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Question 1.1:

Why are solids rigid?

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.

Question 1.2:

Why do solids have a definite volume?

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.

Question 1.3:

Classify the following as amorphous or crystalline solids:

Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper

Amorphous solids

Polyurethane, teflon, cellophane, polyvinyl chloride, fibre glass

Crystalline solids

Naphthalene, benzoic acid, potassium nitrate, copper

Question 1.4:

Why is glass considered a super cooled liquid?

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.

Question 1.5:

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?

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.

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

Question 1.6:

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.

Potassium sulphate → 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 → Ionic solid

Graphite → Covalent or network solid

Rubidium → Metallic solid

Argon → Non-polar molecular solid

Silicon carbide → Covalent or network solid

Question 1.7:

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?

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).

Question 1.8:

Ionic solids conduct electricity in molten state but not in solid state. Explain.

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

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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.

Question 1.9:

What type of solids are electrical conductors, malleable and ductile?

Metallic solids are electrical conductors, malleable, and ductile.

Question 1.10:

Give the significance of a 'lattice point'.

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.

Question 1.11:

Name the parameters that characterize a unit cell.

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 α (between edges b and c), β (between edges a and c), and γ (between edges a and b).

Question 1.12:

Distinguish between

(i) Hexagonal and monoclinic unit cells

(ii) Face-centred and end-centred unit cells

(i) Hexagonal unit cell

For a hexagonal unit cell,

$$a = b \neq c$$

$$\text{and } \alpha = \beta = 90^\circ$$

$$\gamma = 120^\circ$$

Monoclinic unit cell

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For a monoclinic cell,

$$a \neq b \neq c$$

$$\text{and } \alpha = \gamma = 90^\circ$$

$$\beta \neq 90^\circ$$

(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

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

Question 1.13:

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.

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

$$\frac{1}{8}^{\text{th}}$$

Therefore, $\frac{1}{8}$ 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.

Question 1.14:

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

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.

Question 1.15:

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?

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

$$\text{Therefore, number of octahedral voids} = 3.011 \times 10^{23}$$

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

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

Question 1.16:

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

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.

$$\frac{1}{3} \text{ rd}$$

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

$$2 \times \frac{1}{3} = \frac{2}{3} \text{ rd}$$

Therefore, the number of atoms of M is equal to $\frac{2}{3}$ of the number

of atoms of N.

$$= \frac{2}{3} : 1$$

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 $M_2 N_3$.

Question 1.17:

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

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.

Question 1.18:

An element with molar mass $2.7 \times 10^{-2} \text{ kg mol}^{-1}$ forms a cubic unit cell with edge length 405 pm. If its density is $2.7 \times 10^3 \text{ kg m}^{-3}$, what is the nature of the cubic unit cell?

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

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

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

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

It is known that, Avogadro's number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Applying the relation,

$$\begin{aligned} d &= \frac{z, M}{a^3 \cdot N_A} \\ z &= \frac{d \cdot a^3 N_A}{M} \\ &= \frac{2.7 \times 10^3 \text{ kg m}^{-3} \times (4.05 \times 10^{-10} \text{ m})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{2.7 \times 10^{-2} \text{ kg mol}^{-1}} \\ &= 4.004 \\ &= 4 \end{aligned}$$

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*).

Question 1.19:

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

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.

Question 1.20:

What type of stoichiometric defect is shown by:

(i) ZnS (ii) AgBr

i) ZnS shows Frenkel defect.

ii) AgBr shows Frenkel defect as well as Schottky defect.

Question 1.21:

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

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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 Sr^{2+} is added to NaCl, each Sr^{2+} ion replaces two Na^+ ions. However, one Sr^{2+} ion occupies the site of one Na^+ ion and the other site remains vacant. Hence, vacancies are introduced.

Question 1.22:

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

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.

Question 1.23:

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?

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.

Question 1.24:

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

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Question 1.1:

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

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.

Question 1.2:

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

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.

Question 1.3:

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

(i) Tetra phosphorus decoxide (P_4O_{10}) (vii) Graphite

(ii) Ammonium phosphate $(NH_4)_3PO_4$ (viii) Brass

(iii) SiC (ix) Rb

(iv) I_2 (x) LiBr

(v) P_4 (xi) Si

Ionic → (ii) Ammonium phosphate $(NH_4)_3PO_4$, (x) LiBr

Metallic → (viii) Brass, (ix) Rb

Molecular → (i) Tetra phosphorus decoxide (P_4O_{10}), (iv) I_2 , (v) P_4 .

Covalent (network) → (iii) SiC, (vii) Graphite, (xi) Si

Amorphous → (vi) Plastic

Question 1.4:

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(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?

(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

Question 1.5:

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

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 atomic mass of the metal and ' z ' be the number of atoms in the unit cell.

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

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

[Since mass of the unit cell = Number of atoms in the unit cell \times Atomic mass]

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

From equation (i), we have:

$$m = \frac{d a^3}{z} \quad (ii)$$

$$\text{Now, mass of the metal (m)} = \frac{\text{Atomic mass (M)}}{\text{Avogadro's number (N}_A\text{)}}$$

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

Therefore,

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

$$m = \frac{d(abc)N_A}{z} \quad (iv)$$

From equations (iii) and (iv), we can determine the atomic mass of the unknown metal.

Question 1.6:

'Stability of a crystal is reflected in the magnitude 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?

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.

Question 1.7:

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?

- 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

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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.

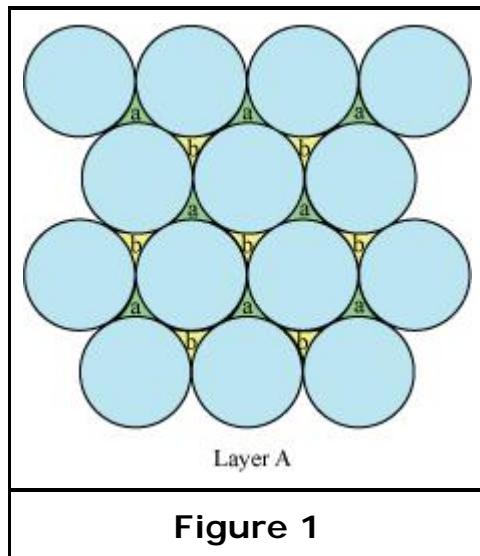
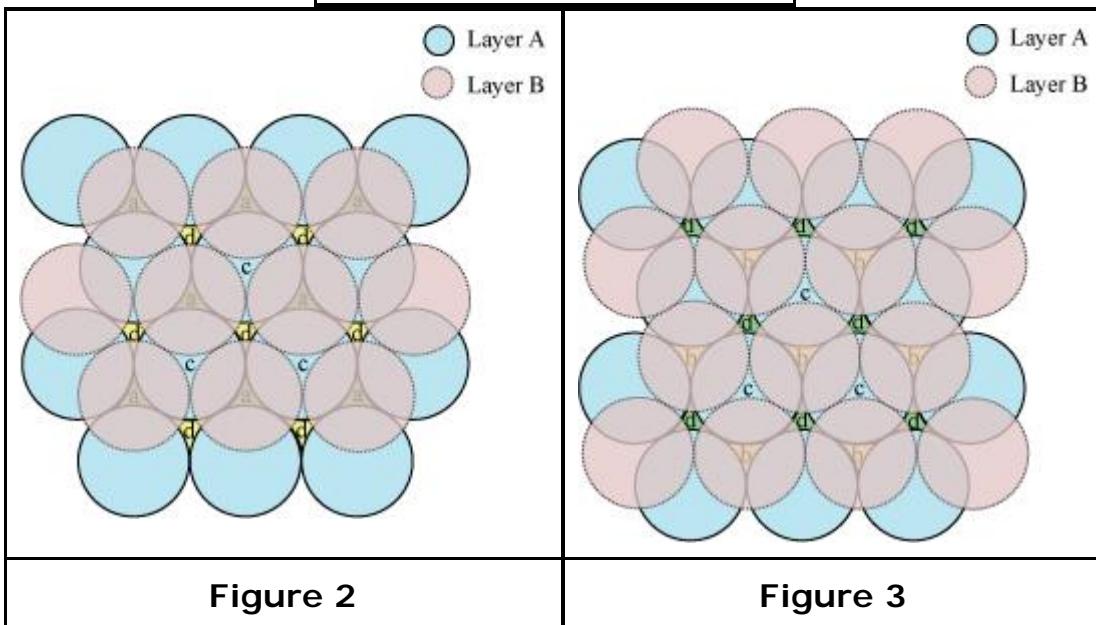


Figure 1



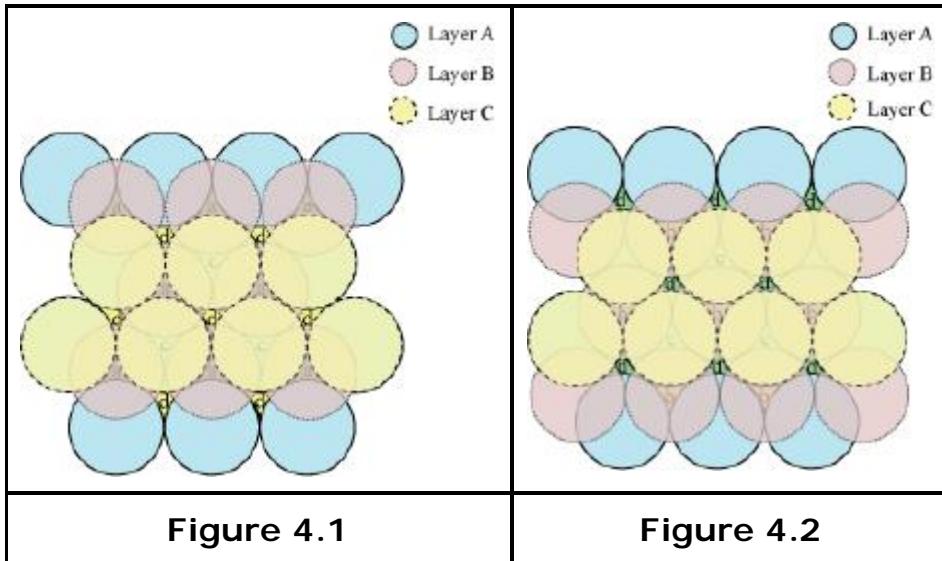
Now, the next layer can be placed over layer B in 2 ways.

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

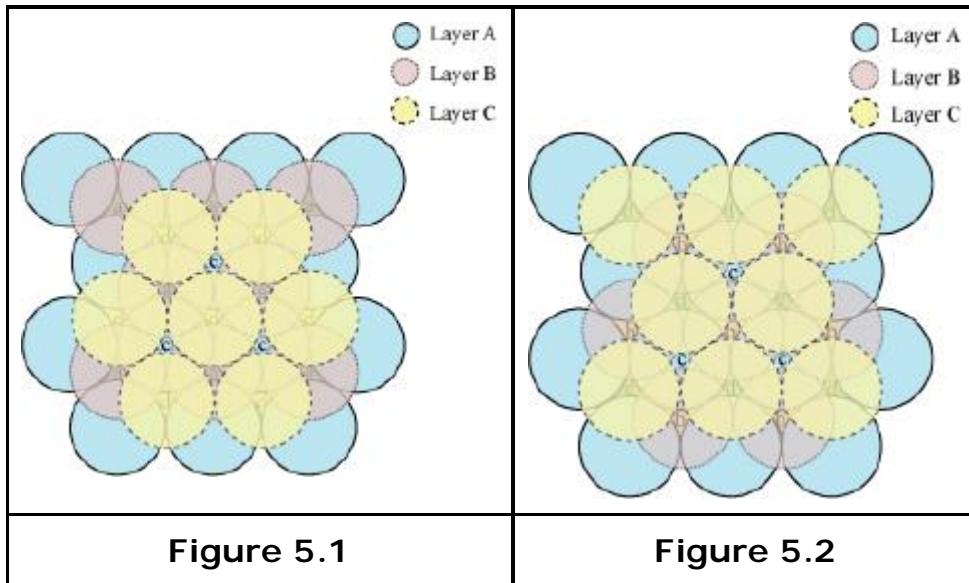
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spheres of layer A. Hence, we can say that the layers in hexagonal close-packing are arranged in an ABAB..... pattern.



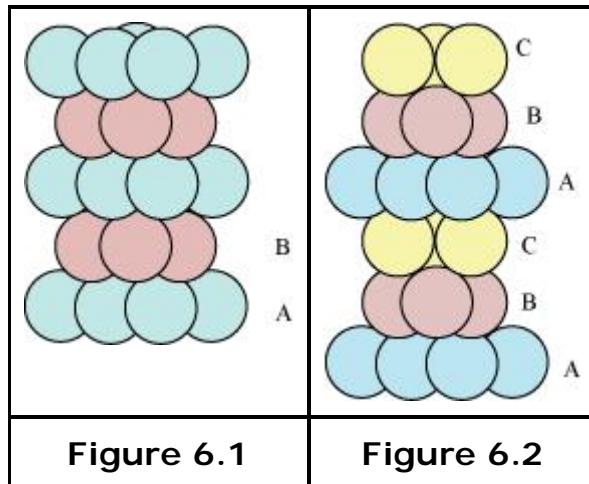
Case 2: When the third layer (layer C) is placed over layer B in such a manner that the spheres of layer C occupy the octahedral voids d.

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.



The side views of hcp and ccp are given in figures 6.1 and 6.2 respectively.

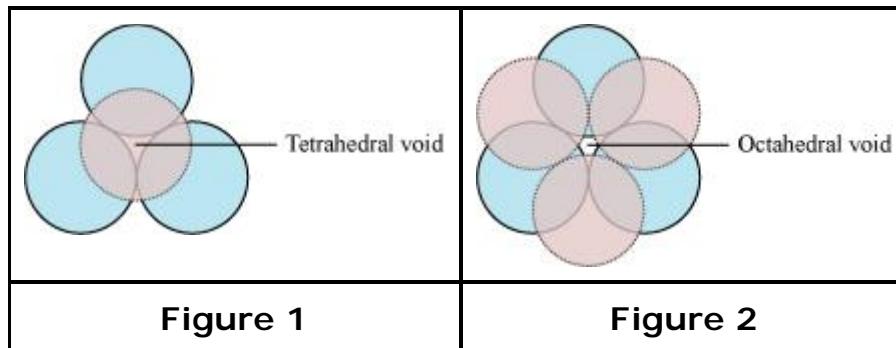
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(ii) The diagrammatic representation of the constituent particles (atoms, ions, or molecules) present in a crystal in a regular three-dimensional arrangement is called crystal lattice.

A unit cell is the smallest three-dimensional portion of a crystal lattice. When repeated again and again in different directions, it generates the entire crystal lattice.

(iii) A void surrounded by 4 spheres is called a tetrahedral void and a void surrounded by 6 spheres is called an octahedral void. Figure 1 represents a tetrahedral void and figure 2 represents an octahedral void.



Question 1.8:

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

(i) There are 14 (8 from the corners + 6 from the faces) lattice points in face-centred cubic.

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(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.

Question 1.9:

Explain

(i) The basis of similarities and differences between metallic and ionic crystals.

(ii) Ionic solids are hard and brittle.

(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.

Question 1.10:

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

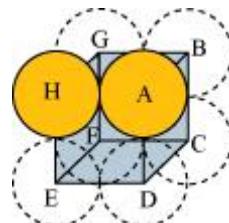
(i) simple cubic

(ii) body-centred cubic

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

(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.



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

So, we can write:

$$a = 2r$$

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.

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

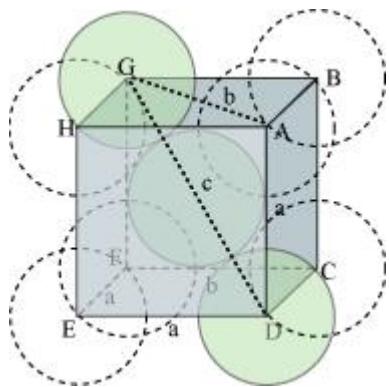
Therefore, volume of the occupied unit cell

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

Hence, packing efficiency

$$\begin{aligned} &= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100\% \\ &= \frac{1}{6}\pi \times 100\% \\ &= \frac{1}{6} \times \frac{22}{7} \times 100\% \\ &= 52.4\% \end{aligned}$$

(ii) Body-centred cubic



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

From ΔFED , we have:

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$$\begin{aligned} b^2 &= a^2 + a^2 \\ \Rightarrow b^2 &= 2a^2 \\ \Rightarrow b &= \sqrt{2}a \end{aligned}$$

Again, from ΔAFD , we have:

$$\begin{aligned} c^2 &= a^2 + b^2 \\ \Rightarrow c^2 &= a^2 + 2a^2 \quad (\text{Since } b^2 = 2a^2) \\ \Rightarrow c^2 &= 3a^2 \\ \Rightarrow c &= \sqrt{3}a \end{aligned}$$

Let the radius of the atom be r .

Length of the body diagonal, $c = 4r$

$$\begin{aligned} \Rightarrow \sqrt{3}a &= 4r \\ \Rightarrow a &= \frac{4r}{\sqrt{3}} \end{aligned}$$

$$\begin{aligned} r &= \frac{\sqrt{3}a}{4} \\ \text{or, } & \end{aligned}$$

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

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

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

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

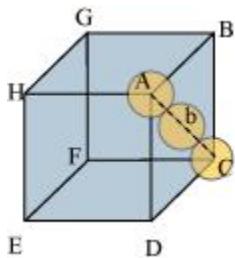
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$$= \frac{\frac{8}{3}\pi r^3}{\left(\frac{4}{\sqrt{3}}r\right)^3} \times 100\%$$

$$= \frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}}r^3} \times 100\% \\ = 68\%$$

(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 ΔABC , we have:

$$\begin{aligned} AC^2 &= BC^2 + AB^2 \\ \Rightarrow b^2 &= a^2 + a^2 \\ \Rightarrow b^2 &= 2a^2 \\ \Rightarrow b &= \sqrt{2a} \end{aligned}$$

Let r be the radius of the atom.

Now, from the figure, it can be observed that:

$$\begin{aligned} b &= 4r \\ \Rightarrow \sqrt{2a} &= 4r \\ \Rightarrow a &= 2\sqrt{2}r \end{aligned}$$

$$a^3 = (2\sqrt{2}r)^3$$

Now, volume of the cube,

We know that the number of atoms per unit cell is 4.

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

So, volume of the occupied unit cell

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

$$\begin{aligned} &= \frac{4\pi \frac{4}{3} r^3}{(2\sqrt{2}r)^3} \times 100\% \\ &= \frac{\frac{16}{3}\pi r^3}{16\sqrt{2}r^3} \times 100\% \end{aligned}$$

$$= 74\%$$

Question 1.11:

Silver crystallises in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3} , calculate the atomic mass of silver

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:

$$\begin{aligned} d &= \frac{z M}{a^3 N_A} \\ \Rightarrow M &= \frac{d a^3 N_A}{z} \\ &= \frac{10.5 \text{ g cm}^{-3} \times (4.077 \times 10^{-8} \text{ cm})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{4} \\ &= 107.13 \text{ gmol}^{-1} \end{aligned}$$

Therefore, atomic mass of silver = 107.13 u

Question 1.12:

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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?

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.

Question 1.13:

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.

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

Atomic mass, M = 93 g mol⁻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:

$$\begin{aligned} d &= \frac{z M}{a^3 N_A} \\ \Rightarrow a^3 &= \frac{z M}{d N_A} \\ &= \frac{2 \times 93 \text{ g mol}^{-1}}{8.55 \text{ g cm}^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1}} \\ &= 3.612 \times 10^{-23} \text{ cm}^3 \end{aligned}$$

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

For body-centred cubic unit cell:

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

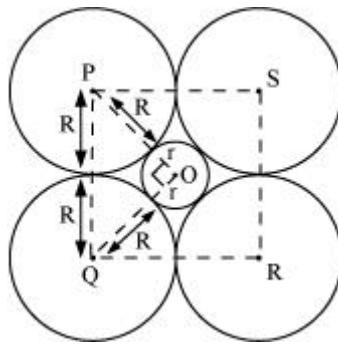
$$= 1.432 \times 10^{-8} \text{ cm}$$

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

$$= 14.32 \text{ nm}$$

Question 1.14:

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



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 ΔPOQ is right-angled

$$\angle POQ = 90^\circ$$

Now, applying Pythagoras theorem, we can write:

$$\begin{aligned} PQ^2 &= PO^2 + OQ^2 \\ \Rightarrow (2R)^2 &= (R+r)^2 + (R+r)^2 \\ \Rightarrow (2R)^2 &= 2(R+r)^2 \\ \Rightarrow 2R^2 &= (R+r)^2 \\ \Rightarrow \sqrt{2}R &= R+r \\ \Rightarrow r &= \sqrt{2}R - R \\ \Rightarrow r &= (\sqrt{2}-1)R \\ \Rightarrow r &= 0.414 R \end{aligned}$$

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Question 1.15:

Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3} .

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, $M = 63.5 \text{ g mol}^{-1}$

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

Applying the relation:

$$\begin{aligned} d &= \frac{zM}{a^3 N_A} \\ &= \frac{4 \times 63.5 \text{ g mol}^{-1}}{(3.61 \times 10^{-8} \text{ cm})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}} \\ &= 8.97 \text{ g cm}^{-3} \end{aligned}$$

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.

Question 1.16:

Analysis shows that nickel oxide has the formula $\text{Ni}_{0.98}\text{O}_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?

The formula of nickel oxide is $\text{Ni}_{0.98}\text{O}_{1.00}$.

Therefore, the ratio of the number of Ni atoms to the number of O atoms,
 $\text{Ni} : \text{O} = 0.98 : 1.00 = 98 : 100$

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 Ni^{2+} ions = $x(+2)$

= $+2x$

And, total charge on Ni^{3+} ions = $(98 - x)(+3)$

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$$= 294 - 3x$$

Since, the compound is neutral, we can write:

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

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

$$\Rightarrow x = 94$$

Therefore, number of Ni^{2+} ions = 94

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

$$= \frac{94}{98}$$

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

$$= 0.959$$

$$\text{Ni}^{3+} = \frac{4}{98}$$

And, fraction of nickel that exists as

$$= 0.041$$

Alternatively, fraction of nickel that exists as $\text{Ni}^{3+} = 1 - 0.959$

$$= 0.041$$

Question 1.17:

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

Semiconductors are substances having conductance in the intermediate range of 10^{-6} to 10^4 $\text{ohm}^{-1}\text{m}^{-1}$.

The two main types of semiconductors are:

(i) n -type semiconductor

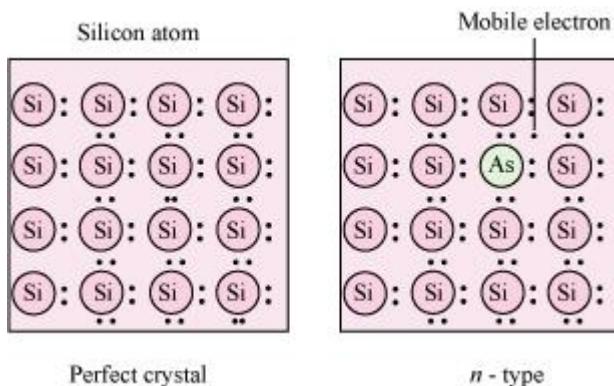
(ii) p -type semiconductor

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

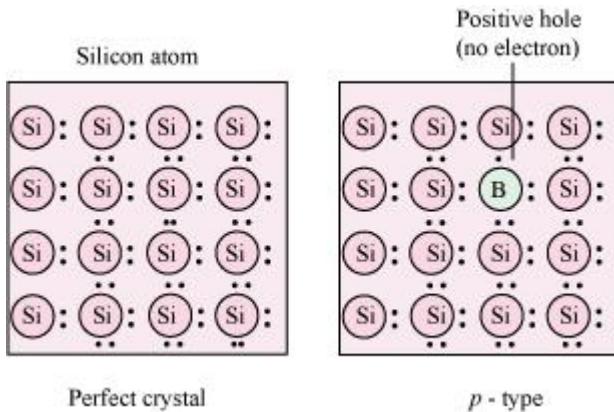
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electrons are used in the formation of four covalent bonds with four neighbouring Si or Ge atoms. The remaining fifth electron becomes delocalised and increases the conductivity of the doped Si or Ge.



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.



Question 1.18:

Non-stoichiometric cuprous oxide, Cu_2O 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?

In the cuprous oxide (Cu_2O) 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 O^{2-} .

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ions. This is because some Cu^+ ions have been replaced by Cu^{2+} ions. Every Cu^{2+} 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

Question 1.19:

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.

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.

$$= \frac{2}{3}x$$

So, number of ferric (Fe^{3+}) ions

Therefore, ratio of the number of Fe^{3+} ions to the number of O^{2-} ions,

$$\text{Fe}^{3+} : \text{O}^{2-} = \frac{2}{3}x : x$$

$$= \frac{2}{3} : 1$$

$$= 2 : 3$$

Hence, the formula of the ferric oxide is Fe_2O_3 .

Question 1.20:

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.

Question 1.20:

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.

(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). So, there will be an extra electron and the semiconductor generated will be an *n*-type semiconductor.

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Question 1.21:

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

For a face-centred unit cell:

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

It is given that the atomic radius, $r = 0.144 \text{ nm}$

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

$$= 0.407 \text{ nm}$$

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

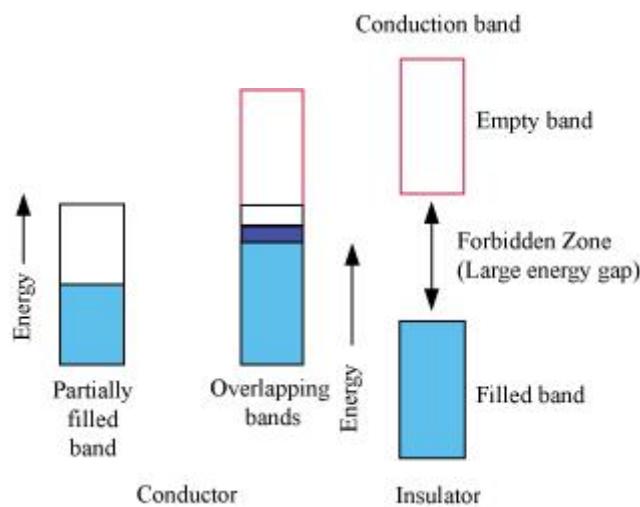
Question 1.22:

In terms of band theory, what is the difference

(i) Between a conductor and an insulator

(ii) Between a conductor and a semiconductor

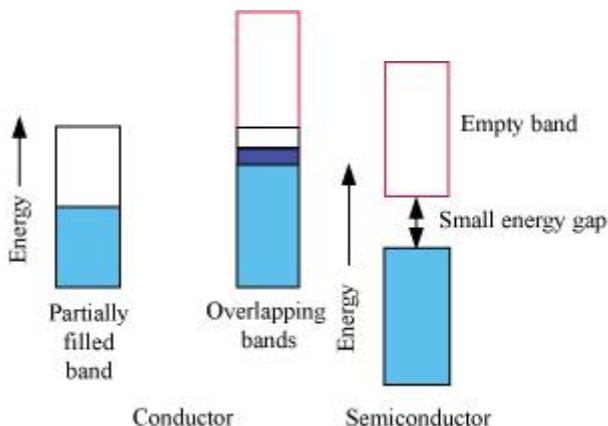
(i) The valence band of a conductor is partially-filled or it overlaps with a higher energy, unoccupied conduction band.



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.

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(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.

Question 1.23:

Explain the following terms with suitable examples:

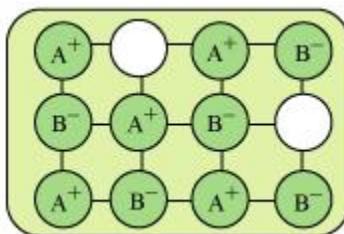
(i) Schottky defect

(ii) Frenkel defect

(iii) Interstitials and

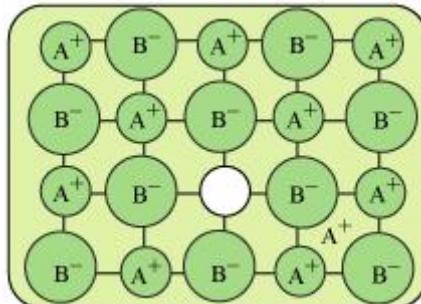
(iv) F-centres

(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 10^6 Schottky pairs per cm^3 at room temperature. Ionic substances containing similar-sized cations and anions show this type of defect. For example: NaCl, KCl, CsCl, AgBr, etc.

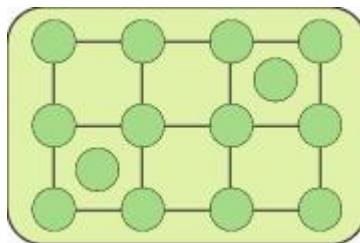


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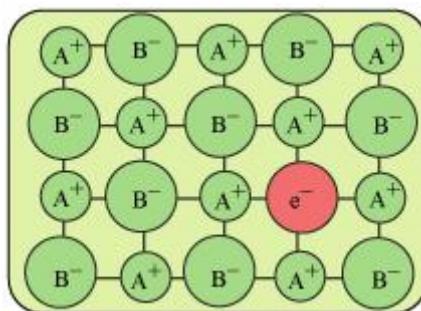
(ii) Frenkel defect: Ionic solids containing large differences in the sizes of ions show this type of defect. When the smaller ion (usually cation) is dislocated from its normal site to an interstitial site, Frenkel defect is created. It creates a vacancy defect as well as an interstitial defect. Frenkel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



Question 1.24:

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?

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(ii) How many unit cells are there in 1.00 cm^3 of aluminium?

(i) For cubic close-packed structure:

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

$$= 2\sqrt{2} \times 125 \text{ pm}$$

$$= 353.55 \text{ pm}$$

$$= 354 \text{ pm (approximately)}$$

(ii) Volume of one unit cell = $(354 \text{ pm})^3$

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

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

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

$$\text{Therefore, number of unit cells in } 1.00 \text{ cm}^3 = \frac{1.00 \text{ cm}^3}{4.4 \times 10^{-23} \text{ cm}^3}$$

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

Question 1.25:

If NaCl is doped with 10^{-3} mol % of SrCl₂, what is the concentration of cation vacancies?

It is given that NaCl is doped with 10^{-3} mol% of SrCl₂.

This means that 100 mol of NaCl is doped with 10^{-3} mol of SrCl₂.

$$\frac{10^{-3}}{100}$$

Therefore, 1 mol of NaCl is doped with 10^{-5} mol of SrCl₂

$$= 10^{-5} \text{ mol of SrCl}_2$$

Cation vacancies produced by one Sr²⁺ ion = 1

∴ Concentration of the cation vacancies

$$\begin{aligned} \text{produced by } 10^{-5} \text{ mol of Sr}^{2+} \text{ ions} &= 10^{-5} \times 6.022 \times 10^{23} \\ &= 6.022 \times 10^{18} \text{ mol}^{-1} \end{aligned}$$

Hence, the concentration of cation vacancies created by SrCl₂ is 6.022×10^{18} per mol of NaCl.

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Question 1.26:

Explain the following with suitable examples:

(i) Ferromagnetism

(ii) Paramagnetism

(iii) Ferrimagnetism

(iv) Antiferromagnetism

(v) 12-16 and 13-15 group compounds.

(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 CrO_2 .

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^{2+} , Fe^{3+} , and Cr^{3+} .

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 .

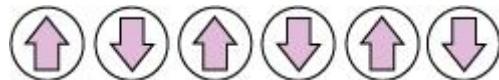
Ferrimagnetic substances are weakly attracted by a magnetic field as compared to ferromagnetic substances. On heating, these substances become paramagnetic.



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Schematic alignment of magnetic moments in ferrimagnetic substances

(iv) Antiferromagnetism: Antiferromagnetic substances have 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 group 15 elements. These compounds are prepared to stimulate average valence of four as in Ge or Si. Indium (III) antimonide (InSb), aluminium phosphide (AlP), 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.

SOLUTION : NCERT QUESTION ANSWER

SOLUTION

Question 2.1:

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

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

$$\begin{aligned} &= \frac{\text{Mass of } C_6H_6}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4} \times 100\% \\ &= \frac{22}{22 + 122} \times 100\% \\ &= 15.28\% \end{aligned}$$

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

$$\begin{aligned} &= \frac{\text{Mass of } CCl_4}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4} \times 100\% \\ &= \frac{122}{22 + 122} \times 100\% \\ &= 84.72\% \end{aligned}$$

Alternatively,

$$\begin{aligned} \text{Mass percentage of } CCl_4 &= (100 - 15.28)\% \\ &= 84.72\% \end{aligned}$$

Question 2.2:

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

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

$$\begin{aligned} \therefore \text{Mass of carbon tetrachloride} &= (100 - 30)\text{g} \\ &= 70 \text{ g} \end{aligned}$$

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

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

SOLUTION : NCERT QUESTION ANSWER

$$\text{C}_6\text{H}_6 = \frac{30}{78} \text{ mol}$$

∴ Number of moles of

$$= 0.3846 \text{ mol}$$

$$\text{Molar mass of carbon tetrachloride (CCl}_4) = 1 \times 12 + 4 \times 35.5$$

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

$$= \frac{70}{154} \text{ mol}$$

∴ Number of moles of CCl₄

$$= 0.4545 \text{ mol}$$

Thus, the mole fraction of C₆H₆ is given as:

$$\frac{\text{Number of moles of C}_6\text{H}_6}{\text{Number of moles of C}_6\text{H}_6 + \text{Number of moles of CCl}_4}$$
$$= \frac{0.3846}{0.3846 + 0.4545}$$

$$= 0.458$$

Question 2.3:

Calculate the molarity of each of the following solutions: (a) 30 g of Co(NO₃)₂. 6H₂O in 4.3 L of solution (b) 30 mL of 0.5 M H₂SO₄ diluted to 500 mL.

Molarity is given by:

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

(a) Molar mass of Co (NO₃)₂.6H₂O = 59 + 2 (14 + 3 × 16) + 6 × 18

$$= 291 \text{ g mol}^{-1}$$

$$= \frac{30}{291} \text{ mol}$$

∴ Moles of Co (NO₃)₂.6H₂O

$$= 0.103 \text{ mol}$$

$$= \frac{0.103 \text{ mol}}{4.3 \text{ L}}$$

Therefore, molarity

SOLUTION : NCERT QUESTION ANSWER

$$= 0.023 \text{ M}$$

(b) Number of moles present in 1000 mL of 0.5 M H_2SO_4 = 0.5 mol

$$\therefore \text{Number of moles present in } 30 \text{ mL of } 0.5 \text{ M } \text{H}_2\text{SO}_4 = \frac{0.5 \times 30}{1000} \text{ mol}$$

$$= 0.015 \text{ mol}$$

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

$$= 0.03 \text{ M}$$

Question 2.4:

Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution.

$$\text{Molar mass of urea } (\text{NH}_2\text{CONH}_2) = 2(1 \times 14 + 2 \times 1) + 1 \times 12 + 1 \times 16$$

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

0.25 molar aqueous solution of urea means:

$$1000 \text{ g of water contains } 0.25 \text{ mol} = (0.25 \times 60) \text{ g of urea}$$

$$= 15 \text{ g of urea}$$

That is,

$$(1000 + 15) \text{ g of solution contains } 15 \text{ g of urea}$$

$$= \frac{15 \times 2500}{1000 + 15} \text{ g}$$

Therefore, 2.5 kg (2500 g) of solution contains

$$= 36.95 \text{ g}$$

$$= 37 \text{ g of urea (approximately)}$$

Hence, mass of urea required = 37 g

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

Question 2.5:

SOLUTION : NCERT QUESTION ANSWER

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.

(a) Molar mass of KI = 39 + 127 = 166 g mol⁻¹

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

That is,

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

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

Therefore, molality of the solution

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

$$= 1.506 \text{ m}$$

$$= 1.51 \text{ m (approximately)}$$

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

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

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

$$= 83.19 \text{ mL}$$

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

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

Therefore, molarity of the solution

$$= 1.45 \text{ M}$$

$$= \frac{20}{166} = 0.12 \text{ mol}$$

(c) Moles of KI

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

Moles of water

SOLUTION : NCERT QUESTION ANSWER

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

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

$$= 0.0263$$

Question 2.6:

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

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.

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

$$= 55.56 \text{ mol}$$

$$\therefore \text{Mole fraction of } \text{H}_2\text{S}, x = \frac{\text{Moles of } \text{H}_2\text{S}}{\text{Moles of } \text{H}_2\text{S} + \text{Moles of water}}$$

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

$$= 0.0035$$

At STP, pressure (p) = 0.987 bar

According to Henry's law:

$$p = K_H x$$

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

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

$$= 282 \text{ bar}$$

Question 2.7:

SOLUTION : NCERT QUESTION ANSWER

Henry's law constant for CO₂ in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO₂ in 500 mL of soda water when packed under 2.5 atm CO₂ pressure at 298 K.

It is given that:

$$K_H = 1.67 \times 10^8 \text{ Pa}$$

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

$$= 2.533125 \times 10^5 \text{ Pa}$$

According to Henry's law:

$$p_{\text{CO}_2} = K_H x$$

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

$$= \frac{2.533125 \times 10^5}{1.67 \times 10^8}$$

$$= 0.00152$$

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

We can write,

[Since, n_{CO_2} is negligible as compared to $n_{\text{H}_2\text{O}}$]

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

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

$$= 27.78 \text{ mol of water}$$

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

Now,

$$p_A = p_A^0 x_A$$

$$p_B = p_B^0 x_B = p_B^0 (1 - x_A)$$

SOLUTION : NCERT QUESTION ANSWER

$$\frac{n_{CO_2}}{27.78} = 0.00152$$

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

Hence, quantity of CO₂ in 500 mL of soda water = (0.042 × 44)g

$$= 1.848 \text{ g}$$

Question 2.8:

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.

It is given that:

$$p_A^0 = 450 \text{ mm of Hg}$$

$$p_B^0 = 700 \text{ mm of Hg}$$

$$p_{\text{total}} = 600 \text{ mm of Hg}$$

From Raoult's law, we have:

Therefore, total pressure, $p_{\text{total}} = p_A + p_B$

$$\Rightarrow p_{\text{total}} = p_A^0 x_A + p_B^0 (1 - x_A)$$

$$\Rightarrow p_{\text{total}} = p_A^0 x_A + p_B^0 - p_B^0 x_A$$

$$\Rightarrow p_{\text{total}} = (p_A^0 - p_B^0)x_A + p_B^0$$

$$\Rightarrow 600 = (450 - 700)x_A + 700$$

$$\Rightarrow -100 = -250x_A$$

$$\Rightarrow x_A = 0.4$$

Therefore, $x_B = 1 - x_A$

$$= 1 - 0.4$$

$$= 0.6$$

SOLUTION : NCERT QUESTION ANSWER

$$\text{Now, } p_A = p_A^0 x_A$$

$$= 450 \times 0.4$$

$$= 180 \text{ mm of Hg}$$

$$p_B = p_B^0 x_B$$

$$= 700 \times 0.6$$

$$= 420 \text{ mm of Hg}$$

Now, in the vapour phase:

$$= \frac{p_A}{p_A + p_B}$$

Mole fraction of liquid A

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

$$= \frac{180}{600}$$

$$= 0.30$$

And, mole fraction of liquid B = 1 - 0.30

$$= 0.70$$

Question 2.9:

Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering

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, $w_2 = 50 \text{ g}$

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

Molecular weight of urea, $M_2 = 60 \text{ g mol}^{-1}$

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

SOLUTION : NCERT QUESTION ANSWER

Now, from Raoult's law, we have:

$$\begin{aligned}
 \frac{p_1^0 - p_1}{p_1^0} &= \frac{n_2}{n_1 + n_2} \\
 \Rightarrow \frac{p_1^0 - p_1}{p_1^0} &= \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1} + \frac{w_2}{M_2}} \\
 \Rightarrow \frac{23.8 - p_1}{23.8} &= \frac{\frac{50}{60}}{\frac{850}{18} + \frac{50}{60}} \\
 \Rightarrow \frac{23.8 - p_1}{23.8} &= \frac{0.83}{47.22 + 0.83} \\
 \Rightarrow \frac{23.8 - p_1}{23.8} &= 0.0173 \\
 \Rightarrow p_1 &= 23.4 \text{ mm of Hg}
 \end{aligned}$$

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

Question 2.10:

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.

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

$$= 0.37 \text{ K}$$

Mass of water, $w_1 = 500 \text{ g}$

Molar mass of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), $M_2 = 11 \times 12 + 22 \times 1 + 11 \times 16$

$$= 342 \text{ g mol}^{-1}$$

Molal elevation constant, $K_b = 0.52 \text{ K kg mol}^{-1}$

We know that:

SOLUTION : NCERT QUESTION ANSWER

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

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

$$= \frac{0.37 \times 342 \times 500}{0.52 \times 1000}$$

$$= 121.67 \text{ g (approximately)}$$

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.

Question 2.11:

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 . $K_f = 3.9 \text{ K kg mol}^{-1}$.

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, $\Delta T_f = 1.5 \text{ K}$

We know that:

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

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

$$= \frac{1.5 \times 176 \times 75}{3.9 \times 1000}$$

$$= 5.08 \text{ g (approx)}$$

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.

