \times 10^{-3} \text{s}^{-1}$ When P = 0.65 atm,

 $P_0 + p = 0.65$

$$\Rightarrow p = 0.65 - P_0$$

$$= 0.65 - 0.5$$

= 0.15 atm

Therefore, when the total pressure is 0.65 atm, pressure of SOCI2is

$$p_{SOCl_2} = P_0 - p$$

$$= 0.5 - 0.15$$

$$= 0.35 atm$$

Therefore, the rate of equation, when total pressure is 0.65 atm, is given by,

Rate =
$$k(P_{SOCI_2})$$

$$= (2.23 \times 10^{-3} \text{s}^{-1}) (0.35 \text{ atm})$$

$$= 7.8 \times 10^{-4} atm s^{-1}$$

Q22:

The rate constant for the decomposition of N₂O₅ at various temperatures is given below:

T/°C	0	20	40	60	80
$10^5 \times k/\text{ s}^{-1}$	0.0787	1.70	25.7	178	2140

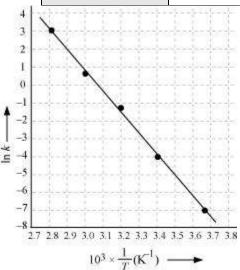
Draw a graph between $\ln k$ and 1/T and calculate the values of A and E_a .

Predict the rate constant at 30 ° and 50 °C.

Answer:

From the given data, we obtain

T/°C	0	20	40	60	80
T/K	273	293	313	333	353
$\frac{1}{T}/\mathrm{K}^{-1}$	3.66×10-3	3.41×10-3	3.19×10 ⁻³	3.0×10-3	2.83 ×10-3
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140
ln k	- 7.147	- 4.075	- 1.359	- 0.577	3.063



Slope of the line,

$$\frac{y_2 - y_1}{x_2 - x_1} = -12.301 \,\mathrm{K}$$

According to Arrhenius equation,

Slope =
$$-\frac{E_a}{R}$$

 $\Rightarrow E_a = -Slope \times R$
= $-(-12.301 \text{ K}) \times (8.314 \text{ J K}^{-1} \text{mol}^{-1})$
= $102.27 \text{ kJ mol}^{-1}$

Again,

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln A = \ln k + \frac{E_a}{RT}$$

When
$$T = 273 \,\mathrm{K}$$
,

$$\ln k = -7.147$$

Then,
$$\ln A = -7.147 + \frac{102.27 \times 10^3}{8.314 \times 273}$$

= 37.911

Therefore,
$$A = 2.91 \times 10^6$$

When
$$T = 30 + 273 \,\mathrm{K} = 303 \,\mathrm{K}$$

$$\frac{1}{T} = 0.0033 \,\mathrm{K} = 3.3 \times 10^{-3} \,\mathrm{K}$$

$$\text{Then, } \text{ at } \frac{1}{T} = 3.3 \times 10^{-3} \, \text{K},$$

$$\ln k = -2.8$$

Therefore,
$$k = 6.08 \times 10^{-2} \text{ s}^{-1}$$

Again, when
$$T = 50 + 273 \,\mathrm{K} = 323 \,\mathrm{K}$$

Q23:

The rate constant for the decomposition of hydrocarbons is 2.418 x 10⁻⁵ s⁻¹at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

Answer:

$$k=2.418 \times 10^{-5} \text{s}^{-1}$$

 E_a = 179.9 kJ mol⁻¹= 179.9 x 10³J mol⁻¹

According to the Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\Rightarrow \ln k = \ln A - \frac{E_a}{RT}$$

$$\Rightarrow \log k = \log A - \frac{E_a}{2.303 \text{ RT}}$$

$$\Rightarrow \log A = \log k + \frac{E_a}{2.303 \text{ RT}}$$

$$= \log \left(2.418 \times 10^{-5} \text{ s}^{-1}\right) + \frac{179.9 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ Jk}^{-1} \text{ mol}^{-1} \times 546 \text{ K}}$$

= (0.3835 - 5) + 17.2082

= 12.5917

Therefore, A = antilog (12.5917)

= $3.9 \times 10^{12} s^{-1}$ (approximately)

Q24:

Consider a certain reaction A \rightarrow Products with $k = 2.0 \times 10^{-2} \text{ s}^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L⁻¹.