SOLUTION : NCERT QUESTION ANSWER

Question 2.12:

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.

It is given that:

$$\text{Volume of water, } V = 450 \text{ mL} = 0.45 \text{ L}$$

$$\text{Temperature, } T = (37 + 273) \text{ K} = 310 \text{ K}$$

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

Number of moles of the polymer,

We know that:

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

Osmotic pressure,

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

$$= 30.98 \text{ Pa}$$

$$= 31 \text{ Pa (approximately)}$$

Question 2.1:

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

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.

SOLUTION : NCERT QUESTION ANSWER

(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.

Question 2.2:

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

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.

Question 2.3:

Define the following terms:

(i) Mole fraction

(ii) Molality

(iii) Molarity

(iv) Mass percentage

(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.,

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all components}}$$

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:

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

SOLUTION : NCERT QUESTION ANSWER

(ii) Molality

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

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

(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:

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

Question 2.4:

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} ?

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.

$$\text{Molar mass of nitric acid (HNO}_3\text{)} = 1 \times 1 + 1 \times 14 + 3 \times 16 = 63 \text{ g mol}^{-1}$$

$$\text{Then, number of moles of HNO}_3 = \frac{68}{63} \text{ mol}$$

$$= 1.079 \text{ mol}$$

Given,

$$\text{Density of solution} = 1.504 \text{ g mL}^{-1}$$

SOLUTION : NCERT QUESTION ANSWER

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

$$= 66.49 \text{ mL}$$

$$= 66.49 \times 10^{-3} \text{ L}$$

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

$$= 16.23 \text{ M}$$

Question 2.5:

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 mL^{-1} , then what shall be the molarity of the solution?

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

Molar mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) = $6 \times 12 + 12 \times 1 + 6 \times 16 = 180 \text{ g mol}^{-1}$

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

$$= 0.056 \text{ mol}$$

$$\therefore \text{Molality of solution} = \frac{0.056 \text{ mol}}{0.09 \text{ kg}} = 0.62 \text{ m}$$

$$\text{Number of moles of water} = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}}$$

$$= 5 \text{ mol}$$

$$(x_g) = \frac{0.056}{0.056 + 5} \\ \Rightarrow \text{Mole fraction of glucose} = 0.011$$

$$\text{And, mole fraction of water } x_w = 1 - x_g$$

$$= 1 - 0.011$$

SOLUTION : NCERT QUESTION ANSWER

$$= 0.989$$

If the density of the solution is 1.2 g mL^{-1} , then the volume of the 100 g solution can be given as:

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

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

$$= 0.67 \text{ M}$$

Question 2.6:

How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and NaHCO_3 containing equimolar amounts of both?

Let the amount of Na_2CO_3 in the mixture be $x \text{ g}$.

Then, the amount of NaHCO_3 in the mixture is $(1 - x) \text{ g}$.

Molar mass of $\text{Na}_2\text{CO}_3 = 2 \times 23 + 1 \times 12 + 3 \times 16$

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

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

Molar mass of $\text{NaHCO}_3 = 1 \times 23 + 1 \times 1 \times 12 + 3 \times 16$

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

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

According to the question,

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

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

$$\Rightarrow 190x = 106$$

SOLUTION : NCERT QUESTION ANSWER

$$\Rightarrow x = 0.5579$$

$$= \frac{0.5579}{106} \text{ mol}$$

Therefore, number of moles of Na_2CO_3

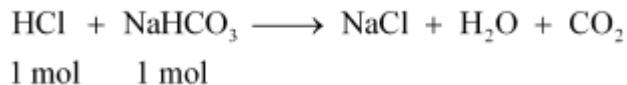
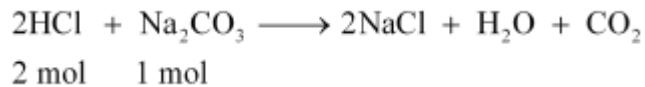
$$= 0.0053 \text{ mol}$$

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

And, number of moles of NaHCO_3

$$= 0.0053 \text{ mol}$$

HCl reacts with Na_2CO_3 and NaHCO_3 according to the following equation.



1 mol of Na_2CO_3 reacts with 2 mol of HCl.

Therefore, 0.0053 mol of Na_2CO_3 reacts with $2 \times 0.0053 \text{ mol} = 0.0106 \text{ mol}$.

Similarly, 1 mol of NaHCO_3 reacts with 1 mol of HCl.

Therefore, 0.0053 mol of NaHCO_3 reacts with 0.0053 mol of HCl.

Total moles of HCl required = $(0.0106 + 0.0053) \text{ mol}$

$$= 0.0159 \text{ mol}$$

In 0.1 M of HCl,

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

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

Therefore, 0.0159 mol of HCl is present in

$$= 159 \text{ mL of the solution}$$

Hence, 159 mL of 0.1 M of HCl is required to react completely with 1 g mixture of Na_2CO_3 and NaHCO_3 , containing equimolar amounts of both.

Question 2.7:

SOLUTION : NCERT QUESTION ANSWER

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

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

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

$$= 75 + 160$$

$$= 235 \text{ g}$$

Total amount of solution = $300 + 400 = 700 \text{ g}$

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

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,

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

$$= 66.43\%$$

Question 2.8:

An antifreeze solution is prepared from 222.6 g of ethylene glycol ($\text{C}_2\text{H}_4(\text{OH})_2$) 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?

Molar mass of ethylene glycol $[\text{C}_2\text{H}_4(\text{OH})_2] = 2 \times 12 + 6 \times 1 + 2 \times 16$

$$= 62 \text{ gmol}^{-1}$$

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

$$= 3.59 \text{ mol}$$

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

Therefore, molality of the solution

$$= 17.95 \text{ m}$$

SOLUTION : NCERT QUESTION ANSWER

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

$$= 422.6 \text{ g}$$

Given,

Density of the solution = 1.072 g mL^{-1}

$$\therefore \text{Volume of the solution} = \frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}}$$

$$= 394.22 \text{ mL}$$

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

$$\Rightarrow \text{Molarity of the solution} = \frac{3.59 \text{ mol}}{0.39422 \times 10^{-3} \text{ L}}$$

$$= 9.11 \text{ M}$$

Question 2.9:

A sample of drinking water was found to be severely contaminated with chloroform (CHCl_3) 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.

(i) 15 ppm (by mass) means 15 parts per million (10^6) of the solution.

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

$$= 1.5 \times 10^{-5} \%$$

(ii) Molar mass of chloroform (CHCl_3) = $1 \times 12 + 1 \times 1 + 3 \times 35.5$

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

Now, according to the question,

15 g of chloroform is present in 10^6 g of the solution.

i.e., 15 g of chloroform is present in $(10^6 - 15) \approx 10^6$ g of water.

SOLUTION : NCERT QUESTION ANSWER

$$\therefore \text{Molality of the solution} = \frac{\frac{15}{119.5} \text{ mol}}{10^6 \times 10^{-3} \text{ kg}} \\ = 1.26 \times 10^{-4} \text{ m}$$

Question 2.10:

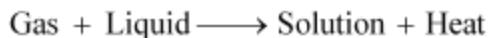
What role does the molecular interaction play in a solution of alcohol and water?

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.

Question 2.11:

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

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.

Question 2.12:

State Henry's law and mention some important applications?

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 CO_2 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

SOLUTION : NCERT QUESTION ANSWER

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.

Question 2.13:

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?

$$\text{Molar mass of ethane (C}_2\text{H}_6\text{)} = 2 \times 12 + 6 \times 1$$

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

$$\therefore \text{Number of moles present in } 6.56 \times 10^{-3} \text{ g of ethane} = \frac{6.56 \times 10^{-3}}{30}$$
$$= 2.187 \times 10^{-3} \text{ mol}$$

Let the number of moles of the solvent be x .

According to Henry's law,

$$p = K_H x$$

$$\Rightarrow 1 \text{ bar} = K_H \cdot \frac{2.187 \times 10^{-3}}{2.187 \times 10^{-3} + x}$$

$$\Rightarrow 1 \text{ bar} = K_H \frac{2.187 \times 10^{-3}}{x} \quad (\text{Since } x \gg 2.187 \times 10^{-3})$$

$$\Rightarrow K_H = \frac{x}{2.187 \times 10^{-3}} \text{ bar}$$

$$\text{Number of moles present in } 5.00 \times 10^{-2} \text{ g of ethane} = \frac{5.00 \times 10^{-2}}{30} \text{ mol}$$

$$= 1.67 \times 10^{-3} \text{ mol}$$

SOLUTION : NCERT QUESTION ANSWER

According to Henry's law,

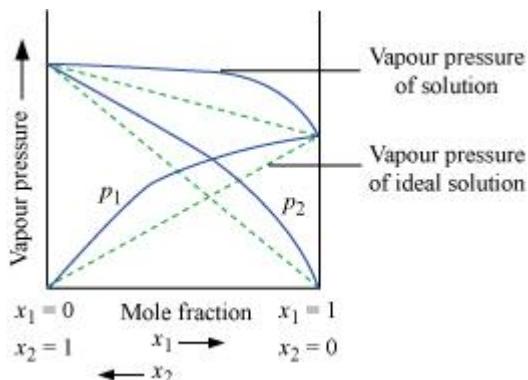
$$\begin{aligned}
 p &= K_H x \\
 &= \frac{x}{2.187 \times 10^{-3}} \times \frac{1.67 \times 10^{-3}}{(1.67 \times 10^{-3}) + x} \\
 &= \frac{x}{2.187 \times 10^{-3}} \times \frac{1.67 \times 10^{-3}}{x} \quad (\text{Since, } x \gg 1.67 \times 10^{-3}) \\
 &= 0.764 \text{ bar}
 \end{aligned}$$

Hence, partial pressure of the gas shall be 0.764 bar.

Question 2.14:

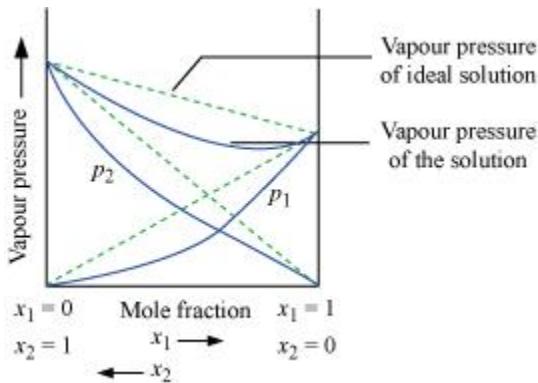
What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{\text{sol}}H$ related to positive and negative deviations from Raoult's law?

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

SOLUTION : NCERT QUESTION ANSWER



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.

$$\Delta_{\text{sol}}H = 0$$

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

$$\therefore \Delta_{\text{sol}}H = \text{Positive}$$

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

$$\therefore \Delta_{\text{sol}}H = \text{Negative}$$

Question 2.15:

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?

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 g mol⁻¹

According to Raoult's law,

SOLUTION : NCERT QUESTION ANSWER

$$\begin{aligned}
 \frac{p_1^0 - p_1}{p_1^0} &= \frac{w_2 \times M_1}{M_2 \times w_1} \\
 \Rightarrow \frac{1.013 - 1.004}{1.013} &= \frac{2 \times 18}{M_2 \times 98} \\
 \Rightarrow \frac{0.009}{1.013} &= \frac{2 \times 18}{M_2 \times 98} \\
 \Rightarrow M_2 &= \frac{1.013 \times 2 \times 18}{0.009 \times 98} \\
 &= 41.35 \text{ g mol}^{-1}
 \end{aligned}$$

Hence, the molar mass of the solute is 41.35 g mol^{-1} .

Question 2.16:

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?

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

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

We know that,

$$\text{Molar mass of heptane (C}_7\text{H}_{16}\text{)} = 7 \times 12 + 16 \times 1$$

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

$$\therefore \text{Number of moles of heptane} = \frac{26}{100} \text{ mol}$$

$$= 0.26 \text{ mol}$$

$$\text{Molar mass of octane (C}_8\text{H}_{18}\text{)} = 8 \times 12 + 18 \times 1$$

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

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

$$= 0.31 \text{ mol}$$

SOLUTION : NCERT QUESTION ANSWER

$$x_1 = \frac{0.26}{0.26 + 0.31}$$

Mole fraction of heptane,

$$= 0.456$$

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

$$= 0.544$$

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

$$= 0.456 \times 105.2$$

$$= 47.97 \text{ kPa}$$

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

$$= 0.544 \times 46.8$$

$$= 25.46 \text{ kPa}$$

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

$$= 47.97 + 25.46$$

$$= 73.43 \text{ kPa}$$

Question 2.17:

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

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

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

$$= 55.56 \text{ mol}$$

Therefore, mole fraction of the solute in the solution is

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

It is given that,

SOLUTION : NCERT QUESTION ANSWER

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,

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

$$\Rightarrow 12.3 - p_1 = 0.2177$$

$$\Rightarrow p_1 = 12.0823$$

$$= 12.08 \text{ kPa (approximately)}$$

Hence, the vapour pressure of the solution is 12.08 kPa

Question 2.18:

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%.

Let the vapour pressure of pure octane be p_1^0 .

Then, the vapour pressure of the octane after dissolving the non-volatile solute is

$$\frac{80}{100} p_1^0 = 0.8 p_1^0.$$

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,

SOLUTION : NCERT QUESTION ANSWER

$$\begin{aligned}
 \frac{p_1^0 - p_1}{p_1^0} &= \frac{w_2 \times M_1}{M_2 \times w_1} \\
 \Rightarrow \frac{p_1^0 - 0.8p_1^0}{p_1^0} &= \frac{w_2 \times 114}{40 \times 114} \\
 \Rightarrow \frac{0.2p_1^0}{p_1^0} &= \frac{w_2}{40} \\
 \Rightarrow 0.2 &= \frac{w_2}{40} \\
 \Rightarrow w_2 &= 8 \text{ g}
 \end{aligned}$$

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

Question 2.19:

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.

(i) Let, the molar mass of the solute be $M \text{ g mol}^{-1}$

$$n_1 = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ mol}$$

Now, the no. of moles of solvent (water),

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

And, the no. of moles of solute,

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

Applying the relation:

SOLUTION : NCERT QUESTION ANSWER

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

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

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

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

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

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

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

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

After the addition of 18 g of water:

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

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

Again, applying the relation:

SOLUTION : NCERT QUESTION ANSWER

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

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

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

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

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

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

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

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

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

SOLUTION : NCERT QUESTION ANSWER

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

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

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

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

$$\Rightarrow 3M = 69$$

$$\Rightarrow M = 23\text{ u}$$

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.

Question 2.20:

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.

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

$$= 2.15 \text{ K}$$

$$\text{Molar mass of sugar (C}_{12}\text{H}_{22}\text{O}_{11}\text{)} = 12 \times 12 + 22 \times 1 + 11 \times 16$$

$$= 342 \text{ g mol}^{-1}$$

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

SOLUTION : NCERT QUESTION ANSWER

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

Now, number of moles of cane sugar

$$= 0.0146 \text{ mol}$$

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

Therefore, molality of the solution,

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

Applying the relation,

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

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

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

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

$$\text{Molar mass of glucose (C}_6\text{H}_{12}\text{O}_6) = 6 \times 12 + 12 \times 1 + 6 \times 16$$

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

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

$$= \frac{5}{180} \text{ mol}$$

\therefore Number of moles of glucose

$$= 0.0278 \text{ mol}$$

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

Therefore, molality of the solution,

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

Applying the relation,

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

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

$$= 4.09 \text{ K (approximately)}$$

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

SOLUTION : NCERT QUESTION ANSWER

Question 2.21:

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 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate atomic masses of A and B.

We know that,

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

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

$$= 110.87 \text{ g mol}^{-1}$$

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

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

Now, we have the molar masses of AB_2 and AB_4 as $110.87 \text{ g mol}^{-1}$ and $196.15 \text{ g mol}^{-1}$ respectively.

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

Now, we can write:

$$x + 2y = 110.87 \quad (\text{i})$$

$$x + 4y = 196.15 \quad (\text{ii})$$

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.

SOLUTION : NCERT QUESTION ANSWER

Question 2.22:

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?

Here,

$$T = 300 \text{ K}$$

$$\pi = 1.52 \text{ bar}$$

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

Applying the relation,

$$\pi = CRT$$

$$\Rightarrow C = \frac{\pi}{RT}$$
$$= \frac{1.52 \text{ bar}}{0.083 \text{ bar L K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$
$$= 0.061 \text{ mol}$$

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

Question 2.23:

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

(i) n-hexane and n-octane

(ii) I₂ and CCl₄

(iii) NaClO₄ and water

(iv) methanol and acetone

(v) acetonitrile (CH₃CN) and acetone (C₃H₆O).

(i) Van der Wall's forces of attraction.

(ii) Van der Wall's forces of attraction.

(iii) Ion-dipole interaction.

SOLUTION : NCERT QUESTION ANSWER

(iv) Dipole-dipole interaction.

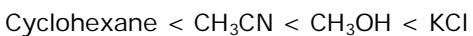
(v) Dipole-dipole interaction.

Question 2.24:

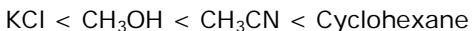
Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl, CH₃OH, CH₃CN.

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:



Therefore, the order of increasing solubility is:



Question 2.25:

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

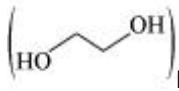
(i) phenol (ii) toluene (iii) formic acid

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

(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 (C₅H₁₁OH) has polar –OH group, but it also contains a very bulky non-polar –C₅H₁₁ group. Thus, pentanol is partially soluble in water.

Question 2.26:

SOLUTION : NCERT QUESTION ANSWER

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.

$$\text{Number of moles present in } 92 \text{ g of } \text{Na}^+ \text{ ions} = \frac{92 \text{ g}}{23 \text{ g mol}^{-1}}$$
$$= 4 \text{ mol}$$

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

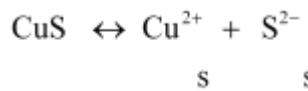
$$= 4 \text{ m}$$

Question 2.27:

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

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

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



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

$$= s \times s$$

$$= s^2$$

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

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

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

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

Question 2.28:

Calculate the mass percentage of aspirin ($\text{C}_9\text{H}_8\text{O}_4$) in acetonitrile (CH_3CN) when 6.5 g of $\text{C}_9\text{H}_8\text{O}_4$ is dissolved in 450 g of CH_3CN .

SOLUTION : NCERT QUESTION ANSWER

6.5 g of $\text{C}_9\text{H}_8\text{O}_4$ is dissolved in 450 g of CH_3CN .

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

$$= 456.5 \text{ g}$$

$$= \frac{6.5}{456.5} \times 100\%$$

Therefore, mass percentage of $\text{C}_9\text{H}_8\text{O}_4$

$$= 1.424\%$$

Question 2.29:

Nalorphene ($\text{C}_{19}\text{H}_{21}\text{NO}_3$), similar to morphine, is used to combat withdrawal

symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg.

Calculate the mass of 1.5×10^{-3} m aqueous solution required for the above dose.

The molar mass of nalorphene ($\text{C}_{19}\text{H}_{21}\text{NO}_3$) is given as:

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

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

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

$$= 0.4665 \text{ g}$$

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

$$= 1000.4665 \text{ g}$$

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

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

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

$$= 3.22 \text{ g}$$

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

SOLUTION : NCERT QUESTION ANSWER

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

Question 2.30:

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

0.15 M solution of benzoic acid in methanol means,

1000 mL of solution contains 0.15 mol of benzoic acid

$$\frac{0.15 \times 250}{1000}$$

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

= 0.0375 mol of benzoic acid

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

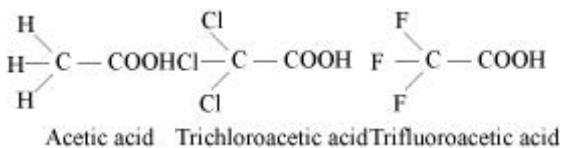
= 122 g mol⁻¹

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

= 4.575 g

Question 2.31:

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.



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

Question 2.32:

Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$

SOLUTION : NCERT QUESTION ANSWER

K kg mol^{-1} .

$$\begin{aligned}\text{Molar mass of } \text{CH}_3\text{CH}_2\text{CHClCOOH} &= 15+14+13+35.5+12+16+16+1 \\ &= 122.5 \text{ g mol}^{-1}\end{aligned}$$

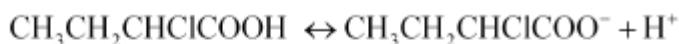
$$\begin{aligned}\text{CH}_3\text{CH}_2\text{CHClCOOH} &= \frac{10 \text{ g}}{122.5 \text{ g mol}^{-1}} \\ \therefore \text{No. of moles present in 10 g of} \\ &= 0.0816 \text{ mol}\end{aligned}$$

It is given that 10 g of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$ is added to 250 g of water.

$$\begin{aligned}&= \frac{0.0186}{250} \times 1000 \\ \therefore \text{Molality of the solution,} \\ &= 0.3264 \text{ mol kg}^{-1}\end{aligned}$$

Let α be the degree of dissociation of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$.

$\text{CH}_3\text{CH}_2\text{CHClCOOH}$ undergoes dissociation according to the following equation:



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

$$\therefore K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)}$$

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

Since α is very small with respect to 1, $1 - \alpha \approx 1$

$$\begin{aligned}\text{Now, } K_a &= \frac{C\alpha^2}{1}\end{aligned}$$

SOLUTION : NCERT QUESTION ANSWER

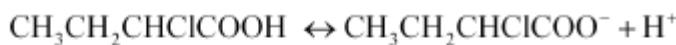
$$\Rightarrow K_a = C\alpha^2$$

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

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

$$= 0.0655$$

Again,



Initial moles	1	0	0
At equilibrium	1 - α	α	α

$$\text{Total moles of equilibrium} = 1 - \alpha + \alpha + \alpha$$

$$= 1 + \alpha$$

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

$$= 1 + \alpha$$

$$= 1 + 0.0655$$

$$= 1.0655$$

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

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

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

$$= 0.65 \text{ K}$$

Question 2.33:

19.5 g of CH_2FCOOH 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

It is given that:

SOLUTION : NCERT QUESTION ANSWER

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

$$w_2 = 19.5 \text{ g}$$

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

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

We know that:

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

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

$$= 72.54 \text{ g mol}^{-1}$$

Therefore, observed molar mass of CH_2FCOOH , $(M_2)_{\text{obs}} = 72.54 \text{ g mol}^{-1}$

The calculated molar mass of CH_2FCOOH is:

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

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

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

Therefore, van't Hoff factor,

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

$$= 1.0753$$

Let α be the degree of dissociation of CH_2FCOOH

	$\text{CH}_2\text{FCOOH} \leftrightarrow \text{CH}_2\text{FCOO}^- + \text{H}^+$		
Initial conc.	$C \text{ mol L}^{-1}$	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$
			Total = $C(1+\alpha)$

SOLUTION : NCERT QUESTION ANSWER

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

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

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

$$= 1.0753 - 1$$

$$= 0.0753$$

Now, the value of K_a is given as:

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

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

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

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

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

$$= 0.5 \text{ M}$$

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

Therefore,

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

$$= \frac{0.5 \times 0.00567}{0.9247}$$

$$= 0.00307 \text{ (approximately)}$$

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

Question 2.34:

SOLUTION : NCERT QUESTION ANSWER

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

Vapour pressure of water, $p_1^0 = 17.535 \text{ mm of Hg}$

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

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

We know that,

Molar mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), $M_2 = 6 \times 12 + 12 \times 1 + 6 \times 16$

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

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,

$$= 0.139 \text{ mol}$$

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

And, number of moles of water,

$$= 25 \text{ mol}$$

We know that,

$$\begin{aligned} \frac{p_1^0 - p_1}{p_1^0} &= \frac{n_1}{n_2 + n_1} \\ \Rightarrow \frac{17.535 - p_1}{17.535} &= \frac{0.139}{0.139 + 25} \\ \Rightarrow 17.535 - p_1 &= \frac{0.139 \times 17.535}{25.139} \end{aligned}$$

$$\Rightarrow 17.535 - p_1 = 0.097$$

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

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

Question 2.35:

SOLUTION : NCERT QUESTION ANSWER

Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm Hg.
Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

Here,

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

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

According to Henry's law,

$$p = k_H x$$

$$\begin{aligned} \Rightarrow x &= \frac{p}{k_H} \\ &= \frac{760 \text{ mm Hg}}{4.27 \times 10^5 \text{ mm Hg}} \\ &= 177.99 \times 10^{-5} \\ &= 178 \times 10^{-5} \text{ (approximately)} \end{aligned}$$

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

Question 2.36:

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.

$$\text{Number of moles of liquid A, } n_A = \frac{100}{140} \text{ mol}$$

$$= 0.714 \text{ mol}$$

$$\text{Number of moles of liquid B, } n_B = \frac{1000}{180} \text{ mol}$$

$$= 5.556 \text{ mol}$$

$$\text{Then, mole fraction of A, } x_A = \frac{n_A}{n_A + n_B}$$

SOLUTION : NCERT QUESTION ANSWER

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

$$= 0.114$$

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

$$= 0.886$$

Vapour pressure of pure liquid B, $p_B^0 = 500$ torr

Therefore, vapour pressure of liquid B in the solution,

$$p_B = p_B^0 x_B$$

$$= 500 \times 0.886$$

$$= 443 \text{ torr}$$

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

\therefore Vapour pressure of liquid A in the solution,

$$p_A = p_{\text{total}} - p_B$$

$$= 475 - 443$$

$$= 32 \text{ torr}$$

Now,

$$p_A = p_A^0 x_A$$

$$\Rightarrow p_A^0 = \frac{p_A}{x_A}$$
$$= \frac{32}{0.114}$$

$$= 280.7 \text{ torr}$$

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

Question 2.37:

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

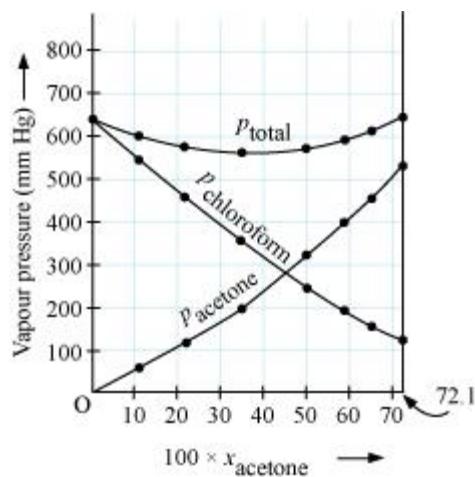
SOLUTION : NCERT QUESTION ANSWER

p_{total} ', $p_{\text{chloroform}}$ ' and p_{acetone} as a function of x_{acetone} . The experimental data observed for different compositions of mixture is.

100 $\times x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{\text{acetone}} / \text{mm Hg}$	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}} / \text{m m Hg}$	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

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
$p_{\text{acetone}} / \text{mm Hg}$	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}} / \text{m m Hg}$	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
$p_{\text{total}} (\text{mm Hg})$	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.

Question 2.38:

SOLUTION : NCERT QUESTION ANSWER

Benzene and toluene form ideal solution over the entire range of composition.

The vapour pressure of pure benzene and naphthalene 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.

$$\text{Molar mass of benzene } (\text{C}_6\text{H}_6) = 6 \times 12 + 6 \times 1$$

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

$$\text{Molar mass of toluene } (\text{C}_6\text{H}_5\text{CH}_3) = 7 \times 12 + 8 \times 1$$

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

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

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

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

$$\text{And, mole fraction of toluene, } x_t = 1 - 0.486 = 0.514$$

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

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

$$\text{Therefore, partial vapour pressure of benzene, } p_b = x_b \times p_b^0$$

$$= 0.486 \times 50.71$$

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

$$\text{And, partial vapour pressure of toluene, } p_t = x_t \times p_t^0$$

SOLUTION : NCERT QUESTION ANSWER

$$= 0.514 \times 32.06$$

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

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

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

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

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

$$= 0.599$$

$$= 0.6$$

Question 2.39:

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 K if the

Henry's law constants for oxygen and nitrogen are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.

Percentage of oxygen (O_2) 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,

$$\text{Partial pressure of oxygen, } p_{O_2} = \frac{20}{100} \times 7600 \text{ mm Hg}$$

$$= 1520 \text{ mm Hg}$$

SOLUTION : NCERT QUESTION ANSWER

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

Partial pressure of nitrogen,

$$= 6004 \text{ mmHg}$$

Now, according to Henry's law:

$$p = K_H \cdot x$$

For oxygen:

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

For nitrogen:

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

Hence, the mole fractions of oxygen and nitrogen in water are 4.61×10^{-5} and 9.22×10^{-5} respectively.

Question 2.40:

Determine the amount of CaCl_2 ($i = 2.47$) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27°C .

We know that,

$$\begin{aligned} \pi &= i \frac{n}{V} RT \\ \Rightarrow \pi &= i \frac{w}{MV} RT \\ \Rightarrow w &= \frac{\pi MV}{i RT} \end{aligned}$$

SOLUTION : NCERT QUESTION ANSWER

$$\pi = 0.75 \text{ atm}$$

$$V = 2.5 \text{ L}$$

$$i = 2.47$$

$$T = (27 + 273) \text{ K} = 300 \text{ K}$$

Here,

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

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

$$= 111 \text{ g mol}^{-1}$$

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

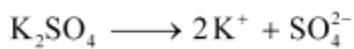
$$= 3.42 \text{ g}$$

Hence, the required amount of CaCl_2 is 3.42 g.

Question 2.41:

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

When K_2SO_4 is dissolved in water, K^+ and SO_4^{2-} ions are produced.



Total number of ions produced = 3

$$\therefore i = 3$$

Given,

$$w = 25 \text{ mg} = 0.025 \text{ g}$$

$$V = 2 \text{ L}$$

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

Also, we know that:

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

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

SOLUTION : NCERT QUESTION ANSWER

Appling the following relation,

$$\begin{aligned}\pi &= i \frac{n}{v} RT \\&= i \frac{w}{M} \frac{1}{v} RT \\&= 3 \times \frac{0.025}{174} \times \frac{1}{2} \times 0.0821 \times 298 \\&= 5.27 \times 10^{-3} \text{ atm}\end{aligned}$$

ELECTROCHEMISTRY NCERT SOLUTION

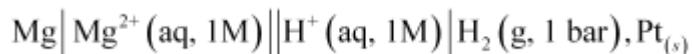
ELECTROCHEMISTRY

Question 3.1:

How would you determine the standard electrode potential of the system $Mg^{2+} | Mg$?

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

A cell, consisting of $Mg | MgSO_4 (aq, 1 \text{ M})$ as the anode and the standard hydrogen electrode as the cathode, is set up.



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_R^\ominus for the standard hydrogen electrode is zero.

$$\therefore E^\ominus = 0 - E_L^\ominus$$

$$= -E_L^\ominus$$

Question 3.2:

Can you store copper sulphate solutions in a zinc pot?

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.

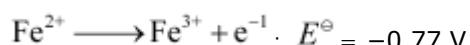


Hence, copper sulphate solution cannot be stored in a zinc pot.

Question 3.3:

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

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

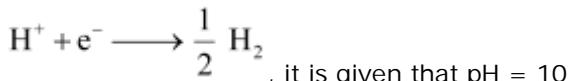


ELECTROCHEMISTRY NCERT SOLUTION

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.

Question 3.4:

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



For hydrogen electrode, , it is given that pH = 10

$$\therefore [\text{H}^+] = 10^{-10} \text{ M}$$

Now, using Nernst equation:

$$H_{\left(\text{H}^+/\frac{1}{2}\text{H}_2\right)} = E_{\left(\text{H}^+/\frac{1}{2}\text{H}_2\right)}^\ominus - \frac{RT}{nF} \ln \left[\frac{1}{[\text{H}^+]} \right]$$

$$= E_{\left(\text{H}^+/\frac{1}{2}\text{H}_2\right)}^\ominus - \frac{0.0591}{1} \log \left[\frac{1}{[\text{H}^+]} \right]$$

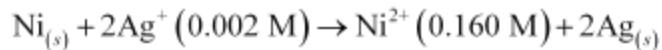
$$= 0 - \frac{0.0591}{1} \log \left[\frac{1}{10^{-10}} \right]$$

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

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

Question 3.5:

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



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

Applying Nernst equation we have:

ELECTROCHEMISTRY NCERT SOLUTION

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

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

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

$$= 1.05 - 0.02955 \log 4 \times 10^4$$

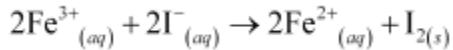
$$= 1.05 - 0.02955 (\log 10000 + \log 4)$$

$$= 1.05 - 0.02955 (4 + 0.6021)$$

$$= 0.914 \text{ V}$$

Question 3.6:

The cell in which the following reactions occurs:



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

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

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

We know that:

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

$$= -2 \times 96487 \times 0.236$$

$$= -45541.864 \text{ J mol}^{-1}$$

$$= -45.54 \text{ kJ mol}^{-1}$$

$$\text{Again, } \Delta_r G^{\ominus} = -2.303RT \log K_c$$

ELECTROCHEMISTRY NCERT SOLUTION

$$\Rightarrow \log K_c = -\frac{\Delta_r G^\ominus}{2.303 RT}$$
$$= -\frac{-45.54 \times 10^3}{2.303 \times 8.314 \times 298}$$
$$= 7.981$$
$$\therefore K_c = \text{Antilog } (7.981)$$
$$= 9.57 \times 10^7$$

Question 3.7:

Why does the conductivity of a solution decrease with dilution?

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.

Question 3.8:

Suggest a way to determine the Λ_m^\ominus value of water.

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

$$\begin{aligned}\Lambda_m^\ominus(\text{H}_2\text{O}) &= \lambda_{\text{H}^+}^\ominus + \lambda_{\text{OH}^-}^\ominus \\ &= (\lambda_{\text{H}^+}^\ominus + \lambda_{\text{Cl}^-}^\ominus) + (\lambda_{\text{Na}^+}^\ominus + \lambda_{\text{OH}^-}^\ominus) - (\lambda_{\text{Na}^+}^\ominus + \lambda_{\text{Cl}^-}^\ominus) \\ \Lambda_m^\ominus(\text{HCl}) + \Lambda_m^\ominus(\text{NaOH}) - \Lambda_m^\ominus(\text{NaCl})\end{aligned}$$

Hence, by knowing the Λ_m^\ominus values of HCl, NaOH, and NaCl, the Λ_m^\ominus value of water can be determined

Question 3.9:

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 $\lambda^\circ(\text{H}^+) =$

ELECTROCHEMISTRY NCERT SOLUTION

= 349.6 S cm² mol⁻¹ and λ° (HCOO⁻) = 54.6 S cm² mol

$$C = 0.025 \text{ mol L}^{-1}$$

$$\Lambda_m = 46.1 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\lambda^{\circ}(H^+) = 349.6 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\lambda^{\circ}(HCOO^-) = 54.6 \text{ Scm}^2 \text{ mol}^{-1}$$

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

$$= 349.6 + 54.6$$

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

Now, degree of dissociation:

$$\begin{aligned}\alpha &= \frac{\Lambda_m(HCOOH)}{\Lambda_m^{\circ}(HCOOH)} \\ &= \frac{46.1}{404.2} \\ &= 0.114 (\text{approximately})\end{aligned}$$

Thus, dissociation constant:

$$\begin{aligned}K &= \frac{c \alpha^2}{(1-\alpha)} \\ &= \frac{(0.025 \text{ mol L}^{-1})(0.114)^2}{(1-0.114)} \\ &= 3.67 \times 10^{-4} \text{ mol L}^{-1}\end{aligned}$$

Question 3.10:

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

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

$$t = 2 \text{ hours} = 2 \times 60 \times 60 \text{ s} = 7200 \text{ s}$$

$$\text{Thus, } Q = It$$

$$= 0.5 \text{ A} \times 7200 \text{ s}$$

ELECTROCHEMISTRY NCERT SOLUTION

$$= 3600 \text{ C}$$

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

Then,

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

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

Question 3.11:

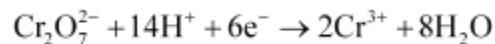
Suggest a list of metals that are extracted electrolytically

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

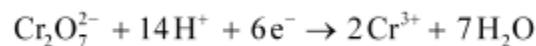
Question 3.12:

What is the quantity of electricity in coulombs needed to reduce 1 mol of

$\text{Cr}_2\text{O}_7^{2-}$? Consider the reaction:



The given reaction is as follows:



Therefore, to reduce 1 mole of $\text{Cr}_2\text{O}_7^{2-}$, the required quantity of electricity will be:

$$= 6 \text{ F}$$

$$= 6 \times 96487 \text{ C}$$

$$= 578922 \text{ C}$$

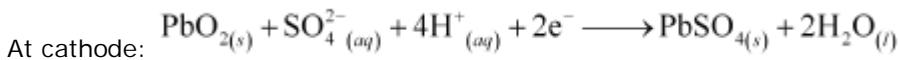
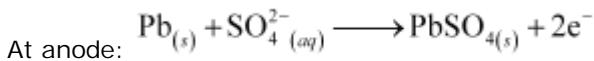
Question 3.13:

Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

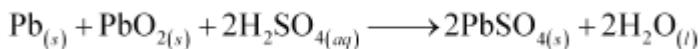
ELECTROCHEMISTRY NCERT SOLUTION

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:



The overall cell reaction is given by,



When a battery is charged, the reverse of all these reactions takes place.

Hence, on charging, $\text{PbSO}_{4(s)}$ present at the anode and cathode is converted into $\text{Pb}_{(s)}$ and $\text{PbO}_{2(s)}$ respectively.

Question 3.14:

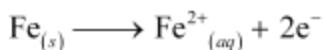
Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Methane and methanol can be used as fuels in fuel cells.

Question 3.15:

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

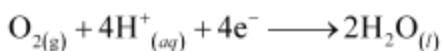
In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,



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

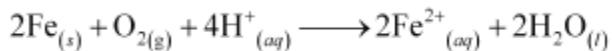
There, in the presence of H^+ ions, the electrons reduce oxygen. This spot behaves as the cathode. These H^+ ions come either from H_2CO_3 , which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.

The reaction corresponding at the cathode is given by,



ELECTROCHEMISTRY NCERT SOLUTION

The overall reaction is:



Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide ($\text{Fe}_2\text{O}_3, x\text{H}_2\text{O}$) i.e., rust.

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

Question 3.1:

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

The following is the order in which the given metals displace each other from the solution of their salts.

Mg, Al, Zn, Fe, Cu

Question 3.2:

Given the standard electrode potentials,

$$\text{K}^{+}/\text{K} = -2.93\text{V}, \text{Ag}^{+}/\text{Ag} = 0.80\text{V},$$

$$\text{Hg}^{2+}/\text{Hg} = 0.79\text{V}$$

$$\text{Mg}^{2+}/\text{Mg} = -2.37\text{ V}, \text{Cr}^{3+}/\text{Cr} = -0.74\text{V}$$

Arrange these metals in their increasing order of reducing power

The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of $\text{K}^{+}/\text{K} < \text{Mg}^{2+}/\text{Mg} < \text{Cr}^{3+}/\text{Cr} < \text{Hg}^{2+}/\text{Hg} < \text{Ag}^{+}/\text{Ag}$.

Hence, the reducing power of the given metals increases in the following order:

Ag < Hg < Cr < Mg < K

Question 3.3:

Depict the galvanic cell in which the reaction $\text{Zn}(s) + 2\text{Ag}^{+}(aq) \rightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$ takes place. Further show:

ELECTROCHEMISTRY NCERT SOLUTION

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode

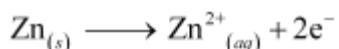
The galvanic cell in which the given reaction takes place is depicted as:



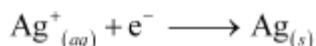
(i) Zn electrode (anode) is negatively charged.

(ii) Ions 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,

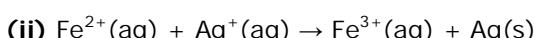
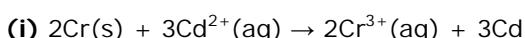


The reaction taking place at the cathode is given by,

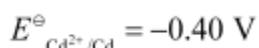
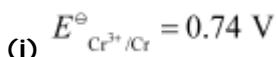


Question 3.4:

Calculate the standard cell potentials of galvanic cells in which the following reactions take place:



Calculate the $\Delta_r G^\ominus$ and equilibrium constant of the reactions



The galvanic cell of the given reaction is depicted as:



ELECTROCHEMISTRY NCERT SOLUTION

Now, the standard cell potential is

$$\begin{aligned} E_{\text{cell}}^{\ominus} &= E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus} \\ &= -0.40 - (-0.74) \\ &= +0.34 \text{ V} \\ \Delta_r G^{\ominus} &= -nFE_{\text{cell}}^{\ominus} \end{aligned}$$

In the given equation,

$$n = 6$$

$$F = 96487 \text{ C mol}^{-1}$$

$$E_{\text{cell}}^{\ominus} = +0.34 \text{ V}$$

$$\begin{aligned} \text{Then, } \Delta_r G^{\ominus} &= -6 \times 96487 \text{ C mol}^{-1} \times 0.34 \text{ V} \\ &= -196833.48 \text{ CV mol}^{-1} \\ &= -196833.48 \text{ J mol}^{-1} \\ &= -196.83 \text{ kJ mol}^{-1} \end{aligned}$$

Again,

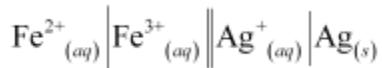
$$\begin{aligned} \Delta_r G^{\ominus} &= -RT \ln K \\ \Rightarrow \Delta_r G^{\ominus} &= -2.303 RT \ln K \\ \Rightarrow \log K &= -\frac{\Delta_r G}{2.303 RT} \\ &= \frac{-196.83 \times 10^3}{2.303 \times 8.314 \times 298} \\ &= 34.496 \\ \therefore K &= \text{antilog (34.496)} \\ &= 3.13 \times 10^{34} \end{aligned}$$

$$\text{(ii) } E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\ominus} = 0.77 \text{ V}$$

$$E_{\text{Ag}^+/\text{Ag}}^{\ominus} = 0.80 \text{ V}$$

ELECTROCHEMISTRY NCERT SOLUTION

The galvanic cell of the given reaction is depicted as:



Now, the standard cell potential is

$$\begin{aligned} E_{\text{cell}}^\ominus &= E_R^\ominus - E_L^\ominus \\ &= 0.80 - 0.77 \\ &= 0.03 \text{ V} \end{aligned}$$

Here, $n = 1$.

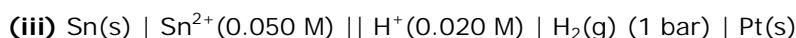
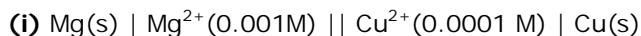
$$\begin{aligned} \Delta_r G^\ominus &= -nFE_{\text{cell}}^\ominus \\ \text{Then, } &= -1 \times 96487 \text{ C mol}^{-1} \times 0.03 \text{ V} \\ &= -2894.61 \text{ J mol}^{-1} \\ &= -2.89 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Again, } \Delta_r G^\ominus = -2.303 RT \ln K$$

$$\begin{aligned} \Rightarrow \log K &= -\frac{\Delta_r G}{2.303 RT} \\ &= \frac{-2894.61}{2.303 \times 8.314 \times 298} \\ &= 0.5073 \\ \therefore K &= \text{antilog (0.5073)} \\ &= 3.2 \text{ (approximately)} \end{aligned}$$

Question 3.5:

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



ELECTROCHEMISTRY NCERT SOLUTION



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

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \\ &= \{0.34 - (-2.36)\} - \frac{0.0591}{2} \log \frac{.001}{.0001} \\ &= 2.7 - \frac{0.0591}{2} \log 10 \end{aligned}$$

$$= 2.7 - 0.02955$$

$$= 2.67 \text{ V (approximately)}$$

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

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2} \\ &= \{0 - (-0.44)\} - \frac{0.0591}{2} \log \frac{0.001}{1^2} \\ &= 0.44 - 0.02955(-3) \end{aligned}$$

$$= 0.52865 \text{ V}$$

$$= 0.53 \text{ V (approximately)}$$

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

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2} \\ &= \{0 - (-0.14)\} - \frac{0.0591}{2} \log \frac{0.050}{(0.020)^2} \end{aligned}$$

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

$$= 0.14 - 0.062$$

$$= 0.078 \text{ V}$$

$$= 0.08 \text{ V (approximately)}$$

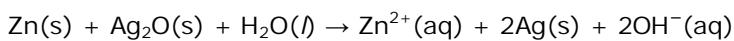
(iv) For the given reaction, the Nernst equation can be given as:

ELECTROCHEMISTRY NCERT SOLUTION

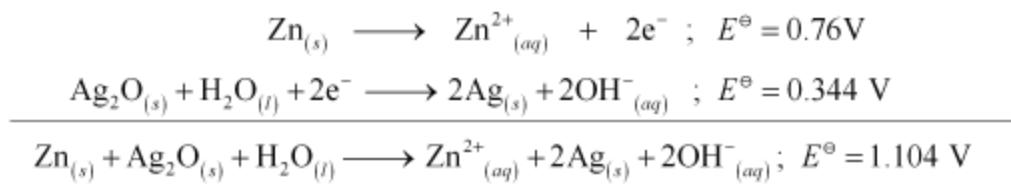
$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2} \\
 &= (0 - 1.09) - \frac{0.0591}{2} \log \frac{1}{(0.010)^2 (0.030)^2} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{0.00000009} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \\
 &= -1.09 - 0.02955 \times \log (1.11 \times 10^7) \\
 &= -1.09 - 0.02955 (0.0453 + 7) \\
 &= -1.09 - 0.208 \\
 &= -1.298 \text{ V}
 \end{aligned}$$

Question 3.6:

In the button cells widely used in watches and other devices the following reaction takes place:



Determine $\Delta_r G^{\ominus}$ and E^{\ominus} for the reaction



$$\therefore E^{\ominus} = 1.104 \text{ V}$$

We know that,

$$\begin{aligned}
 \Delta_r G^{\ominus} &= -nFE^{\ominus} \\
 &= -2 \times 96487 \times 1.04 \\
 &= -213043.296 \text{ J} \\
 &= -213.04 \text{ kJ}
 \end{aligned}$$

Question 3.7:

ELECTROCHEMISTRY NCERT SOLUTION

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

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 κ . If ρ 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 $a = 1$, $l = 1$)

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

Molar conductivity:

Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing 1 mole of the electrolyte kept between two electrodes with the area of cross-section A and distance of unit length.

$$\Lambda_m = \kappa \frac{A}{l}$$

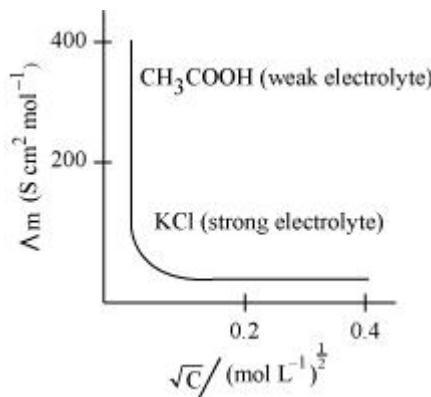
Now, $l = 1$ and $A = V$ (volume containing 1 mole of the electrolyte).

$$\therefore \Lambda_m = \kappa V$$

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

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

ELECTROCHEMISTRY NCERT SOLUTION



Question 3.8:

The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm^{-1} . Calculate its molar conductivity.

Given,

$$\kappa = 0.0248 \text{ S cm}^{-1}$$

$$c = 0.20 \text{ M}$$

$$\therefore \text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{c}$$

$$= \frac{0.0248 \times 1000}{0.2}$$

$$= 124 \text{ Scm}^2 \text{mol}^{-1}$$

Question 3.9:

The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$.

Given,

$$\text{Conductivity, } \kappa = 0.146 \times 10^{-3} \text{ S cm}^{-1}$$

$$\text{Resistance, } R = 1500 \Omega$$

$$\therefore \text{Cell constant} = \kappa \times R$$

$$= 0.146 \times 10^{-3} \times 1500$$

$$= 0.219 \text{ cm}^{-1}$$

ELECTROCHEMISTRY NCERT SOLUTION

Question 3.10:

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

$10^2 \times \kappa / \text{S m}^{-1}$ 1.237 11.85 23.15 55.53 106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m^0 .

Given,

$$\kappa = 1.237 \times 10^{-2} \text{ S m}^{-1}, c = 0.001 \text{ M}$$

$$\text{Then, } \kappa = 1.237 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.0316 \text{ M}^{1/2}$$

$$\begin{aligned}\therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{1.237 \times 10^{-4} \text{ S cm}^{-1}}{0.001 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 123.7 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

$$\kappa = 11.85 \times 10^{-2} \text{ S m}^{-1}, c = 0.010 \text{ M}$$

$$\text{Then, } \kappa = 11.85 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.1 \text{ M}^{1/2}$$

$$\begin{aligned}\therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{11.85 \times 10^{-4} \text{ S cm}^{-1}}{0.010 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 118.5 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

$$\kappa = 23.15 \times 10^{-2} \text{ S m}^{-1}, c = 0.020 \text{ M}$$

$$\text{Then, } \kappa = 23.15 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.1414 \text{ M}^{1/2}$$

ELECTROCHEMISTRY NCERT SOLUTION

$$\begin{aligned}\therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{23.15 \times 10^{-4} \text{ S cm}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 115.8 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

$$\kappa = 55.53 \times 10^{-2} \text{ S m}^{-1}, c = 0.050 \text{ M}$$

$$\text{Then, } \kappa = 55.53 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.2236 \text{ M}^{1/2}$$

$$\begin{aligned}\therefore \kappa &= \frac{\kappa}{c} \\ &= \frac{55.53 \times 10^{-4} \text{ S cm}^{-1}}{0.050 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 111.1 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

$$\kappa = 106.74 \times 10^{-2} \text{ S m}^{-1}, c = 0.100 \text{ M}$$

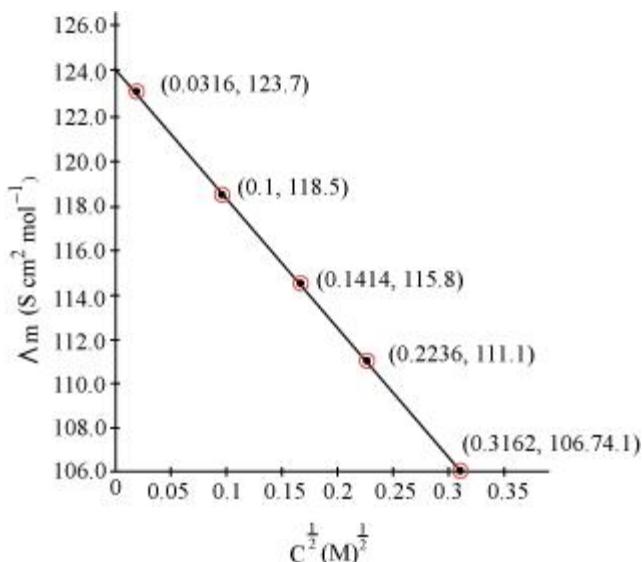
$$\text{Then, } \kappa = 106.74 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.3162 \text{ M}^{1/2}$$

$$\begin{aligned}\therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 106.74 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Now, we have the following data:

$C^{1/2} / M^{1/2}$	0.0316	0.1	0.1414	0.2236	0.3162
$\Lambda_m (\text{S cm}^2 \text{ mol}^{-1})$	123.7	118.5	115.8	111.1	106.74

ELECTROCHEMISTRY NCERT SOLUTION



Since the line intersects Λ_m at $124.0 \text{ S cm}^2 \text{ mol}^{-1}$, $\Lambda_m^0 = 124.0 \text{ S cm}^2 \text{ mol}^{-1}$.

Question 3.11:

Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and if Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

Given, $\kappa = 7.896 \times 10^{-5} \text{ S m}^{-1}$

$$c = 0.00241 \text{ mol L}^{-1}$$

$$\text{Then, molar conductivity, } \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1}}{0.00241 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Again, } \Lambda_m^0 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Now, } \alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}}$$

$$= 0.084$$

ELECTROCHEMISTRY NCERT SOLUTION

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

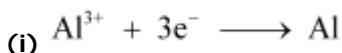
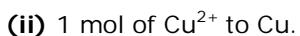
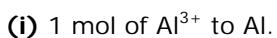
∴ Dissociation constant,

$$= \frac{(0.00241 \text{ mol L}^{-1})(0.084)^2}{(1-0.084)}$$

$$= 1.86 \times 10^{-5} \text{ mol L}^{-1}$$

Question 3.12:

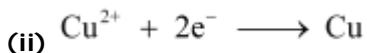
How much charge is required for the following reductions:



∴ Required charge = 3 F

$$= 3 \times 96487 \text{ C}$$

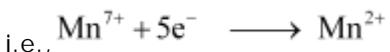
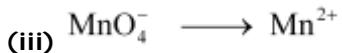
$$= 289461 \text{ C}$$



∴ Required charge = 2 F

$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$



∴ Required charge = 5 F

$$= 5 \times 96487 \text{ C}$$

$$= 482435 \text{ C}$$

ELECTROCHEMISTRY NCERT SOLUTION

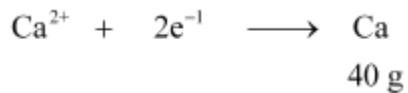
Question 3.13:

How much electricity in terms of Faraday is required to produce

(i) 20.0 g of Ca from molten CaCl_2 .

(ii) 40.0 g of Al from molten Al_2O_3 .

(i) According to the question,



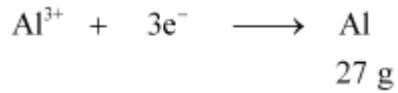
Electricity required to produce 40 g of calcium = 2 F

$$= \frac{2 \times 20}{40} \text{ F}$$

Therefore, electricity required to produce 20 g of calcium

$$= 1 \text{ F}$$

(ii) According to the question,



Electricity required to produce 27 g of Al = 3 F

$$= \frac{3 \times 40}{27} \text{ F}$$

Therefore, electricity required to produce 40 g of Al

$$= 4.44 \text{ F}$$

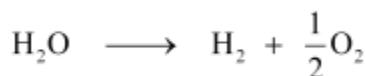
Question 3.14:

How much electricity is required in coulomb for the oxidation of

(i) 1 mol of H_2O to O_2 .

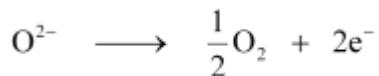
(ii) 1 mol of FeO to Fe_2O_3 .

(i) According to the question,



ELECTROCHEMISTRY NCERT SOLUTION

Now, we can write:

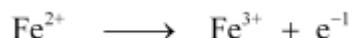


Electricity required for the oxidation of 1 mol of H₂O to O₂ = 2 F

$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$

(ii) According to the question,



Electricity required for the oxidation of 1 mol of FeO to Fe₂O₃ = 1 F

$$= 96487 \text{ C}$$

Question 3.15:

A solution of Ni(NO₃)₂ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Given,

Current = 5A

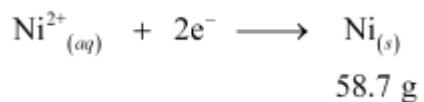
Time = 20 × 60 = 1200 s

∴ Charge = current × time

$$= 5 \times 1200$$

$$= 6000 \text{ C}$$

According to the reaction,



Nickel deposited by 2 × 96487 C = 58.71 g

$$= \frac{58.71 \times 6000}{2 \times 96487} \text{ g}$$

Therefore, nickel deposited by 6000 C

$$= 1.825 \text{ g}$$

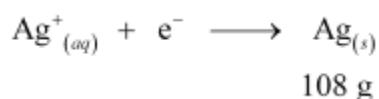
ELECTROCHEMISTRY NCERT SOLUTION

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

Question 3.16:

Three electrolytic cells A,B,C containing solutions of ZnSO_4 , AgNO_3 and CuSO_4 , 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?

According to the reaction:



i.e., 108 g of Ag is deposited by 96487 C.

$$\frac{96487 \times 1.45}{108} \text{ C}$$

Therefore, 1.45 g of Ag is deposited by =

$$= 1295.43 \text{ C}$$

Given,

Current = 1.5 A

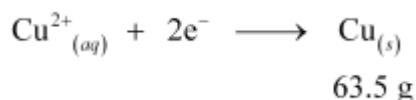
$$\therefore \text{Time} = \frac{1295.43}{1.5} \text{ s}$$

$$= 863.6 \text{ s}$$

$$= 864 \text{ s}$$

$$= 14.40 \text{ min}$$

Again,



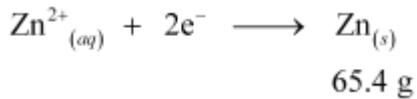
i.e., 2×96487 C of charge deposit = 63.5 g of Cu

$$= \frac{63.5 \times 1295.43}{2 \times 96487} \text{ g}$$

Therefore, 1295.43 C of charge will deposit

$$= 0.426 \text{ g of Cu}$$

ELECTROCHEMISTRY NCERT SOLUTION



i.e., 2×96487 C of charge deposit = 65.4 g of Zn

$$= \frac{65.4 \times 1295.43}{2 \times 96487} \text{ g}$$

Therefore, 1295.43 C of charge will deposit

= 0.439 g of Zn

Question 3.17:

Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:

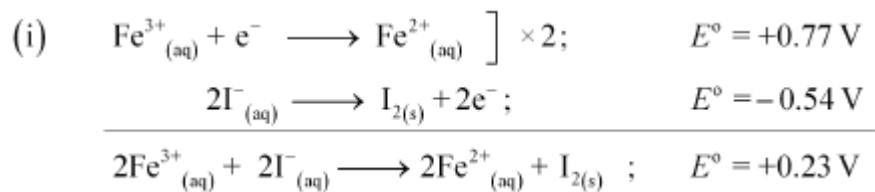
(i) $\text{Fe}^{3+}_{(aq)}$ and $\text{I}^-_{(aq)}$

(ii) $\text{Ag}^+_{(aq)}$ and $\text{Cu}_{(s)}$

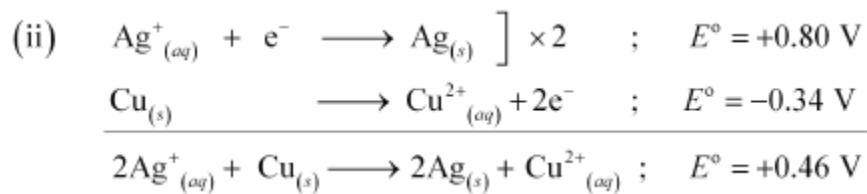
(iii) $\text{Fe}^{3+}_{(aq)}$ and $\text{Br}^-_{(aq)}$

(iv) $\text{Ag}_{(s)}$ and $\text{Fe}^{3+}_{(aq)}$

(v) $\text{Br}_2_{(aq)}$ and $\text{Fe}^{2+}_{(aq)}$.

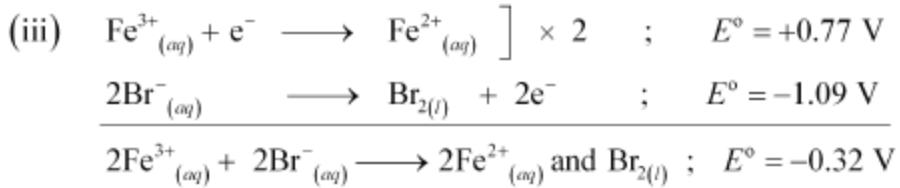


Since E° for the overall reaction is positive, the reaction between $\text{Fe}^{3+}_{(aq)}$ and $\text{I}^-_{(aq)}$ is feasible.

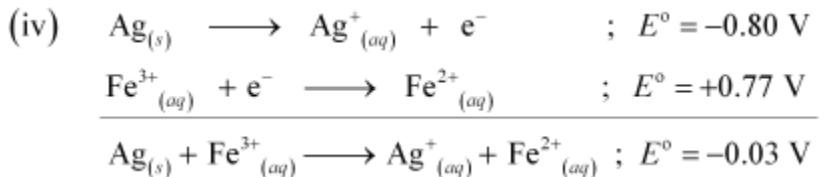


Since E° for the overall reaction is positive, the reaction between $\text{Ag}^+_{(aq)}$ and $\text{Cu}_{(s)}$ is feasible.

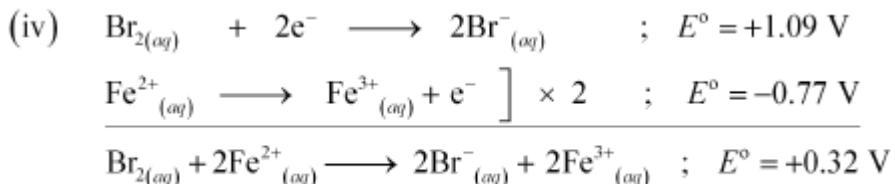
ELECTROCHEMISTRY NCERT SOLUTION



Since E° for the overall reaction is negative, the reaction between $\text{Fe}^{3+}_{(aq)}$ and $\text{Br}^-_{(aq)}$ is not feasible.



Since E° for the overall reaction is negative, the reaction between $\text{Ag}_{(s)}$ and $\text{Fe}^{3+}_{(aq)}$ is not feasible.



Since E° for the overall reaction is positive, the reaction between $\text{Br}_2(aq)$ and $\text{Fe}^{2+}_{(aq)}$ is feasible.

Question 3.18:

Predict the products of electrolysis in each of the following:

(i) An aqueous solution of AgNO_3 with silver electrodes.

(ii) An aqueous solution of AgNO_3 with platinum electrodes.

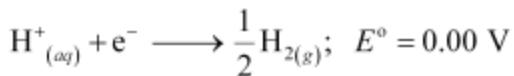
(iii) A dilute solution of H_2SO_4 with platinum electrodes.

(iv) An aqueous solution of CuCl_2 with platinum electrodes.

(i) At cathode:

The following reduction reactions compete to take place at the cathode.

ELECTROCHEMISTRY NCERT SOLUTION



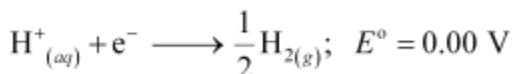
The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

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:

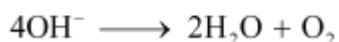
The following reduction reactions compete to take place at the cathode.



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:

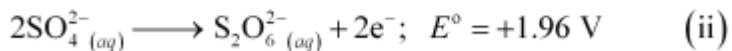
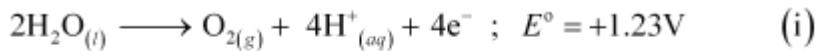
Since Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or O_2 ions can be oxidized at the anode. But OH^- ions having a lower discharge potential and get preference and decompose to liberate O_2 .



(iii) At the cathode, the following reduction reaction occurs to produce H_2 gas.



At the anode, the following processes are possible.

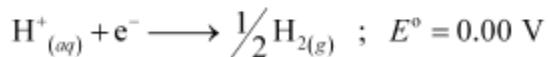
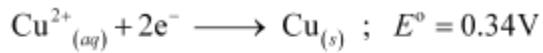


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For dilute sulphuric acid, reaction (i) is preferred to produce O₂ gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At cathode:

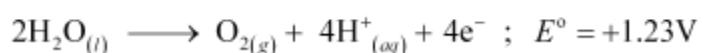
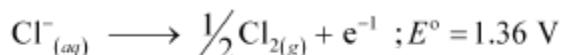
The following reduction reactions compete to take place at the cathode.



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.



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

CHEMICAL KINETICS : NCERT SOLUTION

CHEMICAL KINETICS

Question 4.1:

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.

$$\text{Average rate of reaction} = -\frac{\Delta[R]}{\Delta t}$$

$$= -\frac{[R]_2 - [R]_1}{t_2 - t_1}$$

$$= -\frac{0.02 - 0.03}{25} \text{ M min}^{-1}$$

$$= -\frac{-0.01}{25} \text{ M min}^{-1}$$

$$= 4 \times 10^{-4} \text{ M min}^{-1}$$

$$= \frac{4 \times 10^{-4}}{60} \text{ M s}^{-1}$$

$$= 6.67 \times 10^{-6} \text{ M s}^{-1}$$

Question 4.2:

In a reaction, $2A \rightarrow \text{Products}$, 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?

$$\text{Average rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t}$$

CHEMICAL KINETICS : NCERT SOLUTION

$$= -\frac{1}{2} \frac{[A]_2 - [A]_1}{t_2 - t_1}$$

$$= -\frac{1}{2} \frac{0.4 - 0.5}{10}$$

$$= -\frac{1}{2} \frac{-0.1}{10}$$

$$= 0.005 \text{ mol L}^{-1} \text{ min}^{-1}$$

$$= 5 \times 10^{-3} \text{ M min}^{-1}$$

Question 4.3:

For a reaction, $A + B \rightarrow \text{Product}$; the rate law is given by, $r = k[A]^{1/2}[B]^2$. What is the order of the reaction?

$$= \frac{1}{2} + 2$$

The order of the reaction

$$= 2 \frac{1}{2}$$

$$= 2.5$$

Question 4.4:

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?

The reaction $X \rightarrow Y$ follows second order kinetics.

Therefore, the rate equation for this reaction will be:

$$\text{Rate} = k[X]^2 \quad (1)$$

Let $[X] = a \text{ mol L}^{-1}$, then equation (1) can be written as:

$$\text{Rate}_1 = k \cdot (a)^2$$

$$= ka^2$$

If the concentration of X is increased to three times, then $[X] = 3a \text{ mol L}^{-1}$

CHEMICAL KINETICS : NCERT SOLUTION

Now, the rate equation will be:

$$\text{Rate} = k (3a)^2$$

$$= 9(ka^2)$$

Hence, the rate of formation will increase by 9 times.

Question 4.5:

A first order reaction has a rate constant $1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

From the question, we can write down the following information:

Initial amount = 5 g

Final concentration = 3 g

Rate constant = $1.15 \times 10^{-3} \text{ s}^{-1}$

We know that for a 1st order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219$$

$$= 444.38 \text{ s}$$

$$= 444 \text{ s (approx)}$$

Question 4.6:

Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

We know that for a 1st order reaction,

$$t_{1/2} = \frac{0.693}{k}$$

CHEMICAL KINETICS : NCERT SOLUTION

It is given that $t_{1/2} = 60 \text{ min}$

$$\therefore k = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{60}$$

$$= 0.01155 \text{ min}^{-1}$$

$$= 1.155 \text{ min}^{-1}$$

Or $k = 1.925 \times 10^{-4} \text{ s}^{-1}$

Question 4.7:

What will be the effect of temperature on rate constant?

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,

$$k = A e^{-E_a/RT}$$

Where,

A is the Arrhenius factor or the frequency factor

T is the temperature

R is the gas constant

E_a is the activation energy

Question 4.8:

The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K . Calculate E_a .

It is given that $T_1 = 298 \text{ K}$

$$\therefore T_2 = (298 + 10) \text{ K}$$

$$= 308 \text{ K}$$

We also know that the rate of the reaction doubles when temperature is increased by 10° .

CHEMICAL KINETICS : NCERT SOLUTION

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:

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$\Rightarrow \log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$\Rightarrow E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

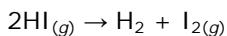
$$= 52897.78 \text{ J mol}^{-1}$$

$$= 52.9 \text{ kJ mol}^{-1}$$

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

Question 4.9:

The activation energy for the reaction



is $209.5 \text{ kJ mol}^{-1}$ at 581K . Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

In the given case:

$$E_a = 209.5 \text{ kJ mol}^{-1} = 209500 \text{ J mol}^{-1}$$

$$T = 581 \text{ K}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as:

CHEMICAL KINETICS : NCERT SOLUTION

$$x = e^{-E_a/RT}$$

$$\Rightarrow \ln x = -E_a / RT$$

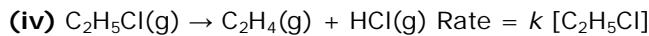
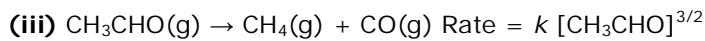
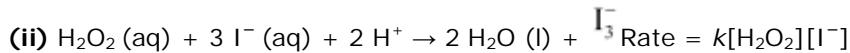
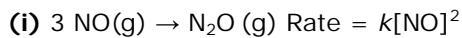
$$\Rightarrow \log x = -\frac{E_a}{2.303 RT}$$

$$\Rightarrow \log x = \frac{209500 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 581} = 18.8323$$

$$\begin{aligned} \text{Now, } x &= \text{Anti log}(18.8323) \\ &= \text{Anti log } 19.1677 \\ &= 1.471 \times 10^{-19} \end{aligned}$$

Question 4.1:

From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.



(i) Given rate = $k [\text{NO}]^2$

Therefore, order of the reaction = 2

$$k = \frac{\text{Rate}}{[\text{NO}]^2}$$

Dimension of

$$\begin{aligned} &= \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})^2} \\ &= \frac{\text{mol L}^{-1} \text{ s}^{-1}}{\text{mol}^2 \text{ L}^{-2}} \\ &= \text{L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

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(ii) Given rate = $k [H_2O_2] [I^-]$

Therefore, order of the reaction = 2

$$k = \frac{\text{Rate}}{[H_2O_2][I^-]}$$

Dimension of

$$= \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})}$$

$$= \text{L mol}^{-1} \text{s}^{-1}$$

(iii) Given rate = $k [CH_3CHO]^{3/2}$

$$k = \frac{\text{Rate}}{[CH_3CHO]^{\frac{3}{2}}}$$

Dimension of

$$= \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^{\frac{3}{2}}}$$

$$= \frac{\text{mol L}^{-1} \text{s}^{-1}}{\text{mol}^{\frac{3}{2}} \text{L}^{\frac{-3}{2}}}$$

$$= L^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ s}^{-1}$$

(iv) Given rate = $k [C_2H_5Cl]$

Therefore, order of the reaction = 1

$$k = \frac{\text{Rate}}{[C_2H_5Cl]}$$

Dimension of

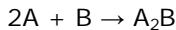
$$= \frac{\text{mol L}^{-1} \text{s}^{-1}}{\text{mol L}^{-1}}$$

$$= \text{s}^{-1}$$

Question 4.2:

For the reaction:

CHEMICAL KINETICS : NCERT SOLUTION



the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1 \text{ mol L}^{-1}$, $[B] = 0.2 \text{ mol L}^{-1}$. Calculate the rate of reaction after $[A]$ is reduced to 0.06 mol L^{-1} .

The initial rate of the reaction is

$$\begin{aligned}\text{Rate} &= k [A][B]^2 \\ &= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) (0.1 \text{ mol L}^{-1}) (0.2 \text{ mol L}^{-1})^2 \\ &= 8.0 \times 10^{-9} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}\end{aligned}$$

When $[A]$ is reduced from 0.1 mol L^{-1} to 0.06 mol L^{-1} , the concentration of A reacted = $(0.1 - 0.06) \text{ mol L}^{-1} = 0.04 \text{ mol L}^{-1}$

$$\begin{aligned}&= \frac{1}{2} \times 0.04 \text{ mol L}^{-1} \\ \text{Therefore, concentration of B reacted} &\quad = 0.02 \text{ mol L}^{-1}\end{aligned}$$

Then, concentration of B available, $[B] = (0.2 - 0.02) \text{ mol L}^{-1}$

$$= 0.18 \text{ mol L}^{-1}$$

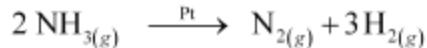
After $[A]$ is reduced to 0.06 mol L^{-1} , the rate of the reaction is given by,

$$\begin{aligned}\text{Rate} &= k [A][B]^2 \\ &= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) (0.06 \text{ mol L}^{-1}) (0.18 \text{ mol L}^{-1})^2 \\ &= 3.89 \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

Question 4.3:

The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$?

The decomposition of NH_3 on platinum surface is represented by the following equation.



Therefore,

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

However, it is given that the reaction is of zero order.

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Therefore,

$$-\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k$$
$$= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Therefore, the rate of production of N_2 is

$$\frac{d[\text{N}_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

And, the rate of production of H_2 is

$$\frac{d[\text{H}_2]}{dt} = 3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$
$$= 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Question 4.4:

The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and the reaction rate is given by

$$\text{Rate} = k [\text{CH}_3\text{OCH}_3]^{3/2}$$

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.,

$$\text{Rate} = k (p_{\text{CH}_3\text{OCH}_3})^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

If pressure is measured in bar and time in minutes, then

$$\text{Unit of rate} = \text{bar min}^{-1}$$

$$\text{Rate} = k (p_{\text{CH}_3\text{OCH}_3})^{3/2}$$

$$\Rightarrow k = \frac{\text{Rate}}{(p_{\text{CH}_3\text{OCH}_3})^{3/2}}$$

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$$(k) = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}}$$

Therefore, unit of rate constants

$$= \text{bar}^{-1/2} \text{ min}^{-1}$$

Question 4.5:

Mention the factors that affect the rate of a chemical reaction

The factors that affect the rate of a reaction are as follows.

- (i) Concentration of reactants (pressure in case of gases)
- (ii) Temperature
- (iii) Presence of a catalyst

Question 4.6:

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?

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

$$R' = k(2a)^2$$

$$= 4ka^2$$

$$= 4 R$$

Therefore, the rate of the reaction would increase by 4 times.

$$[A] = \frac{1}{2}a$$

- (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

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$$\begin{aligned} R'' &= k \left(\frac{1}{2}a \right)^2 \\ &= \frac{1}{4}ka \\ &= \frac{1}{4}R \end{aligned}$$

$\frac{1}{4}$

Therefore, the rate of the reaction would be reduced to $\frac{1}{4}$.

Question 4.7:

What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

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, k is the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

T is the temperature, and

E_a is the energy of activation for the reaction

Question 4.8:

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.

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$$= \frac{d[\text{Ester}]}{dt}$$

(i) Average rate of reaction between the time interval, 30 to 60 seconds,

$$\begin{aligned} &= \frac{0.31 - 0.17}{60 - 30} \\ &= \frac{0.14}{30} \\ &= 4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

(ii) For a pseudo first order reaction,

$$k = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]}$$

$$k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31}$$

For $t = 30 \text{ s}$,

$$= 1.911 \times 10^{-2} \text{ s}^{-1}$$

$$k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17}$$

For $t = 60 \text{ s}$,

$$= 1.957 \times 10^{-2} \text{ s}^{-1}$$

$$k_3 = \frac{2.303}{90} \log \frac{0.55}{0.085}$$

For $t = 90 \text{ s}$,

$$= 2.075 \times 10^{-2} \text{ s}^{-1}$$

$$k = \frac{k_1 + k_2 + k_3}{3}$$

Then, average rate constant,

$$\begin{aligned} &= \frac{(1.911 \times 10^{-2}) + (1.957 \times 10^{-2}) + (2.075 \times 10^{-2})}{3} \\ &= 1.98 \times 10^{-2} \text{ s}^{-1} \end{aligned}$$

Question 4.9:

A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

CHEMICAL KINETICS : NCERT SOLUTION

(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?

(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

$$\begin{aligned}-\frac{d[R]}{dt} &= k[A][3B]^2 \\ &= 9 \cdot k[A][B]^2\end{aligned}$$

Therefore, the rate of reaction will increase 9 times.

(iii) When the concentrations of both A and B are doubled,

$$\begin{aligned}-\frac{d[R]}{dt} &= k[A][B]^2 \\ &= k[2A][2B]^2 \\ &= 8 \cdot k[A][B]^2\end{aligned}$$

Therefore, the rate of reaction will increase 8 times

Question 4.10:

In a reaction between A and B, the initial rate of reaction (r_0) 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?

Let the order of the reaction with respect to A be x and with respect to B be y .

Therefore,

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$$r_0 = k[A]^x [B]^y$$

$$5.07 \times 10^{-5} = k[0.20]^x [0.30]^y \quad (\text{i})$$

$$5.07 \times 10^{-5} = k[0.20]^x [0.10]^y \quad (\text{ii})$$

$$1.43 \times 10^{-4} = k[0.40]^x [0.05]^y \quad (\text{iii})$$

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

$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k[0.40]^x [0.05]^y}{k[0.20]^x [0.30]^y}$$

$$\Rightarrow \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{[0.40]^x}{[0.20]^x} \quad \left[\begin{array}{l} \text{Since } y = 0, \\ [0.05]^y = [0.30]^y = 1 \end{array} \right]$$

$$\Rightarrow 2.821 = 2^x$$

$$\Rightarrow \log 2.821 = x \log 2 \quad (\text{Taking log on both sides})$$

$$\Rightarrow x = \frac{\log 2.821}{\log 2}$$

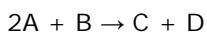
$$= 1.496$$

$$= 1.5 \text{ (approximately)}$$

Hence, the order of the reaction with respect to A is 1.5 and with respect to B is zero.

Question 4.11:

The following results have been obtained during the kinetic studies of the reaction:



CHEMICAL KINETICS : NCERT SOLUTION

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.

Let the order of the reaction with respect to A be x and with respect to B be y .

Therefore, rate of the reaction is given by,

$$\text{Rate} = k[A]^x [B]^y$$

According to the question,

$$6.0 \times 10^{-3} = k[0.1]^x [0.1]^y \quad (\text{i})$$

$$7.2 \times 10^{-2} = k[0.3]^x [0.2]^y \quad (\text{ii})$$

$$2.88 \times 10^{-1} = k[0.3]^x [0.4]^y \quad (\text{iii})$$

$$2.40 \times 10^{-2} = k[0.4]^x [0.1]^y \quad (\text{iv})$$

Dividing equation (iv) by (i), we obtain

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^x [0.1]^y}{k[0.1]^x [0.1]^y}$$

$$\Rightarrow 4 = \frac{[0.4]^x}{[0.1]^x}$$

$$\Rightarrow 4 = \left(\frac{0.4}{0.1}\right)^x$$

$$\Rightarrow (4)^1 = 4^x$$

$$\Rightarrow x = 1$$

Dividing equation (iii) by (ii), we obtain

CHEMICAL KINETICS : NCERT SOLUTION

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k[0.3]^x [0.4]^y}{k[0.3]^x [0.2]^y}$$

$$\Rightarrow 4 = \left(\frac{0.4}{0.2}\right)^y$$

$$\Rightarrow 4 = 2^y$$

$$\Rightarrow 2^2 = 2^y$$

$$\Rightarrow y = 2$$

Therefore, the rate law is

$$\text{Rate} = k[A][B]^2$$

$$\Rightarrow k = \frac{\text{Rate}}{[A][B]^2}$$

From experiment I, we obtain

$$k = \frac{6.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.1 \text{ mol L}^{-1})(0.1 \text{ mol L}^{-1})^2}$$

$$= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

From experiment II, we obtain

$$k = \frac{7.2 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.3 \text{ mol L}^{-1})(0.2 \text{ mol L}^{-1})^2}$$

$$= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

From experiment III, we obtain

$$k = \frac{2.88 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.3 \text{ mol L}^{-1})(0.4 \text{ mol L}^{-1})^2}$$

$$= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

From experiment IV, we obtain

$$k = \frac{2.40 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.4 \text{ mol L}^{-1})(0.1 \text{ mol L}^{-1})^2}$$

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$$= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

Therefore, rate constant, $k = 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$

Question 4.12:

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	--

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,

$$\text{Rate} = k [A]^1 [B]^0$$

$$\Rightarrow \text{Rate} = k [A]$$

From experiment I, we obtain

$$2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = k (0.1 \text{ mol L}^{-1})$$

$$\Rightarrow k = 0.2 \text{ min}^{-1}$$

From experiment II, we obtain

$$4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = 0.2 \text{ min}^{-1} [A]$$

$$\Rightarrow [A] = 0.2 \text{ mol L}^{-1}$$

From experiment III, we obtain

$$\text{Rate} = 0.2 \text{ min}^{-1} \times 0.4 \text{ mol L}^{-1}$$

$$= 0.08 \text{ mol L}^{-1} \text{ min}^{-1}$$

From experiment IV, we obtain

$$2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = 0.2 \text{ min}^{-1} [A]$$

$$\Rightarrow [A] = 0.1 \text{ mol L}^{-1}$$

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Question 4.13:

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}

The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$

Here,

$$= \frac{0.693}{5730} \text{ years}^{-1}$$

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$= \frac{2.303}{\frac{0.693}{5730}} \log \frac{100}{80}$$

$$= 1845 \text{ years (approximately)}$$

Hence, the age of the sample is 1845 years

(i) Half life, $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$= \frac{0.693}{200 \text{ s}^{-1}}$$

$$= 3.47 \text{ s (approximately)}$$

(ii) Half life, $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$= \frac{0.693}{2 \text{ min}^{-1}}$$

$$= 0.35 \text{ min (approximately)}$$

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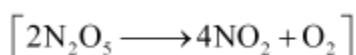
$$(iii) \text{ Half life, } t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$= \frac{0.693}{4 \text{ years}^{-1}}$$

= 0.173 years (approximately)

Question 4.15:

The experimental data for decomposition of N_2O_5



in gas phase at 318K are given below:

$t(\text{s})$	0	40	80	120	160	200	240	280	320
$10^2 \times [\text{N}_2\text{O}_5] \text{ mol}$	1.6 3	1.3 6	1.1 4	0.9 3	0.7 8	0.6 4	0.5 3	0.4 3	0.3 5

(i) Plot $[\text{N}_2\text{O}_5]$ against t .

(ii) Find the half-life period for the reaction.

(iii) Draw a graph between $\log [\text{N}_2\text{O}_5]$ and t .

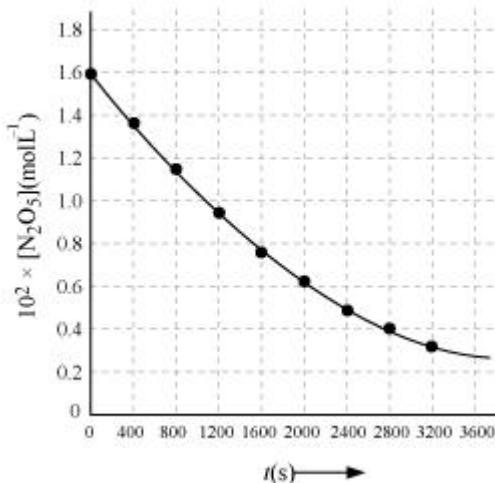
(iv) What is the rate law?