Answer:

 $k=2.0 \times 10^{-2} s^{-1}$

T = 100 s

[A]_o= 1.0 moL⁻¹

Since the unit of kis s⁻¹, the given reaction is a first order reaction.

$$k = \frac{2.303}{t} \log \frac{\left[A\right]_0}{\left[A\right]}$$

Therefore,

$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \log \frac{1.0}{[A]}$$

$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \left(-\log[A]\right)$$

$$\Rightarrow -\log[A] = \frac{2.0 \times 10^{-2} \times 100}{2.303}$$

$$\Rightarrow [A] = \operatorname{anti} \log \left(-\frac{2.0 \times 10^{-2} \times 100}{2.303}\right)$$

= 0.135 mol L-1(approximately)

Hence, the remaining concentration of A is 0.135 mol L⁻¹.

Q25:

Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2}$ = 3.00 hours. What fraction of sample of sucrose remains after 8 hours?

Answer:

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

It is given that, $t_{1/2}$ = 3.00 hours

$$k = \frac{0.693}{t_{1/2}}$$
 Therefore,

$$= \frac{0.693}{3} \ h^{-1}$$

 $= 0.231 h^{-1}$

Then, 0.231 h
$$^{-1}$$
 = $\frac{2.303}{8 \text{ h}} log \frac{\left[R\right]_0}{\left[R\right]}$

$$\Rightarrow \log \frac{[R]_0}{[R]} = \frac{0.231 \,\mathrm{h}^{-1} \times 8 \,\mathrm{h}}{2.303}$$

$$\Rightarrow \frac{[R]_0}{[R]} = \mathrm{antilog}(0.8024)$$

$$\Rightarrow \frac{[R]_0}{[R]} = 6.3445$$

$$\Rightarrow \frac{[R]}{[R]_0} = 0.1576 \,\mathrm{(approx)}$$

$$= 0.158$$

Hence, the fraction of sample of sucrose that remains after 8 hours is 0.158.

Q26:

The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} \text{ s}^{-1}) \text{ e}^{-28000 \text{ K/T}}$$

Calculate Ea.

Answer:

The given equation is

$$k = (4.5 \times 10^{11} \text{ s}^{-1}) \text{ e}^{-28000 \text{ K/T}}$$
 (i)

Arrhenius equation is given by,

$$k = Ae^{-E_{\sigma}/RT}$$
 (ii)

From equation (i) and (ii), we obtain

$$\frac{E_a}{RT} = \frac{28000 \text{ K}}{T}$$

$$\Rightarrow E_a = R \times 28000 \text{ K}$$

$$= 8.314 \text{ J K}^{-1} \text{mol}^{-1} \times 28000 \text{ K}$$

= 232792 J mol-1

= 232.792 kJ mol-1

Q27:

The rate constant for the first order decomposition of H₂O₂is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4 \text{ K/}T$$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?

Answer:

Arrhenius equation is given by,

$$k = Ae^{-E_{\sigma}/RT}$$

$$\Rightarrow \ln k = \ln \mathbf{A} - \frac{E_a}{\mathbf{R}T}$$

$$\Rightarrow \ln k = \log A - \frac{E_a}{RT}$$

$$\Rightarrow \log k = \log A - \frac{E_a}{2.303 \text{ RT}}$$
 (i)

The given equation is

$$\log k = 14.34 - 1.25 \times 10^4 \text{ K/T}$$
 (ii)

From equation (i) and (ii), we obtain

$$\frac{E_a}{2.303 \text{ R}T} = \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\Rightarrow E_a = 1.25 \times 10^4 \text{ K} \times 2.303 \times \text{ R}$$

=
$$1.25 \times 10^{4}$$
K × 2.303×8.314 J K⁻¹mol⁻¹

= 239.34 kJ mol⁻¹

Also, when $t_{1/2}$ = 256 minutes,

$$k = \frac{0.693}{t_{1/2}}$$
$$= \frac{0.693}{256}$$

$$= 2.707 \times 10^{-3} \text{min}^{-1}$$

$$= 4.51 \times 10^{-5} \text{s}^{-1}$$

It is also given that, $\log k = 14.34 - 1.25 \times 10^4 \text{K/}T$

$$\Rightarrow \log(4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^{4} \text{ K}}{T}$$

$$\Rightarrow \log(0.654 - 05) = 14.34 - \frac{1.25 \times 10^{4} \text{ K}}{T}$$

$$\Rightarrow \frac{1.25 \times 10^{4} \text{ K}}{T} = 18.686$$

$$\Rightarrow T = \frac{1.25 \times 10^{4} \text{ K}}{18.686}$$

= 668.95 K

= 669 K (approximately)

Q28:

The decomposition of A into product has value of k as 4.5 x 10 $^{\circ}$ s⁻¹ at 10 $^{\circ}$ C and energy of activation 60 kJ mol⁻¹. At what temperature would k be 1.5 x 10 $^{\circ}$ s⁻¹?