(v) Calculate the rate constant.

(vi) Calculate the half-life period from k and compare it with (ii).

i.

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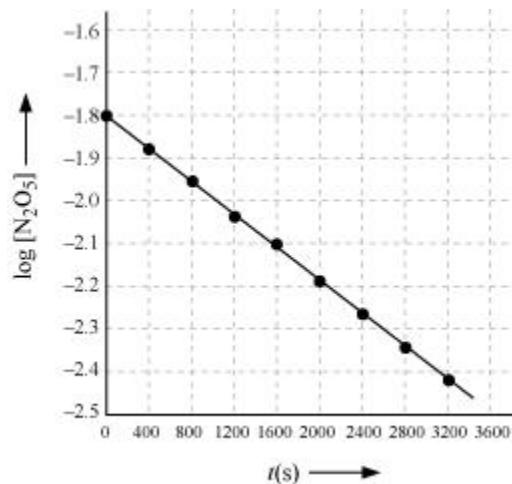
$$\frac{1.630 \times 10^2}{2} \text{ mol L}^{-1} = 81.5 \text{ mol L}^{-1},$$

(ii) Time corresponding to the concentration, $\frac{1.630 \times 10^2}{2} \text{ mol L}^{-1} = 81.5 \text{ mol L}^{-1}$, is the half life. From the graph, the half life is obtained as 1450 s.

(iii)

$t(s)$	$10^2 \times [N_2O_5] / mol L^{-1}$	$\log[N_2O_5]$
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

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(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

$$\text{Rate} = k[N_2O_5]$$

(v) From the plot, $\log[N_2O_5]$ v/s t , we obtain

$$\begin{aligned}\text{Slope} &= \frac{-2.46 - (-1.79)}{3200 - 0} \\ &= \frac{-0.67}{3200}\end{aligned}$$

Again, slope of the line of the plot $\log[N_2O_5]$ v/s t is given by

$$-\frac{k}{2.303}$$

Therefore, we obtain,

$$-\frac{k}{2.303} = -\frac{0.67}{3200}$$

$$\Rightarrow k = 4.82 \times 10^{-4} \text{ s}^{-1}$$

(vi) Half-life is given by,

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$$\begin{aligned}t_{1/2} &= \frac{0.639}{k} \\&= \frac{0.693}{4.82 \times 10^{-4}} \text{ s} \\&= 1.438 \times 10^3 \text{ s} \\&= 1438 \text{ s}\end{aligned}$$

This value, 1438 s, is very close to the value that was obtained from the graph

Question 4.16:

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 $1/16^{\text{th}}$ value?

It is known that,

$$\begin{aligned}t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\&= \frac{2.303}{60 \text{ s}^{-1}} \log \frac{1}{1/16} \\&= \frac{2.303}{60 \text{ s}^{-1}} \log 16 \\&= 4.6 \times 10^{-2} \text{ s (approximately)}\end{aligned}$$

Hence, the required time is $4.6 \times 10^{-2} \text{ s}$.

Question 4.17:

During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If $1\mu\text{g}$ of ^{90}Sr 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.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \text{ y}^{-1}$$

Here,

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

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$$\begin{aligned}
 &\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]} \\
 &\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} (-\log [R]) \\
 &\Rightarrow \log [R] = -\frac{10 \times 0.693}{2.303 \times 28.1} \\
 &\Rightarrow [R] = \text{antilog}(-0.1071) \\
 &\quad = \text{antilog}(\bar{1.8929}) \\
 &\quad = 0.7814 \mu\text{g}
 \end{aligned}$$

Therefore, 0.7814 μg of ^{90}Sr will remain after 10 years.

Again,

$$\begin{aligned}
 t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\
 &\Rightarrow 60 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]} \\
 &\Rightarrow \log [R] = -\frac{60 \times 0.693}{2.303 \times 28.1} \\
 &\Rightarrow [R] = \text{antilog}(-0.6425) \\
 &\quad = \text{antilog}(\bar{1.3575}) \\
 &\quad = 0.2278 \mu\text{g}
 \end{aligned}$$

Therefore, 0.2278 μg of ^{90}Sr will remain after 60 years

Question 4.18:

For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction

For a first order reaction, the time required for 99% completion is

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$$\begin{aligned}t_1 &= \frac{2.303}{k} \log \frac{100}{100-99} \\&= \frac{2.303}{k} \log 100 \\&= 2 \times \frac{2.303}{k}\end{aligned}$$

For a first order reaction, the time required for 90% completion is

$$\begin{aligned}t_2 &= \frac{2.303}{k} \log \frac{100}{100-90} \\&= \frac{2.303}{k} \log 10 \\&= \frac{2.303}{k}\end{aligned}$$

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.

Question 4.19:

A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$\begin{aligned}k &= \frac{2.303}{40 \text{ min}} \log \frac{100}{100-30} \\&= \frac{2.303}{40 \text{ min}} \log \frac{10}{7} \\&= 8.918 \times 10^{-3} \text{ min}^{-1}\end{aligned}$$

Therefore, $t_{1/2}$ of the decomposition reaction is

$$\begin{aligned}t_{1/2} &= \frac{0.693}{k} \\&= \frac{0.693}{8.918 \times 10^{-3}} \text{ min}\end{aligned}$$

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= 77.7 min (approximately)

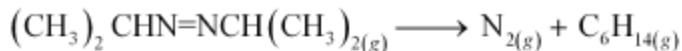
Question 4.20:

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

The decomposition of azoisopropane to hexane and nitrogen at 543 K is represented by the following equation.



At $t = 0$	P_0	0	0
At $t = t$	$P_0 - p$	p	p

$$\text{After time, } t, \text{ total pressure, } P_t = (P_0 - p) + p + p$$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

$$\text{Therefore, } P_0 - p = P_0 - (P_t - P_0)$$

$$= 2P_0 - P_t$$

For a first order reaction,

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{P_0}{P_0 - p} \\ &= \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t} \end{aligned}$$

$$\text{When } t = 360 \text{ s, } k = \frac{2.303}{360 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 54.0}$$

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$$= 2.175 \times 10^{-3} \text{ s}^{-1}$$

$$k = \frac{2.303}{720 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 63.0}$$

When $t = 720 \text{ s}$,

$$= 2.235 \times 10^{-3} \text{ s}^{-1}$$

Hence, the average value of rate constant is

$$k = \frac{(2.175 \times 10^{-3}) + (2.235 \times 10^{-3})}{2} \text{ s}^{-1}$$

$$= 2.21 \times 10^{-3} \text{ s}^{-1}$$

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

Question 4.21:

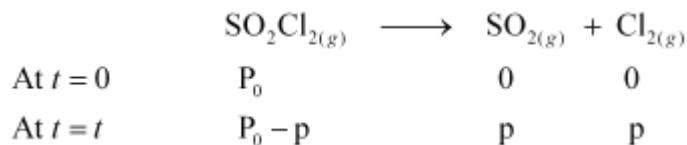
The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.



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

The thermal decomposition of SO_2Cl_2 at a constant volume is represented by the following equation.



$$\text{After time, } t, \text{ total pressure, } P_t = (P_0 - p) + p + p$$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

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Therefore, $P_0 - p = P_0 - (P_t - P_0)$

$$= 2 P_0 - P_t$$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - p}$$

$$= \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

$$k = \frac{2.303}{100 \text{ s}} \log \frac{0.5}{2 \times 0.5 - 0.6}$$

When $t = 100 \text{ s}$,

$$= 2.231 \times 10^{-3} \text{ s}^{-1}$$

When $P_t = 0.65 \text{ atm}$,

$$P_0 + p = 0.65$$

$$\Rightarrow p = 0.65 - P_0$$

$$= 0.65 - 0.5$$

$$= 0.15 \text{ atm}$$

Therefore, when the total pressure is 0.65 atm, pressure of SOCl_2 is

$$P_{\text{SOCl}_2} = P_0 - p$$

$$= 0.5 - 0.15$$

$$= 0.35 \text{ atm}$$

Therefore, the rate of equation, when total pressure is 0.65 atm, is given by,

$$\text{Rate} = k(P_{\text{SOCl}_2})$$

$$= (2.23 \times 10^{-3} \text{ s}^{-1}) (0.35 \text{ atm})$$

$$= 7.8 \times 10^{-4} \text{ atm s}^{-1}$$

Question 4.22:

The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

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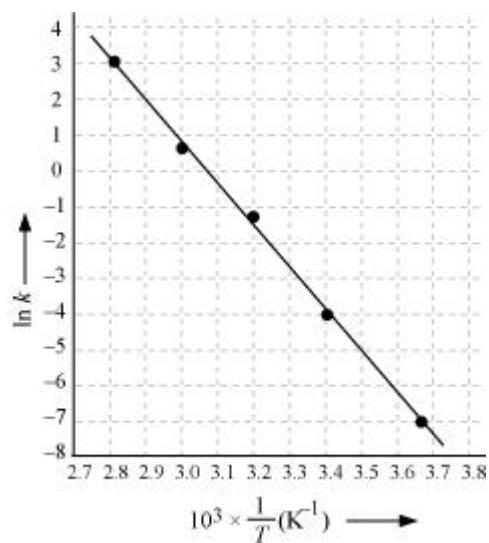
$T/^\circ\text{C}$	0	20	40	60	80
$10^5 \times k/\text{s}^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between $\ln k$ and $1/T$ and calculate the values of A and E_a .

Predict the rate constant at 30°C and 50°C .

From the given data, we obtain

$T/^\circ\text{C}$	0	20	40	60	80
T/K	273	293	313	333	353
$\frac{1}{T}/\text{K}^{-1}$	3.66×10^{-3}	3.41×10^{-3}	3.19×10^{-3}	3.0×10^{-3}	2.83×10^{-3}
$10^5 \times k/\text{s}^{-1}$	0.0787	1.70	25.7	178	2140
$\ln k$	-7.147	-4.075	-1.359	-0.577	3.063



Slope of the line,

$$\frac{y_2 - y_1}{x_2 - x_1} = -12.301 \text{ K}$$

According to Arrhenius equation,

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$$\begin{aligned}
 \text{Slope} &= -\frac{E_a}{R} \\
 \Rightarrow E_a &= -\text{Slope} \times R \\
 &= -(-12.301 \text{ K}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \\
 &= 102.27 \text{ kJ mol}^{-1}
 \end{aligned}$$

Again,

$$\begin{aligned}
 \ln k &= \ln A - \frac{E_a}{RT} \\
 \ln A &= \ln k + \frac{E_a}{RT}
 \end{aligned}$$

When $T = 273 \text{ K}$,

$$\ln k = -7.147$$

$$\begin{aligned}
 \text{Then, } \ln A &= -7.147 + \frac{102.27 \times 10^3}{8.314 \times 273} \\
 &= 37.911
 \end{aligned}$$

$$\text{Therefore, } A = 2.91 \times 10^6$$

When $T = 30 + 273 \text{ K} = 303 \text{ K}$,

$$\frac{1}{T} = 0.0033 \text{ K} = 3.3 \times 10^{-3} \text{ K}$$

$$\begin{aligned}
 \text{Then, at } \frac{1}{T} &= 3.3 \times 10^{-3} \text{ K,} \\
 \ln k &= -2.8
 \end{aligned}$$

$$\text{Therefore, } k = 6.08 \times 10^{-2} \text{ s}^{-1}$$

Again, when $T = 50 + 273 \text{ K} = 323 \text{ K}$,

$$\frac{1}{T} = 0.0031 \text{ K} = 3.1 \times 10^{-3} \text{ K}$$

$$\begin{aligned}
 \text{Then, at } \frac{1}{T} &= 3.1 \times 10^{-3} \text{ K,} \\
 \ln k &= -2.8
 \end{aligned}$$

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$$\ln k = -0.5$$

$$\text{Therefore, } k = 0.607 \text{ s}^{-1}$$

Question 4.23:

The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5} \text{ s}^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor

$$k = 2.418 \times 10^{-5} \text{ s}^{-1}$$

$$T = 546 \text{ K}$$

$$E_a = 179.9 \text{ kJ mol}^{-1} = 179.9 \times 10^3 \text{ J mol}^{-1}$$

According to the Arrhenius equation,

$$k = A e^{-E_a/RT}$$

$$\Rightarrow \ln k = \ln A - \frac{E_a}{RT}$$

$$\Rightarrow \log k = \log A - \frac{E_a}{2.303 RT}$$

$$\begin{aligned}\Rightarrow \log A &= \log k + \frac{E_a}{2.303 RT} \\ &= \log(2.418 \times 10^{-5} \text{ s}^{-1}) + \frac{179.9 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 546 \text{ K}}\end{aligned}$$

$$= (0.3835 - 5) + 17.2082$$

$$= 12.5917$$

Therefore, $A = \text{antilog}(12.5917)$

$$= 3.9 \times 10^{12} \text{ s}^{-1} \text{ (approximately)}$$

Question 4.24:

Consider a certain reaction $A \rightarrow \text{Products}$ 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} .

$$k = 2.0 \times 10^{-2} \text{ s}^{-1}$$

$$T = 100 \text{ s}$$

$$[A]_0 = 1.0 \text{ mol L}^{-1}$$

Since the unit of k is s^{-1} , the given reaction is a first order reaction.

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$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

Therefore,

$$\begin{aligned} \Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} &= \frac{2.303}{100 \text{ s}} \log \frac{1.0}{[A]} \\ \Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} &= \frac{2.303}{100 \text{ s}} (-\log [A]) \\ \Rightarrow -\log [A] &= \frac{2.0 \times 10^{-2} \times 100}{2.303} \\ \Rightarrow [A] &= \text{anti log} \left(-\frac{2.0 \times 10^{-2} \times 100}{2.303} \right) \\ &= 0.135 \text{ mol L}^{-1} \text{ (approximately)} \end{aligned}$$

Hence, the remaining concentration of A is 0.135 mol L^{-1} .

Question 4.25:

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?

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,

$$= \frac{0.693}{3} \text{ h}^{-1}$$

$$= 0.231 \text{ h}^{-1}$$

$$= \frac{2.303}{8 \text{ h}} \log \frac{[R]_0}{[R]}$$

Then, 0.231 h^{-1}

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$$\Rightarrow \log \frac{[R]_0}{[R]} = \frac{0.231 \text{ h}^{-1} \times 8 \text{ h}}{2.303}$$

$$\Rightarrow \frac{[R]_0}{[R]} = \text{antilog}(0.8024)$$

$$\Rightarrow \frac{[R]_0}{[R]} = 6.3445$$

$$\begin{aligned}\Rightarrow \frac{[R]}{[R]_0} &= 0.1576 \text{ (approx)} \\ &= 0.158\end{aligned}$$

Hence, the fraction of sample of sucrose that remains after 8 hours is 0.158.

Question 4.26:

The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K}/T}$$

Calculate E_a .

The given equation is

$$k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K}/T} \text{ (i)}$$

Arrhenius equation is given by,

$$k = A e^{-E_a/RT} \text{ (ii)}$$

From equation (i) and (ii), we obtain

$$\frac{E_a}{RT} = \frac{28000 \text{ K}}{T}$$

$$\Rightarrow E_a = R \times 28000 \text{ K}$$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 28000 \text{ K}$$

$$= 232792 \text{ J mol}^{-1}$$

$$= 232.792 \text{ kJ mol}^{-1}$$

Question 4.27:

The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

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$$\log k = 14.34 - 1.25 \times 10^4 \text{ K}/T$$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?

Arrhenius equation is given by,

$$k = A e^{-E_a/RT}$$

$$\begin{aligned} \Rightarrow \ln k &= \ln A - \frac{E_a}{RT} \\ \Rightarrow \ln k &= \log A - \frac{E_a}{RT} \\ \Rightarrow \log k &= \log A - \frac{E_a}{2.303 RT} \end{aligned} \quad (\text{i})$$

The given equation is

$$\log k = 14.34 - 1.25 \times 10^4 \text{ K}/T \quad (\text{ii})$$

From equation (i) and (ii), we obtain

$$\begin{aligned} \frac{E_a}{2.303 RT} &= \frac{1.25 \times 10^4 \text{ K}}{T} \\ \Rightarrow E_a &= 1.25 \times 10^4 \text{ K} \times 2.303 \times R \\ &= 1.25 \times 10^4 \text{ K} \times 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 239339.3 \text{ J mol}^{-1} \text{ (approximately)} \\ &= 239.34 \text{ kJ mol}^{-1} \end{aligned}$$

Also, when $t_{1/2} = 256$ minutes,

$$\begin{aligned} k &= \frac{0.693}{t_{1/2}} \\ &= \frac{0.693}{256} \\ &= 2.707 \times 10^{-3} \text{ min}^{-1} \\ &= 4.51 \times 10^{-5} \text{ s}^{-1} \end{aligned}$$

It is also given that, $\log k = 14.34 - 1.25 \times 10^4 \text{ K}/T$

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$$\Rightarrow \log(4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\Rightarrow \log(0.654 - 05) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\Rightarrow \frac{1.25 \times 10^4 \text{ K}}{T} = 18.686$$

$$\Rightarrow T = \frac{1.25 \times 10^4 \text{ K}}{18.686}$$

$$= 668.95 \text{ K}$$

$$= 669 \text{ K (approximately)}$$

Question 4.28:

The decomposition of A into product has value of k as $4.5 \times 10^3 \text{ s}^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1} . At what temperature would k be $1.5 \times 10^4 \text{ s}^{-1}$?

From Arrhenius equation, we obtain

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\text{Also, } k_1 = 4.5 \times 10^3 \text{ s}^{-1}$$

$$T_1 = 273 + 10 = 283 \text{ K}$$

$$k_2 = 1.5 \times 10^4 \text{ s}^{-1}$$

$$E_a = 60 \text{ kJ mol}^{-1} = 6.0 \times 10^4 \text{ J mol}^{-1}$$

Then,

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{6.0 \times 10^4 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$\Rightarrow 0.5229 = 3133.627 \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$\Rightarrow \frac{0.5229 \times 283 T_2}{3133.627} = T_2 - 283$$

$$\Rightarrow 0.0472 T_2 = T_2 - 283$$

$$\Rightarrow 0.9528 T_2 = 283$$

$$\Rightarrow T_2 = 297.019 \text{ K (approximately)}$$

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$$= 297 \text{ K}$$

$$= 24^\circ\text{C}$$

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

Question 4.29:

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

$$4 \times 10^{10} \text{ s}^{-1}. \text{ Calculate } k \text{ at } 318 \text{ K and } E_a.$$

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$\text{At } 298 \text{ K, } t = \frac{2.303}{k} \log \frac{100}{90}$$

$$= \frac{0.1054}{k}$$

$$\text{At } 308 \text{ K, } t' = \frac{2.303}{k'} \log \frac{100}{75}$$

$$= \frac{0.2877}{k'}$$

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

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$$\log \frac{k'}{k} = \frac{E_a}{2.303R} \left(\frac{T' - T}{TT'} \right)$$

$$\log(2.7296) = \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{298 \times 308} \right)$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log(2.7296)}{308 - 298}$$

$$= 76640.096 \text{ J mol}^{-1}$$

$$= 76.64 \text{ kJ mol}^{-1}$$

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

$$\log k = \log A - \frac{E_a}{2.303 R T}$$

$$= \log(4 \times 10^{10}) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318}$$

$$= (0.6021 + 10) - 12.5876$$

$$= -1.9855$$

Therefore, $k = \text{Antilog}(-1.9855)$

$$= 1.034 \times 10^{-2} \text{ s}^{-1}$$

Question 4.30:

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.

From Arrhenius equation, we obtain

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$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

It is given that, $k_2 = 4k_1$

$$T_1 = 293\text{ K}$$

$$T_2 = 313\text{ K}$$

$$\text{Therefore, } \log \frac{4k_1}{k_2} = \frac{E_a}{2.303 \times 8.314} \left(\frac{313 - 293}{293 \times 313} \right)$$

$$\Rightarrow 0.6021 = \frac{20 \times E_a}{2.303 \times 8.314 \times 293 \times 313}$$

$$\Rightarrow E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$$

$$= 52863.33 \text{ J mol}^{-1}$$

$$= 52.86 \text{ kJ mol}^{-1}$$

Hence, the required energy of activation is $52.86 \text{ kJ mol}^{-1}$.

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Question 5.1:

Write any two characteristics of Chemisorption

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.

Question 5.2:

Why does physisorption decrease with the increase of temperature?

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.

Question 5.3:

Why are powdered substances more effective adsorbents than their crystalline forms?

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.

Question 5.4:

Why is it necessary to remove CO when ammonia is obtained by Haber's process?

It is important to remove CO in the synthesis of ammonia as CO adversely affects the activity of the iron catalyst, used in Haber's process.

Question 5.5:

Why is the ester hydrolysis slow in the beginning and becomes faster after sometime?

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

Question 5.6:

What is the role of desorption in the process of catalysis?

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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.

Question 5.7:

What modification can you suggest in the Hardy-Schulze law?

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'

Question 5.8:

Why is it essential to wash the precipitate with water before estimating it quantitatively?

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

Question 5.1:

Distinguish between the meaning of the terms adsorption and absorption.

Give one example of each.

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.

Question 5.2:

What is the difference between physisorption and chemisorption?

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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 $20\text{-}40 \text{ kJ mol}^{-1}$.	Enthalpy of adsorption is high as chemical bonds are formed. The values lie in the range of $40\text{-}400 \text{ kJ mol}^{-1}$.
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.

Question 5.3:

Give reason why a finely divided substance is more effective as an adsorbent.

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.

Question 5.4:

What are the factors which influence the adsorption of a gas on a solid?

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

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The greater the surface area of the adsorbent, the greater is the adsorption of a gas on the solid surface.

(3) Effect of pressure

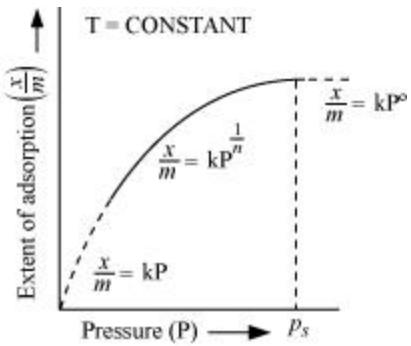
Adsorption is a reversible process and is accompanied by a decrease in pressure. Therefore, adsorption increases with an increase in pressure.

(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

Question 5.5:

What is an adsorption isotherm? Describe Freundlich adsorption isotherm.



$$\left(\frac{x}{m} \right)$$

The plot between the extent of adsorption $\left(\frac{x}{m} \right)$ 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.

$$\frac{x}{m}$$

From the given plot it is clear that at pressure P_s , $\frac{x}{m}$ reaches the maximum value. P_s is called the saturation pressure. Three cases arise from the graph now.

Case I - At low pressure:

$$\frac{x}{m}$$

The plot is straight and sloping, indicating that the pressure is directly proportional to $\frac{x}{m}$ i.e.,

$$\frac{x}{m} \propto P.$$

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$$\frac{x}{m} = k P \quad (k \text{ is a constant})$$

Case II - At high pressure:

$$\frac{x}{m}$$

When pressure exceeds the saturated pressure, $\frac{x}{m}$ becomes independent of P values.

$$\frac{x}{m} \propto P^\alpha$$

$$\frac{x}{m} = k P^\alpha$$

Case III - At intermediate pressure:

$$\frac{x}{m}$$

At intermediate pressure, $\frac{x}{m}$ depends on P raised to the powers between 0 and 1. This relationship is known as the Freundlich adsorption isotherm.

$$\frac{x}{m} \propto P^{\frac{1}{n}}$$

$$\frac{x}{m} = k P^{\frac{1}{n}} \quad n > 1$$

Now, taking log:

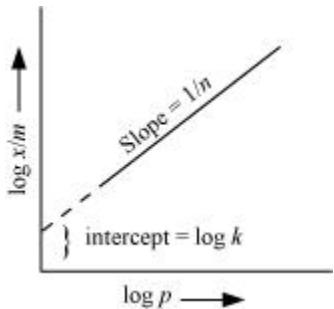
$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

$$\left(\frac{x}{m} \right)$$

On plotting the graph between $\log \left(\frac{x}{m} \right)$ and $\log P$, a straight line is obtained with the slope

$$\frac{1}{n}$$

equal to $\frac{1}{n}$ and the intercept equal to $\log k$.



Question 5.6:

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What do you understand by activation of adsorbent? How is it achieved?

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

Question 5.7:

What role does adsorption play in heterogeneous catalysis?

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

Question 5.8:

Why is adsorption always exothermic?

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.

$$\therefore \Delta G = \Delta H - T\Delta S$$

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Since ΔS is negative, ΔH has to be negative to make ΔG negative. Hence, adsorption is always exothermic

Question 5.9:

How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?

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

Question 5.10:

Discuss the effect of pressure and temperature on the adsorption of gases on solids.

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

Question 5.11:

What are lyophilic and lyophobic sols? Give one example of each type. Why are hydrophobic sols easily coagulated?

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(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

Question 5.12:

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?

(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.

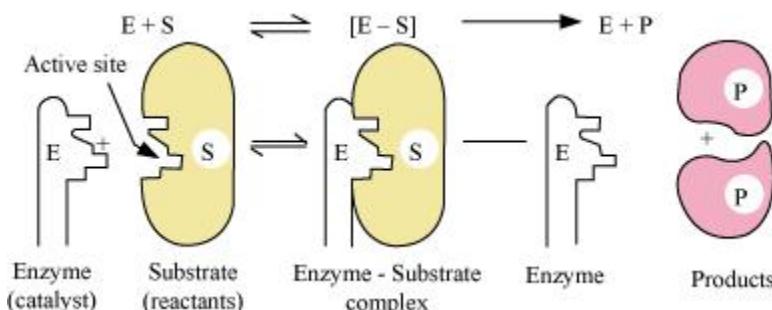
(iii) Certain substances tend to behave like normal electrolytes at lower concentrations. However, at higher concentrations, these substances behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called aggregated colloids

Question 5.13:

What are enzymes? Write in brief the mechanism of enzyme catalysis.

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'.

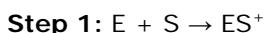
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Mechanism of enzyme catalysis:

On the surface of the enzymes, various cavities are present with characteristic shapes. These cavities possess active groups such as $-NH_2$, $-COOH$, 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,



(Activated complex)



Question 5.14:

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?

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

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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).

Question 5.15:

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?

(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

Question 5.16:

What are emulsions? What are their different types? Give example of each type.

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

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Question 5.17:

What is demulsification? Name two demulsifiers.

The process of decomposition of an emulsion into its constituent liquids is called demulsification. Examples of demulsifiers are surfactants, ethylene oxide, etc

Question 5.18:

Action of soap is due to emulsification and micelle formation. Comment.

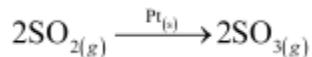
The cleansing action of soap is due to emulsification and micelle formation. Soaps are basically sodium and potassium salts of long chain fatty acids, $R-COO^-Na^+$. The end of the molecule to which the sodium is attached is polar in nature, while the alkyl-end is non-polar. Thus, a soap molecule contains 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

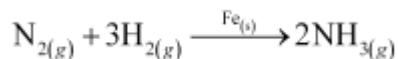
Question 5.19:

Give four examples of heterogeneous catalysis.

(i) Oxidation of sulphur dioxide to form sulphur trioxide. In this reaction, Pt acts as a catalyst.

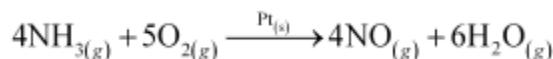


(ii) Formation of ammonia by the combination of dinitrogen and dihydrogen in the presence of finely divided iron.

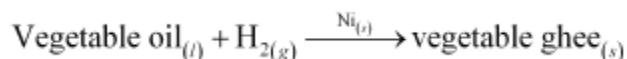


This process is called the Haber's process.

(iii) Oswald's process: Oxidation of ammonia to nitric oxide in the presence of platinum.



(iv) Hydrogenation of vegetable oils in the presence of Ni.



Question 5.20:

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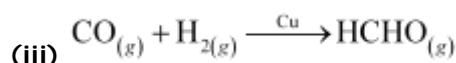
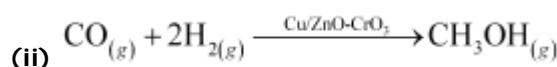
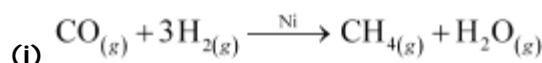
What do you mean by activity and selectivity of catalysts?

(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.



Question 5.21:

Describe some features of catalysis by zeolites.

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.

Question 5.22:

What is shape selective catalysis?

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.

Question 5.23:

Explain the following terms:

(i) Electrophoresis (ii) Coagulation

(iii) Dialysis (iv) Tyndall effect.

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(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

Question 5.24:

Give four uses of emulsions.

Four uses of emulsions:

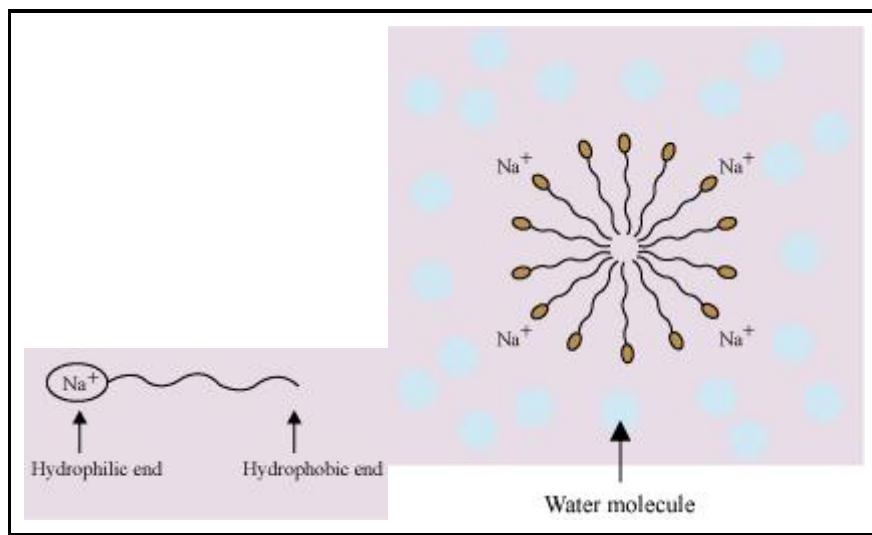
- (i) Cleansing action of soaps is based on the formation of emulsions.
- (ii) Digestion of fats in intestines takes place by the process of emulsification.
- (iii) Antiseptics and disinfectants when added to water form emulsions.
- (iv) The process of emulsification is used to make medicines

Question 5.25:

What are micelles? Give an example of a micelles system.

Micelle formation is done by substances such as soaps and detergents when dissolved in water. The molecules of such substances contain a hydrophobic and a hydrophilic part. When present in water, these substances arrange themselves in spherical structures in such a manner that their hydrophobic parts are present towards the centre, while the hydrophilic parts are pointing towards the outside (as shown in the given figure). This is known as micelle formation.

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Question 5.26:

Explain the terms with suitable examples:

- (i) Alcosol (ii) Aerosol (iii) Hydrosol

(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

Question 5.27:

Comment on the statement that "colloid is not a substance but a state of substance".

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.

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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

ELECTROCHEMISTRY NCERT SOLUTION

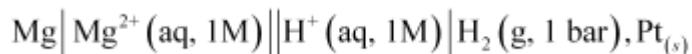
ELECTROCHEMISTRY

Question 3.1:

How would you determine the standard electrode potential of the system $Mg^{2+} \mid Mg$?

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

A cell, consisting of $Mg \mid MgSO_4 \text{ (aq 1 M)}$ as the anode and the standard hydrogen electrode as the cathode, is set up.



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_R^\ominus for the standard hydrogen electrode is zero.

$$\therefore E^\ominus = 0 - E_L^\ominus$$

$$= -E_L^\ominus$$

Question 3.2:

Can you store copper sulphate solutions in a zinc pot?

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.

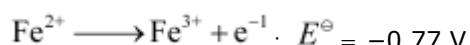


Hence, copper sulphate solution cannot be stored in a zinc pot.

Question 3.3:

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

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

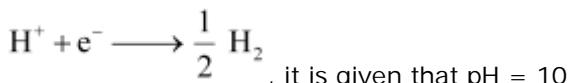


ELECTROCHEMISTRY NCERT SOLUTION

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.

Question 3.4:

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



For hydrogen electrode, , it is given that pH = 10

$$\therefore [\text{H}^+] = 10^{-10} \text{ M}$$

Now, using Nernst equation:

$$E_{\left(\text{H}^+/\frac{1}{2}\text{H}_2\right)} = E_{\left(\text{H}^+/\frac{1}{2}\text{H}_2\right)}^\ominus - \frac{RT}{nF} \ln \left[\frac{1}{[\text{H}^+]} \right]$$

$$= E_{\left(\text{H}^+/\frac{1}{2}\text{H}_2\right)}^\ominus - \frac{0.0591}{1} \log \left[\frac{1}{[\text{H}^+]} \right]$$

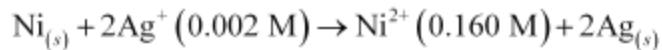
$$= 0 - \frac{0.0591}{1} \log \left[\frac{1}{10^{-10}} \right]$$

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

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

Question 3.5:

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



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

Applying Nernst equation we have:

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

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

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

$$= 1.05 - 0.02955 \log 4 \times 10^4$$

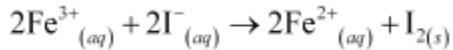
$$= 1.05 - 0.02955 (\log 10000 + \log 4)$$

$$= 1.05 - 0.02955 (4 + 0.6021)$$

$$= 0.914 \text{ V}$$

Question 3.6:

The cell in which the following reactions occurs:



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

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

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

We know that:

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

$$= -2 \times 96487 \times 0.236$$

$$= -45541.864 \text{ J mol}^{-1}$$

$$= -45.54 \text{ kJ mol}^{-1}$$

$$\text{Again, } \Delta_r G^{\ominus} = -2.303RT \log K_c$$

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$$\Rightarrow \log K_c = -\frac{\Delta_r G^\ominus}{2.303 RT}$$
$$= -\frac{-45.54 \times 10^3}{2.303 \times 8.314 \times 298}$$
$$= 7.981$$

$$\therefore K_c = \text{Antilog } (7.981)$$

$$= 9.57 \times 10^7$$

Question 3.7:

Why does the conductivity of a solution decrease with dilution?

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.

Question 3.8:

Suggest a way to determine the Λ_m^\ominus value of water.

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

$$\begin{aligned}\Lambda_{m(H_2O)}^\ominus &= \lambda_{H^+}^\ominus + \lambda_{OH^-}^\ominus \\ &= (\lambda_{H^+}^\ominus + \lambda_{Cl^-}^\ominus) + (\lambda_{Na^+}^\ominus + \lambda_{OH^-}^\ominus) - (\lambda_{Na^+}^\ominus + \lambda_{Cl^-}^\ominus) \\ \Lambda_{m(HCl)}^\ominus + \Lambda_{m(NaOH)}^\ominus - \Lambda_{m(NaCl)}^\ominus\end{aligned}$$

Hence, by knowing the Λ_m^\ominus values of HCl, NaOH, and NaCl, the Λ_m^\ominus value of water can be determined

Question 3.9:

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

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

Calculate its degree of dissociation and dissociation constant. Given $\lambda^\circ(H^+)$

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= 349.6 S cm² mol⁻¹ and λ° (HCOO⁻) = 54.6 S cm² mol

$$C = 0.025 \text{ mol L}^{-1}$$

$$\Lambda_m = 46.1 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\lambda^{\circ}(H^+) = 349.6 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\lambda^{\circ}(HCOO^-) = 54.6 \text{ Scm}^2 \text{ mol}^{-1}$$

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

$$= 349.6 + 54.6$$

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

Now, degree of dissociation:

$$\begin{aligned}\alpha &= \frac{\Lambda_m(HCOOH)}{\Lambda_m^{\circ}(HCOOH)} \\ &= \frac{46.1}{404.2} \\ &= 0.114 (\text{approximately})\end{aligned}$$

Thus, dissociation constant:

$$\begin{aligned}K &= \frac{c \alpha^2}{(1-\alpha)} \\ &= \frac{(0.025 \text{ mol L}^{-1})(0.114)^2}{(1-0.114)} \\ &= 3.67 \times 10^{-4} \text{ mol L}^{-1}\end{aligned}$$

Question 3.10:

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

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

$$t = 2 \text{ hours} = 2 \times 60 \times 60 \text{ s} = 7200 \text{ s}$$

$$\text{Thus, } Q = It$$

$$= 0.5 \text{ A} \times 7200 \text{ s}$$

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$$= 3600 \text{ C}$$

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

Then,

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

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

Question 3.11:

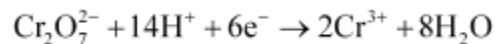
Suggest a list of metals that are extracted electrolytically

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

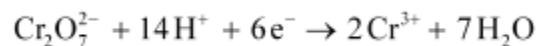
Question 3.12:

What is the quantity of electricity in coulombs needed to reduce 1 mol of

$\text{Cr}_2\text{O}_7^{2-}$? Consider the reaction:



The given reaction is as follows:



Therefore, to reduce 1 mole of $\text{Cr}_2\text{O}_7^{2-}$, the required quantity of electricity will be:

$$= 6 \text{ F}$$

$$= 6 \times 96487 \text{ C}$$

$$= 578922 \text{ C}$$

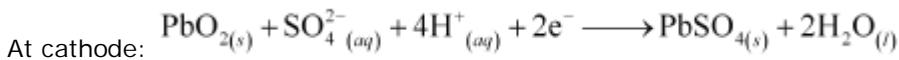
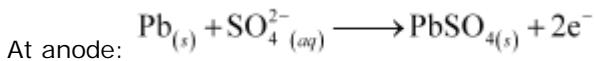
Question 3.13:

Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

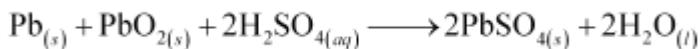
ELECTROCHEMISTRY NCERT SOLUTION

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:



The overall cell reaction is given by,



When a battery is charged, the reverse of all these reactions takes place.

Hence, on charging, $\text{PbSO}_{4(s)}$ present at the anode and cathode is converted into $\text{Pb}_{(s)}$ and $\text{PbO}_{2(s)}$ respectively.

Question 3.14:

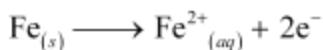
Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Methane and methanol can be used as fuels in fuel cells.

Question 3.15:

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

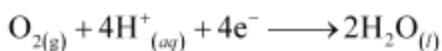
In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,



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

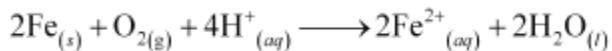
There, in the presence of H^+ ions, the electrons reduce oxygen. This spot behaves as the cathode. These H^+ ions come either from H_2CO_3 , which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.

The reaction corresponding at the cathode is given by,



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The overall reaction is:



Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide ($\text{Fe}_2\text{O}_3, x\text{H}_2\text{O}$) i.e., rust.

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

Question 3.1:

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

The following is the order in which the given metals displace each other from the solution of their salts.

Mg, Al, Zn, Fe, Cu

Question 3.2:

Given the standard electrode potentials,

$$\text{K}^{+}/\text{K} = -2.93\text{V}, \text{Ag}^{+}/\text{Ag} = 0.80\text{V},$$

$$\text{Hg}^{2+}/\text{Hg} = 0.79\text{V}$$

$$\text{Mg}^{2+}/\text{Mg} = -2.37\text{ V}, \text{Cr}^{3+}/\text{Cr} = -0.74\text{V}$$

Arrange these metals in their increasing order of reducing power

The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of $\text{K}^{+}/\text{K} < \text{Mg}^{2+}/\text{Mg} < \text{Cr}^{3+}/\text{Cr} < \text{Hg}^{2+}/\text{Hg} < \text{Ag}^{+}/\text{Ag}$.

Hence, the reducing power of the given metals increases in the following order:

Ag < Hg < Cr < Mg < K

Question 3.3:

Depict the galvanic cell in which the reaction $\text{Zn}(s) + 2\text{Ag}^{+}(aq) \rightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$ takes place. Further show:

ELECTROCHEMISTRY NCERT SOLUTION

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode

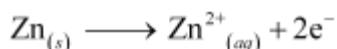
The galvanic cell in which the given reaction takes place is depicted as:



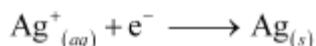
(i) Zn electrode (anode) is negatively charged.

(ii) Ions 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,

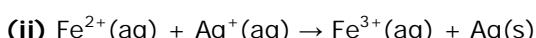
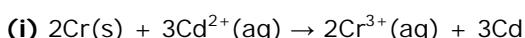


The reaction taking place at the cathode is given by,

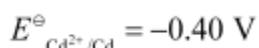
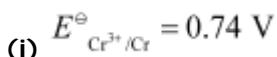


Question 3.4:

Calculate the standard cell potentials of galvanic cells in which the following reactions take place:



Calculate the $\Delta_r G^\ominus$ and equilibrium constant of the reactions



The galvanic cell of the given reaction is depicted as:



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Now, the standard cell potential is

$$\begin{aligned} E_{\text{cell}}^{\ominus} &= E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus} \\ &= -0.40 - (-0.74) \\ &= +0.34 \text{ V} \\ \Delta_r G^{\ominus} &= -nFE_{\text{cell}}^{\ominus} \end{aligned}$$

In the given equation,

$$n = 6$$

$$F = 96487 \text{ C mol}^{-1}$$

$$E_{\text{cell}}^{\ominus} = +0.34 \text{ V}$$

$$\begin{aligned} \text{Then, } \Delta_r G^{\ominus} &= -6 \times 96487 \text{ C mol}^{-1} \times 0.34 \text{ V} \\ &= -196833.48 \text{ CV mol}^{-1} \\ &= -196833.48 \text{ J mol}^{-1} \\ &= -196.83 \text{ kJ mol}^{-1} \end{aligned}$$

Again,

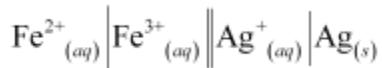
$$\begin{aligned} \Delta_r G^{\ominus} &= -RT \ln K \\ \Rightarrow \Delta_r G^{\ominus} &= -2.303 RT \ln K \\ \Rightarrow \log K &= -\frac{\Delta_r G}{2.303 RT} \\ &= \frac{-196.83 \times 10^3}{2.303 \times 8.314 \times 298} \\ &= 34.496 \\ \therefore K &= \text{antilog (34.496)} \\ &= 3.13 \times 10^{34} \end{aligned}$$

$$\text{(ii) } E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\ominus} = 0.77 \text{ V}$$

$$E_{\text{Ag}^+/\text{Ag}}^{\ominus} = 0.80 \text{ V}$$

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The galvanic cell of the given reaction is depicted as:



Now, the standard cell potential is

$$\begin{aligned} E_{\text{cell}}^\ominus &= E_R^\ominus - E_L^\ominus \\ &= 0.80 - 0.77 \\ &= 0.03 \text{ V} \end{aligned}$$

Here, $n = 1$.

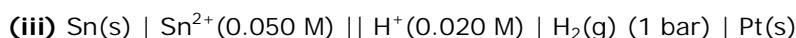
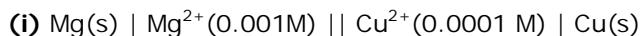
$$\begin{aligned} \Delta_r G^\ominus &= -nFE_{\text{cell}}^\ominus \\ \text{Then, } &= -1 \times 96487 \text{ C mol}^{-1} \times 0.03 \text{ V} \\ &= -2894.61 \text{ J mol}^{-1} \\ &= -2.89 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Again, } \Delta_r G^\ominus = -2.303 RT \ln K$$

$$\begin{aligned} \Rightarrow \log K &= -\frac{\Delta_r G}{2.303 RT} \\ &= \frac{-2894.61}{2.303 \times 8.314 \times 298} \\ &= 0.5073 \\ \therefore K &= \text{antilog (0.5073)} \\ &= 3.2 \text{ (approximately)} \end{aligned}$$

Question 3.5:

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



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

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \\ &= \{0.34 - (-2.36)\} - \frac{0.0591}{2} \log \frac{.001}{.0001} \\ &= 2.7 - \frac{0.0591}{2} \log 10 \end{aligned}$$

$$= 2.7 - 0.02955$$

$$= 2.67 \text{ V (approximately)}$$

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

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2} \\ &= \{0 - (-0.44)\} - \frac{0.0591}{2} \log \frac{0.001}{1^2} \\ &= 0.44 - 0.02955(-3) \end{aligned}$$

$$= 0.52865 \text{ V}$$

$$= 0.53 \text{ V (approximately)}$$

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

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2} \\ &= \{0 - (-0.14)\} - \frac{0.0591}{2} \log \frac{0.050}{(0.020)^2} \end{aligned}$$

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

$$= 0.14 - 0.062$$

$$= 0.078 \text{ V}$$

$$= 0.08 \text{ V (approximately)}$$

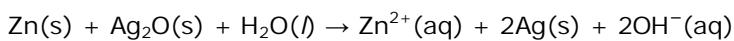
(iv) For the given reaction, the Nernst equation can be given as:

ELECTROCHEMISTRY NCERT SOLUTION

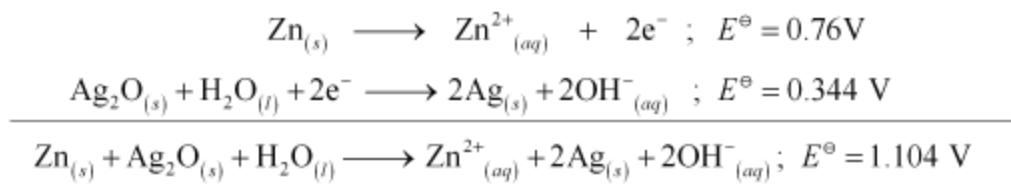
$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2} \\
 &= (0 - 1.09) - \frac{0.0591}{2} \log \frac{1}{(0.010)^2 (0.030)^2} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{0.00000009} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \\
 &= -1.09 - 0.02955 \times \log (1.11 \times 10^7) \\
 &= -1.09 - 0.02955 (0.0453 + 7) \\
 &= -1.09 - 0.208 \\
 &= -1.298 \text{ V}
 \end{aligned}$$

Question 3.6:

In the button cells widely used in watches and other devices the following reaction takes place:



Determine $\Delta_r G^{\ominus}$ and E^{\ominus} for the reaction



$$\therefore E^{\ominus} = 1.104 \text{ V}$$

We know that,

$$\begin{aligned}
 \Delta_r G^{\ominus} &= -nFE^{\ominus} \\
 &= -2 \times 96487 \times 1.04 \\
 &= -213043.296 \text{ J} \\
 &= -213.04 \text{ kJ}
 \end{aligned}$$

Question 3.7:

ELECTROCHEMISTRY NCERT SOLUTION

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

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 κ . If ρ 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 $a = 1$, $l = 1$)

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

Molar conductivity:

Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing 1 mole of the electrolyte kept between two electrodes with the area of cross-section A and distance of unit length.

$$\Lambda_m = \kappa \frac{A}{l}$$

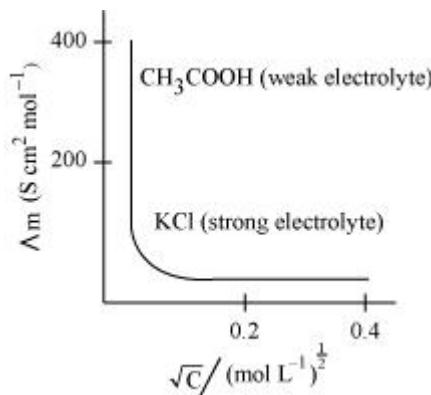
Now, $l = 1$ and $A = V$ (volume containing 1 mole of the electrolyte).

$$\therefore \Lambda_m = \kappa V$$

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

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

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Question 3.8:

The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm^{-1} . Calculate its molar conductivity.

Given,

$$\kappa = 0.0248 \text{ S cm}^{-1}$$

$$c = 0.20 \text{ M}$$

$$\therefore \text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{c}$$

$$= \frac{0.0248 \times 1000}{0.2}$$

$$= 124 \text{ Scm}^2 \text{mol}^{-1}$$

Question 3.9:

The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$.

Given,

$$\text{Conductivity, } \kappa = 0.146 \times 10^{-3} \text{ S cm}^{-1}$$

$$\text{Resistance, } R = 1500 \Omega$$

$$\therefore \text{Cell constant} = \kappa \times R$$

$$= 0.146 \times 10^{-3} \times 1500$$

$$= 0.219 \text{ cm}^{-1}$$

ELECTROCHEMISTRY NCERT SOLUTION

Question 3.10:

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

$10^2 \times \kappa / \text{S m}^{-1}$ 1.237 11.85 23.15 55.53 106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m^0 .

Given,

$$\kappa = 1.237 \times 10^{-2} \text{ S m}^{-1}, c = 0.001 \text{ M}$$

$$\text{Then, } \kappa = 1.237 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.0316 \text{ M}^{1/2}$$

$$\begin{aligned}\therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{1.237 \times 10^{-4} \text{ S cm}^{-1}}{0.001 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 123.7 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

$$\kappa = 11.85 \times 10^{-2} \text{ S m}^{-1}, c = 0.010 \text{ M}$$

$$\text{Then, } \kappa = 11.85 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.1 \text{ M}^{1/2}$$

$$\begin{aligned}\therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{11.85 \times 10^{-4} \text{ S cm}^{-1}}{0.010 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 118.5 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

$$\kappa = 23.15 \times 10^{-2} \text{ S m}^{-1}, c = 0.020 \text{ M}$$

$$\text{Then, } \kappa = 23.15 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.1414 \text{ M}^{1/2}$$

ELECTROCHEMISTRY NCERT SOLUTION

$$\begin{aligned}\therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{23.15 \times 10^{-4} \text{ S cm}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 115.8 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

$$\kappa = 55.53 \times 10^{-2} \text{ S m}^{-1}, c = 0.050 \text{ M}$$

$$\text{Then, } \kappa = 55.53 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.2236 \text{ M}^{1/2}$$

$$\begin{aligned}\therefore \kappa &= \frac{\kappa}{c} \\ &= \frac{55.53 \times 10^{-4} \text{ S cm}^{-1}}{0.050 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 111.1 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

$$\kappa = 106.74 \times 10^{-2} \text{ S m}^{-1}, c = 0.100 \text{ M}$$

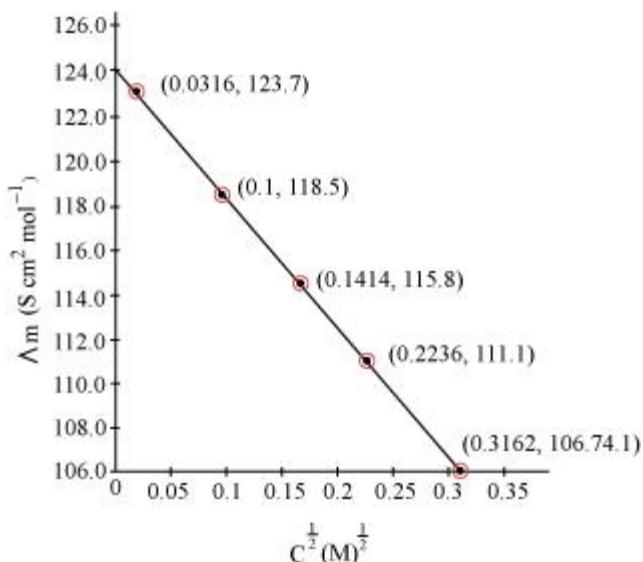
$$\text{Then, } \kappa = 106.74 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.3162 \text{ M}^{1/2}$$

$$\begin{aligned}\therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 106.74 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Now, we have the following data:

$C^{1/2} / M^{1/2}$	0.0316	0.1	0.1414	0.2236	0.3162
$\Lambda_m (\text{S cm}^2 \text{ mol}^{-1})$	123.7	118.5	115.8	111.1	106.74

ELECTROCHEMISTRY NCERT SOLUTION



Since the line intersects Λ_m at $124.0 \text{ S cm}^2 \text{ mol}^{-1}$, $\Lambda_m^0 = 124.0 \text{ S cm}^2 \text{ mol}^{-1}$.

Question 3.11:

Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and if Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

Given, $\kappa = 7.896 \times 10^{-5} \text{ S m}^{-1}$

$$c = 0.00241 \text{ mol L}^{-1}$$

$$\text{Then, molar conductivity, } \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1}}{0.00241 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Again, } \Lambda_m^0 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Now, } \alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}}$$

$$= 0.084$$

ELECTROCHEMISTRY NCERT SOLUTION

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

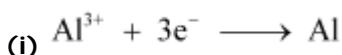
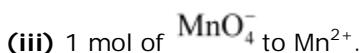
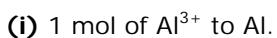
∴ Dissociation constant,

$$= \frac{(0.00241 \text{ mol L}^{-1})(0.084)^2}{(1-0.084)}$$

$$= 1.86 \times 10^{-5} \text{ mol L}^{-1}$$

Question 3.12:

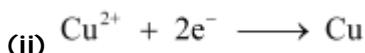
How much charge is required for the following reductions:



∴ Required charge = 3 F

$$= 3 \times 96487 \text{ C}$$

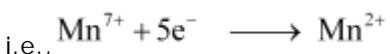
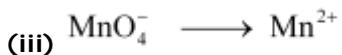
$$= 289461 \text{ C}$$



∴ Required charge = 2 F

$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$



∴ Required charge = 5 F

$$= 5 \times 96487 \text{ C}$$

$$= 482435 \text{ C}$$

ELECTROCHEMISTRY NCERT SOLUTION

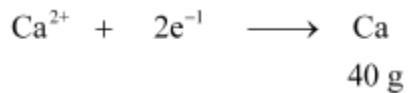
Question 3.13:

How much electricity in terms of Faraday is required to produce

(i) 20.0 g of Ca from molten CaCl_2 .

(ii) 40.0 g of Al from molten Al_2O_3 .

(i) According to the question,



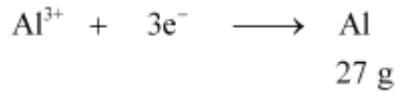
Electricity required to produce 40 g of calcium = 2 F

$$= \frac{2 \times 20}{40} \text{ F}$$

Therefore, electricity required to produce 20 g of calcium

$$= 1 \text{ F}$$

(ii) According to the question,



Electricity required to produce 27 g of Al = 3 F

$$= \frac{3 \times 40}{27} \text{ F}$$

Therefore, electricity required to produce 40 g of Al

$$= 4.44 \text{ F}$$

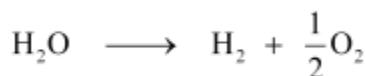
Question 3.14:

How much electricity is required in coulomb for the oxidation of

(i) 1 mol of H_2O to O_2 .

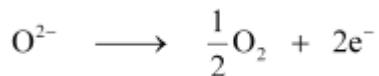
(ii) 1 mol of FeO to Fe_2O_3 .

(i) According to the question,



ELECTROCHEMISTRY NCERT SOLUTION

Now, we can write:

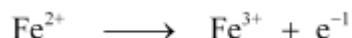


Electricity required for the oxidation of 1 mol of H₂O to O₂ = 2 F

$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$

(ii) According to the question,



Electricity required for the oxidation of 1 mol of FeO to Fe₂O₃ = 1 F

$$= 96487 \text{ C}$$

Question 3.15:

A solution of Ni(NO₃)₂ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Given,

Current = 5A

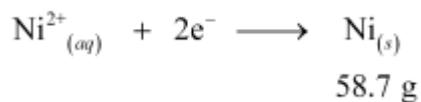
Time = 20 × 60 = 1200 s

∴ Charge = current × time

$$= 5 \times 1200$$

$$= 6000 \text{ C}$$

According to the reaction,



Nickel deposited by 2 × 96487 C = 58.71 g

$$= \frac{58.71 \times 6000}{2 \times 96487} \text{ g}$$

Therefore, nickel deposited by 6000 C

$$= 1.825 \text{ g}$$

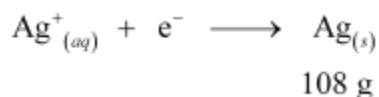
ELECTROCHEMISTRY NCERT SOLUTION

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

Question 3.16:

Three electrolytic cells A,B,C containing solutions of ZnSO_4 , AgNO_3 and CuSO_4 , 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?

According to the reaction:



i.e., 108 g of Ag is deposited by 96487 C.

$$\frac{96487 \times 1.45}{108} \text{ C}$$

Therefore, 1.45 g of Ag is deposited by =

$$= 1295.43 \text{ C}$$

Given,

Current = 1.5 A

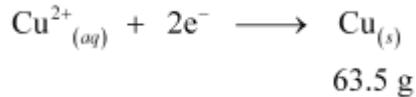
$$\therefore \text{Time} = \frac{1295.43}{1.5} \text{ s}$$

$$= 863.6 \text{ s}$$

$$= 864 \text{ s}$$

$$= 14.40 \text{ min}$$

Again,



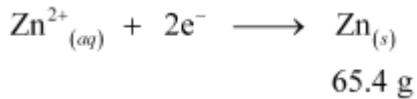
i.e., 2×96487 C of charge deposit = 63.5 g of Cu

$$= \frac{63.5 \times 1295.43}{2 \times 96487} \text{ g}$$

Therefore, 1295.43 C of charge will deposit

$$= 0.426 \text{ g of Cu}$$

ELECTROCHEMISTRY NCERT SOLUTION



i.e., 2×96487 C of charge deposit = 65.4 g of Zn

$$= \frac{65.4 \times 1295.43}{2 \times 96487} \text{ g}$$

Therefore, 1295.43 C of charge will deposit

= 0.439 g of Zn

Question 3.17:

Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:

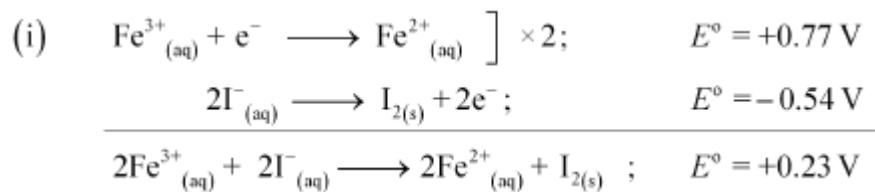
(i) $\text{Fe}^{3+}_{(aq)}$ and $\text{I}^-_{(aq)}$

(ii) $\text{Ag}^+_{(aq)}$ and $\text{Cu}_{(s)}$

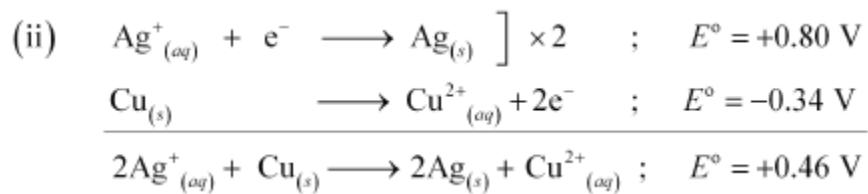
(iii) $\text{Fe}^{3+}_{(aq)}$ and $\text{Br}^-_{(aq)}$

(iv) $\text{Ag}_{(s)}$ and $\text{Fe}^{3+}_{(aq)}$

(v) $\text{Br}_2_{(aq)}$ and $\text{Fe}^{2+}_{(aq)}$.

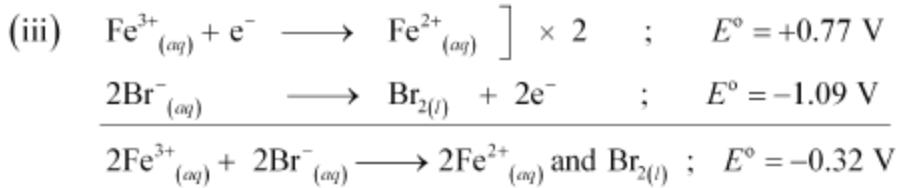


Since E° for the overall reaction is positive, the reaction between $\text{Fe}^{3+}_{(aq)}$ and $\text{I}^-_{(aq)}$ is feasible.

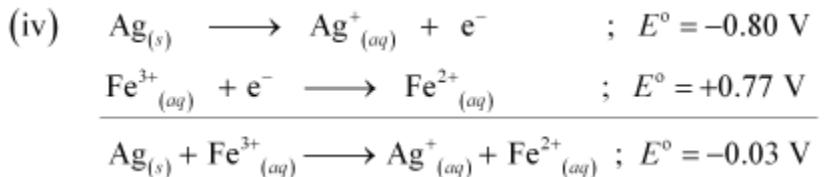


Since E° for the overall reaction is positive, the reaction between $\text{Ag}^+_{(aq)}$ and $\text{Cu}_{(s)}$ is feasible.

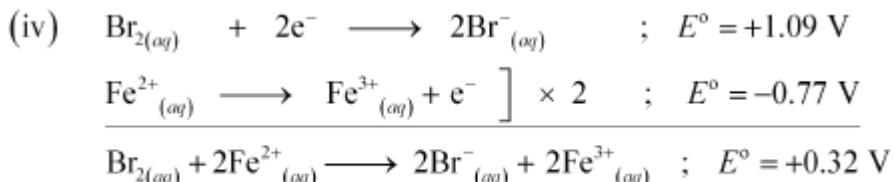
ELECTROCHEMISTRY NCERT SOLUTION



Since E° for the overall reaction is negative, the reaction between $\text{Fe}^{3+}_{(aq)}$ and $\text{Br}^-_{(aq)}$ is not feasible.



Since E° for the overall reaction is negative, the reaction between $\text{Ag}_{(s)}$ and $\text{Fe}^{3+}_{(aq)}$ is not feasible.



Since E° for the overall reaction is positive, the reaction between $\text{Br}_2(aq)$ and $\text{Fe}^{2+}_{(aq)}$ is feasible.

Question 3.18:

Predict the products of electrolysis in each of the following:

(i) An aqueous solution of AgNO_3 with silver electrodes.

(ii) An aqueous solution of AgNO_3 with platinum electrodes.

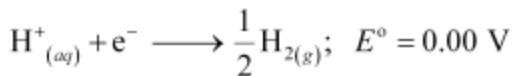
(iii) A dilute solution of H_2SO_4 with platinum electrodes.

(iv) An aqueous solution of CuCl_2 with platinum electrodes.

(i) At cathode:

The following reduction reactions compete to take place at the cathode.

ELECTROCHEMISTRY NCERT SOLUTION



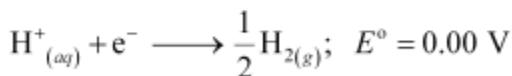
The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

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:

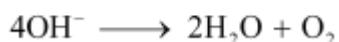
The following reduction reactions compete to take place at the cathode.



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:

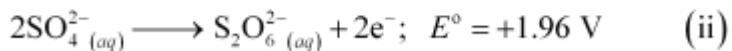
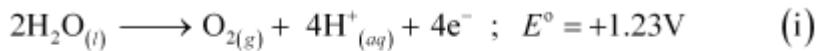
Since Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or O_2 ions can be oxidized at the anode. But OH^- ions having a lower discharge potential and get preference and decompose to liberate O_2 .



(iii) At the cathode, the following reduction reaction occurs to produce H_2 gas.



At the anode, the following processes are possible.

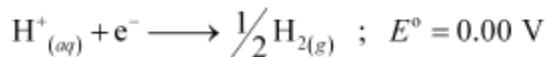
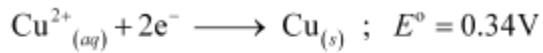


ELECTROCHEMISTRY NCERT SOLUTION

For dilute sulphuric acid, reaction (i) is preferred to produce O₂ gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At cathode:

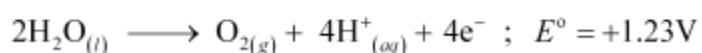
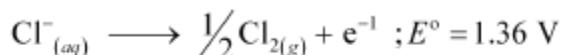
The following reduction reactions compete to take place at the cathode.



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.



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

P BLOCK ELEMENT : NCERT SOLUTION

P BLOCK ELEMENT

Question 7.1:

Why are pentahalides more covalent than trihalides?

Answer

In pentahalides, the oxidation state is +5 and in trihalides, the oxidation state is +3. Since the metal ion with a high charge has more polarizing power, pentahalides are more covalent than trihalides.

Question 7.2:

Why is BiH_3 the strongest reducing agent amongst all the hydrides of

Group 15 elements?

Answer

As we move down a group, the atomic size increases and the stability of the hydrides of group 15 elements decreases. Since the stability of hydrides decreases on moving from NH_3 to BiH_3 , the reducing character of the hydrides increases on moving from NH_3 to BiH_3 .

Question 7.3:

Why is N_2 less reactive at room temperature?

Answer

The two N atoms in N_2 are bonded to each other by very strong triple covalent bonds. The bond dissociation energy of this bond is very high. As a result, N_2 is less reactive at room temperature.

Question 7.4:

Mention the conditions required to maximise the yield of ammonia.

Answer

Ammonia is prepared using the Haber's process. The yield of ammonia can be maximized under the following conditions:

- (i) High pressure ($\square 200 \text{ atm}$)
- (ii) A temperature of $\square 700 \text{ K}$
- (iii) Use of a catalyst such as iron oxide mixed with small amounts of K_2O and Al_2O_3

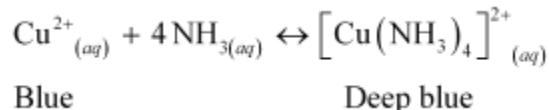
P BLOCK ELEMENT : NCERT SOLUTION

Question 7.5:

How does ammonia react with a solution of Cu^{2+} ?

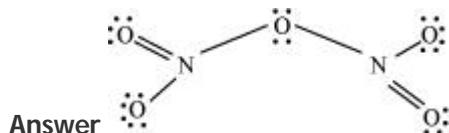
Answer

NH_3 acts as a Lewis base. It donates its electron pair and forms a linkage with metal ion.



Question 7.6:

What is the covalence of nitrogen in N_2O_5 ?



From the structure of N_2O_5 , it is evident that the covalence of nitrogen is 4

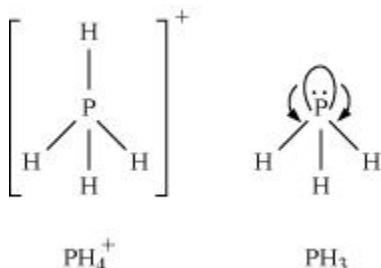
Question 7.7:

Bond angle in PH_4^+ is higher than that in PH_3 . Why?

Answer

In PH_3 , P is sp^3 hybridized. Three orbitals are involved in bonding with three hydrogen atoms and the fourth one contains a lone pair. As lone pair-bond pair repulsion is stronger than bond pair-bond pair repulsion, the tetrahedral shape associated with sp^3 bonding is changed to

pyramidal. PH_3 combines with a proton to form PH_4^+ in which the lone pair is absent. Due to the absence of lone pair in PH_4^+ , there is no lone pair-bond pair repulsion. Hence, the bond angle in PH_4^+ is higher than the bond angle in PH_3 .



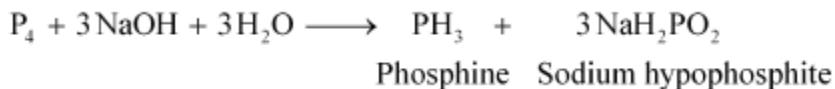
Question 7.8:

P BLOCK ELEMENT : NCERT SOLUTION

What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO₂?

Answer

White phosphorous dissolves in boiling NaOH solution (in a CO₂ atmosphere) to give phosphine, PH₃.



Question 7.9:

What happens when PCl₅ is heated?

Answer

All the bonds that are present in PCl₅ are not similar. It has three equatorial and two axial bonds. The equatorial bonds are stronger than the axial ones. Therefore, when PCl₅ is heated strongly, it decomposes to form PCl₃.

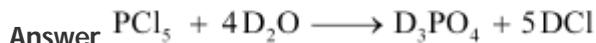


Question 7.10:

Write a balanced equation for the hydrolytic reaction of PCl₅ in heavy water.



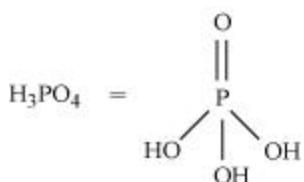
Therefore, the net reaction can be written as



Question 7.11:

What is the basicity of H₃PO₄?

Answer



P BLOCK ELEMENT : NCERT SOLUTION

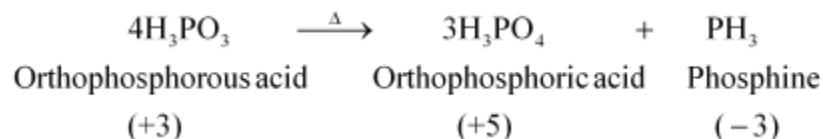
Since there are three OH groups present in H_3PO_4 , its basicity is three i.e., it is a tribasic acid.

Question 7.12:

What happens when H_3PO_3 is heated?

Answer

H_3PO_3 , on heating, undergoes disproportionation reaction to form PH_3 and H_3PO_4 . The oxidation numbers of P in H_3PO_3 , PH_3 , and H_3PO_4 are +3, -3, and +5 respectively. As the oxidation number of the same element is decreasing and increasing during a particular reaction, the reaction is a disproportionation reaction.



Question 7.13:

List the important sources of sulphur.

Answer

Sulphur mainly exists in combined form in the earth's crust primarily as sulphates [gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), baryte (BaSO_4)] and sulphides [(galena (PbS), zinc blends (ZnS), copper pyrites (CuFeS_2))]

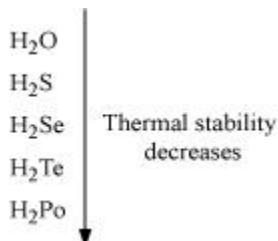
Question 7.14:

Write the order of thermal stability of the hydrides of Group 16 elements.

Answer

The thermal stability of hydrides decreases on moving down the group. This is due to a decrease in the bond dissociation enthalpy (H-E) of hydrides on moving down the group.

Therefore,



Question 7.15:

P BLOCK ELEMENT : NCERT SOLUTION

Why is H₂O a liquid and H₂S a gas?

Answer

H₂O has oxygen as the central atom. Oxygen has smaller size and higher electronegativity as compared to sulphur. Therefore, there is extensive hydrogen bonding in H₂O, which is absent in H₂S. Molecules of H₂S are held together only by weak van der Waal's forces of attraction.

Hence, H₂O exists as a liquid while H₂S as a solid.

Question 7.16:

Which of the following does not react with oxygen directly?

Zn, Ti, Pt, Fe

Answer

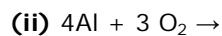
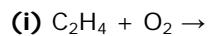
Discussion

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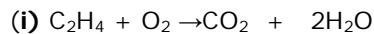
Pt is a noble metal and does not react very easily. All other elements, Zn, Ti, Fe, are quite reactive. Hence, oxygen does not react with platinum (Pt) directly

Question 7.17:

Complete the following reactions:



Answer



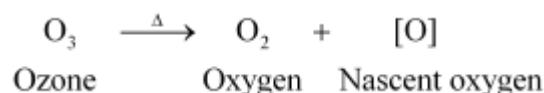
Question 7.18:

Why does O₃ act as a powerful oxidising agent?

Answer

P BLOCK ELEMENT : NCERT SOLUTION

Ozone is not a very stable compound under normal conditions and decomposes readily on heating to give a molecule of oxygen and nascent oxygen. Nascent oxygen, being a free radical, is very reactive.



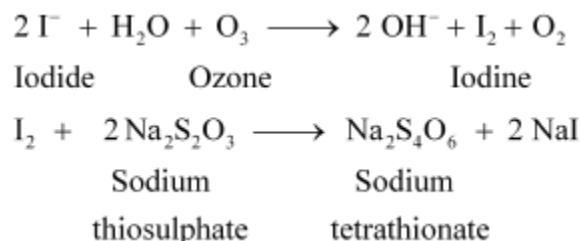
Therefore, ozone acts as a powerful oxidising agent.

Question 7.19:

How is O₃ estimated quantitatively?

Answer

Quantitatively, ozone can be estimated with the help of potassium iodide. When ozone is made to react with potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated. This liberated iodine can be titrated against a standard solution of sodium thiosulphate using starch as an indicator. The reactions involved in the process are given below.



Question 7.20:

What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?

Answer

SO₂ acts as a reducing agent when passed through an aqueous solution containing Fe(III) salt. It reduces Fe(III) to Fe(II) i.e., ferric ions to ferrous ions.



Question 7.21:

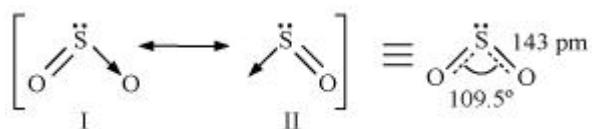
Comment on the nature of two S–O bonds formed in SO₂ molecule. Are the two S–O bonds in this molecule equal?

Answer

The electronic configuration of S is 1s² 2s² 2p⁶ 3s² 3p⁴.

P BLOCK ELEMENT : NCERT SOLUTION

During the formation of SO_2 , one electron from $3p$ orbital goes to the $3d$ orbital and S undergoes sp^2 hybridization. Two of these orbitals form sigma bonds with two oxygen atoms and the third contains a lone pair. p -orbital and d -orbital contain an unpaired electron each. One of these electrons forms $p\pi-p\pi$ bond with one oxygen atom and the other forms $p\pi-d\pi$ bond with the other oxygen. This is the reason SO_2 has a bent structure. Also, it is a resonance hybrid of structures I and II.



Both S–O bonds are equal in length (143 pm) and have a multiple bond character

Question 7.22:

How is the presence of SO_2 detected?

Answer

SO_2 is a colourless and pungent smelling gas.

It can be detected with the help of potassium permanganate solution. When SO_2 is passed through an acidified potassium permanganate solution, it decolorizes the solution as it reduces MnO_4^- ions to Mn^{2+} ions.



Question 7.23:

Mention three areas in which H_2SO_4 plays an important role.

Answer

Sulphuric acid is an important industrial chemical and is used for a lot of purposes. Some important uses of sulphuric acid are given below.

- (i) It is used in fertilizer industry. It is used to make various fertilizers such as ammonium sulphate and calcium super phosphate.
- (ii) It is used in the manufacture of pigments, paints, and detergents.
- (iii) It is used in the manufacture of storage batteries

Question 7.24:

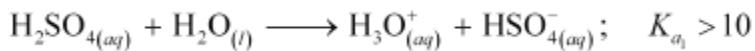
Write the conditions to maximize the yield of H_2SO_4 by Contact process.

Answer Question 7.25:

P BLOCK ELEMENT : NCERT SOLUTION

Why is $K_{a_2} \ll K_{a_1}$ for H_2SO_4 in water?

Answer



It can be noticed that $K_{a_1} \gg K_{a_2}$

This is because a neutral H_2SO_4 has a much higher tendency to lose a proton than the negatively charged HSO_{4}^- . Thus, the former is a much stronger acid than the latter

Manufacture of sulphuric acid by Contact process involves three steps.

1. Burning of ores to form SO_2
2. Conversion of SO_2 to SO_3 by the reaction of the former with O_2
(V_2O_5 is used in this process as a catalyst.)
3. Absorption of SO_3 in H_2SO_4 to give oleum ($\text{H}_2\text{S}_2\text{O}_7$)

The key step in this process is the second step. In this step, two moles of gaseous reactants combine to give one mole of gaseous product. Also, this reaction is exothermic. Thus, in accordance with Le Chatelier's principle, to obtain the maximum amount of SO_3 gas, temperature should be low and pressure should be high

Question 7.26:

Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of F_2 and Cl_2 .

Answer

Fluorine is a much stronger oxidizing agent than chlorine. The oxidizing power depends on three factors.

1. Bond dissociation energy
2. Electron gain enthalpy
3. Hydration enthalpy

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The electron gain enthalpy of chlorine is more negative than that of fluorine. However, the bond dissociation energy of fluorine is much lesser than that of chlorine. Also, because of its small size, the hydration energy of fluorine is much higher than that of chlorine. Therefore, the latter two factors more than compensate for the less negative electron gain enthalpy of fluorine. Thus, fluorine is a much stronger oxidizing agent than chlorine

Question 7.27:

Give two examples to show the anomalous behaviour of fluorine.

Answer

Anomalous behaviour of fluorine

(i) It forms only one oxoacid as compared to other halogens that form a number of oxoacids.

(ii) Ionisation enthalpy, electronegativity, and electrode potential of fluorine are much higher than expected

Question 7.28:

Sea is the greatest source of some halogens. Comment.

Answer

Sea water contains chlorides, bromides, and iodides of Na, K, Mg, and Ca. However, it primarily contains NaCl. The deposits of dried up sea beds contain sodium chloride and carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$. Marine life also contains iodine in their systems. For example, sea weeds contain upto 0.5% iodine as sodium iodide. Thus, sea is the greatest source of halogens

Question 7.29:

Give the reason for bleaching action of Cl_2 .

Answer

When chlorine reacts with water, it produces nascent oxygen. This nascent oxygen then combines with the coloured substances present in the organic matter to oxidize them into colourless substances.



Coloured substances + [O] → Oxidized colourless substance

Question 7.30:

Name two poisonous gases which can be prepared from chlorine gas.

Answer

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Two poisonous gases that can be prepared from chlorine gas are

- (i) Phosgene (COCl_2)
- (ii) Mustard gas ($\text{CICH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$)

Question 7.31:

Why is ICl more reactive than I_2 ?

Answer

ICl is more reactive than I_2 because $\text{I}-\text{Cl}$ bond in ICl is weaker than $\text{I}-\text{I}$ bond in I_2

Question 7.32:

Why is helium used in diving apparatus?

Answer

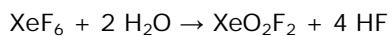
Air contains a large amount of nitrogen and the solubility of gases in liquids increases with increase in pressure. When sea divers dive deep into the sea, large amount of nitrogen dissolves in their blood. When they come back to the surface, solubility of nitrogen decreases and it separates from the blood and forms small air bubbles. This leads to a dangerous medical condition called bends. Therefore, air in oxygen cylinders used for diving is diluted with helium gas. This is done as He is sparingly less soluble in blood

Question 7.33:

Balance the following equation: $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + \text{HF}$

Answer

Balanced equation



Question 7.34:

Why has it been difficult to study the chemistry of radon?

Answer

It is difficult to study the chemistry of radon because it is a radioactive substance having a half-life of only 3.82 days. Also, compounds of radon such as RnF_2 have not been isolated. They have only been identified

Question 7.1:

P BLOCK ELEMENT : NCERT SOLUTION

Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.

Answer

General trends in group 15 elements

(i) Electronic configuration: All the elements in group 15 have 5 valence electrons. Their general electronic configuration is $ns^2 np^3$.

(ii) Oxidation states: All these elements have 5 valence electrons and require three more electrons to complete their octets. However, gaining electrons is very difficult as the nucleus will have to attract three more electrons. This can take place only with nitrogen as it is the smallest in size and the distance between the nucleus and the valence shell is relatively small. The remaining elements of this group show a formal oxidation state of -3 in their covalent compounds. In addition to the -3 state, N and P also show -1 and -2 oxidation states.

All the elements present in this group show +3 and +5 oxidation states. However, the stability of +5 oxidation state decreases down a group, whereas the stability of +3 oxidation state increases. This happens because of the inert pair effect.

(iii) Ionization energy and electronegativity

First ionization decreases on moving down a group. This is because of increasing atomic sizes. As we move down a group, electronegativity decreases, owing to an increase in size.

(iv) Atomic size: On moving down a group, the atomic size increases. This increase in the atomic size is attributed to an increase in the number of shells

Question 7.2:

Why does the reactivity of nitrogen differ from phosphorus?

Answer

Nitrogen is chemically less reactive. This is because of the high stability of its molecule, N_2 . In N_2 , the two nitrogen atoms form a triple bond. This triple bond has very high bond strength, which is very difficult to break. It is because of nitrogen's small size that it is able to form $p\pi-p\pi$ bonds with itself. This property is not exhibited by atoms such as phosphorus. Thus, phosphorus is more reactive than nitrogen.

Question 7.3:

Discuss the trends in chemical reactivity of group 15 elements.

Answer

Discussion

Share

General trends in chemical properties of group – 15

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(i) Reactivity towards hydrogen:

The elements of group 15 react with hydrogen to form hydrides of type EH_3 , where E = N, P, As, Sb, or Bi. The stability of hydrides decreases on moving down from NH_3 to BiH_3 .

(ii) Reactivity towards oxygen:

The elements of group 15 form two types of oxides: E_2O_3 and E_2O_5 , where E = N, P, As, Sb, or Bi. The oxide with the element in the higher oxidation state is more acidic than the other. However, the acidic character decreases on moving down a group.

(iii) Reactivity towards halogens:

The group 15 elements react with halogens to form two series of salts: EX_3 and EX_5 . However, nitrogen does not form NX_5 as it lacks the d -orbital. All trihalides (except NX_3) are stable.

(iv) Reactivity towards metals:

The group 15 elements react with metals to form binary compounds in which metals exhibit -3 oxidation states

Question 7.4:

Why does NH_3 form hydrogen bond but PH_3 does not?

Answer

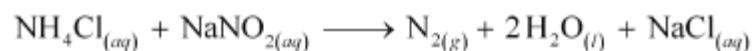
Nitrogen is highly electronegative as compared to phosphorus. This causes a greater attraction of electrons towards nitrogen in NH_3 than towards phosphorus in PH_3 . Hence, the extent of hydrogen bonding in PH_3 is very less as compared to NH_3

Question 7.5:

How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.

Answer

An aqueous solution of ammonium chloride is treated with sodium nitrite.



NO and HNO_3 are produced in small amounts. These are impurities that can be removed on passing nitrogen gas through aqueous sulphuric acid, containing potassium dichromate

Question 7.6:

How is ammonia manufactured industrially?