Answer:

From Arrhenius equation, we obtain

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \,\text{R}} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Also, $k_1 = 4.5 \times 10^3 \,\mathrm{s}^{-1}$

$$T_1 = 273 + 10 = 283 \text{ K}$$

$$k_2 = 1.5 \times 10^4 \,\mathrm{s}^{-1}$$

$$E_a = 60 \text{ kJ mol}^{-1} = 6.0 \times 10^4 \text{ J mol}^{-1}$$

Then,

$$\log \frac{1.5 \times 10^{4}}{4.5 \times 10^{3}} = \frac{6.0 \times 10^{4} \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{T_{2} - 283}{283 T_{2}} \right)$$

$$\Rightarrow 0.5229 = 3133.627 \left(\frac{T_{2} - 283}{283 T_{2}} \right)$$

$$\Rightarrow \frac{0.5229 \times 283 T_{2}}{3133.627} = T_{2} - 283$$

$$\Rightarrow 0.0472 T_{2} = T_{2} - 283$$

$$\Rightarrow 0.9528 T_{2} = 283$$

$$\Rightarrow T_{2} = 297.019 \text{ K (approximately)}$$

= 297 K

= 24°C

Hence, *k* would be $1.5 \times 10^4 \, \text{s}^{-1}$ at 24° C.

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q29:

The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is 4×10^{10} s⁻¹. Calculate k at 318 K and E_a .

Answer:

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

$$t = \frac{2.303}{k} \log \frac{100}{90}$$

$$= \frac{0.1054}{k}$$
At 308 K,
$$t' = \frac{2.303}{k'} \log \frac{100}{75}$$

$$= \frac{2.2877}{k'}$$

According to the question,

$$t = t'$$

$$\Rightarrow \frac{0.1054}{k} = \frac{0.2877}{k'}$$

$$\Rightarrow \frac{k'}{k} = 2.7296$$

From Arrhenius equation, we obtain

$$\log \frac{k'}{k} = \frac{E_a}{2.303 \,\text{R}} \left(\frac{T' - T}{TT'} \right)$$

$$\log (2.7296) = \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{298 \times 308} \right)$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log(2.7296)}{308 - 298}$$

$$= 76640.096 \,\text{J mol}^{-1}$$

$$= 76.64 \,\text{kJ mol}^{-1}$$

To calculate k at 318 K,

It is given that,
$$A = 4 \times 10^{10} \,\text{s}^{-1}$$
, $T = 318 \,\text{K}$

Again, from Arrhenius equation, we obtain

$$\log k = \log A - \frac{E_a}{2.303 \,\mathrm{R} \,T}$$

$$= \log \left(4 \times 10^{10}\right) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318}$$

$$= \left(0.6021 + 10\right) - 12.5876$$

$$= -1.9855$$

Therefore,
$$k = \text{Antilog}(-1.9855)$$

= $1.034 \times 10^{-2} \text{ s}^{-1}$

Q30:

The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Answer:

From Arrhenius equation, we obtain

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \,\text{R}} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$
It is given that, $k_2 = 4k_1$

$$T_1 = 293 \,\text{K}$$

$$T_2 = 313 \,\text{K}$$
Therefore, $\log \frac{4k_1}{k_2} = \frac{E_a}{2.303 \times 8.314} \left(\frac{313 - 293}{293 \times 313} \right)$

$$\Rightarrow 0.6021 = \frac{20 \times E_a}{2.303 \times 8.314 \times 293 \times 313}$$

$$\Rightarrow E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$$

$$= 52863.33 \,\text{J mol}^{-1}$$

$$= 52.86 \,\text{kJ mol}^{-1}$$

Hence, the required energy of activation is 52.86 kJmol⁻¹.

NCERT Solutions for Class 12 Chemistry Part 1 Chapter 5

Surface Chemistry Class 12

used in Haber's process.