Answer

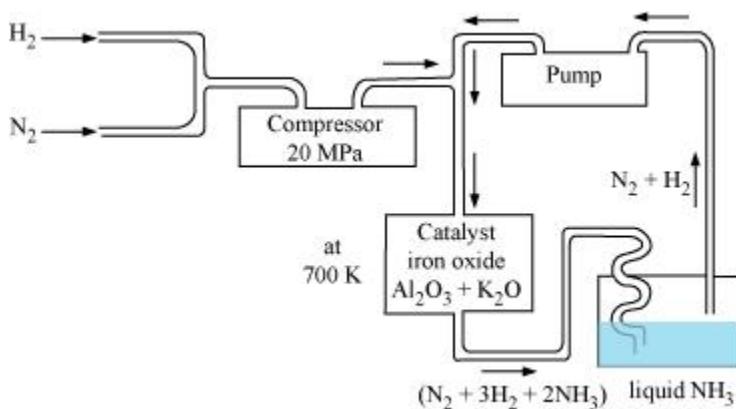
P BLOCK ELEMENT : NCERT SOLUTION

Ammonia is prepared on a large-scale by the Haber's process.



The optimum conditions for manufacturing ammonia are:

- (i) Pressure (around $200 \times 10^5 \text{ Pa}$)
- (ii) Temperature (4700 K)
- (iii) Catalyst such as iron oxide with small amounts of Al_2O_3 and K_2O

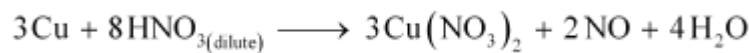


Question 7.7:

Illustrate how copper metal can give different products on reaction with HNO_3 .

Answer

Concentrated nitric acid is a strong oxidizing agent. It is used for oxidizing most metals. The products of oxidation depend on the concentration of the acid, temperature, and also on the material undergoing oxidation.



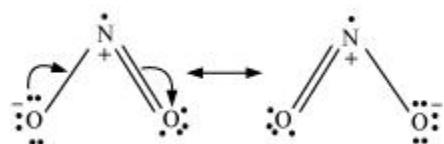
Question 7.8:

Give the resonating structures of NO_2 and N_2O_5 .

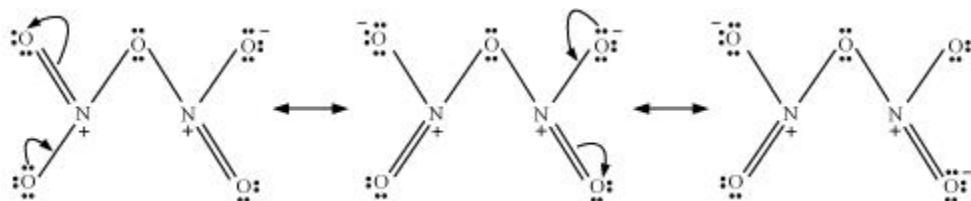
Answer

(1)

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(2)



Question 7.9:

The HNH angle value is higher than HPH, HAsH and HSbH angles. Why? [Hint: Can be explained on the basis of sp^3 hybridisation in NH_3 and only $s-p$ bonding between hydrogen and other elements of the group].

Answer

Hydride NH_3 PH_3 AsH_3 SbH_3

H–M–H angle 107° 92° 91° 90°

The above trend in the H–M–H bond angle can be explained on the basis of the electronegativity of the central atom. Since nitrogen is highly electronegative, there is high electron density around nitrogen. This causes greater repulsion between the electron pairs around nitrogen, resulting in maximum bond angle. We know that electronegativity decreases on moving down a group. Consequently, the repulsive interactions between the electron pairs decrease, thereby decreasing the H–M–H bond angle

Question 7.10:

Why does $\text{R}_3\text{P}=\text{O}$ exist but $\text{R}_3\text{N}=\text{O}$ does not (R = alkyl group)?

Answer

N (unlike P) lacks the d -orbital. This restricts nitrogen to expand its coordination number beyond four. Hence, $\text{R}_3\text{N}=\text{O}$ does not exist

Question 7.11:

Explain why NH_3 is basic while BiH_3 is only feebly basic.

Answer

NH_3 is distinctly basic while BiH_3 is feebly basic.

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Nitrogen has a small size due to which the lone pair of electrons is concentrated in a small region. This means that the charge density per unit volume is high. On moving down a group, the size of the central atom increases and the charge gets distributed over a large area decreasing the electron density. Hence, the electron donating capacity of group 15 element hydrides decreases on moving down the group

Question 7.12:

Nitrogen exists as diatomic molecule and phosphorus as P_4 . Why?

Answer

Nitrogen owing to its small size has a tendency to form $p\pi-p\pi$ multiple bonds with itself. Nitrogen thus forms a very stable diatomic molecule, N_2 . On moving down a group, the tendency to form $p\pi-p\pi$ bonds decreases (because of the large size of heavier elements). Therefore, phosphorus (like other heavier metals) exists in the P_4 state

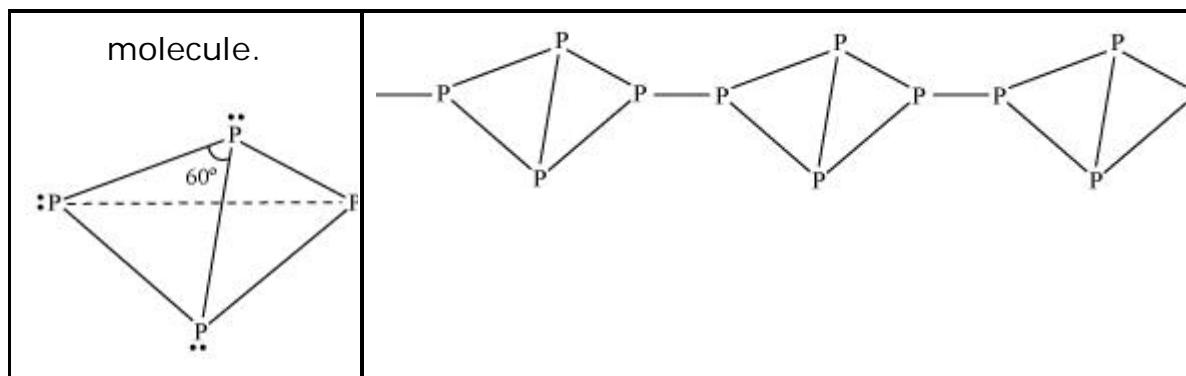
Question 7.13:

Write main differences between the properties of white phosphorus and red phosphorus.

Answer

White phosphorus	Red Phosphorus
It is a soft and waxy solid. It possesses a garlic smell.	It is a hard and crystalline solid, without any smell.
It is poisonous.	It is non-poisonous.
It is insoluble in water but soluble in carbon disulphide.	It is insoluble in both water and carbon disulphide.
It undergoes spontaneous combustion in air.	It is relatively less reactive.
In both solid and vapour states, it exists as a P_4	It exists as a chain of tetrahedral P_4 units.

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Question 7.14:

Why does nitrogen show catenation properties less than phosphorus?

Answer

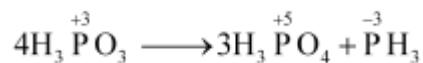
Catenation is much more common in phosphorous compounds than in nitrogen compounds. This is because of the relative weakness of the N–N single bond as compared to the P–P single bond. Since nitrogen atom is smaller, there is greater repulsion of electron density of two nitrogen atoms, thereby weakening the N–N single bond

Question 7.15:

Give the disproportionation reaction of H_3PO_3 .

Answer

On heating, orthophosphorus acid (H_3PO_3) disproportionates to give orthophosphoric acid (H_3PO_4) and phosphine (PH_3). The oxidation states of P in various species involved in the reaction are mentioned below.



Question 7.16:

Can PCl_5 act as an oxidising as well as a reducing agent? Justify.

Answer

PCl_5 can only act as an oxidizing agent. The highest oxidation state that P can show is +5. In PCl_5 , phosphorus is in its highest oxidation state (+5). However, it can decrease its oxidation state and act as an oxidizing agent

Question 7.17:

P BLOCK ELEMENT : NCERT SOLUTION

Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

Answer

The elements of group 16 are collectively called chalcogens.

(i) Elements of group 16 have six valence electrons each. The general electronic configuration of these elements is $ns^2 np^4$, where n varies from 2 to 6.

(ii) Oxidation state:

As these elements have six valence electrons ($ns^2 np^4$), they should display an oxidation state of -2 . However, only oxygen predominantly shows the oxidation state of -2 owing to its high electronegativity. It also exhibits the oxidation state of -1 (H_2O_2), zero (O_2), and $+2$ (OF_2). However, the stability of the -2 oxidation state decreases on moving down a group due to a decrease in the electronegativity of the elements. The heavier elements of the group show an oxidation state of $+2$, $+4$, and $+6$ due to the availability of d -orbitals.

(iii) Formation of hydrides:

These elements form hydrides of formula H_2E , where $E = O, S, Se, Te, Po$. Oxygen and sulphur also form hydrides of type H_2E_2 . These hydrides are quite volatile in nature

Question 7.18:

Why is dioxygen a gas but sulphur a solid?

Answer

Oxygen is smaller in size as compared to sulphur. Due to its smaller size, it can effectively form $p\pi-p\pi$ bonds and form O_2 ($O=O$) molecule. Also, the intermolecular forces in oxygen are weak van der Waal's, which cause it to exist as gas. On the other hand, sulphur does not form M_2 molecule but exists as a puckered structure held together by strong covalent bonds. Hence, it is a solid

Question 7.19:

Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as -141

and 702 kJ mol^{-1} respectively, how can you account for the formation of a

large number of oxides having O^{2-} species and not O^- ?

(Hint: Consider lattice energy factor in the formation of compounds).

Answer

Stability of an ionic compound depends on its lattice energy. More the lattice energy of a compound, more stable it will be.

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Lattice energy is directly proportional to the charge carried by an ion. When a metal combines with oxygen, the lattice energy of the oxide involving O^{2-} ion is much more than the oxide involving O^- ion. Hence, the oxide having O^{2-} ions are more stable than oxides having O^- . Hence, we can say that formation of O^{2-} is energetically more favourable than formation of O^- .

Question 7.20:

Which aerosols deplete ozone?

Answer

Freons or chlorofluorocarbons (CFCs) are aerosols that accelerate the depletion of ozone. In the presence of ultraviolet radiations, molecules of CFCs break down to form chlorine-free radicals that combine with ozone to form oxygen

Question 7.21:

Describe the manufacture of H_2SO_4 by contact process?

Answer

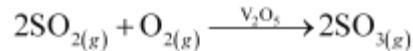
Sulphuric acid is manufactured by the contact process. It involves the following steps:

Step (i):

Sulphur or sulphide ores are burnt in air to form SO_2 .

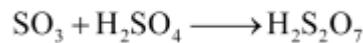
Step (ii):

By a reaction with oxygen, SO_2 is converted into SO_3 in the presence of V_2O_5 as a catalyst.



Step (iii):

SO_3 produced is absorbed on H_2SO_4 to give $H_2S_2O_7$ (oleum).



This oleum is then diluted to obtain H_2SO_4 of the desired concentration.

In practice, the plant is operated at 2 bar (pressure) and 720 K (temperature). The sulphuric acid thus obtained is 96-98% pure

Question 7.22:

How is SO_2 an air pollutant?

Answer

P BLOCK ELEMENT : NCERT SOLUTION

Sulphur dioxide causes harm to the environment in many ways:

1. It combines with water vapour present in the atmosphere to form sulphuric acid. This causes acid rain. Acid rain damages soil, plants, and buildings, especially those made of marble.
2. Even in very low concentrations, SO_2 causes irritation in the respiratory tract. It causes throat and eye irritation and can also affect the larynx to cause breathlessness.
3. It is extremely harmful to plants. Plants exposed to sulphur dioxide for a long time lose colour from their leaves. This condition is known as chlorosis. This happens because the formation of chlorophyll is affected by the presence of sulphur dioxide

Question 7.23:

Why are halogens strong oxidising agents?

Answer

The general electronic configuration of halogens is np^5 , where $n = 2-6$. Thus, halogens need only one more electron to complete their octet and to attain the stable noble gas configuration. Also, halogens are highly electronegative with low dissociation energies and high negative electron gain enthalpies. Therefore, they have a high tendency to gain an electron. Hence, they act as strong oxidizing agents

Question 7.24:

Explain why fluorine forms only one oxoacid, HOF .

Answer

Fluorine forms only one oxoacid i.e., HOF because of its high electronegativity and small size

Question 7.25:

Explain why inspite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.

Answer

Both chlorine and oxygen have almost the same electronegativity values, but chlorine rarely forms hydrogen bonding. This is because in comparison to chlorine, oxygen has a smaller size and as a result, a higher electron density per unit volume

Question 7.26:

Write two uses of ClO_2 .

Answer

P BLOCK ELEMENT : NCERT SOLUTION

Uses of ClO_2 :

- (i) It is used for purifying water.
- (ii) It is used as a bleaching agent

Question 7.27:

Why are halogens coloured?

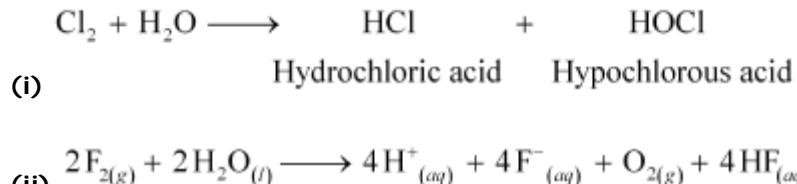
Answer

Almost all halogens are coloured. This is because halogens absorb radiations in the visible region. This results in the excitation of valence electrons to a higher energy region. Since the amount of energy required for excitation differs for each halogen, each halogen displays a different colour.

Question 7.28:

Write the reactions of F_2 and Cl_2 with water.

Answer

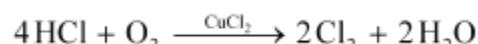


Question 7.29:

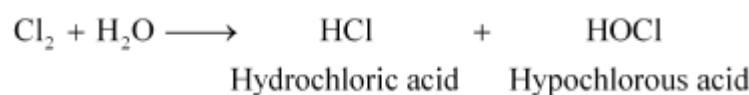
How can you prepare Cl_2 from HCl and HCl from Cl_2 ? Write reactions only.

Answer

- (i) Cl_2 can be prepared from HCl by Deacon's process.



- (ii) HCl can be prepared from Cl_2 on treating it with water.



Question 7.30:

What inspired N. Bartlett for carrying out reaction between Xe and PtF_6 ?

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Answer

Neil Bartlett initially carried out a reaction between oxygen and PtF_6^- . This resulted in the formation of a red compound, $\text{O}_2^+[\text{PtF}_6]^-$.

Later, he realized that the first ionization energy of oxygen (1175 kJ/mol) and Xe (1170 kJ/mol) is almost the same. Thus, he tried to prepare a compound with Xe and PtF_6^- . He was successful and a red-coloured compound, $\text{Xe}^+[\text{PtF}_6]^-$ was formed.

Question 7.31:

What are the oxidation states of phosphorus in the following:

(i) H_3PO_3 (ii) PCl_3 (iii) Ca_3P_2

(iv) Na_3PO_4 (v) POF_3 ?

Answer

Let the oxidation state of P be x

(i) H_3PO_3

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

$$3+x-6=0$$

$$x-3=0$$

$$x=+3$$

(ii) PCl_3

$$x+3(-1)=0$$

$$x-3=0$$

$$x=+3$$

(iii) Ca_3P_2

$$3(+2)+2(x)=0$$

$$6+2x=0$$

$$2x=-6$$

$$x=-3$$

(iv) Na_3PO_4

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$$3(+1) + x + 4(-2) = 0$$

$$3 + x - 8 = 0$$

$$x - 5 = 0$$

$$x = +5$$

(v) POF_3

$$x + (-2) + 3(-1) = 0$$

$$x - 5 = 0$$

$$x = +5$$

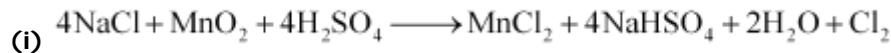
Question 7.32:

Write balanced equations for the following:

(i) NaCl is heated with sulphuric acid in the presence of MnO_2 .

(ii) Chlorine gas is passed into a solution of NaI in water.

Answer

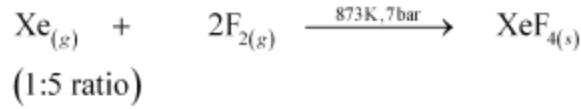
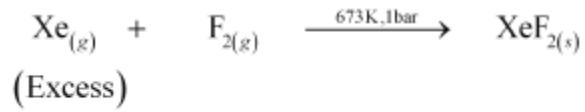


Question 7.33:

How are xenon fluorides XeF_2 , XeF_4 and XeF_6 obtained?

Answer

XeF_2 , XeF_4 , and XeF_6 are obtained by a direct reaction between Xe and F_2 . The condition under which the reaction is carried out determines the product.



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Question 7.34:

With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

Answer

ClO^- is isoelectronic to ClF . Also, both species contain 26 electrons in all as shown.

$$\text{Total electrons } \text{ClO}^- = 17 + 8 + 1 = 26$$

$$\text{In } \text{ClF} = 17 + 9 = 26$$

ClF acts like a Lewis base as it accepts electrons from F to form ClF_3

Question 7.35:

How are XeO_3 and XeOF_4 prepared?

Answer

(i) XeO_3 can be prepared in two ways as shown.



(ii) XeOF_4 can be prepared using XeF_6 .



Question 7.36:

Arrange the following in the order of property indicated for each set:

(i) F_2 , Cl_2 , Br_2 , I_2 - increasing bond dissociation enthalpy.

(ii) HF, HCl, HBr, HI - increasing acid strength.

(iii) NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 – increasing base strength.

Answer

(i) Bond dissociation energy usually decreases on moving down a group as the atomic size increases. However, the bond dissociation energy of F_2 is lower than that of Cl_2 and Br_2 . This is due to the small atomic size of fluorine. Thus, the increasing order for bond dissociation energy among halogens is as follows:

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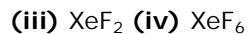
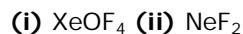
The bond dissociation energy of H-X molecules where X = F, Cl, Br, I, decreases with an increase in the atomic size. Since H-I bond is the weakest, HI is the strongest acid.



On moving from nitrogen to bismuth, the size of the atom increases while the electron density on the atom decreases. Thus, the basic strength decreases

Question 7.37:

Which one of the following does not exist?

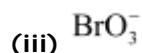
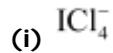


Answer

NeF_2 does not exist

Question 7.38:

Give the formula and describe the structure of a noble gas species which is isostructural with:

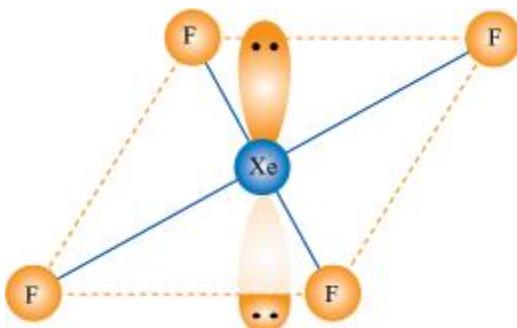


Answer

(i)

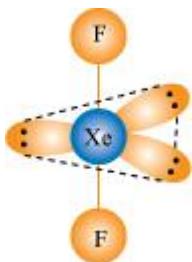
XeF_4 is isoelectronic with ICl_4^- and has square planar geometry.

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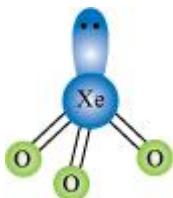
(ii)

XeF₂ is isoelectronic to IBr_2^- and has a linear structure.



(iii)

XeO₃ is isostructural to BrO_3^- and has a pyramidal molecular structure.



Question 7.39:

Why do noble gases have comparatively large atomic sizes?

Answer

Noble gases do not form molecules. In case of noble gases, the atomic radii corresponds to van der Waal's radii. On the other hand, the atomic radii of other elements correspond to their covalent radii. By definition, van der Waal's radii are larger than covalent radii. It is for this reason that noble gases are very large in size as compared to other atoms belonging to the same period

Question 7.40:

List the uses of Neon and argon gases.

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Answer

Uses of neon gas:

- (i) It is mixed with helium to protect electrical equipments from high voltage.
- (ii) It is filled in discharge tubes with characteristic colours.
- (iii) It is used in beacon lights.

Uses of Argon gas:

- (i) Argon along with nitrogen is used in gas-filled electric lamps. This is because Ar is more inert than N.
- (ii) It is usually used to provide an inert temperature in a high metallurgical process.
- (iii) It is also used in laboratories to handle air-sensitive substances

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Question 8.1:

Silver atom has completely filled *d* orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

Answer

Ag has a completely filled $4d$ orbital ($4d^{10} 5s^1$) in its ground state. Now, silver displays two oxidation states (+1 and +2). In the +1 oxidation state, an electron is removed from the *s*-orbital. However, in the +2 oxidation state, an electron is removed from the *d*-orbital. Thus, the *d*-orbital now becomes incomplete ($4d^9$). Hence, it is a transition element

Question 8.2:

In the series Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomization of zinc is the lowest, i.e., 126 kJ mol⁻¹. Why?

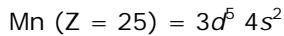
Answer

The extent of metallic bonding an element undergoes decides the enthalpy of atomization. The more extensive the metallic bonding of an element, the more will be its enthalpy of atomization. In all transition metals (except Zn, electronic configuration: $3d^{10} 4s^2$), there are some unpaired electrons that account for their stronger metallic bonding. Due to the absence of these unpaired electrons, the inter-atomic electronic bonding is the weakest in Zn and as a result, it has the least enthalpy of atomization

Question 8.3:

Which of the $3d$ series of the transition metals exhibits the largest number of oxidation states and why?

Answer



Mn has the maximum number of unpaired electrons present in the *d*-subshell (5 electrons). Hence, Mn exhibits the largest number of oxidation states, ranging from +2 to +7

Question 8.4:

The $E^\theta(M^{2+}/M)$ value for copper is positive (+0.34V). What is possibly the reason for this?

(Hint: consider its high $\Delta_a H^\theta$ and low $\Delta_{\text{hyd}} H^\theta$)

Answer

The $E^\theta(M^{2+}/M)$ value of a metal depends on the energy changes involved in the following:

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1. Sublimation: The energy required for converting one mole of an atom from the solid state to the gaseous state.



2. Ionization: The energy required to take out electrons from one mole of atoms in the gaseous state.



3. Hydration: The energy released when one mole of ions are hydrated.



Now, copper has a high energy of atomization and low hydration energy. Hence, the $E^\theta(M^{2+}/M)$ value for copper is positive

Question 8.5:

How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements?

Answer

Ionization enthalpies are found to increase in the given series due to a continuous filling of the inner d -orbitals. The irregular variations of ionization enthalpies can be attributed to the extra stability of configurations such as d^0 , d^5 , d^{10} . Since these states are exceptionally stable, their ionization enthalpies are very high.

In case of first ionization energy, Cr has low ionization energy. This is because after losing one electron, it attains the stable configuration ($3d^5$). On the other hand, Zn has exceptionally high first ionization energy as an electron has to be removed from stable and fully-filled orbitals ($3d^{10} 4s^2$).

Second ionization energies are higher than the first since it becomes difficult to remove an electron when an electron has already been taken out. Also, elements like Cr and Cu have exceptionally high second ionization energies as after losing the first electron, they have attained the stable configuration (Cr^{+} : $3d^5$ and Cu^{+} : $3d^{10}$). Hence, taking out one electron more from this stable configuration will require a lot of energy

Question 8.6:

Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

Answer

Both oxide and fluoride ions are highly electronegative and have a very small size. Due to these properties, they are able to oxidize the metal to its highest oxidation state

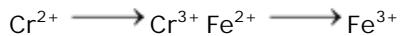
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Question 8.7:

Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why?

Answer

The following reactions are involved when Cr^{2+} and Fe^{2+} act as reducing agents.



The $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$ value is -0.41 V and $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ is $+0.77$ V. This means that Cr^{2+} can be easily oxidized to Cr^{3+} , but Fe^{2+} does not get oxidized to Fe^{3+} easily. Therefore, Cr^{2+} is a better reducing agent than Fe^{3+} .

Question 8.8:

Calculate the 'spin only' magnetic moment of $\text{M}^{2+}_{(aq)}$ ion ($Z = 27$).

Answer

$$Z = 27$$

$$\Rightarrow [\text{Ar}] 3d^7 4s^2$$

$$\therefore \text{M}^{2+} = [\text{Ar}] 3d^7$$

$$3d^7 = \boxed{\begin{array}{|c|c|c|c|c|c|} \hline \uparrow & \downarrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array}}$$

i.e., 3 unpaired electrons

$$\therefore n = 3$$

$$\Rightarrow \sqrt{n(n+2)} = \mu$$

$$\Rightarrow \sqrt{3(3+2)} = \mu$$

$$\Rightarrow \sqrt{15} = \mu$$

$$\mu \approx 4 \text{ BM}$$

Question 8.9:

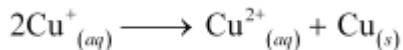
Explain why Cu^+ ion is not stable in aqueous solutions?

Answer

In an aqueous medium, Cu^{2+} is more stable than Cu^+ . This is because although energy is required to remove one electron from Cu^+ to Cu^{2+} , high hydration energy of Cu^{2+}

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compensates for it. Therefore, Cu^+ ion in an aqueous solution is unstable. It disproportionates to give Cu^{2+} and Cu.



Question 8.10:

Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Answer

In actinoids, $5f$ orbitals are filled. These $5f$ orbitals have a poorer shielding effect than $4f$ orbitals (in lanthanoids). Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more than that experienced by lanthanoids. Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

Question 8.1:

Write down the electronic configuration of:

(i) Cr^{3+} + (iii) Cu^+ (v) Co^{2+} (vii) Mn^{2+}

(ii) Pm^{3+} (iv) Ce^{4+} (vi) Lu^{2+} (viii) Th^{4+}

Answer

(i) Cr^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

Or, $[\text{Ar}]^{18} 3d^3$

(ii) Pm^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^4$

Or, $[\text{Xe}]^{54} 3d^3$

(iii) Cu^+ : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Or, $[\text{Ar}]^{18} 3d^{10}$

(iv) Ce^{4+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

Or, $[\text{Xe}]^{54}$

(v) Co^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

Or, $[\text{Ar}]^{18} 3d^7$

(vi) Lu^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^1$

Or, $[\text{Xe}]^{54} 2f^{14} 3d^3$

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(vii) Mn^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Or, $[\text{Ar}]^{18} 3d^5$

(viii) Th^{4+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^4 5s^2 5p^6 5d^{10} 6s^2 6s^6$

Or, $[\text{Rn}]^{86}$

Question 8.2:

Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

Answer

Electronic configuration of Mn^{2+} is $[\text{Ar}]^{18} 3d^5$.

Electronic configuration of Fe^{2+} is $[\text{Ar}]^{18} 3d^6$.

It is known that half-filled and fully-filled orbitals are more stable. Therefore, Mn in (+2) state has a stable d^5 configuration. This is the reason Mn^{2+} shows resistance to oxidation to Mn^{3+} . Also, Fe^{2+} has $3d^6$ configuration and by losing one electron, its configuration changes to a more stable $3d^5$ configuration. Therefore, Fe^{2+} easily gets oxidized to Fe^{+3} oxidation state

Question 8.3:

Explain briefly how +2 state becomes more and more stable in the first half

of the first row transition elements with increasing atomic number?

Answer

The oxidation states displayed by the first half of the first row of transition metals are given in the table below.

	Sc	Ti	V	Cr	Mn
	+ 2	+ 2	+ 2	+ 2	
	+ 3	+ 3	+ 3	+ 3	+ 3
Oxidation state			+ 4	+ 4	+ 4
			+ 5	+ 5	+ 6
				+ 6	+ 7

It can be easily observed that except Sc, all others metals display +2 oxidation state. Also, on moving from Sc to Mn, the atomic number increases from 21 to 25. This means the number of electrons in the 3d-orbital also increases from 1 to 5.

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$$\text{Sc (+2)} = d^1$$

$$\text{Ti (+2)} = d^2$$

$$\text{V (+2)} = d^3$$

$$\text{Cr (+2)} = d^4$$

$$\text{Mn (+2)} = d^5$$

+2 oxidation state is attained by the loss of the two 4s electrons by these metals. Since the number of *d* electrons in (+2) state also increases from Ti(+2) to Mn(+ 2), the stability of +2 state increases (as *d*-orbital is becoming more and more half-filled). Mn (+2) has d^5 electrons (that is half-filled *d* shell, which is highly stable)

Question 8.4:

To what extent do the electronic configurations decide the stability of

oxidation states in the first series of the transition elements? Illustrate

your answer with examples.

Answer

The elements in the first-half of the transition series exhibit many oxidation states with Mn exhibiting maximum number of oxidation states (+2 to +7). The stability of +2 oxidation state increases with the increase in atomic number. This happens as more electrons are getting filled in the *d*-orbital. However, Sc does not show +2 oxidation state. Its electronic configuration is $4s^2 3d^1$. It loses all the three electrons to form Sc^{3+} . +3 oxidation state of Sc is very stable as by losing all three electrons, it attains stable noble gas configuration, [Ar]. Ti (+ 4) and V(+5) are very stable for the same reason. For Mn, +2 oxidation state is very stable as after losing two electrons, its *d*-orbital is exactly half-filled, [Ar] $3d^5$

Question 8.5:

What may be the stable oxidation state of the transition element with the

following *d* electron configurations in the ground state of their atoms : $3d^3$,

$3d^5$, $3d^8$ and $3d^4$?

Answer

	Electronic configuration in ground state	Stable oxidation states
--	---	-------------------------

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(i)	$3d^3$ (Vanadium)	+2, +3, +4 and +5
(ii)	$3d^5$ (Chromium)	+3, +4, +6
(iii)	$3d^5$ (Manganese)	+2, +4, +6, +7
(iv)	$3d^8$ (Cobalt)	+2, +3
(v)	$3d^4$	There is no $3d^4$ configuration in ground state.

Question 8.6:

Name the oxometal anions of the first series of the transition metals in

which the metal exhibits the oxidation state equal to its group number.

Answer

(i) Vanadate, VO_3^-

Oxidation state of V is + 5.

(ii) Chromate, CrO_4^{2-}

Oxidation state of Cr is + 6.

(iii) Permanganate, MnO_4^-

Oxidation state of Mn is + 7

Question 8.7:

What is lanthanoid contraction? What are the consequences of lanthanoid

contraction?

Answer

As we move along the lanthanoid series, the atomic number increases gradually by one. This means that the number of electrons and protons present in an atom also increases by one. As electrons are being added to the same shell, the effective nuclear charge increases. This happens because the increase in nuclear attraction due to the addition of proton is more pronounced than the increase in the interelectronic repulsions due to the addition of electron. Also, with the increase in atomic number, the number of electrons in the $4f$ orbital also increases. The $4f$ electrons have poor shielding effect. Therefore, the effective nuclear charge experienced by the outer electrons increases. Consequently, the attraction of the nucleus for

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the outermost electrons increases. This results in a steady decrease in the size of lanthanoids with the increase in the atomic number. This is termed as lanthanoid contraction.

Consequences of lanthanoid contraction

- (i) There is similarity in the properties of second and third transition series.
 - ii. Separation of lanthanoids is possible due to lanthanide contraction.
- (iii) It is due to lanthanide contraction that there is variation in the basic strength of lanthanide hydroxides. (Basic strength decreases from La(OH)_3 to Lu(OH)_3 .)

Question 8.8:

What are the characteristics of the transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements?

Answer

Transition elements are those elements in which the atoms or ions (in stable oxidation state) contain partially filled *d*-orbital. These elements lie in the *d*-block and show a transition of properties between *s*-block and *p*-block. Therefore, these are called transition elements.

Elements such as Zn, Cd, and Hg cannot be classified as transition elements because these have completely filled *d*-subshell

Question 8.9:

In what way is the electronic configuration of the transition elements different from that of the non-transition elements?

Answer

Transition metals have a partially filled *d*-orbital. Therefore, the electronic configuration of transition elements is $(n - 1)d^{1-10} ns^{0-2}$.

The non-transition elements either do not have a *d*-orbital or have a fully filled *d*-orbital. Therefore, the electronic configuration of non-transition elements is ns^{1-2} or $ns^2 np^{1-6}$

Question 8.10:

What are the different oxidation states exhibited by the lanthanoids?

Answer

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In the lanthanide series, +3 oxidation state is most common i.e., Ln(III) compounds are predominant. However, +2 and +4 oxidation states can also be found in the solution or in solid compounds.

Question 8.11:

Explain giving reasons:

- (i) Transition metals and many of their compounds show paramagnetic behaviour.
- (ii) The enthalpies of atomisation of the transition metals are high.
- (iii) The transition metals generally form coloured compounds.
- (iv) Transition metals and their many compounds act as good catalyst.

Answer

(i) Transition metals show paramagnetic behaviour. Paramagnetism arises due to the presence of unpaired electrons with each electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. However, in the first transition series, the orbital angular momentum is quenched. Therefore, the resulting paramagnetism is only because of the unpaired electron.

(ii) Transition elements have high effective nuclear charge and a large number of valence electrons. Therefore, they form very strong metallic bonds. As a result, the enthalpy of atomization of transition metals is high.

(iii) Most of the complexes of transition metals are coloured. This is because of the absorption of radiation from visible light region to promote an electron from one of the d -orbitals to another. In the presence of ligands, the d -orbitals split up into two sets of orbitals having different energies. Therefore, the transition of electrons can take place from one set to another. The energy required for these transitions is quite small and falls in the visible region of radiation. The ions of transition metals absorb the radiation of a particular wavelength and the rest is reflected, imparting colour to the solution.

(iv) The catalytic activity of the transition elements can be explained by two basic facts.

(a) Owing to their ability to show variable oxidation states and form complexes, transition metals form unstable intermediate compounds. Thus, they provide a new path with lower activation energy, E_a , for the reaction.

(b) Transition metals also provide a suitable surface for the reactions to occur.

Question 8.12:

What are interstitial compounds? Why are such compounds well known for

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transition metals?

Answer

Transition metals are large in size and contain lots of interstitial sites. Transition elements can trap atoms of other elements (that have small atomic size), such as H, C, N, in the interstitial sites of their crystal lattices. The resulting compounds are called interstitial compounds

Question 8.13:

How is the variability in oxidation states of transition metals different from

that of the non-transition metals? Illustrate with examples.

Answer

In transition elements, the oxidation state can vary from +1 to the highest oxidation state by removing all its valence electrons. Also, in transition elements, the oxidation states differ by 1 (Fe^{2+} and Fe^{3+} ; Cu^+ and Cu^{2+}). In non-transition elements, the oxidation states differ by 2, for example, +2 and +4 or +3 and +5, etc

Question 8.14:

Describe the preparation of potassium dichromate from iron chromite ore.

What is the effect of increasing pH on a solution of potassium dichromate?

Answer

Potassium dichromate is prepared from chromite ore $(\text{FeCr}_2\text{O}_4)$ in the following steps.

Step (1): Preparation of sodium chromate



Step (2): Conversion of sodium chromate into sodium dichromate



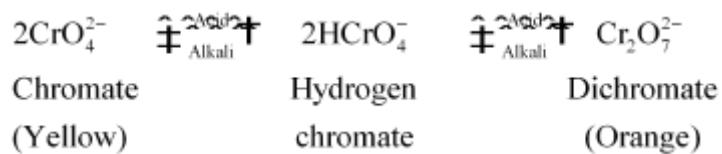
Step(3): Conversion of sodium dichromate to potassium dichromate



Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration.

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The dichromate ion $(\text{Cr}_2\text{O}_7^{2-})$ exists in equilibrium with chromate (CrO_4^{2-}) ion at pH 4. However, by changing the pH, they can be interconverted.



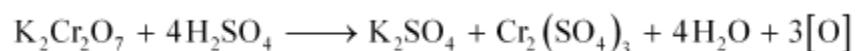
Question 8.15:

Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

- (i) iodide (ii) iron(II) solution and (iii) H_2S

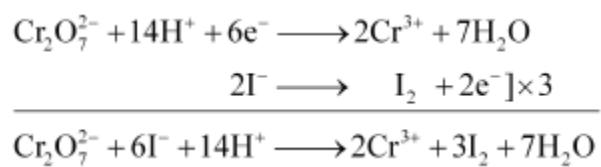
Answer

$\text{K}_2\text{Cr}_2\text{O}_7$ acts as a very strong oxidising agent in the acidic medium.

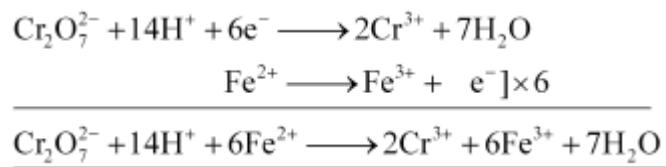


$\text{K}_2\text{Cr}_2\text{O}_7$ takes up electrons to get reduced and acts as an oxidising agent. The reaction of $\text{K}_2\text{Cr}_2\text{O}_7$ with other iodide, iron (II) solution, and H_2S are given below.

- (i) $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes iodide to iodine.

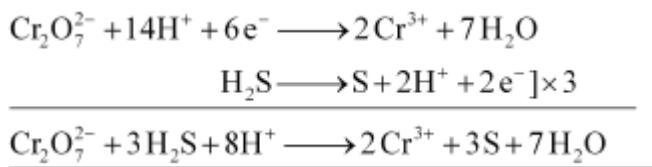


- (ii) $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes iron (II) solution to iron (III) solution i.e., ferrous ions to ferric ions.



- (iii) $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes H_2S to sulphur.

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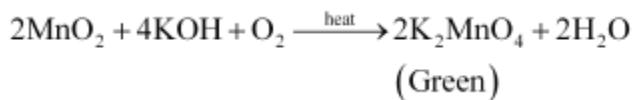
Question 8.16:

Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii) SO_2 and (iii) oxalic acid?

Write the ionic equations for the reactions.

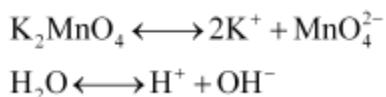
Answer

Potassium permanganate can be prepared from pyrolusite (MnO_2). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as KNO_3 or KClO_4 , to give K_2MnO_4 .

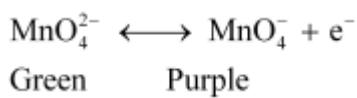


The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution.

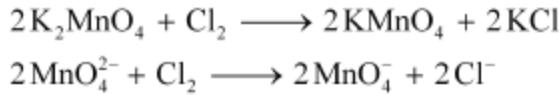
Electrolytic oxidation



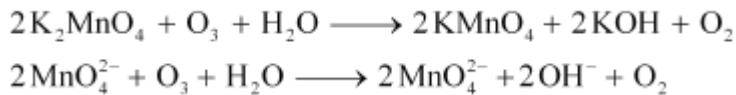
At anode, manganate ions are oxidized to permanganate ions.



Oxidation by chlorine

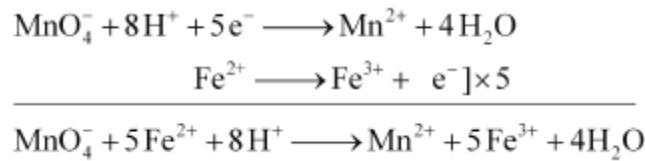


Oxidation by ozone

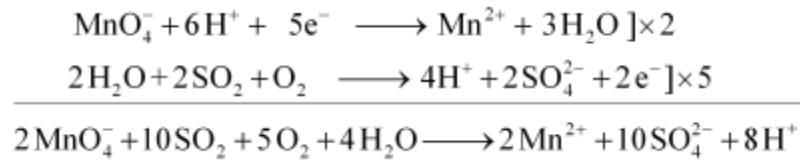


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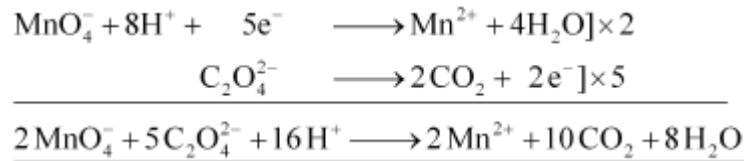
(i) Acidified KMnO_4 solution oxidizes Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.



(ii) Acidified potassium permanganate oxidizes SO_2 to sulphuric acid.



(iii) Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide.



Question 8.17:

For M^{2+}/M and $\text{M}^{3+}/\text{M}^{2+}$ systems, the E^\ominus values for some metals are as follows:

$\text{Cr}^{2+}/\text{Cr} -0.9\text{V}$

$\text{Cr}^3/\text{Cr}^{2+} -0.4\text{ V}$

$\text{Mn}^{2+}/\text{Mn} -1.2\text{V}$

$\text{Mn}^{3+}/\text{Mn}^{2+} +1.5\text{ V}$

$\text{Fe}^{2+}/\text{Fe} -0.4\text{V}$

$\text{Fe}^3/\text{Fe}^{2+} +0.8\text{ V}$

Use this data to comment upon:

(i) The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+} and

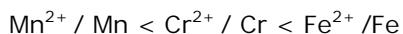
(ii) The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

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Answer

(i) The E^\ominus value for $\text{Fe}^{3+}/\text{Fe}^{2+}$ is higher than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$ and lower than that for $\text{Mn}^{3+}/\text{Mn}^{2+}$. So, the reduction of Fe^{3+} to Fe^{2+} is easier than the reduction of Mn^{3+} to Mn^{2+} , but not as easy as the reduction of Cr^{3+} to Cr^{2+} . Hence, Fe^{3+} is more stable than Mn^{3+} , but less stable than Cr^{3+} . These metal ions can be arranged in the increasing order of their stability as: $\text{Mn}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+}$

(ii) The reduction potentials for the given pairs increase in the following order.



So, the oxidation of Fe to Fe^{2+} is not as easy as the oxidation of Cr to Cr^{2+} and the oxidation of Mn to Mn^{2+} . Thus, these metals can be arranged in the increasing order of their ability to get oxidised as: $\text{Fe} < \text{Cr} < \text{Mn}$

Question 8.18:

Predict which of the following will be coloured in aqueous solution? Ti^{3+} , V^{3+} , Cu^+ , Sc^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} . Give reasons for each.

Answer

Only the ions that have electrons in *d*-orbital will be coloured. The ions in which *d*-orbital is empty will be colourless.

Element	Atomic Number	Ionic State	Electronic configuration in ionic state
Ti	22	Ti^{3+}	[Ar] $3d^1$
V	23	V^{3+}	[Ar] $3d^2$
Cu	29	Cu^+	[Ar] $3d^{10}$
Sc	21	Sc^{3+}	[Ar]
Mn	25	Mn^{2+}	[Ar] $3d^5$
Fe	26	Fe^{3+}	[Ar] $3d^5$
Co	27	Co^{2+}	[Ar] $3d^7$

From the above table, it can be easily observed that only Sc^{3+} has an empty *d*-orbital. All other ions, except Sc^{3+} , will be coloured in aqueous solution because of *d-d* transitions

Question 8.19:

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Compare the stability of +2 oxidation state for the elements of the first transition series.

Answer

Sc			+3				
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

From the above table, it is evident that the maximum number of oxidation states is shown by Mn, varying from +2 to +7. The number of oxidation states increases on moving from Sc to Mn. On moving from Mn to Zn, the number of oxidation states decreases due to a decrease in the number of available unpaired electrons. The relative stability of the +2 oxidation state increases on moving from top to bottom. This is because on moving from top to bottom, it becomes more and more difficult to remove the third electron from the *d*-orbital.

Question 8.20:

Compare the chemistry of actinoids with that of the lanthanoids with special reference to:

- (i) electronic configuration (iii) oxidation state
- (ii) atomic and ionic sizes and (iv) chemical reactivity.

Answer

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(i) Electronic configuration

The general electronic configuration for lanthanoids is $[Xe]^{54} 4f^{0-14} 5d^{0-1} 6s^2$ and that for actinoids is $[Rn]^{86} 5f^{1-14} 6d^{0-1} 7s^2$. Unlike $4f$ orbitals, $5f$ orbitals are not deeply buried and participate in bonding to a greater extent.

(ii) Oxidation states

The principal oxidation state of lanthanoids is (+3). However, sometimes we also encounter oxidation states of + 2 and + 4. This is because of extra stability of fully-filled and half-filled orbitals. Actinoids exhibit a greater range of oxidation states. This is because the $5f$, $6d$, and $7s$ levels are of comparable energies. Again, (+3) is the principal oxidation state for actinoids. Actinoids such as lanthanoids have more compounds in +3 state than in +4 state.

(iii) Atomic and Ionic sizes

Similar to lanthanoids, actinoids also exhibit actinoid contraction (overall decrease in atomic and ionic radii). The contraction is greater due to the poor shielding effect of $5f$ orbitals.

iv. Chemical reactivity

In the lanthanide series, the earlier members of the series are more reactive. They have reactivity that is comparable to Ca. With an increase in the atomic number, the lanthanides start behaving similar to Al. Actinoids, on the other hand, are highly reactive metals, especially when they are finely divided. When they are added to boiling water, they give a mixture of oxide and hydride. Actinoids combine with most of the non-metals at moderate temperatures. Alkalies have no action on these actinoids. In case of acids, they are slightly affected by nitric acid (because of the formation of a protective oxide layer).

Question 8.21:

How would you account for the following:

- (i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.
- (ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
- (iii) The d^1 configuration is very unstable in ions.

Answer

(i) Cr^{2+} is strongly reducing in nature. It has a d^4 configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3 configuration can be written as t_{2g}^3 configuration, which is a more stable configuration. In the case of Mn^{3+} (d^4), it acts as an oxidizing agent and gets reduced to Mn^{2+} (d^5). This has an exactly half-filled d -orbital and is highly stable.

(ii) Co(II) is stable in aqueous solutions. However, in the presence of strong field complexing reagents, it is oxidized to Co (III). Although the 3rd ionization energy for Co is high, but the

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higher amount of crystal field stabilization energy (CFSE) released in the presence of strong field ligands overcomes this ionization energy.

(iii) The ions in d^1 configuration tend to lose one more electron to get into stable d^0 configuration. Also, the hydration or lattice energy is more than sufficient to remove the only electron present in the d -orbital of these ions. Therefore, they act as reducing agents

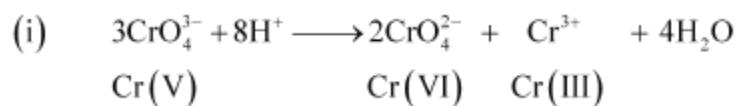
Question 8.22:

What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

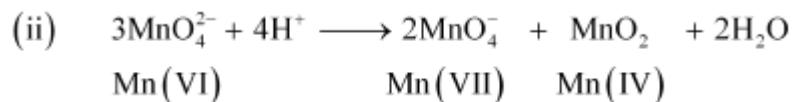
Answer

It is found that sometimes a relatively less stable oxidation state undergoes an oxidation-reduction reaction in which it is simultaneously oxidised and reduced. This is called disproportionation.

For example,



Cr(V) is oxidized to Cr(VI) and reduced to Cr(III).



Mn (VI) is oxidized to Mn (VII) and reduced to Mn (IV).

Question 8.23:

Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

Answer

In the first transition series, Cu exhibits +1 oxidation state very frequently. It is because Cu (+1) has an electronic configuration of [Ar] $3d^{10}$. The completely filled d -orbital makes it highly stable

Question 8.24:

Calculate the number of unpaired electrons in the following gaseous ions: Mn^{3+} , Cr^{3+} , V^{3+} and Ti^{3+} . Which one of these is the most stable in aqueous solution?

Answer

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	Gaseous ions	Number of unpaired electrons
(i)	Mn ³⁺ , [Ar]3d ⁴	4
(ii)	Cr ³⁺ , [Ar]3d ³	3
(iii)	V ³⁺ , [Ar]3d ²	2
(vi)	Ti ³⁺ , [Ar]3d ¹	1

Cr³⁺ is the most stable in aqueous solutions owing to a t_{2g}^3 configuration

Question 8.25:

Give examples and suggest reasons for the following features of the transition metal chemistry:

- (i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
- (ii) A transition metal exhibits highest oxidation state in oxides and fluorides.
- (iii) The highest oxidation state is exhibited in oxoanions of a metal.

Answer

(i) In the case of a lower oxide of a transition metal, the metal atom has a low oxidation state. This means that some of the valence electrons of the metal atom are not involved in bonding. As a result, it can donate electrons and behave as a base.

On the other hand, in the case of a higher oxide of a transition metal, the metal atom has a high oxidation state. This means that the valence electrons are involved in bonding and so, they are unavailable. There is also a high effective nuclear charge.

As a result, it can accept electrons and behave as an acid.

For example, Mn^{II}O is basic and $\text{Mn}_2\overset{\text{VII}}{\text{O}}_7$ is acidic.

(ii) Oxygen and fluorine act as strong oxidising agents because of their high electronegativities and small sizes. Hence, they bring out the highest oxidation states from the transition metals. In other words, a transition metal exhibits higher oxidation states in oxides and fluorides. For example, in OsF₆ and V₂O₅, the oxidation states of Os and V are +6 and +5 respectively.

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(iii) Oxygen is a strong oxidising agent due to its high electronegativity and small size. So, oxo-anions of a metal have the highest oxidation state. For example, in MnO_4^- , the oxidation state of Mn is +7

Question 8.26:

Indicate the steps in the preparation of:

(i) $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore.

(ii) KMnO_4 from pyrolusite ore.

Answer

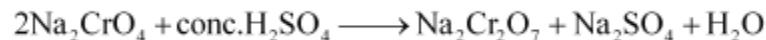
(i)

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is prepared from chromite ore (FeCr_2O_4) in the following steps.

Step (1): Preparation of sodium chromate



Step (2): Conversion of sodium chromate into sodium dichromate

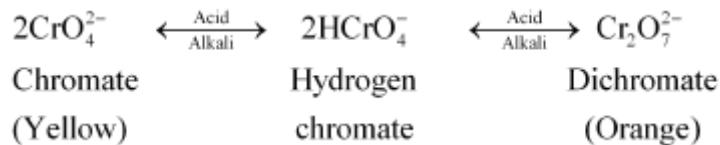


Step(3): Conversion of sodium dichromate to potassium dichromate



Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration.

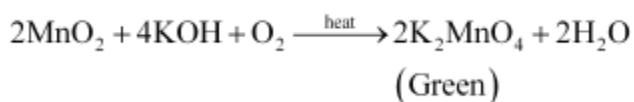
The dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) exists in equilibrium with chromate (CrO_4^{2-}) ion at pH 4. However, by changing the pH, they can be interconverted.



(ii)

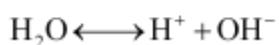
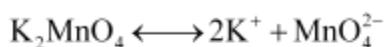
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Potassium permanganate (KMnO_4) can be prepared from pyrolusite (MnO_2). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as KNO_3 or KClO_4 , to give K_2MnO_4 .



The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution.

Electrolytic oxidation



At anode, manganate ions are oxidized to permanganate ions.



Green Purple

Oxidation by chlorine



Oxidation by ozone



Question 8.27:

What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

Answer

An alloy is a solid solution of two or more elements in a metallic matrix. It can either be a partial solid solution or a complete solid solution. Alloys are usually found to possess different physical properties than those of the component elements.

An important alloy of lanthanoids is Mischmetal. It contains lanthanoids (94–95%), iron (5%), and traces of S, C, Si, Ca, and Al.

Uses

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(1) Mischmetal is used in cigarettes and gas lighters.

(2) It is used in flame throwing tanks.

(3) It is used in tracer bullets and shells

Question 8.28:

What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104.

Answer

Inner transition metals are those elements in which the last electron enters the *f*-orbital. The elements in which the 4*f* and the 5*f* orbitals are progressively filled are called *f*-block elements. Among the given atomic numbers, the atomic numbers of the inner transition elements are 59, 95, and 102

Question 8.29:

The chemistry of the actinoid elements is not so smooth as that of the Lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

Answer

Lanthanoids primarily show three oxidation states (+2, +3, +4). Among these oxidation states, +3 state is the most common. Lanthanoids display a limited number of oxidation states because the energy difference between 4*f*, 5*d*, and 6*s* orbitals is quite large. On the other hand, the energy difference between 5*f*, 6*d*, and 7*s* orbitals is very less. Hence, actinoids display a large number of oxidation states. For example, uranium and plutonium display +3, +4, +5, and +6 oxidation states while neptunium displays +3, +4, +5, and +7. The most common oxidation state in case of actinoids is also +3

Question 8.30:

Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

Answer

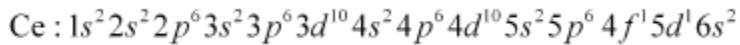
The last element in the actinoid series is lawrencium, Lr. Its atomic number is 103 and its electronic configuration is $[\text{Rn}]5f^{14} 6d^1 7s^2$. The most common oxidation state displayed by it is +3; because after losing 3 electrons it attains stable f^{14} configuration

Question 8.31:

Use Hund's rule to derive the electronic configuration of Ce^{3+} ion and calculate its magnetic moment on the basis of 'spin-only' formula.

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Answer



Magnetic moment can be calculated as:

$$\mu = \sqrt{n(n+2)}$$

Where,

n = number of unpaired electrons

In Ce, $n = 2$

$$\begin{aligned}\text{Therefore, } \mu &= \sqrt{2(2+2)} \\ &= \sqrt{2 \times 4} \\ &= \sqrt{8} \\ &= 2\sqrt{2} \\ &= 2.828 \text{ BM}\end{aligned}$$

Question 8.32:

Name the members of the lanthanoid series which exhibit +4 oxidation state and those which exhibit +2 oxidation state. Try to correlate this type of behavior with the electronic configurations of these elements.

Answer

The lanthanides that exhibit +2 and +4 states are shown in the given table. The atomic numbers of the elements are given in the parenthesis.

+2	+4
Nd (60)	Ce (58)
Sm (62)	Pr (59)
Eu (63)	Nd (60)
Tm (69)	Tb (65)
Yb (70)	Dy (66)

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Ce after forming Ce^{4+} attains a stable electronic configuration of [Xe].

Tb after forming Tb^{4+} attains a stable electronic configuration of [Xe] $4f^7$.

Eu after forming Eu^{2+} attains a stable electronic configuration of [Xe] $4f^7$.

Yb after forming Yb^{2+} attains a stable electronic configuration of [Xe] $4f^{14}$.

Question 8.33:

Compare the chemistry of the actinoids with that of lanthanoids with reference to:

- (i) electronic configuration
- (ii) oxidation states and
- (iii) chemical reactivity.

Answer

Electronic configuration

The general electronic configuration for lanthanoids is $[\text{Xe}]^{54} 4f^{0-14} 5d^{0-1} 6s^2$ and that for actinoids is $[\text{Rn}]^{86} 5f^{1-14} 6d^{0-1} 7s^2$. Unlike $4f$ orbitals, $5f$ orbitals are not deeply buried and participate in bonding to a greater extent.

Oxidation states

The principal oxidation state of lanthanoids is (+3). However, sometimes we also encounter oxidation states of + 2 and + 4. This is because of extra stability of fully-filled and half-filled orbitals. Actinoids exhibit a greater range of oxidation states. This is because the $5f$, $6d$, and $7s$ levels are of comparable energies. Again, (+3) is the principal oxidation state for actinoids. Actinoids such as lanthanoids have more compounds in +3 state than in +4 state.

Chemical reactivity

In the lanthanide series, the earlier members of the series are more reactive. They have reactivity that is comparable to Ca. With an increase in the atomic number, the lanthanides start behaving similar to Al. Actinoids, on the other hand, are highly reactive metals, especially when they are finely divided. When they are added to boiling water, they give a mixture of oxide and hydride. Actinoids combine with most of the non-metals at moderate temperatures. Alkalies have no action on these actinoids. In case of acids, they are slightly affected by nitric acid (because of the formation of a protective oxide layer).

Question 8.34:

Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.

Answer

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Atomic number	Electronic configuration
61	$[\text{Xe}]^{54} 4f^5 5d^0 6s^2$
91	$[\text{Rn}]^{86} 5f^2 6d^1 7s^2$
101	$[\text{Rn}]^{86} 5f^{13} 5d^0 7s^2$
109	$[\text{Rn}]^{86} 5f^{14} 6d^7 7s^2$

Question 8.35:

Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:

- (i) electronic configurations,
- (ii) oxidation states,
- (iii) ionisation enthalpies, and
- (iv) atomic sizes.

Answer

(i) In the 1st, 2nd and 3rd transition series, the 3d, 4d and 5d orbitals are respectively filled.

We know that elements in the same vertical column generally have similar electronic configurations.

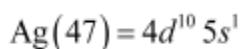
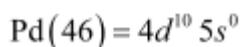
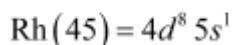
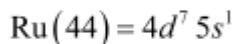
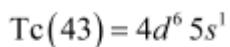
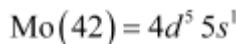
In the first transition series, two elements show unusual electronic configurations:

$$\text{Cr}(24) = 3d^5 4s^1$$

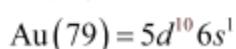
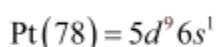
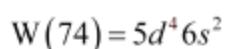
$$\text{Cu}(29) = 3d^{10} 4s^1$$

Similarly, there are exceptions in the second transition series. These are:

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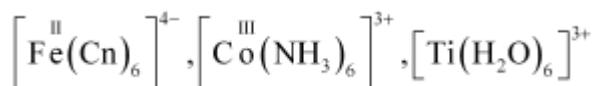
There are some exceptions in the third transition series as well. These are:



As a result of these exceptions, it happens many times that the electronic configurations of the elements present in the same group are dissimilar.

(ii) In each of the three transition series the number of oxidation states shown by the elements is the maximum in the middle and the minimum at the extreme ends.

However, +2 and +3 oxidation states are quite stable for all elements present in the first transition series. All metals present in the first transition series form stable compounds in the +2 and +3 oxidation states. The stability of the +2 and +3 oxidation states decreases in the second and the third transition series, wherein higher oxidation states are more important.



For example $\left[\text{Fe}(\text{Cn})_6 \right]^{4-}$, $\left[\text{Co}(\text{NH}_3)_6 \right]^{3+}$, $\left[\text{Ti}(\text{H}_2\text{O})_6 \right]^{3+}$ are stable complexes, but no such complexes are known for the second and third transition series such as Mo, W, Rh, In. They form complexes in which their oxidation states are high. For example: WCl_6 , ReF_7 , RuO_4 , etc.

(iii) In each of the three transition series, the first ionisation enthalpy increases from left to right. However, there are some exceptions. The first ionisation enthalpies of the third transition series are higher than those of the first and second transition series. This occurs due to the poor shielding effect of 4f electrons in the third transition series.

Certain elements in the second transition series have higher first ionisation enthalpies than elements corresponding to the same vertical column in the first transition series. There are also elements in the 2nd transition series whose first ionisation enthalpies are lower than those of the elements corresponding to the same vertical column in the 1st transition series.

(iv) Atomic size generally decreases from left to right across a period. Now, among the three transition series, atomic sizes of the elements in the second transition series are greater than those of the elements corresponding to the same vertical column in the first transition series. However, the atomic sizes of the elements in the third transition series are virtually the same

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as those of the corresponding members in the second transition series. This is due to lanthanoid contraction

Question 8.36:

Write down the number of 3d electrons in each of the following ions:

Ti^{2+} , V^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , CO^{2+} , Ni^{2+} and Cu^{2+} .

Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions (octahedral).

Answer

Metal ion	Number of <i>d</i> -electrons	Filling of <i>d</i> -orbitals
Ti^{2+}	2	t_{2g}^2
V^{2+}	3	t_{2g}^3
Cr^{3+}	3	t_{2g}^3
Mn^{2+}	5	$t_{2g}^3 e_g^2$
Fe^{2+}	6	$t_{2g}^4 e_g^2$
Fe^{3+}	5	$t_{2g}^3 e_g^2$
CO^{2+}	7	$t_{2g}^5 e_g^2$
Ni^{2+}	8	$t_{2g}^6 e_g^2$
Cu^{2+}	9	$t_{2g}^6 e_g^3$

Question 8.37:

Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

Answer

The properties of the elements of the first transition series differ from those of the heavier transition elements in many ways.

D AND F BLOCK ELEMENT NCERT SOLUTION

(i) The atomic sizes of the elements of the first transition series are smaller than those of the heavier elements (elements of 2nd and 3rd transition series).

However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction.

(ii) +2 and +3 oxidation states are more common for elements in the first transition series, while higher oxidation states are more common for the heavier elements.

(iii) The enthalpies of atomisation of the elements in the first transition series are lower than those of the corresponding elements in the second and third transition series.

(iv) The melting and boiling points of the first transition series are lower than those of the heavier transition elements. This is because of the occurrence of stronger metallic bonding (M–M bonding).

(v) The elements of the first transition series form low-spin or high-spin complexes depending upon the strength of the ligand field. However, the heavier transition elements form only low-spin complexes, irrespective of the strength of the ligand field

Question 8.38:

What can be inferred from the magnetic moment values of the following complex species?

Example Magnetic Moment (BM)



Answer

Magnetic moment (μ) is given as
$$\mu = \sqrt{n(n+2)}$$

For value $n = 1$,
$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.732$$

For value $n = 2$,
$$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$$

For value $n = 3$,
$$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$$

For value $n = 4$,
$$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.899$$

D AND F BLOCK ELEMENT NCERT SOLUTION

For value $n = 5$, $\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92$

(i) $K_4[Mn(CN)_6]$

For in transition metals, the magnetic moment is calculated from the spin-only formula. Therefore,

$$\sqrt{n(n+2)} = 2.2$$

We can see from the above calculation that the given value is closest to $n = 1$. Also, in this complex, Mn is in the +2 oxidation state. This means that Mn has 5 electrons in the d -orbital.

Hence, we can say that CN^- is a strong field ligand that causes the pairing of electrons.

(ii) $[Fe(H_2O)_6]^{2+}$

$$\sqrt{n(n+2)} = 5.3$$

We can see from the above calculation that the given value is closest to $n = 4$. Also, in this complex, Fe is in the +2 oxidation state. This means that Fe has 6 electrons in the d -orbital.

Hence, we can say that H_2O is a weak field ligand and does not cause the pairing of electrons.

(iii) $K_2[MnCl_4]$

$$\sqrt{n(n+2)} = 5.9$$

We can see from the above calculation that the given value is closest to $n = 5$. Also, in this complex, Mn is in the +2 oxidation state. This means that Mn has 5 electrons in the d -orbital.

Hence, we can say that Cl^- is a weak field ligand and does not cause the pairing of electrons.

COORDINATION COMPOUND AND ITS CHEMISTRY

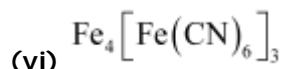
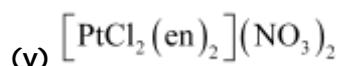
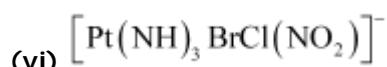
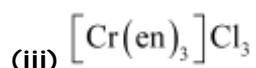
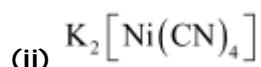
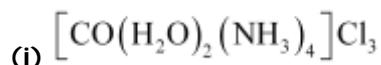
COORDINATION COMPOUND AND ITS CHEMISTRY

Question 9.1:

Write the formulas for the following coordination compounds:

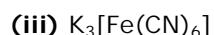
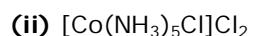
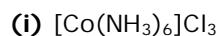
- (i) Tetraamminediaquacobalt(III) chloride
- (ii) Potassium tetracyanonickelate(II)
- (iii) Tris(ethane-1,2-diamine) chromium(III) chloride
- (iv) Amminebromidochloridonitrito-N-platinato(II)
- (v) Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate
- (vi) Iron(III) hexacyanoferrate(II)

Answer



Question 9.2:

Write the IUPAC names of the following coordination compounds:



COORDINATION COMPOUND AND ITS CHEMISTRY

(iv) $K_3[Fe(C_2O_4)_3]$

(v) $K_2[PdCl_4]$

(vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

Answer

(i) Hexaamminecobalt(III) chloride

(ii) Pentaamminechloridocobalt(III) chloride

(iii) Potassium hexacyanoferrate(III)

(iv) Potassium trioxalatoferrate(III)

(v) Potassium tetrachloridopalladate(II)

(vi) Diamminechlorido(methylamine)platinum(II) chloride

Question 9.3:

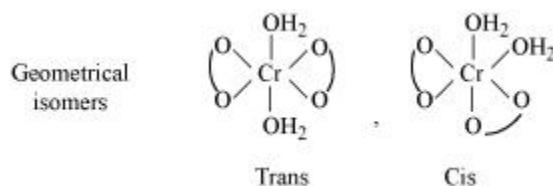
Indicate the types of isomerism exhibited by the following complexes and

draw the structures for these isomers:

- i. $K[Cr(H_2O)_2(C_2O_4)_2]$
- ii. $[Co(en)_3]Cl_3$
- iii. $[Co(NH_3)_5(NO_2)](NO_3)_2$
- iv. $[Pt(NH_3)(H_2O)Cl_2]$

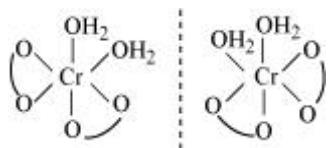
Answer

- i. Both geometrical (*cis*-, *trans*-) isomers for $K[Cr(H_2O)_2(C_2O_4)_2]$ can exist. Also, optical isomers for *cis*-isomer exist.

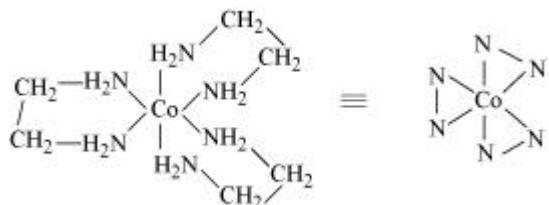


Trans-isomer is optically inactive. On the other hand, *cis*-isomer is optically active.

COORDINATION COMPOUND AND ITS CHEMISTRY



(ii) Two optical isomers for $[\text{CO}(\text{en})_3]\text{Cl}_3$ exist.

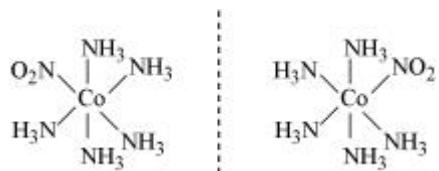


Two optical isomers are possible for this structure.



(iii) $[\text{CO}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$

A pair of optical isomers:



It can also show linkage isomerism.

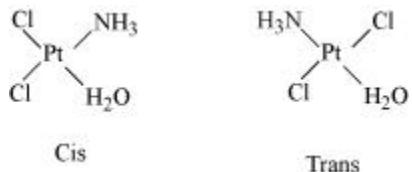
$[\text{CO}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$ and $[\text{CO}(\text{NH}_3)_5(\text{ONO})](\text{NO}_3)_2$

It can also show ionization isomerism.

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$ $[\text{CO}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)(\text{NO}_2)$

(iv) Geometrical (*cis*-, *trans*-) isomers of $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$ can exist.

COORDINATION COMPOUND AND ITS CHEMISTRY

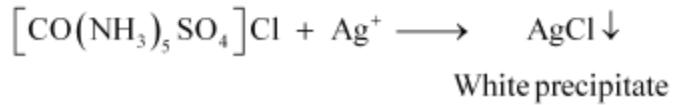
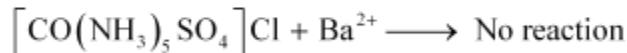
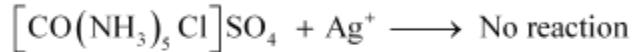
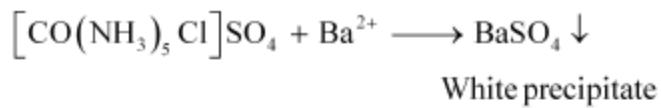


Question 9.4:

Give evidence that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ are ionization isomers.

Answer

When ionization isomers are dissolved in water, they ionize to give different ions. These ions then react differently with different reagents to give different products.



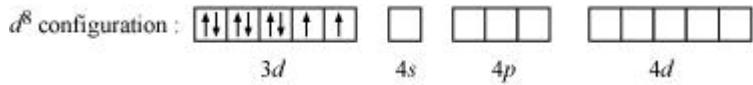
Question 9.5:

Explain on the basis of valence bond theory that $[\text{Ni}(\text{CN})_4]^{2-}$ ion with square

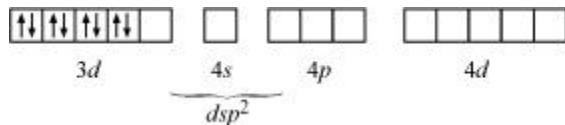
planar structure is diamagnetic and the $[\text{NiCl}_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Answer

Ni is in the +2 oxidation state i.e., in d^8 configuration.



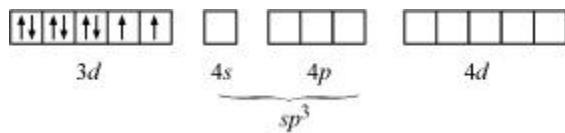
There are 4 CN^- ions. Thus, it can either have a tetrahedral geometry or square planar geometry. Since CN^- ion is a strong field ligand, it causes the pairing of unpaired $3d$ electrons.



COORDINATION COMPOUND AND ITS CHEMISTRY

It now undergoes dsp^2 hybridization. Since all electrons are paired, it is diamagnetic.

In case of $[NiCl_4]^{2-}$, Cl^- ion is a weak field ligand. Therefore, it does not lead to the pairing of unpaired $3d$ electrons. Therefore, it undergoes sp^3 hybridization.



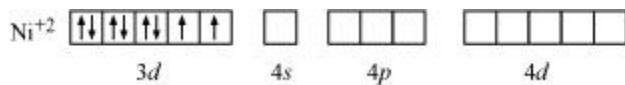
Since there are 2 unpaired electrons in this case, it is paramagnetic in nature

Question 9.6:

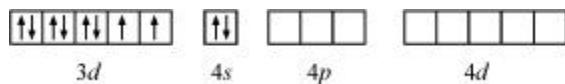
$[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

Answer

Though both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ are tetrahedral, their magnetic characters are different. This is due to a difference in the nature of ligands. Cl^- is a weak field ligand and it does not cause the pairing of unpaired $3d$ electrons. Hence, $[NiCl_4]^{2-}$ is paramagnetic.



In $Ni(CO)_4$, Ni is in the zero oxidation state i.e., it has a configuration of $3d^8 4s^2$.



But CO is a strong field ligand. Therefore, it causes the pairing of unpaired $3d$ electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to sp^3 hybridization. Since no unpaired electrons are present in this case, $[Ni(CO)_4]$ is diamagnetic.

Question 9.7:

$[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

Answer

In both $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, Fe exists in the +3 oxidation state i.e., in d^5 configuration.



Since CN^- is a strong field ligand, it causes the pairing of unpaired electrons. Therefore, there is only one unpaired electron left in the d -orbital.



COORDINATION COMPOUND AND ITS CHEMISTRY

Therefore,

$$\begin{aligned}\mu &= \sqrt{n(n+2)} \\ &= \sqrt{1(1+2)} \\ &= \sqrt{3} \\ &= 1.732 \text{ BM}\end{aligned}$$

On the other hand, H_2O is a weak field ligand. Therefore, it cannot cause the pairing of electrons. This means that the number of unpaired electrons is 5.

Therefore,

$$\begin{aligned}\mu &= \sqrt{n(n+2)} \\ &= \sqrt{5(5+2)} \\ &= \sqrt{35} \\ &\approx 6 \text{ BM}\end{aligned}$$

Thus, it is evident that $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic, while $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic

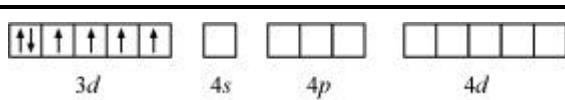
Question 9.8:

Explain $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex.

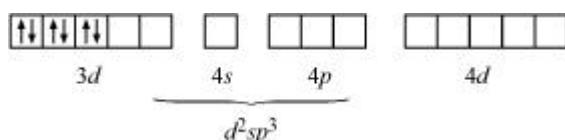
Answer

$[\text{Co}(\text{NH}_3)_6]^{3+}$	$[\text{Ni}(\text{NH}_3)_6]^{2+}$
Oxidation state of cobalt = +3	Oxidation state of Ni = +2
Electronic configuration of cobalt $= d^6$	Electronic configuration of nickel $= d^8$

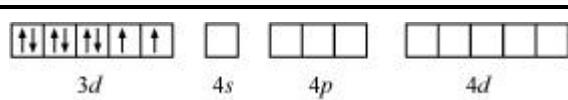
COORDINATION COMPOUND AND ITS CHEMISTRY



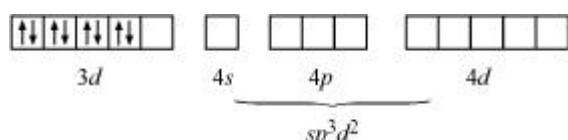
NH₃ being a strong field ligand causes the pairing. Therefore, Ni can undergo d^2sp^3 hybridization.



Hence, it is an inner orbital complex.



If NH₃ causes the pairing, then only one 3d orbital is empty. Thus, it cannot undergo d^2sp^3 hybridization. Therefore, it undergoes sp^3d^2 hybridization.

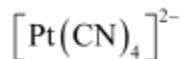


Hence, it forms an outer orbital complex

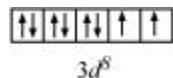
Question 9.9:

Predict the number of unpaired electrons in the square planar [Pt(CN)₄]²⁻ ion.

Answer



In this complex, Pt is in the +2 state. It forms a square planar structure. This means that it undergoes d^2 hybridization. Now, the electronic configuration of Pd(+2) is 5d⁸.

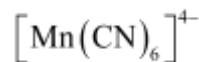
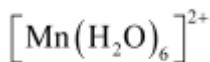


CN⁻ being a strong field ligand causes the pairing of unpaired electrons. Hence, there are no unpaired electrons in $[\text{Pt}(\text{CN})_4]^{2-}$.

Question 9.10:

The hexaquo manganese(II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

Answer



COORDINATION COMPOUND AND ITS CHEMISTRY

Mn is in the +2 oxidation state.

The electronic configuration is d^5 .

The crystal field is octahedral.

Water is a weak field ligand.

Therefore, the arrangement of the electrons in $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is $t2g3eg2$.

Mn is in the +2 oxidation state.

The electronic configuration is d^5 .

The crystal field is octahedral.

Cyanide is a strong field ligand.

Therefore, the arrangement of

the electrons in $[\text{Mn}(\text{CN})_6]^{4-}$ is

$t2g5eg0$.

Hence, hexaaquo manganese (II) ion has five unpaired electrons, while hexacyano ion has only one unpaired electron

Question 9.11:

Calculate the overall complex dissociation equilibrium constant for the $\text{Cu}(\text{NH}_3)_4^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13} .

Answer

$$\beta_4 = 2.1 \times 10^{13}$$

The overall complex dissociation equilibrium constant is the reciprocal of the overall stability constant, β_4 .

$$\frac{1}{\beta_4} = \frac{1}{2.1 \times 10^{13}}$$
$$\therefore = 4.7 \times 10^{-14}$$

Question 9.1:

Explain the bonding in coordination compounds in terms of Werner's postulates.

Answer

Werner's postulates explain the bonding in coordination compounds as follows:

(i) A metal exhibits two types of valencies namely, primary and secondary valencies. Primary valencies are satisfied by negative ions while secondary valencies are satisfied by both negative and neutral ions.

COORDINATION COMPOUND AND ITS CHEMISTRY

(In modern terminology, the primary valency corresponds to the oxidation number of the metal ion, whereas the secondary valency refers to the coordination number of the metal ion.

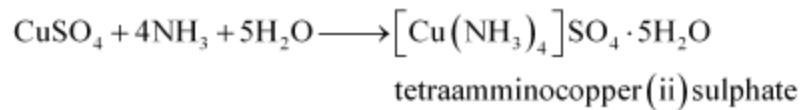
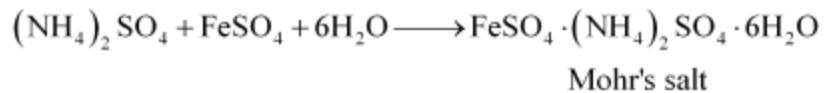
(ii) A metal ion has a definite number of secondary valencies around the central atom. Also, these valencies project in a specific direction in the space assigned to the definite geometry of the coordination compound.

(iii) Primary valencies are usually ionizable, while secondary valencies are non-ionizable

Question 9.2:

FeSO_4 solution mixed with $(\text{NH}_4)_2\text{SO}_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but CuSO_4 solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

Answer



Both the compounds i.e., $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ fall under the category of addition compounds with only one major difference i.e., the former is an example of a double salt, while the latter is a coordination compound.

A double salt is an addition compound that is stable in the solid state but that which breaks up into its constituent ions in the dissolved state. These compounds exhibit individual properties

of their constituents. For e.g. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ breaks into Fe^{2+} , NH_4^+ , and SO_4^{2-} ions. Hence, it gives a positive test for Fe^{2+} ions.

A coordination compound is an addition compound which retains its identity in the solid as well as in the dissolved state. However, the individual properties of the constituents are lost. This

happens because $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ does not show the test for Cu^{2+} . The ions present in the solution of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ are $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and SO_4^{2-}

Question 9.3:

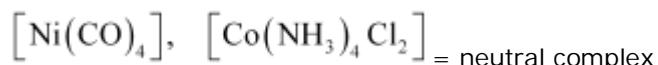
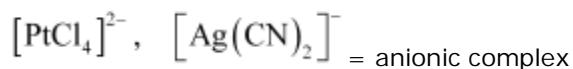
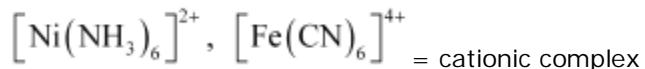
Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Answer

COORDINATION COMPOUND AND ITS CHEMISTRY

(i) Coordination entity:

A coordination entity is an electrically charged radical or species carrying a positive or negative charge. In a coordination entity, the central atom or ion is surrounded by a suitable number of neutral molecules or negative ions (called ligands). For example:



(ii) Ligands

The neutral molecules or negatively charged ions that surround the metal atom in a

coordination entity or a coordinal complex are known as ligands. For example, $\ddot{\text{N}}\text{H}_3$, $\text{H}_2\ddot{\text{O}}$, Cl^- , OH^- . Ligands are usually polar in nature and possess at least one unshared pair of valence electrons.

(iii) Coordination number:

The total number of ligands (either neutral molecules or negative ions) that get attached to the central metal atom in the coordination sphere is called the coordination number of the central metal atom. It is also referred to as its ligancy.

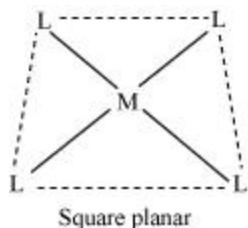
For example:

- In the complex, $\text{K}_2[\text{PtCl}_6]$, there are six chloride ions attached to Pt in the coordinate sphere. Therefore, the coordination number of Pt is 6.
- Similarly, in the complex $[\text{Ni}(\text{NH}_3)_4]\text{Cl}_2$, the coordination number of the central atom (Ni) is 4.

(vi) Coordination polyhedron:

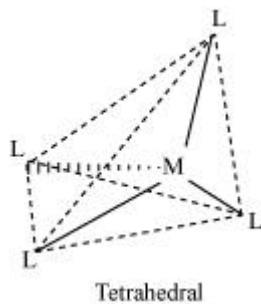
Coordination polyhedrons about the central atom can be defined as the spatial arrangement of the ligands that are directly attached to the central metal ion in the coordination sphere. For example:

(a)



COORDINATION COMPOUND AND ITS CHEMISTRY

(b) Tetrahedral



(v) **Homoleptic complexes:**

These are those complexes in which the metal ion is bound to only one kind of a donor group.

For e.g.: $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{PtCl}_4]^{2-}$ etc.

(vi) **Heteroleptic complexes:**

Heteroleptic complexes are those complexes where the central metal ion is bound to more than one type of a donor group.

For e.g.: $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2]^+$, $[\text{Co}(\text{NH}_3)_5 \text{Cl}]^{2+}$

Question 9.4:

What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

Answer

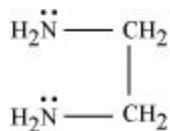
A ligand may contain one or more unshared pairs of electrons which are called the donor sites of ligands. Now, depending on the number of these donor sites, ligands can be classified as follows:

(a) **Unidentate ligands:** Ligands with only one donor site are called unidentate ligands. For

e.g., $\ddot{\text{N}}\text{H}_3$, Cl^- etc.

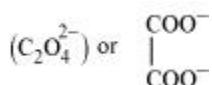
(b) **Didentate ligands:** Ligands that have two donor sites are called didentate ligands. For e.g.,

(a) Ethane-1,2-diamine



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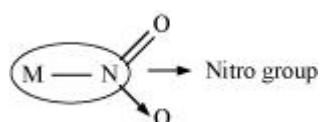
(b) Oxalate ion



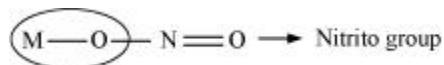
(c) Ambidentate ligands:

Ligands that can attach themselves to the central metal atom through two different atoms are called ambidentate ligands. For example:

(a)



(The donor atom is N)



(The donor atom is oxygen)

(b)



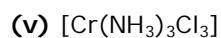
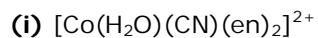
(The donor atom is S)



(The donor atom is N)

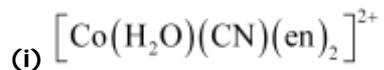
Question 9.5:

Specify the oxidation numbers of the metals in the following coordination entities:



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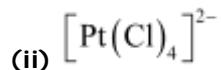
Answer



Let the oxidation number of Co be x .

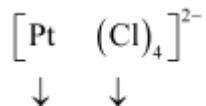
The charge on the complex is +2.

$$\begin{array}{cccccc} \left[\text{Co} & (\text{H}_2\text{O}) & (\text{CN}) & (\text{en})_2 \right]^{2+} \\ \downarrow & \downarrow & \downarrow & \downarrow \\ x & + & 0 & + (-1) & + 2(0) = +2 \\ x - 1 & = & +2 \\ x & = & +3 \end{array}$$



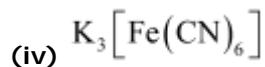
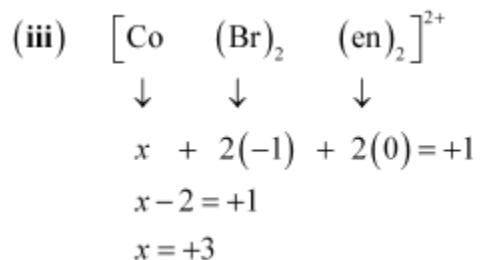
Let the oxidation number of Pt be x .