Chapter 5 Surface Chemistry Exercise Solutions
In text: Solutions of Questions on Page Number: 127
Q1:
Write any two characteristics of Chemisorption.
Answer:
1. Chemisorption is highly specific in nature. It occurs only if there is a possibility of chemical bonding between the adsorbent and the adsorbate.
2. Like physisorption, chemisorption also increases with an increase in the surface area of the adsorbent.
Q2:
Why does physisorption decrease with the increase of temperature?
Answer:
Physisorption is exothermic in nature. Therefore, in accordance with Le-Chateliere's principle, it decreases with an increase in temperature. This means that physisorption occurs more readily at a lower temperature.
Q3:
Why are powdered substances more effective adsorbents than their crystalline forms?
Answer:
Powdered substances are more effective adsorbents than their crystalline forms because when a substance is powdered, its surface area increases and physisorption is directly proportional to the surface area of the adsorbent.
Q4:
Why is it necessary to remove CO when ammonia is obtained by Haber's process?
Answer:
It is important to remove CO in the synthesis of ammonia as CO adversely affects the activity of the iron catalyst,

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\mathbf{a}	15	
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Why is the ester hydrolysis slow in the beginning and becomes faster after sometime?

Answer:

Ester hydrolysis can be represented as:

The acid produced in the reaction acts as a catalyst and makes the reaction faster. Substances that act as catalysts in the same reaction in which they are obtained as products are known as autocatalysts.

Q6:

What is the role of desorption in the process of catalysis?

Answer:

The role of desorption in the process of catalysis is to make the surface of the solid catalyst free for the fresh adsorption of the reactants on the surface.

Q7:

What modification can you suggest in the Hardy-Schulze law?

Answer:

Hardy-Schulze law states that 'the greater the valence of the flocculating ion added, the greater is its power to cause precipitation.'

This law takes into consideration only the charge carried by an ion, not its size. The smaller the size of an ion, the more will be its polarising power. Thus, Hardy-Schulze law can be modified in terms of the polarising power of the flocculating ion. Thus, the modified Hardy-Schulze law can be stated as 'the greater the polarising power of the flocculating ion added, the greater is its power to cause precipitation.'

Q8:

Why is it essential to wash the precipitate with water before estimating it quantitatively?

Answer:

When a substance gets precipitated, some ions that combine to form the precipitate get adsorbed on the surface of the precipitate. Therefore, it becomes important to wash the precipitate before estimating it quantitatively in order to remove these adsorbed ions or other such impurities.

<< Previous Chapter 4 : Chemical KineticsNext Chapter 6 : General Principles and Processes of Isolation of Elements >>

Exercise: Solutions of Questions on Page Number: 146

Q1:

Distinguish between the meaning of the terms adsorption and absorption.

Give one example of each.

Answer:

Adsorption is a surface phenomenon of accumulation of molecules of a substance at the surface rather than in the bulk of a solid or liquid. The substance that gets adsorbed is called the 'adsorbate' and the substance on whose surface the adsorption takes place is called the 'adsorbent'. Here, the concentration of the adsorbate on the surface of the adsorbent increases. In adsorption, the substance gets concentrated at the surface only. It does not penetrate through the surface to the bulk of the solid or liquid. For example, when we dip a chalk stick into an ink solution, only its surface becomes coloured. If we break the chalk stick, it will be found to be white from inside.

On the other hand, the process of *absorption* is a bulk phenomenon. In absorption, the substance gets uniformly distributed throughout the bulk of the solid or liquid.

Q2:

What is the difference between physisorption and chemisorption?

Answer:

	Physisorption	Chemisorption
1.	In this type of adsorption, the adsorbate is attached to the surface of the adsorbent with weak van der Waal's forces of attraction.	In this type of adsorption, strong chemical bonds are formed between the adsorbate and the surface of the adsorbent.
2.	No new compound is formed in the process.	New compounds are formed at the surface of the adsorbent.
3.	It is generally found to be reversible in nature.	It is usually irreversible in nature.
4.	Enthalpy of adsorption is low as weak van der Waal's forces of attraction are involved. The values lie in the range of 20-40 kJ mol.	Enthalpy of adsorption is high as chemical bonds are formed. The values lie in the range of 40-400 kJ mol ⁻¹ .
5.	It is favoured by low temperature conditions.	It is favoured by high temperature conditions.
6.	It is an example of multi-layer adsorption	It is an example of mono-layer adsorption.

Q3:

Give reason why a finely divided substance is more effective as an adsorbent.

Answer:

Adsorption is a surface phenomenon. Therefore, adsorption is directly proportional to the surface area. A finely divided substance has a large surface area. Both physisorption and chemisorption increase with an increase in the surface area. Hence, a finely divided substance behaves as a good adsorbent.

Q4:

What are the factors which influence the adsorption of a gas on a solid?

Answer:

There are various factors that affect the rate of adsorption of a gas on a solid surface.

(1) Nature of the gas:

Easily liquefiable gases such as NH_3 , HCl etc. are adsorbed to a great extent in comparison to gases such as H_2 , O_2 etc. This is because Van der Waal's forces are stronger in easily liquefiable gases.

(2) Surface area of the solid

The greater the surface area of the adsorbent, the greater is the adsorption of a gas on the solid surface.

(3) Effect of pressure

Adsorption is a reversible process and is accompanied by a decrease in pressure. Therefore, adsorption increases with an increase in pressure.

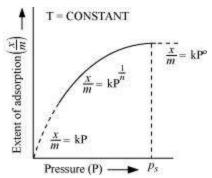
(4) Effect of temperature

Adsorption is an exothermic process. Thus, in accordance with Le-Chatelier's principle, the magnitude of adsorption decreases with an increase in temperature.

Q5:

What is an adsorption isotherm? Describe Freundlich adsorption isotherm.

Answer:



The plot between the extent of adsorption m against the pressure of gas (P) at constant temperature (T) is called the adsorption isotherm.

Freundlich adsorption isotherm:

Freundlich adsorption isotherm gives an empirical relationship between the quantity of gas adsorbed by the unit mass of solid adsorbent and pressure at a specific temperature.

From the given plot it is clear that at pressure P_s , m reaches the maximum valve. P_s is called the saturation pressure. Three cases arise from the graph now.

Case I- At low pressure:

$$\frac{x}{m} = \frac{x}{m} \alpha P.$$
 The plot is straight and sloping, indicating that the pressure in directly proportional to $\frac{x}{m}$ i.e.,

$$\frac{x}{m} = k P$$
 (k is a constant)

Case II- At high pressure:

When pressure exceeds the saturated pressure, m becomes independent of P values.

$$\frac{x}{m} \alpha P^{\circ}$$

$$\frac{x}{m} = k P^{\circ}$$

Case III- At intermediate pressure:

At intermediate pressure, m depends on P raised to the powers between 0 and 1. This relationship is known as the Freundlich adsorption isotherm.

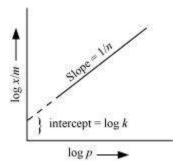
$$\frac{x}{m} \alpha P^{\frac{1}{n}}$$

$$\frac{x}{m} = kP^{\frac{1}{n}} \qquad n >$$

Now, taking log:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

On plotting the graph between log $\frac{x}{m}$ and log P, a straight line is obtained with the slope equal to $\frac{1}{n}$ and the intercept equal to log k.



Q6:

What do you understand by activation of adsorbent? How is it achieved?

Answer:

By activating an adsorbent, we tend to increase the adsorbing power of the adsorbent. Some ways to activate an adsorbent are:

- (i) By increasing the surface area of the adsorbent. This can be done by breaking it into smaller pieces or powdering it
- (ii) Some specific treatments can also lead to the activation of the adsorbent. For example, wood charcoal is activated by heating it between 650 K and 1330 K in vacuum or air. It expels all the gases absorbed or adsorbed and thus, creates a space for adsorption of gases.

Q7:

What role does adsorption play in heterogeneous catalysis?

Answer:

Heterogeneous catalysis:

A catalytic process in which the catalyst and the reactants are present in different phases is known as a heterogeneous catalysis. This heterogeneous catalytic action can be explained in terms of the adsorption theory. The mechanism of catalysis involves the following steps:

- (i) Adsorption of reactant molecules on the catalyst surface.
- (ii) Occurrence of a chemical reaction through the formation of an intermediate.
- (iii) De-sorption of products from the catalyst surface
- (iv) Diffusion of products away from the catalyst surface.

In this process, the reactants are usually present in the gaseous state and the catalyst is present in the solid state. Gaseous molecules are then adsorbed on the surface of the catalyst. As the concentration of reactants on the surface of the catalyst increases, the rate of reaction also increases. In such reactions, the products have very less affinity for the catalyst and are quickly desorbed, thereby making the surface free for other reactants.

Q8:

Why is adsorption always exothermic?

Answer:

Adsorption is always exothermic. This statement can be explained in two ways.

- (i) Adsorption leads to a decrease in the residual forces on the surface of the adsorbent. This causes a decrease in the surface energy of the adsorbent. Therefore, adsorption is always exothermic.
- (ii) ΔH of adsorption is always negative. When a gas is adsorbed on a solid surface, its movement is restricted leading to a decrease in the entropy of the gas i.e., ΔS is negative. Now for a process to be spontaneous, ΔG should be negative.
- $\Delta G = \Delta H T\Delta S$

Since ΔS is negative, ΔH has to be negative to make ΔG negative. Hence, adsorption is always exothermic.

Q9:

How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?

Answer:

One criterion for classifying colloids is the physical state of the dispersed phase and dispersion medium. Depending upon the type of the dispersed phase and dispersion medium (solid, liquid, or gas), there can be eight types of colloidal systems.

Dispersed phase		Dispersion medium	Type of colloid	Example
1.	Solid	Solid	Solid Sol	Gemstone
2.	Solid	Liquid	Sol	Paint
3.	Solid	Gas	Aerosol	Smoke
4.	Liquid	Solid	Gel	Cheese
5.	Liquid	Liquid	Emulsion	Milk
6.	Liquid	Gas	Aerosol	Fog
7.	Gas	Solid	Solid foam	Pumice stone
8.	Gas	Liquid	Foam	Froth

Q10:

Discuss the effect of pressure and temperature on the adsorption of gases on solids.

Answer:

Effect of pressure

Adsorption is a reversible process and is accompanied by a decrease in pressure. Therefore, adsorption increases with an increase in pressure.

Effect of temperature

Adsorption is an exothermic process. Thus, in accordance with Le-Chatelier's principle, the magnitude of adsorption decreases with an increase in temperature.

Q11:

What are lyophilic and lyophobic sols? Give one example of each type. Why are hydrophobic sols easily coaqulated?

Answer:

(i) Lyophilic sols:

Colloidal sols that are formed by mixing substances such as gum, gelatin, starch, etc. with a suitable liquid (dispersion medium) are called lyophilic sols. These sols are reversible in nature i.e., if two constituents of the sol are separated by any means (such as evaporation), then the sol can be prepared again by simply mixing the dispersion medium with the dispersion phase and shaking the mixture.

(ii) Lyophobic sols:

When substances such as metals and their sulphides etc. are mixed with the dispersion medium, they do not form colloidal sols. Their colloidal sols can be prepared only by special methods. Such sols are called lyophobic sols. These sols are irreversible in nature. For example: sols of metals.

Now, the stability of hydrophilic sols depends on two things- the presence of a charge and the salvation of colloidal particles. On the other hand, the stability of hydrophobic sols is only because of the presence of a charge. Therefore, the latter are much less stable than the former. If the charge of hydrophobic sols is removed (by addition of electrolytes), then the particles present in them come closer and form aggregates, leading to precipitation.

Q12:

What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids?

Answer:

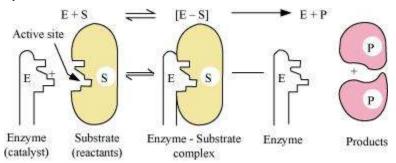
- (i) In multi-molecular colloids, the colloidal particles are an aggregate of atoms or small molecules with a diameter of less than 1 nm. The molecules in the aggregate are held together by van der Waal's forces of attraction. Examples of such colloids include gold sol and sulphur sol.
- (ii) In macro-molecular colloids, the colloidal particles are large molecules having colloidal dimensions. These particles have a high molecular mass. When these particles are dissolved in a liquid, sol is obtained. For example: starch, nylon, cellulose, etc.
- (iii) Certain substances tend to behave like normal electrolytes at lower concentrations. However, at higher concentrations, these substances behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called aggregated colloids.

Q13:

What are enzymes? Write in brief the mechanism of enzyme catalysis.

Answer:

Enzymes are basically protein molecules of high molecular masses. These form colloidal solutions when dissolved in water. These are complex, nitrogenous organic compounds produced by living plants and animals. Enzymes are also called 'biochemical catalysts'.



Mechanism of enzyme catalysis:

On the surface of the enzymes, various cavities are present with characteristic shapes. These cavities possess active groups such as -NH₂, -COOH, etc. The reactant molecules having a complementary shape fit into the cavities just like a key fits into a lock. This leads to the formation of an activated complex. This complex then decomposes to give the product.

Hence,

Step 1: $E + S \rightarrow ES^+$

(Activated complex)

Step 2: $ES^+ \rightarrow E + P$

Q14:

How are colloids classified on the basis of

(i) Physical states of components

- (ii) Nature of dispersion medium and
- (iii) Interaction between dispersed phase and dispersion medium?

Answer:

Colloids can be classified on various bases:

- (i) On the basis of the physical state of the components (by components we mean the dispersed phase and dispersion medium). Depending on whether the components are solids, liquids, or gases, we can have eight types of colloids.
- (ii) On the basis of the dispersion medium, sols can be divided as:

Dispersion medium	Name of sol
Water	Aquasol or hydrosol
Alcohol	Alcosol
Benzene	Benzosol
Gases	Aerosol

(iii) On the basis of the nature of the interaction between the dispersed phase and dispersion medium, the colloids can be classified as lyophilic (solvent attracting) and lyophobic (solvent repelling).

Q15:

Explain what is observed

- (i) When a beam of light is passed through a colloidal sol.
- (ii) An electrolyte, NaCl is added to hydrated ferric oxide sol.
- (iii) Electric current is passed through a colloidal sol?

Answer:

- (i) When a beam of light is passed through a colloidal solution, then scattering of light is observed. This is known as the Tyndall effect. This scattering of light illuminates the path of the beam in the colloidal solution.
- (ii) When NaCl is added to ferric oxide sol, it dissociates to give Na⁺ and Cl⁻ ions. Particles of ferric oxide sol are positively charged. Thus, they get coagulated in the presence of negatively charged Cl⁻ ions.
- (iii) The colloidal particles are charged and carry either a positive or negative charge. The dispersion medium carries an equal and opposite charge. This makes the whole system neutral. Under the influence of an electric current, the colloidal particles move towards the oppositely charged electrode. When they come in contact with the electrode, they lose their charge and coagulate.

Q16:

What are emulsions? What are their different types? Give example of each type. Answer: The colloidal solution in which both the dispersed phase and dispersion medium are liquids is called an emulsion. There are two types of emulsions: (a) Oil in water type: Here, oil is the dispersed phase while water is the dispersion medium. For example: milk, vanishing cream, etc. (b) Water in oil type: Here, water is the dispersed phase while oil is the dispersion medium. For example: cold cream, butter, etc. Q17: What is demulsification? Name two demulsifiers. Answer: The process of decomposition of an emulsion into its constituent liquids is called demulsification. Examples of demulsifiers are surfactants, ethylene oxide, etc. Q18: Action of soap is due to emulsification and micelle formation. Comment. Answer: The cleansing action of soap is due to emulsification and micelle formation. Soaps are basically sodium and potassium salts of long chain fatty acids, R-COO Na*. The end of the molecule to which the sodium is attached is polar in nature, while the alkyl-end is non-polar. Thus, a soap molecule contains a hydrophilic (polar) and a hydrophobic (non-polar) part. When soap is added to water containing dirt, the soap molecules surround the dirt particles in such a manner that their hydrophobic parts get attached to the dirt molecule and the hydrophilic parts point away from the dirt molecule. This is known as micelle formation. Thus, we can say that the polar group dissolves in water while the non-polar group dissolves in the dirt particle. Now, as these micelles are negatively charged, they do not coalesce and a stable emulsion is formed. Q19: Give four examples of heterogeneous catalysis. Answer:

(i) Oxidation of sulphur dioxide to form sulphur trioxide. In this reaction, Pt acts as a catalyst.

$$2SO_{2(g)} \xrightarrow{Pt_{(s)}} 2SO_{3(g)}$$

(ii) Formation of ammonia by the combination of dinitrogen and dihydrogen in the presence of finely divided iron.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe_{(s)}} 2NH_{3(g)}$$

This process is called the Haber's process.

(iii) Oswald's process: Oxidation of ammonia to nitric oxide in the presence of platinum.

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt_{(s)}} 4NO_{(g)} + 6H_2O_{(g)}$$

(iv) Hydrogenation of vegetable oils in the presence of Ni.

Vegetable
$$oil_{(i)} + H_{2(g)} \xrightarrow{Ni_{(i)}} vegetable ghee_{(s)}$$

Q20:

What do you mean by activity and selectivity of catalysts?

Answer:

(a) Activity of a catalyst:

The activity of a catalyst is its ability to increase the rate of a particular reaction. Chemisorption is the main factor in deciding the activity of a catalyst. The adsorption of reactants on the catalyst surface should be neither too strong nor too weak. It should just be strong enough to make the catalyst active.

(b) Selectivity of the catalyst:

The ability of the catalyst to direct a reaction to yield a particular product is referred to as the selectivity of the catalyst. For example, by using different catalysts, we can get different products for the reaction between H₂ and CO.

$$CO_{(g)} + 3H_{2(g)} \xrightarrow{Ni} CH_{4(g)} + H_2O_{(g)}$$

(ii)
$$CO_{(g)} + 2H_{2(g)} \xrightarrow{Cu \times ZnO \cdot CrO_3} CH_3OH_{(g)}$$

(iii)
$$CO_{(g)} + H_{2(g)} \xrightarrow{Cu} HCHO_{(g)}$$

Q21:

Describe some features of catalysis by zeolites.

Answer:

Zeolites are alumino-silicates that are micro-porous in nature. Zeolites have a honeycomb-like structure, which makes them shape-selective catalysts. They have an extended 3D-network of silicates in which some silicon atoms are

replaced by aluminium atoms, giving them an Al-O-Si framework. The reactions taking place in zeolites are very sensitive to the pores and cavity size of the zeolites. Zeolites are commonly used in the petrochemical industry.

Q22:

What is shape selective catalysis?

Answer:

A catalytic reaction which depends upon the pore structure of the catalyst and on the size of the reactant and the product molecules is called shape-selective catalysis. For example, catalysis by zeolites is a shape-selective catalysis. The pore size present in the zeolites ranges from 260-740 pm. Thus, molecules having a pore size more than this cannot enter the zeolite and undergo the reaction.

Q23:

Explain the following terms:

- (i) Electrophoresis (ii) Coagulation
- (iii) Dialysis (iv) Tyndall effect.

Answer:

(i) Electrophoresis:

The movement of colloidal particles under the influence of an applied electric field is known as electrophoresis. Positively charged particles move to the cathode, while negatively charged particles move towards the anode. As the particles reach oppositely charged electrodes, they become neutral and get coagulated.

(ii) Coagulation:

The process of settling down of colloidal particles i.e., conversion of a colloid into a precipitate is called coagulation.

(iii) Dialysis

The process of removing a dissolved substance from a colloidal solution by the means of diffusion through a membrane is known as dialysis. This process is based on the principle that ions and small molecules can pass through animal membranes unlike colloidal particles.

(iv) Tyndall effect:

When a beam of light is allowed to pass through a colloidal solution, it becomes visible like a column of light. This is known as the Tyndall effect. This phenomenon takes place as particles of colloidal dimensions scatter light in all directions.

Q24:

Give four uses of emulsions.

Answer:

Four uses of emulsions:

- (i) Cleansing action of soaps is based on the formation of emulsions.
- (ii) Digestion of fats in intestines takes place by the process of emulsification.
- (iii) Antiseptics and disinfectants when added to water form emulsions.
- (iv) The process of emulsification is used to make medicines.

Q25:

Give four uses of emulsions.

Answer:

Four uses of emulsions:

- (i) Cleansing action of soaps is based on the formation of emulsions.
- (ii) Digestion of fats in intestines takes place by the process of emulsification.
- (iii) Antiseptics and disinfectants when added to water form emulsions.
- (iv) The process of emulsification is used to make medicines.

Q26:

Explain the terms with suitable examples:

(i) Alcosol (ii) Aerosol (iii) Hydrosol

Answer:

(i) Alcosol:

A colloidal solution having alcohol as the dispersion medium and a solid substance as the dispersed phase is called an alcosol.

For example: colloidal sol of cellulose nitrate in ethyl alcohol is an alcosol.

(ii) Aerosol:

A colloidal solution having a gas as the dispersion medium and a solid as the dispersed phase is called an aerosol.

For example: fog

(iii) Hydrosol

A colloidal solution having water as the dispersion medium and a solid as the dispersed phase is called a hydrosol.

For example: starch sol or gold sol

Q27:

Comment on the statement that "colloid is not a substance but a state of substance".

Answer:

Common salt (a typical crystalloid in an aqueous medium) behaves as a colloid in a benzene medium. Hence, we can say that a colloidal substance does not represent a separate class of substances. When the size of the solute particle lies between 1 nm and 1000 nm, it behaves as a colloid.

Hence, we can say that colloid is not a substance but a state of the substance which is dependent on the size of the particle. A colloidal state is intermediate between a true solution and a suspension.