The charge on the complex is -2.

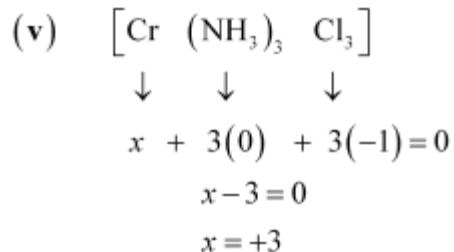
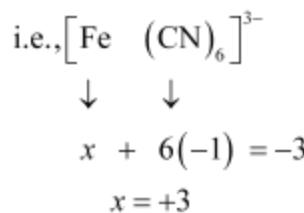


$$x + 4(-1) = -2$$

$$x = +2$$



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Question 9.6:

Using IUPAC norms write the formulas for the following:

- (i) Tetrahydroxozincate(II)
- (ii) Potassium tetrachloridopalladate(II)
- (iii) Diamminedichloridoplatinum(II)
- (iv) Potassium tetracyanonickelate(II)
- (v) Pentaamminenitrito-O-cobalt(III)
- (vi) Hexaamminecobalt(III) sulphate
- (vii) Potassium tri(oxalato)chromate(III)
- (viii) Hexaammineplatinum(IV)
- (ix) Tetrabromidocuprate(II)
- (x) Pentaamminenitrito-N-cobalt(III)

Answer

(i) $[\text{Zn}(\text{OH})_4]^{2-}$

(ii) $\text{K}_2[\text{PdCl}_4]$

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- (iii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
(iv) $\text{K}_2[\text{Ni}(\text{CN})_4]$
(v) $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{2+}$
(vi) $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$
(vii) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
(viii) $[\text{Pt}(\text{NH}_3)_6]^{4+}$
(ix) $[\text{Cu}(\text{Br})_4]^{2-}$
(x) $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{2+}$

Question 9.7:

Using IUPAC norms write the systematic names of the following:

- (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
(ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$
(iii) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
(iv) $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$
(v) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
(vi) $[\text{NiCl}_4]^{2-}$
(vii) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$
(viii) $[\text{Co}(\text{en})_3]^{3+}$
(ix) $[\text{Ni}(\text{CO})_4]$

Answer

- (i) Hexaamminecobalt(III) chloride
(ii) Diamminechlorido(methylamine) platinum(II) chloride
(iii) Hexaquatitanium(III) ion
(iv) Tetraamminichloridonitrito-N-Cobalt(III) chloride

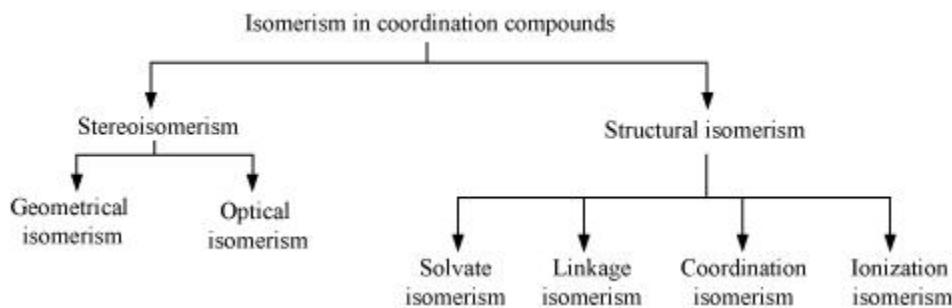
COORDINATION COMPOUND AND ITS CHEMISTRY

- (v) Hexaquamanganese(II) ion
- (vi) Tetrachloridonickelate(II) ion
- (vii) Hexaamminenickel(II) chloride
- (viii) Tris(ethane-1, 2-diammine) cobalt(III) ion
- (ix) Tetracarbonylnickel(0)

Question 9.8:

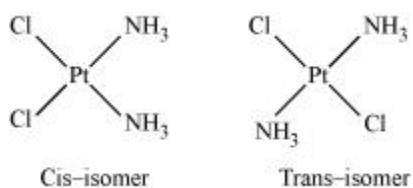
List various types of isomerism possible for coordination compounds, giving an example of each.

Answer



(a) Geometric isomerism:

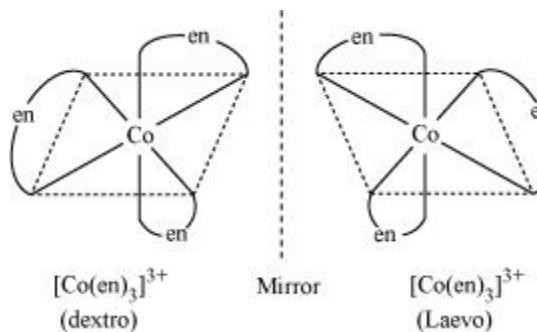
This type of isomerism is common in heteroleptic complexes. It arises due to the different possible geometric arrangements of the ligands. For example:



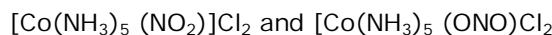
(b) Optical isomerism:

This type of isomerism arises in chiral molecules. Isomers are mirror images of each other and are non-superimposable.

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(c) Linkage isomerism: This type of isomerism is found in complexes that contain ambidentate ligands. For example:



Yellow form Red form

(d) Coordination isomerism:

This type of isomerism arises when the ligands are interchanged between cationic and anionic entities of different metal ions present in the complex.



(e) Ionization isomerism:

This type of isomerism arises when a counter ion replaces a ligand within the coordination sphere. Thus, complexes that have the same composition, but furnish different ions when dissolved in water are called ionization isomers. For e.g., $\text{Co}(\text{NH}_3)_5\text{SO}_4\text{Br}$ and $\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$.

(f) Solvate isomerism:

Solvate isomers differ by whether or not the solvent molecule is directly bonded to the metal ion or merely present as a free solvent molecule in the crystal lattice.



Violet Blue-green Dark green

Question 9.9:

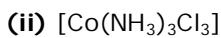
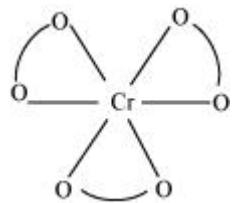
How many geometrical isomers are possible in the following coordination entities?

- (i) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ (ii) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

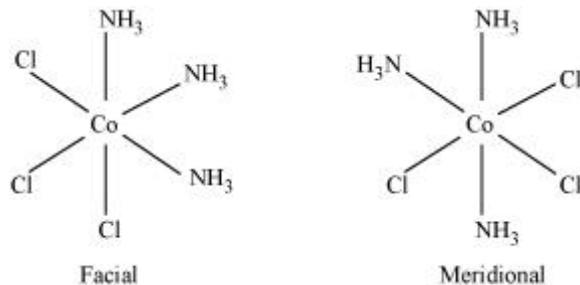
Answer

- (i) For $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, no geometric isomer is possible as it is a bidentate ligand.

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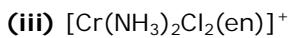
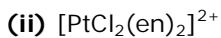
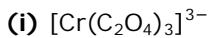


Two geometrical isomers are possible.

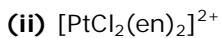
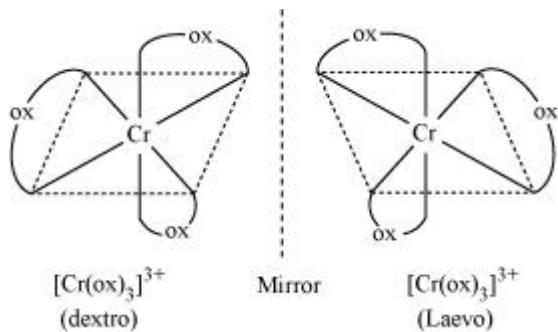
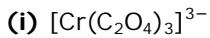


Question 9.10:

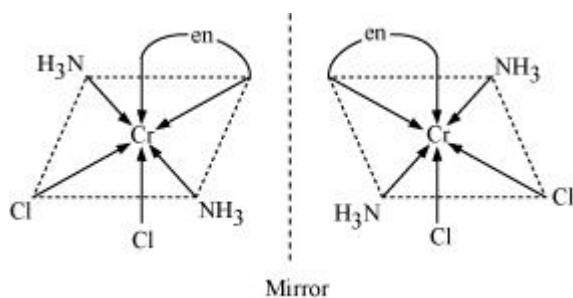
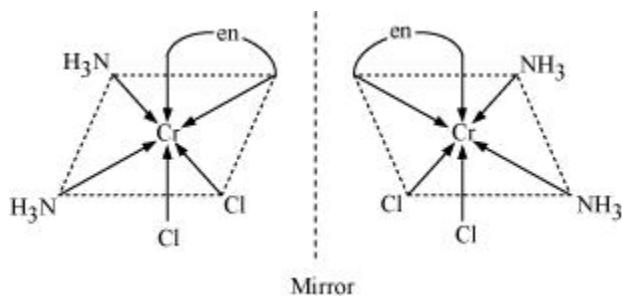
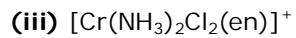
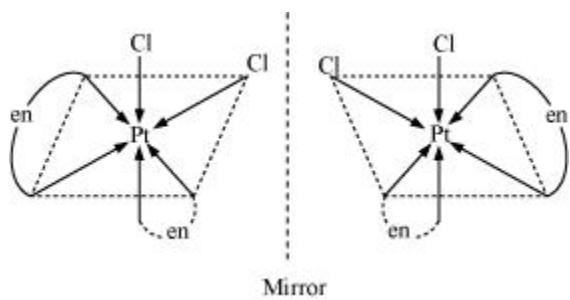
Draw the structures of optical isomers of:



Answer

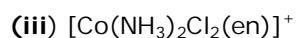
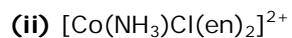


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Question 9.11:

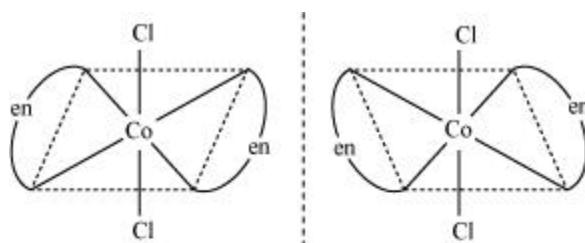
Draw all the isomers (geometrical and optical) of:



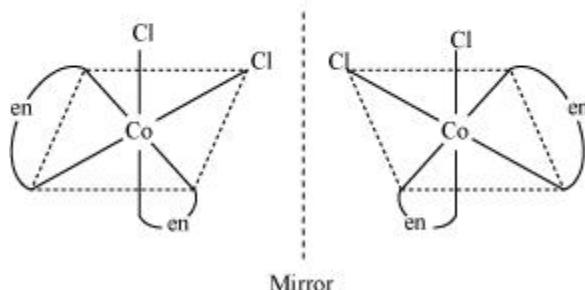
Answer



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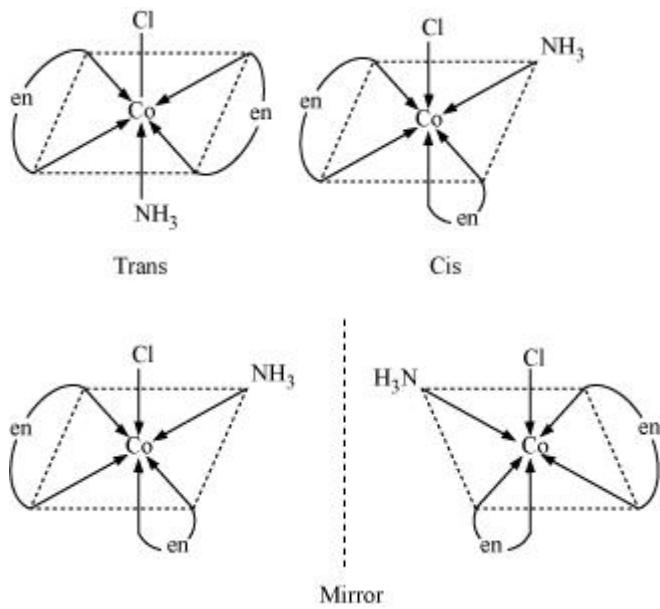
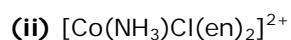


$\text{Trans } [\text{CoCl}_2(\text{en})_2]^+$ isomer-optically inactive
 (Superimposable mirror images)



$\text{Cis } [\text{CoCl}_2(\text{en})_2]^+$ isomer-optically active
 (Non-superimposable mirror images)

In total, three isomers are possible.

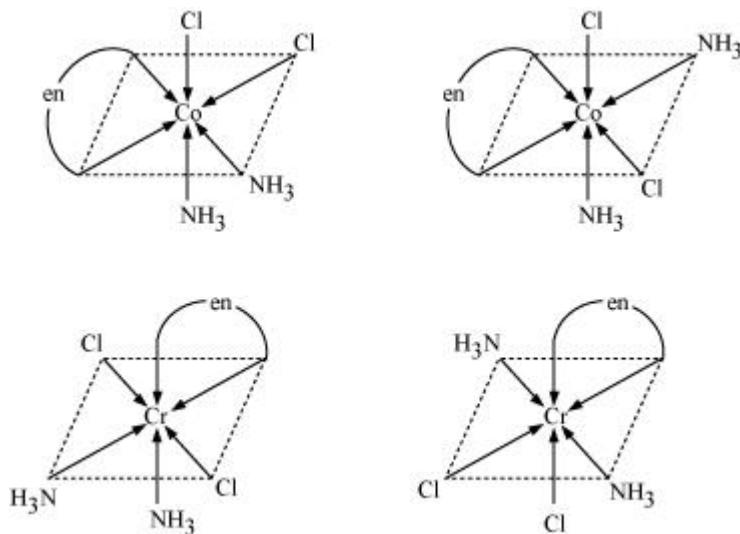


Trans-isomers are optically inactive.

Cis-isomers are optically active.

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(iii) $[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$

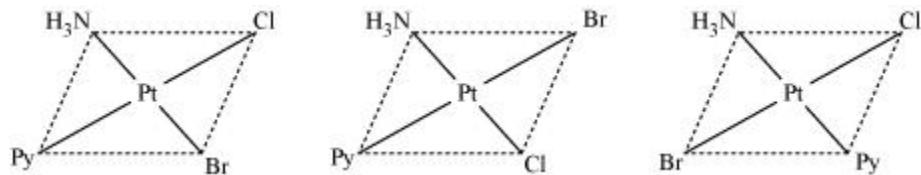


Question 9.12:

Write all the geometrical isomers of $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$ and how many of these will exhibit optical isomers?

Answer

$[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$



From the above isomers, none will exhibit optical isomers. Tetrahedral complexes rarely show optical isomerization. They do so only in the presence of unsymmetrical chelating agents.

Question 9.13:

Aqueous copper sulphate solution (blue in colour) gives:

- (i)** a green precipitate with aqueous potassium fluoride, and
- (ii)** a bright green solution with aqueous potassium chloride

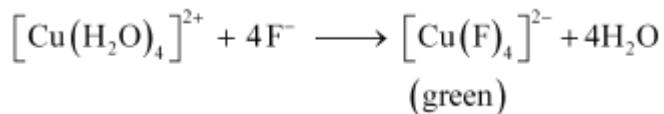
Explain these experimental results.

Answer

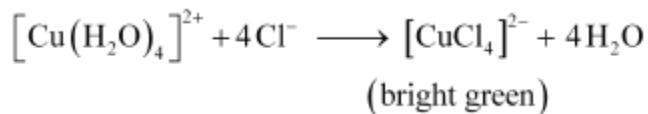
COORDINATION COMPOUND AND ITS CHEMISTRY

Aqueous CuSO_4 exists as $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$. It is blue in colour due to the presence of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ions.

(i) When KF is added:



(ii) When KCl is added:

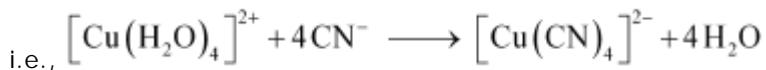
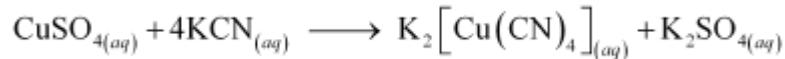


In both these cases, the weak field ligand water is replaced by the F^- and Cl^- ions

Question 9.14:

What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $\text{H}_2\text{S(g)}$ is passed through this solution?

Answer



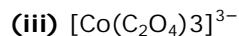
Thus, the coordination entity formed in the process is $\text{K}_2[\text{Cu}(\text{CN})_4]$. $\text{K}_2[\text{Cu}(\text{CN})_4]$ is a very stable complex, which does not ionize to give Cu^{2+} ions when added to water. Hence, Cu^{2+} ions are not precipitated when $\text{H}_2\text{S}_{(g)}$ is passed through the solution

Question 9.15:

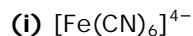
Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i) $[\text{Fe}(\text{CN})_6]^{4-}$

COORDINATION COMPOUND AND ITS CHEMISTRY



Answer



In the above coordination complex, iron exists in the +II oxidation state.

Fe^{2+} : Electronic configuration is $3d^6$

Orbitals of Fe^{2+} ion:

$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	\square	\square	\square	\square
$3d$	$4s$	$4p$						

As CN^- is a strong field ligand, it causes the pairing of the unpaired $3d$ electrons.

$1\downarrow$	$1\downarrow$	$1\downarrow$	\square	\square	\square	\square	\square
$3d$	$4s$	$4p$					

Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3 .

d^2sp^3 hybridized orbitals of Fe^{2+} are:

$1\downarrow$	$1\downarrow$	$1\downarrow$	\square	\square	\square	\square	\square
d^2sp^3							

6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3 orbitals.

Then,

$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$
6 pairs of electrons from 6 CN^- ions							

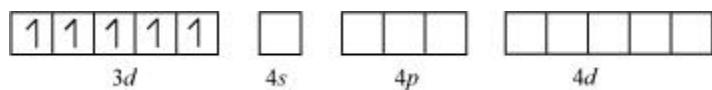
Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).



In this complex, the oxidation state of Fe is +3.

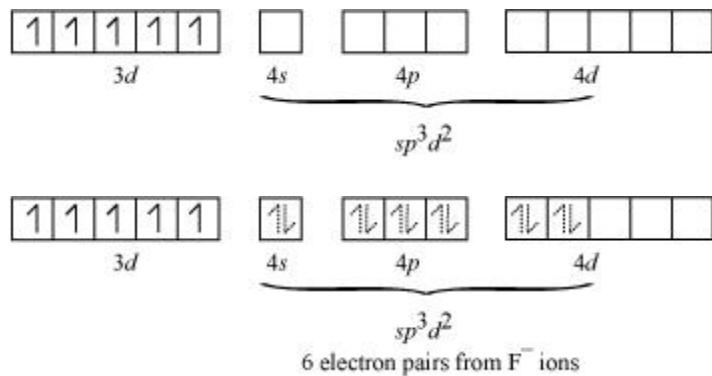
COORDINATION COMPOUND AND ITS CHEMISTRY

Orbitals of Fe^{+3} ion:



There are 6 F^- ions. Thus, it will undergo d^2sp^3 or sp^3d^2 hybridization. As F^- is a weak field ligand, it does not cause the pairing of the electrons in the $3d$ orbital. Hence, the most feasible hybridization is sp^3d^2 .

sp^3d^2 hybridized orbitals of Fe are:

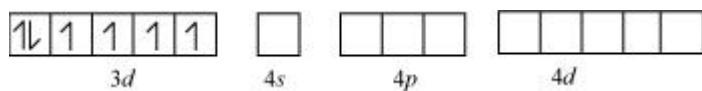


Hence, the geometry of the complex is found to be octahedral.

(iii) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$

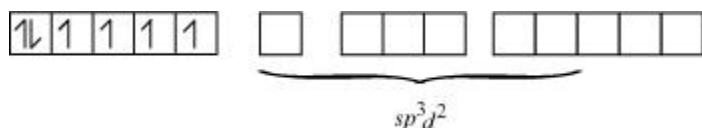
Cobalt exists in the +3 oxidation state in the given complex.

Orbitals of Co^{3+} ion:



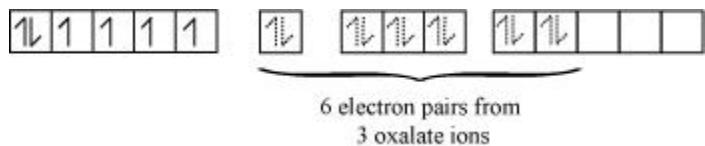
Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the $3d$ orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.

sp^3d^2 hybridization of Co^{3+} :



The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.

COORDINATION COMPOUND AND ITS CHEMISTRY

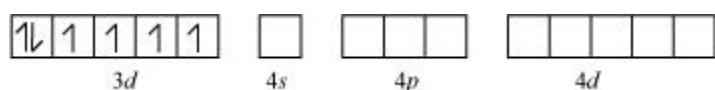


Hence, the geometry of the complex is found to be octahedral.



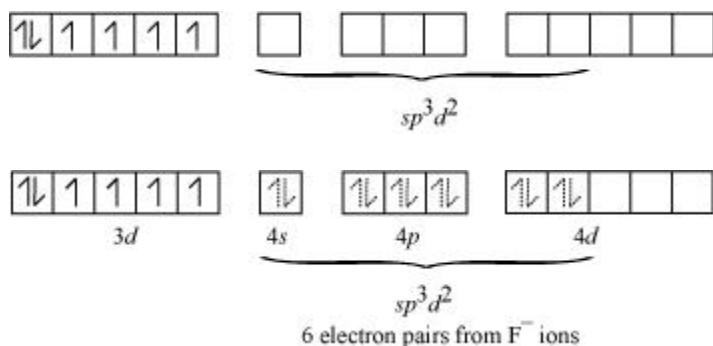
Cobalt exists in the +3 oxidation state.

Orbitals of Co^{3+} ion:



Again, fluoride ion is a weak field ligand. It cannot cause the pairing of the 3d electrons. As a result, the Co^{3+} ion will undergo sp^3d^2 hybridization.

sp^3d^2 hybridized orbitals of Co^{3+} ion are:



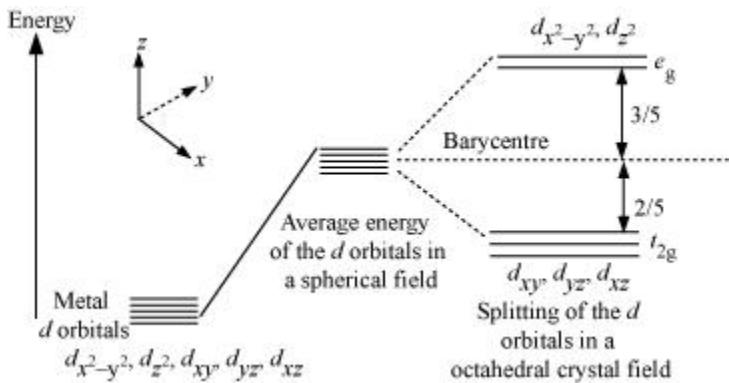
Hence, the geometry of the complex is octahedral and paramagnetic

Question 9.16:

Draw figure to show the splitting of d orbitals in an octahedral crystal field.

Answer

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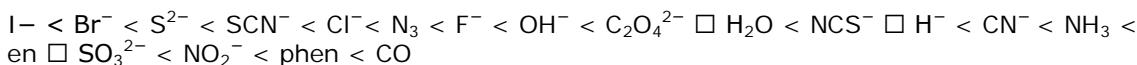
The splitting of the d orbitals in an octahedral field takes place in such a way that $d_{x^2-y^2}$ and d_{z^2} experience a rise in energy and form the e_g level, while d_{xy} , d_{yz} and d_{zx} experience a fall in energy and form the t_{2g} level

Question 9.17:

What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

Answer

A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values. The ligands present on the R.H.S of the series are strong field ligands while that on the L.H.S are weak field ligands. Also, strong field ligands cause higher splitting in the d orbitals than weak field ligands.



Question 9.18:

What is crystal field splitting energy? How does the magnitude of Δ_o decide the actual configuration of d -orbitals in a coordination entity?

Answer

The degenerate d -orbitals (in a spherical field environment) split into two levels i.e., e_g and t_{2g} in the presence of ligands. The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting while the energy difference between the two levels (e_g and t_{2g}) is called the crystal-field splitting energy. It is denoted by Δ_o .

After the orbitals have split, the filling of the electrons takes place. After 1 electron (each) has been filled in the three t_{2g} orbitals, the filling of the fourth electron takes place in two ways. It can enter the e_g orbital (giving rise to $t_{2g}^3 e_g^1$ like electronic configuration) or the pairing of the electrons can take place in the t_{2g} orbitals (giving rise to $t_{2g}^4 e_g^0$ like electronic configuration). If the Δ_o value of a ligand is less than the pairing energy (P), then the electrons enter the e_g orbital. On the other hand, if the Δ_o value of a ligand is more than the pairing energy (P), then the electrons enter the t_{2g} orbital.

COORDINATION COMPOUND AND ITS CHEMISTRY

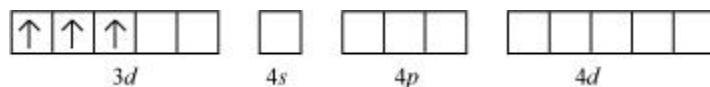
Question 9.19:

$[\text{Cr}(\text{NH}_3)_6]^{3+}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic. Explain why?

Answer

Cr is in the +3 oxidation state i.e., d^3 configuration. Also, NH_3 is a weak field ligand that does not cause the pairing of the electrons in the $3d$ orbital.

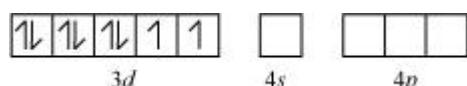
Cr^{3+}



Therefore, it undergoes d^2sp^3 hybridization and the electrons in the $3d$ orbitals remain unpaired. Hence, it is paramagnetic in nature.

In $[\text{Ni}(\text{CN})_4]^{2-}$, Ni exists in the +2 oxidation state i.e., d^8 configuration.

Ni^{2+} :



CN^- is a strong field ligand. It causes the pairing of the $3d$ orbital electrons. Then, Ni^{2+} undergoes dsp^2 hybridization.



As there are no unpaired electrons, it is diamagnetic

Question 9.20:

A solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green but a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. Explain.

Answer

In $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $\text{H}_2\ddot{\text{O}}$ is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+} . In this complex, the d electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of $d-d$ transition is present. Hence, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is coloured.

In $[\text{Ni}(\text{CN})_4]^{2-}$, the electrons are all paired as CN^- is a strong field ligand. Therefore, $d-d$ transition is not possible in $[\text{Ni}(\text{CN})_4]^{2-}$. Hence, it is colourless

Question 9.21:

COORDINATION COMPOUND AND ITS CHEMISTRY

$[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ are of different colours in dilute solutions. Why?

Answer

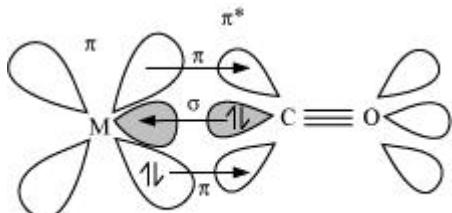
The colour of a particular coordination compound depends on the magnitude of the crystal-field splitting energy, Δ . This CFSE in turn depends on the nature of the ligand. In case of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, the colour differs because there is a difference in the CFSE. Now, CN^- is a strong field ligand having a higher CFSE value as compared to the CFSE value of water. This means that the absorption of energy for the intra $d-d$ transition also differs. Hence, the transmitted colour also differs.

Question 9.22:

Discuss the nature of bonding in metal carbonyls.

Answer

The metal-carbon bonds in metal carbonyls have both σ and π characters. A σ bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal. A π bond is formed by the donation of a pair of electrons from the filled metal d orbital into the vacant anti-bonding π^* orbital (also known as back bonding of the carbonyl group). The σ bond strengthens the π bond and vice-versa. Thus, a synergic effect is created due to this metal-ligand bonding. This synergic effect strengthens the bond between CO and the metal.



Synergic bonding in metal carbonyls

Question 9.23:

Give the oxidation state, d -orbital occupation and coordination number of the central metal ion in the following complexes:

(i) $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$

(ii) cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$

(iii) $(\text{NH}_4)_2[\text{CoF}_4]$

(iv) $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$

Answer

(i) $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$

COORDINATION COMPOUND AND ITS CHEMISTRY

The central metal ion is Co.

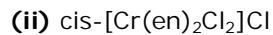
Its coordination number is 6.

The oxidation state can be given as:

$$x - 6 = -3$$

$$x = +3$$

The *d* orbital occupation for Co^{3+} is $t_{2g}^6 e_g^0$.



The central metal ion is Cr.

The coordination number is 6.

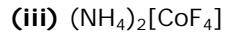
The oxidation state can be given as:

$$x + 2(0) + 2(-1) = +1$$

$$x - 2 = +1$$

$$x = +3$$

The *d* orbital occupation for Cr^{3+} is t_{2g}^3 .



The central metal ion is Co.

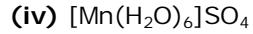
The coordination number is 4.

The oxidation state can be given as:

$$x - 4 = -2$$

$$x = +2$$

The *d* orbital occupation for Co^{2+} is $e_g^4 t_{2g}^3$.



The central metal ion is Mn.

The coordination number is 6.

The oxidation state can be given as:

$$x + 0 = +2$$

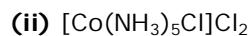
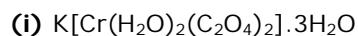
COORDINATION COMPOUND AND ITS CHEMISTRY

$$x = +2$$

The d orbital occupation for Mn is $t_{2g}^3 e_g^2$

Question 9.24:

Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:



Answer

(i) Potassium diaquadioxalatochromate (III) trihydrate.

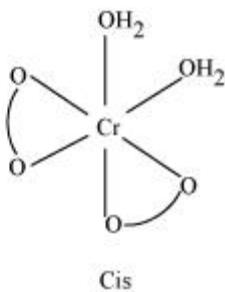
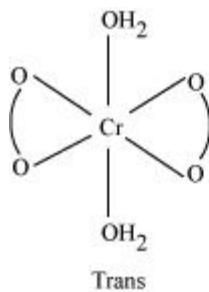
Oxidation state of chromium = 3

Electronic configuration: $3d^3$: t_{2g}^3

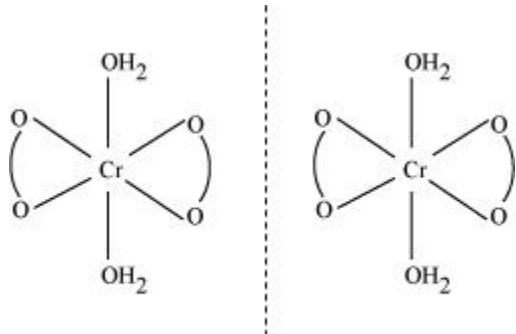
Coordination number = 6

Shape: octahedral

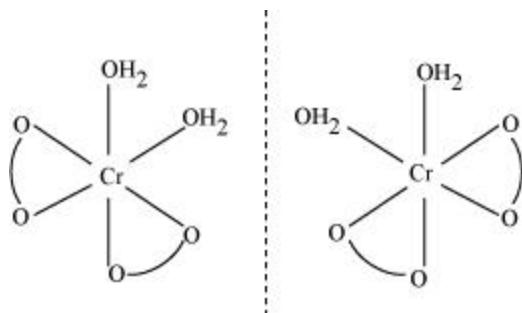
Stereochemistry:



COORDINATION COMPOUND AND ITS CHEMISTRY



Trans is optically inactive



Cis is optically active

$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)}$$

$$= \sqrt{3(3+2)}$$

$$= \sqrt{15}$$

4BM

(ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

IUPAC name: Pentaamminechloridocobalt(III) chloride

Oxidation state of Co = +3

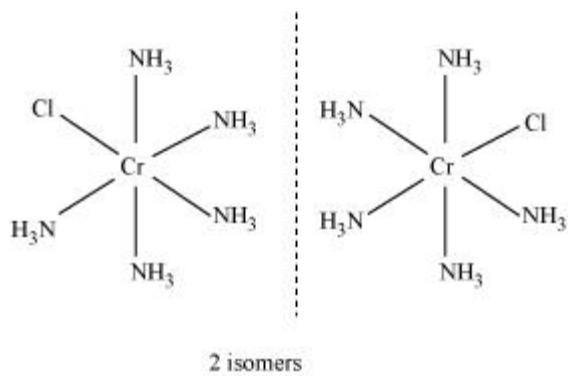
Coordination number = 6

Shape: octahedral.

Electronic configuration: d^6 : t_{2g}^6 .

Stereochemistry:

COORDINATION COMPOUND AND ITS CHEMISTRY



Magnetic Moment = 0

(iii) $\text{CrCl}_3(\text{py})_3$

IUPAC name: Trichloridotripyridinechromium (III)

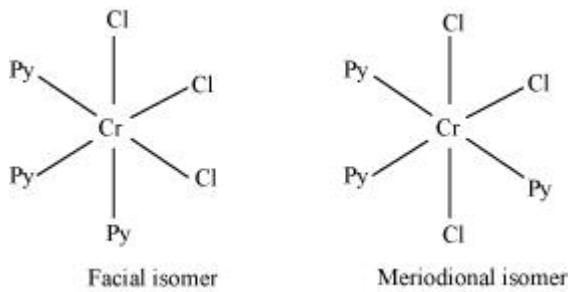
Oxidation state of chromium = +3

Electronic configuration for d^3 = t_{2g}^3

Coordination number = 6

Shape: octahedral.

Stereochemistry:



Both isomers are optically active. Therefore, a total of 4 isomers exist.

$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)}$$

$$\begin{aligned} &= \sqrt{3(3+2)} \\ &= \sqrt{15} \end{aligned}$$

□ 4BM

(iv) $\text{Cs}[\text{FeCl}_4]$

COORDINATION COMPOUND AND ITS CHEMISTRY

IUPAC name: Caesium tetrachloroferrate (III)

Oxidation state of Fe = +3

Electronic configuration of d^6 = $e_g^2 t_{2g}^3$

Coordination number = 4

Shape: tetrahedral

Stereochemistry: optically inactive

Magnetic moment:

$$\mu = \sqrt{n(n+2)}$$

$$= \sqrt{5(5+2)}$$

$$= \sqrt{35} \sim 6 \text{ BM}$$

(v) $\text{K}_4[\text{Mn}(\text{CN})_6]$

Potassium hexacyanomanganate(II)

Oxidation state of manganese = +2

Electronic configuration: d^5+ : t_{2g}^5

Coordination number = 6

Shape: octahedral.

Stereochemistry: optically inactive

$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)}$$

$$= \sqrt{1(1+2)}$$

$$= \sqrt{3}$$

$$= 1.732 \text{ BM}$$

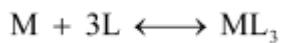
Question 9.25:

What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

Answer

COORDINATION COMPOUND AND ITS CHEMISTRY

The stability of a complex in a solution refers to the degree of association between the two species involved in a state of equilibrium. Stability can be expressed quantitatively in terms of stability constant or formation constant.



$$\text{Stability constant, } \beta = \frac{[ML_3]}{[M][L]^3}$$

For this reaction, the greater the value of the stability constant, the greater is the proportion of ML_3 in the solution.

Stability can be of two types:

(a) Thermodynamic stability:

The extent to which the complex will be formed or will be transformed into another species at the point of equilibrium is determined by thermodynamic stability.

(b) Kinetic stability:

This helps in determining the speed with which the transformation will occur to attain the state of equilibrium.

Factors that affect the stability of a complex are:

(a) **Charge on the central metal ion:** The greater the charge on the central metal ion, the greater is the stability of the complex.

2. **Basic nature of the ligand:** A more basic ligand will form a more stable complex.

2. **Presence of chelate rings:** Chelation increases the stability of complexes

Question 9.26:

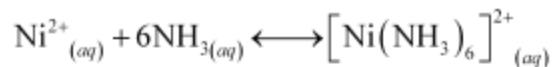
What is meant by the *chelate effect*? Give an example.

Answer

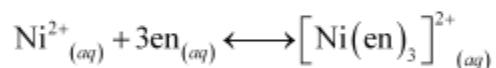
When a ligand attaches to the metal ion in a manner that forms a ring, then the metal-ligand association is found to be more stable. In other words, we can say that complexes containing chelate rings are more stable than complexes without rings. This is known as the chelate effect.

For example:

COORDINATION COMPOUND AND ITS CHEMISTRY

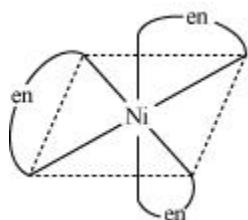


$$\log\beta = 7.99$$



$$\log\beta = 18.1$$

(more stable)



Question 9.27:

Discuss briefly giving an example in each case the role of coordination compounds in:

- (i) biological system
- (ii) medicinal chemistry
- (iii) analytical chemistry
- (iv) extraction/metallurgy of metals

Answer

(i) Role of coordination compounds in biological systems:

We know that photosynthesis is made possible by the presence of the chlorophyll pigment. This pigment is a coordination compound of magnesium. In the human biological system, several coordination compounds play important roles. For example, the oxygen-carrier of blood, i.e., haemoglobin, is a coordination compound of iron.

(ii) Role of coordination compounds in medicinal chemistry:

Certain coordination compounds of platinum (for example, *cis*-platin) are used for inhibiting the growth of tumours.

(iii) Role of coordination compounds in analytical chemistry:

During salt analysis, a number of basic radicals are detected with the help of the colour changes they exhibit with different reagents. These colour changes are a result of the coordination compounds or complexes that the basic radicals form with different ligands.

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(iii) Role of coordination compounds in extraction or metallurgy of metals:

The process of extraction of some of the metals from their ores involves the formation of complexes. For example, in aqueous solution, gold combines with cyanide ions to form $[\text{Au}(\text{CN})_2]$. From this solution, gold is later extracted by the addition of zinc metal

Question 9.28:

How many ions are produced from the complex $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ in solution?

(i) 6

(ii) 4

(iii) 3

(iv) 2

Answer

(iii) The given complex can be written as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$.

Thus, $[\text{Co}(\text{NH}_3)_6]^+$ along with two Cl^- ions are produced

Question 9.29:

Amongst the following ions which one has the highest magnetic moment value?

(i) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

(ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

(iii) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

Answer

(i) No. of unpaired electrons in $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} = 3$

$$\text{Then, } \mu = \sqrt{n(n+2)}$$

$$= \sqrt{3(3+2)}$$

$$= \sqrt{15}$$

$$\sim 4 \text{ BM}$$

(ii) No. of unpaired electrons in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} = 4$

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$$\text{Then, } \mu = \sqrt{4(4+2)}$$

$$= \sqrt{24}$$

$$\sim 5 \text{ BM}$$

(iii) No. of unpaired electrons in $[\text{Zn}(\text{H}_2\text{O})_6]^{2+} = 0$

Hence, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ has the highest magnetic moment value

Question 9.30:

The oxidation number of cobalt in $\text{K}[\text{Co}(\text{CO})_4]$ is

(i) +1

(ii) +3

(iii) -1

(iv) -3

Answer

We know that CO is a neutral ligand and K carries a charge of +1.

Therefore, the complex can be written as $\text{K}^+[\text{Co}(\text{CO})_4]^-$. Therefore, the oxidation number of Co in the given complex is -1. Hence, option (iii) is correct

Question 9.31:

Amongst the following, the most stable complex is

(i) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

(ii) $[\text{Fe}(\text{NH}_3)_6]^{3+}$

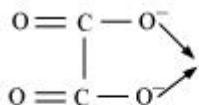
(iii) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$

(iv) $[\text{FeCl}_6]^{3-}$

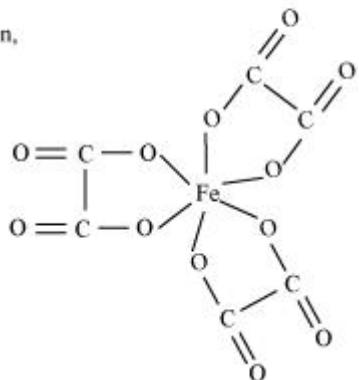
Answer

We know that the stability of a complex increases by chelation. Therefore, the most stable complex is $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$.

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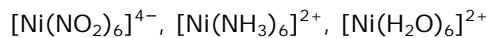


Then,



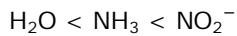
Question 9.32:

What will be the correct order for the wavelengths of absorption in the visible region for the following:

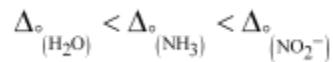


Answer

The central metal ion in all the three complexes is the same. Therefore, absorption in the visible region depends on the ligands. The order in which the CFSE values of the ligands increases in the spectrochemical series is as follows:



Thus, the amount of crystal-field splitting observed will be in the following order:



Hence, the wavelengths of absorption in the visible region will be in the order:

