

1

Solid State

Multiple Choice Questions (MCQs)

Q. 1 Which of the following conditions favours the existence of a substance in the solid state?

- (a) High temperature
- (b) Low temperature
- (c) High thermal energy
- (d) Weak cohesive forces

Ans. (b) At low temperature existence of a substance in solid state is due to

- (a) slow molecular motion and
- (b) strong cohesive forces

These two forces hold the constituent particles together thus causes existence of substance in solid state.

Q. 2 Which of the following is not a characteristic of a crystalline solid?

- (a) Definite and characteristic heat of fusion
- (b) Isotropic nature
- (c) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal
- (d) A true solid

Ans. (b) Crystalline solid is anisotropic in nature as this solid shows different physical properties such as electrical resistance, refractive index in different directions.

Note Isotropic and anisotropic properties are related to amorphous solid and crystalline solid which can be clearly understood as

Property	Types of solid	Physical properties
Isotropy	Amorphous solid	Same value
Anisotropy	Crystalline solid	Different values

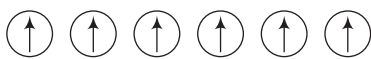
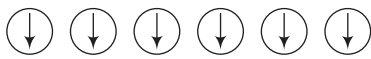


Q. 3 Which of the following is an amorphous solid?

- (a) Graphite (C)
- (b) Quartz glass (SiO_2)
- (c) Chrome alum
- (d) Silicon carbide (SiC)

Ans. (b) Quartz glass (SiO_2) is an amorphous solid due to its short range order of constituent particles.

Note Quartz is a crystalline solid while quartz glass is an amorphous solid.

Q. 4 Which of the following arrangements shows schematic alignment of magnetic moments of antiferromagnetic substances?

- (a) 
- (b) 
- (c) 
- (d) 

Ans. (d) The substances which have domain structure are oppositely oriented and cancel each other's magnetic field are known as antiferromagnetic substances.



**Schematic arrangement of
antiferromagnetic substance**

Q. 5 Which of the following is true about the value of refractive index of quartz glass?

- (a) Same in all directions (b) Different in different directions
(c) Cannot be measured (d) Always zero

Ans. (a) Since, quartz glass is an amorphous solid having short range order of constituents. Hence, value of refractive index is same in all directions, can be measured and not be equal to zero always.

Q. 6 Which of the following statement is not true about amorphous solids?

- (a) On heating they may become crystalline at certain temperature
(b) They may become crystalline on keeping for long time
(c) Amorphous solids can be moulded by heating
(d) They are anisotropic in nature

Ans. (d) Amorphous solids are isotropic in nature because it has no long range order and any physical property will be same on all direction. On the other hand, anisotropic nature is a characteristic feature of crystalline solid.

Q. 7 The sharp melting point of crystalline solids is due to

- (a) a regular arrangement of constituent particles observed over a short distance in the crystal lattice
(b) a regular arrangement of constituent particles observed over a long distance in the crystal lattice
(c) same arrangement of constituent particles in different directions
(d) different arrangement of constituent particles in different directions

Ans. (b) Crystalline solid has regular arrangement of constituent particles observed over a long distance in the crystal lattice. Due to this regular arrangement crystalline solid have sharp melting point.

Q. 8 Iodine molecules are held in the crystals lattice by

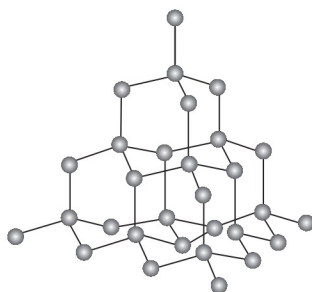
- (a) London forces
- (b) dipole-dipole interactions
- (c) covalent bonds
- (d) coulombic forces

Ans. (a) Iodine molecules are a class of non-polar molecular solid in which constituents molecules are held together by London or dispersion forces. These solids are soft and non-conductor of electricity.

Q. 9 Which of the following is a network solid?

- (a) SO_2 (solid)
- (b) I_2
- (c) Diamond
- (d) H_2O (ice)

Ans. (c) Diamond is a giant molecule in which constituent atoms are held together by covalent bond. Hence, this is a network solid.



Network structure of atom

Q. 10 Which of the following solids is not an electrical conductor?

- | | | | |
|-------------------|---------------------|----------------------------|-----------------------------|
| 1. Mg(s) | 2. TiO (s) | 3. $\text{I}_2 (\text{s})$ | 4. $\text{H}_2\text{O (s)}$ |
| (a) Only 1 | (b) Only 2 | (c) 3 and 4 | (d) 2, 3 and 4 |

Ans. (c) Iodine is a non-polar molecular solid in which iodine molecules are held together by London force or dispersion force. This is soft and non-conductor of electricity. Water is a hydrogen bonded molecular solid in which H and O are held together by polar covalent bond and each water molecule held together by hydrogen bonding. Due to non-ionic nature, they are not electrical conductor.

Q. 11 Which of the following is not the characteristic of ionic solids?

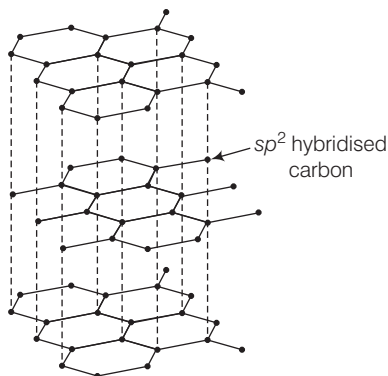
- (a) Very low value of electrical conductivity in the molten state
- (b) Brittle nature
- (c) Very strong forces of interactions
- (d) Anisotropic nature

Ans. (a) Ionic solids easily dissociated into its ions in molten state and show high electrical conductivity. So, statement (a) is incorrect while ionic solids are anisotropic and brittle linked with very strong force of interactions.

Q. 12 Graphite is a good conductor of electricity due to the presence of

- (a) lone pair of electrons
- (b) free valence electrons
- (c) cations
- (d) anions

Ans. (b) Graphite is a good conductor of electricity due to presence of free valence electrons. In graphite, each carbon is sp^2 hybridised having one free electron which makes graphite a good conductor of electricity.



Q. 13 Which of the following oxides behaves as conductor or insulator depending upon temperature?

- (a) TiO (b) SiO_2 (c) TiO_3 (d) MgO

Ans. (c) Certain metal oxides like VO_2 , VO , VO_3 and TiO_3 show metallic or insulating property depending upon temperature. As temperature varies metallic or insulating property varies. This is due to variation in energy gap between conduction band and valence band.

Q. 14 Which of the following oxides shows electrical properties like metals?

- (a) SiO_2 (b) MgO (c) $SO_2(s)$ (d) CrO_2

Ans. (d) CrO_2 , TiO and ReO_3 are some typical metal oxides which show electrical conductivity similar to metal. While SiO_2 , MgO and SO_2 are oxides of metal, semimetal and non-metal which do not show electrical properties.

Q. 15 The lattice site in a pure crystal cannot be occupied by

- (a) molecule (b) ion (c) electron (d) atom

Ans. (c) Each point in a lattice is known as lattice point which are either atom or molecule or ion which are joined together by a straight line to bring out geometry of lattice in pure crystal constituents are arranged in fixed stoichiometric ratio.

Hence, existence of free electrons are not possible, it is possible on in case of imperfection in solid.

Q. 16 Graphite cannot be classified as

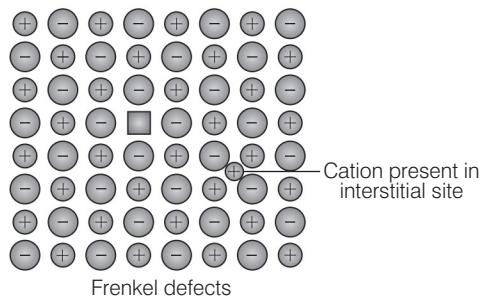
- (a) conducting solid (b) network solid
(c) covalent solid (d) ionic solid

Ans. (d) Graphite can't be classified as ionic solid as graphite is not made up of ions. It is made up of carbon atoms covalently bonded to three carbon atoms so, it is a covalent solid. Since, the formation of covalent bond occurs throughout the crystal therefore, it is a type of network solid. Due to presence of free electron graphite is also classified as conductor solid.

Q. 17 Cations are present in the interstitial sites in

- (a) Frenkel defect
- (b) Schottky defect
- (c) vacancy defect
- (d) metal deficiency defect

Ans. (a) When smaller ion (usually cation) is dislocated from its normal site in crystal and move to interstitial site is known as Frenkel defect as shown below



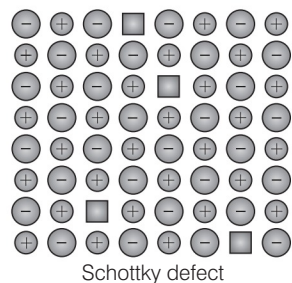
Q. 18 Schottky defect is observed in crystals when

- (a) some cations move from their lattice site to interstitial sites
- (b) equal number of cations and anions are missing from the lattice
- (c) some lattice sites are occupied by electrons
- (d) some impurity is present in the lattice

Ans. (b) Schottky defect is observed in crystal when equal number of cations and anions are missing from the lattice. Thus, density of solid decreases.

When some cations move from their lattice site to interstitial site is known as Frenkel defect. When some impurity is present on crystal is known as impurity defect.

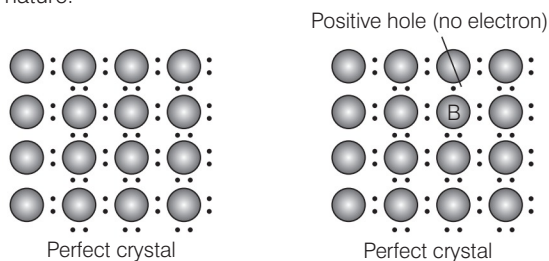
When lattice site is occupied by electron, this type of defect is known as metal excess defect. Hence, except (b) all statements are incorrect regarding Schottky defect.



Q. 19 Which of the following is true about the charge acquired by p - type semiconductors?

- (a) Positive
- (b) Neutral
- (c) Negative
- (d) Depends on concentration of *p* impurity

Ans. (b) When group 13 elements are doped in group 14 element, it creates a hole in a molecule but the molecule as a whole remain neutral. Thus, *p* -type semiconductor is neutral in nature.

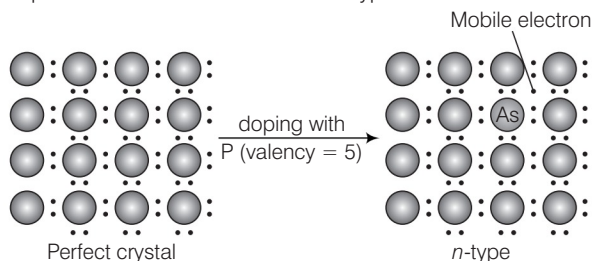


Q. 20 To get a *n*-type semiconductor from silicon, it should be doped with a substance with valency

- (a) 2 (b) 1 (c) 3 (d) 5

Ans. (d) To get a *n*-type semiconductor from silicon, it should be doped with a substance with valence 5.

e.g., Si doped with P lead to formation of *n*-type semiconductor as shown below



Q. 21 The total number of tetrahedral voids in the face centred unit cell is

- (a) 6 (b) 8 (c) 10 (d) 12

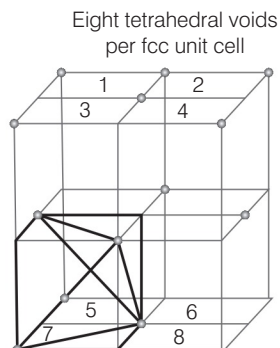
💡 Thinking Process

If number of atoms in fcc unit cell = N

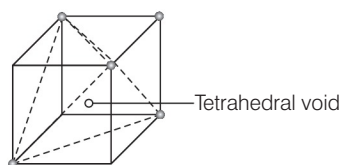
Number of tetrahedral voids = $2N$

Number of octahedral voids = N

Ans. (b) Fcc unit cell contains 8 tetrahedral voids at centre of each 8 smaller cube of an unit cell as shown below



Each cube represented by numeric 1, 2, 3, 4, 5, 6, 7, 8 contain one tetrahedral voids.



Each cube contain one tetrahedral void at its body centre as shown above

Number of atoms in fcc unit cell = 4

Number of octahedral voids = 4

Number of tetrahedral voids = 8

Q. 22 Which of the following point defects are shown by AgBr(s) crystals?

1. Schottky defect
2. Frenkel defect
3. Metal excess defect
4. Metal deficiency defect

(a) 1 and 2 (b) 3 and 4 (c) 1 and 3 (d) 2 and 4

Ans. (a) AgBr shows both Schottky as well as Frenkel defect. In AgBr, both Ag^+ and Br^- ions are absent from the lattice causing Schottky defect. However, Ag^+ ions are mobile so they have a tendency to move aside the lattice and trapped in interstitial site hence, cause Frenkel defect.

Q. 23 In which pair most efficient packing is present?

- (a) hcp and bcc (b) hcp and ccp
(c) bcc and ccp (d) bcc and simple cubic cell

Ans. (b) Packing efficiency is the percentage of total filled space by particles and it can be calculated as packing efficiency

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

Since, packing efficiency for hcp or ccp is calculated to be 74% which is maximum among all type of crystals.

Q. 24 The percentage of empty space in a body centred cubic arrangement is

.....

- (a) 74 (b) 68 (c) 32 (d) 26

Ans. (c) Packing efficiency for bcc arrangement is 68% which represents total filled space in the unit cell. Hence, empty space in a body centred arrangement is $100 - 68 = 32\%$.

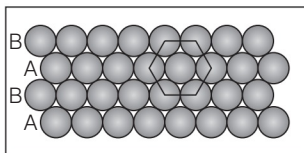
Note Here, empty space in bcc arrangement is asked therefore empty space in any crystal packing can be calculated as empty space in unit cell $= 100 - \text{packing efficiency}$

Q. 25 Which of the following statement is not true about the hexagonal close packing?

- (a) The coordination number is 12
(b) It has 74% packing efficiency
(c) Tetrahedral voids of the second layer are covered by the spheres of the third layer
(d) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer

Ans. (d) Hexagonal close packing can be arranged by two layers

A and B one over another which can be diagrammatically represented as



Here, we can see easily that 1st layer and 4th layer are not exactly aligned.

Thus, statement (d) is not correct while other statements (a), (b) and (c) are true.

Q. 26 In which of the following structures coordination number for cations and anions in the packed structure will be same?

- (a) Cl^- ions form fcc lattice and Na^+ ions occupy all octahedral voids of the unit cell
- (b) Ca^{2+} ions form fcc lattice and F^- ions occupy all the eight tetrahedral voids of the unit cell
- (c) O^{2-} ions form fcc lattice and Na^+ ions occupy all the eight tetrahedral voids of the unit cell
- (d) S^{2-} ions form fcc lattice and Zn^{2+} ions go into alternate tetrahedral voids of the unit cell

Ans. (a) NaCl crystal have rock salt structure having fcc lattice in which Cl^- ions are present at fcc lattice points and face centre and Na^+ occupies all the octahedral void of given unit cell.

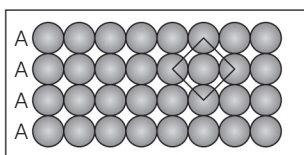
Where, coordination number of $\text{Na}^+ = 6$

coordination number of $\text{Cl}^- = 6$

Q. 27 What is the coordination number in a square close packed structure in two dimensions?

- (a) 2
- (b) 3
- (c) 4
- (d) 6

Ans. (c) Coordination number in a square closed packed structure in two dimensions is equal to 4 as shown below



Cubic closed structure

Q. 28 Which kind of defects are introduced by doping?

- (a) Dislocation defect
- (b) Schottky defect
- (c) Frenkel defect
- (d) Electronic defect

Ans. (d) When electron rich or electron deficient impurity is added to a perfect crystal it introduces electronic defect in them.

Q. 29 Silicon doped with electron rich impurity forms

- (a) *p*-type semiconductor
- (b) *n*-type semiconductor
- (c) intrinsic semiconductor
- (d) insulator

Ans. (b) Silicon doped with electron rich impurity such as phosphorus forms a *n*-type semiconductor. This is due to presence of mobile electron.

Q. 30 Which of the following statements is not true?

- (a) Paramagnetic substances are weakly attracted by magnetic field
- (b) Ferromagnetic substances cannot be magnetised permanently
- (c) The domains in antiferromagnetic substances are oppositely oriented with respect to each other
- (d) Pairing of electrons cancels their magnetic moment in the diamagnetic substances

Ans. (b) Ferromagnetic substances can be magnetised by applying magnetic field to it and magnetic property persist within it even after removal of magnetic field.
Hence, choice (b) is the correct answer while other three choices are correct.

Q. 31 Which of the following is not true about the ionic solids?

- (a) Bigger ions form the close packed structure
- (b) Smaller ions occupy either the tetrahedral or the octahedral voids depending upon their size
- (c) Occupation of all the voids is not necessary
- (d) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions occupying the voids

Ans. (d) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions present at the lattice points. As we know the radii of octahedral or tetrahedral void is related to radii of atoms (r) as

$$\text{Radius of octahedral void } (R_o) = 0.414 r$$

$$\text{Radius of tetrahedral void } (R_t) = 0.225 r$$

Where, r = radius of bigger atom involved.

Q. 32 A ferromagnetic substance becomes a permanent magnet when it is placed in a magnetic field because

- (a) all the domains get oriented in the direction of magnetic field
- (b) all the domains get oriented in the direction opposite to the direction of magnetic field
- (c) domains get oriented randomly
- (d) domains are not affected by magnetic field

Ans. (a) When a ferromagnetic substance is placed in a magnetic field it becomes a permanent magnet because all the domains get oriented in the direction of magnetic field even after removal of applied magnetic field.

Q. 33 The correct order of the packing efficiency in different types of unit cells is

- (a) fcc < bcc < simple cubic
- (b) fcc > bcc > simple cubic
- (c) fcc < bcc > simple cubic
- (d) bcc < fcc > simple cubic

Ans. (b) Packing efficiency in different types of unit cells can be tabulated as

Unit cell	Packing efficiency
fcc	74%
bcc	68%
Simple cubic	52%

Hence, correct order is fcc (74%) > bcc (68%) > simple cubic (52%).

Q. 34 Which of the following defects is also known as dislocation defect?

- (a) Frenkel defect
- (b) Schottky defect
- (c) Non-stoichiometric defect
- (d) Simple interstitial defect

Ans. (a) Frenkel defect is also known as dislocation defect because in Frenkel defect atoms present in crystal lattice is dislocated to interstitial site.

Q. 35 In the cubic close packing, the unit cell has

- (a) 4 tetrahedral voids each of which is shared by four adjacent unit cells
- (b) 4 tetrahedral voids within the unit cell
- (c) 8 tetrahedral voids each of which is shared by four adjacent unit cells
- (d) 8 tetrahedral voids within the unit cells

Ans. (d) In the cubic close packing the unit cell has 8 tetrahedral voids within it and are located at each eight smaller cube of an unit cell.

Q. 36 The edge lengths of the unit cells in terms of the radius of spheres constituting fcc, bcc and simple cubic unit cells are respectively

- (a) $2\sqrt{2}r, \frac{4r}{\sqrt{3}}, 2r$
- (b) $\frac{4r}{\sqrt{3}}, 2\sqrt{2}r, 2r$
- (c) $2r, 2\sqrt{2}r, \frac{4r}{\sqrt{3}}$
- (d) $2r, \frac{4r}{\sqrt{3}}, 2\sqrt{2}r$

Ans. (a) Edge length for different types of unit cells can be tabulated as

Types of unit cell	Edge length
fcc	$2\sqrt{2}r$
bcc	$\frac{4}{\sqrt{3}}r$
scc	$2r$

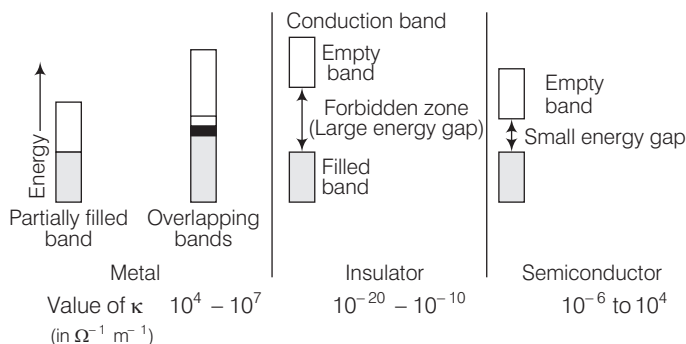
Q. 37 Which of the following represents correct order of conductivity in solids?

- (a) $\kappa_{\text{metals}} \gg \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
- (b) $\kappa_{\text{metals}} \ll \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
- (c) $\kappa_{\text{metals}} \cdot \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} = \text{zero}$
- (d) $\kappa_{\text{metals}} < \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} \neq \text{zero}$

Thinking Process

Look at the option and choose the correct answer using the concept that metal have maximum value of κ and insulator has minimum value.

Ans. (a) Conductivity of metal, insulator and semiconductors can be represented in the term of κ (Kappa) which depends upon energy gap between valence band and conduction band.



Hence, correct order is

$$\kappa_{\text{metals}} \gg \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$$

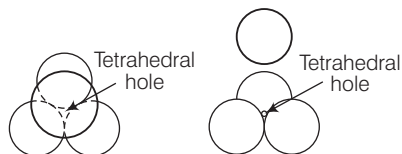
Multiple Choice Questions (More Than One Options)

Q. 38 Which of the following is not true about the voids formed in 3 dimensional hexagonal close packed structure?

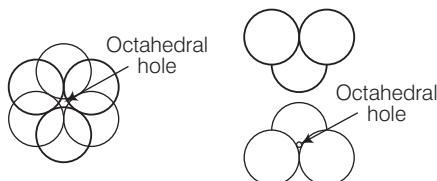
- (a) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer
- (b) All the triangular voids are not covered by the spheres of the second layer
- (c) Tetrahedral voids are formed when the triangular voids in the second layer lie above the triangular voids in the first layer and the triangular shapes of these voids do not overlap
- (d) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer

Ans. (c, d)

Tetrahedral voids are formed when the triangular void in the second layer lie exactly above the triangular voids in the first layer and the triangular shape of these voids oppositely overlap.



Octahedral voids are formed when triangular void of second layer is not exactly overlap with similar void in first layer.



Q. 39 The value of magnetic moment is zero in the case of antiferromagnetic substances because the domains

- (a) get oriented in the direction of the applied magnetic field
- (b) get oriented opposite to the direction of the applied magnetic field
- (c) are oppositely oriented with respect to each other without the application of magnetic field
- (d) cancel out each other's magnetic moment

Ans. (c, d)

In the case of antiferromagnetic substances, the magnetic moment becomes zero because the domains are oppositely oriented with respect to each other without the application of magnetic field which cancel out each other.

Q. 40 Which of the following statements are not true?

- (a) Vacancy defect results in a decrease in the density of the substance
- (b) Interstitial defects results in an increase in the density of the substance
- (c) Impurity defect has no effect on the density of the substance
- (d) Frenkel defect results in an increase in the density of the substance

Ans. (c, d)

Statements (c) and (d) can be correctly written as (c) Impurity defect changes the density of substance as impurity has different density than the ion present on perfect crystal. e.g., When SrCl_2 is added to the NaCl crystal it causes impurity defect.

(d) Frenkel defect results neither decrease nor increase in density of substance.

Q. 41 Which of the following statements are true about metals?

- (a) Valence band overlaps with conduction band
- (b) The gap between valence band and conduction band is negligible
- (c) The gap between valence band and conduction band cannot be determined
- (d) Valence band may remain partially filled

Ans. (a, b, d)

Option (a), (b) and (d) are true, option (c) can be correctly stated as the gap between valence band and conduction band can be determined. The gap between valence band and conduction band decide the conductivity of material.

Q. 42 Under the influence of electric field, which of the following statement is true about the movement of electrons and holes in a p-type semiconductor?

- (a) Electron will move towards the positively charged plate through electron holes
- (b) Holes will appear to be moving towards the negatively charged plate
- (c) Both electrons and holes appear to move towards the positively charged plate
- (d) Movement of electrons is not related to the movement of holes

Ans. (a, b)

In p-type semiconductor, the conductivity is due to existence of hole. When electric field is applied to p-type semiconductor hole starts moving towards negatively charged plate and electron towards positively charged plate.

Q. 43 Which of the following statements are true about semiconductors?

- (a) Silicon doped with electron rich impurity is a p-type semiconductor
- (b) Silicon doped with an electron rich impurity is an n-type semiconductor
- (c) Delocalised electrons increase the conductivity of doped silicon
- (d) An electron vacancy increases the conductivity of n-type semiconductor

Ans. (b, c)

Silicon doped with an electron rich impurity is an n-type semiconductor. Conductivity of n-type semiconductor is due to presence of free electron delocalisation of electrons increases the conductivity of doped silicon due to increase in mobility of electron.

Q. 44 An excess of potassium ions makes KCl crystals appear violet or lilac in colour since

- (a) some of the anionic sites are occupied by an unpaired electron
- (b) some of the anionic sites are occupied by a pair of electrons
- (c) there are vacancies at some anionic sites
- (d) F-centres are created which impart colour to the crystals

Ans. (a, d)

When KCl crystals are heated it leads the disposition of potassium ion on surface of KCl. The Cl^- ions diffuse to the surface of crystal and loss electron by potassium atom to form K^+ ion released electron occupies anionic site which is known as F-centre and impart colour to the crystal.

Q. 45 The number of tetrahedral voids per unit cell in NaCl crystal is

- (a) 4
- (b) 8
- (c) twice the number of octahedral voids
- (d) four times the number of octahedral voids

Ans. (b, c)

NaCl has a rock salt type structure having fcc arrangement.

Total number of atoms per unit cell = 4

∴ Number of tetrahedral voids = $2 \times 4 = 8$

Number of octahedral voids = 4

Hence, (b) and (c) are correct choices.

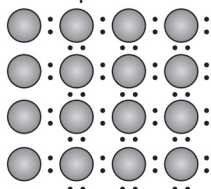
Q. 46 Amorphous solids can also be called

- (a) pseudo solids
- (b) true solids
- (c) super cooled liquids
- (d) super cooled solids

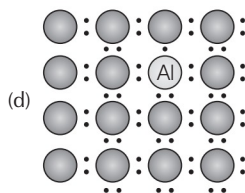
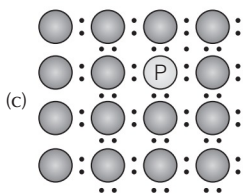
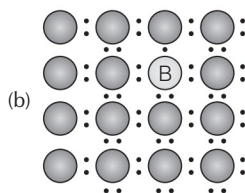
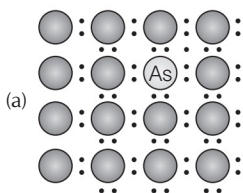
Ans. (a, c)

Amorphous solid has short range order which has a tendency to flow very slowly. Hence, it is also known as pseudo solids or super cooled liquids. Glass panes fixed to windows or doors of old buildings are invariably observed to be thicker at bottom than at the top. These are examples of amorphous solids.

Q. 47 A perfect crystal of silicon (fig) is doped with some elements as given in the options. Which of these options shows n-type semiconductors?



Pure crystal



Ans. (a, c)

n-type semiconductor When group 15 elements are doped into a perfect crystal it leads to formation of n-type semiconductor.

Here, in (a) as (group 15, period 3) is doped to perfect Si-crystal and in (c) as (group 15, period 2) is doped to perfect Si-crystal.

Q. 48 Which of the following statements are correct?

- (a) Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic
- (b) Ferrimagnetic substances do not lose ferrimagnetism on heating and remain ferrimagnetic
- (c) Antiferromagnetic substances have domain structures similar to ferromagnetic substances and their magnetic moments are not cancelled by each other
- (d) In ferromagnetic substances, all the domains get oriented in the direction of magnetic field and remain as such even after removing magnetic field

Ans. (a, d)

Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic. In ferrimagnetic substance domains are aligned in parallel and antiparallel direction in unequal numbers.

In ferromagnetic substances, all the domains get oriented in the direction of magnetic field and remain as such even after removing magnetic field.

Hence, (a) and (d) are correct choices.

Q. 49 Which of the following features are not shown by quartz glass?

- (a) This is a crystalline solid
- (b) Refractive index is same in all the directions
- (c) This has definite heat of fusion
- (d) This is also called super cooled liquid

Ans. (a, c)

Quartz glass is an amorphous solid so it has not definite heat of fusion. This is due to short range order of molecule while quartz glass is also known as super cooled liquid and isotropic in nature.

Q. 50 Which of the following cannot be regarded as molecular solid?

- (a) SiC (silicon carbide)
- (b) AlN
- (c) Diamond
- (d) I₂

Ans. (a, b, c)

SiC, AlN and diamond are examples of network solid as they have three dimensional structure while, I₂ is a molecular solid, because such solid particles are held together by dipole-dipole interactions.

Q. 51 In which of the following arrangements octahedral voids are formed?

- (a) hcp
- (b) bcc
- (c) simple cubic
- (d) fcc

Ans. (a, d)

In hcp and fcc arrangement octahedral voids are formed. In fcc the octahedral voids are observed at edge and centre of cube while in bcc and simple cubic, no any octahedral voids are observed.

Q. 52 Frenkel defect is also known as

- (a) stoichiometric defect
- (b) dislocation defect
- (c) impurity defect
- (d) non-stoichiometric defect

Ans. (a, b)

Frenkel defect arises when the smaller ion (usually cation) is dislocated from its original site to interstitial site, this is also known as dislocation defect. Since, stoichiometry of substance persists so, it is categorised as stoichiometric defect.

Q. 53 Which of the following defects decrease the density?

- (a) Interstitial defect
- (b) Vacancy defect
- (c) Frenkel defect
- (d) Schottky defect

Ans. (b, d)

Vacancy and Schottky defects which lead to decrease the density both are the types of a stoichiometric defect. In case of Frenkel defect and interstitial defect, there is no change in density of substance.

Short Answer Type Questions

Q. 54 Why are liquids and gases categorised as fluids?

Ans. Liquids and gases have the tendency to flow, *i.e.*, their molecules can move freely from one place to another. Therefore, they are known as fluids. *e.g.*, glass panes fixed to windows or doors of old buildings are sometimes found to be thicker at bottom. This is due to ability of glass to flow.

Q. 55 Why are solids incompressible?

Ans. The distance between the constituent particles is very less in solids. On bringing them still closer repulsion will start between electron clouds of these particles. Hence, they cannot be brought further close together and are incompressible.

Q. 56 In spite of long range order in the arrangement of particles why are the crystals usually not perfect?

Ans. Crystals have long range repeated pattern of arrangement of constituent particles but in the process of crystallisation some deviations from the ideal arrangement (*i.e.*, defects) may be introduced, therefore, crystals are usually not perfect.

Q. 57 Why does table salt, NaCl sometimes appear yellow in colour?

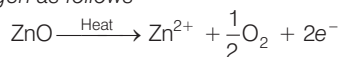
Ans. Yellow colour in NaCl is due to metal excess defect due to which unpaired electrons occupy anionic sites, known as F-centres. These electrons absorb energy from the visible region for the excitation which makes crystal appear yellow.

Q. 58 Why is FeO(s) not formed in stoichiometric composition?

Ans. In the crystals of FeO, some of the Fe^{2+} cations are replaced by Fe^{3+} ions. Three Fe^{2+} ions are replaced by two Fe^{3+} ions to make up the loss of positive charge. Eventually there would be less amount of metal as compared to stoichiometric composition.

Q. 59 Why does white ZnO (s) become yellow upon heating?

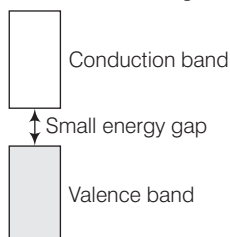
Ans. On heating ZnO loses oxygen as follows



Zn^{2+} ions and electrons move to interstitial sites and F-centres are formed which impart yellow colour to ZnO(s).

Q. 60 Why does the electrical conductivity of semiconductors increase with rise in temperature?

Ans. The gap between conduction band and valence band is small in semiconductors. Therefore, electrons from the valence band can jump to the conduction band on increasing temperature. Thus, they become more conducting as the temperature increases.



Q. 61 Explain why does conductivity of germanium crystals increase on doping with gallium?

Ans. On doping germanium with gallium some of the positions of lattice of germanium are occupied by gallium. Gallium atom has only three valence electrons. Therefore, fourth valency of nearby germanium atom is not satisfied and the place remains vacant.

This place is deficient of electrons and is therefore called electron hole or electron vacancy. Electron from neighbouring atom comes and fills the hole, thereby creating a hole in its original position.

Under the influence of electric field electrons move towards positively charged plates through these and conduct electricity. The holes appear to move towards negatively charged plates.

Q. 62 In a compound, nitrogen atoms (N) make cubic close packed lattice and metal atoms (M) occupy one-third of the tetrahedral voids present. Determine the formula of the compound formed by M and N?

Ans. Let the number of N atoms in ccp is x

$$\therefore \text{Number of tetrahedral voids} = 2x$$

$$\therefore \text{Number of } M \text{ atoms} = \frac{1}{3} \times 2x$$

$$\frac{\text{Number of N atoms}}{\text{Number of } M \text{ atoms}} = \frac{3x}{2x} = \frac{3}{2}$$

So, the formula of the compound is M_2N_3 .

Q. 63 Under which situations can an amorphous substance change to crystalline form?

Ans. On heating, amorphous substances change to crystalline form at some temperature some objects from ancient civilisation are found to be milky in appearance. This is due to crystallisation.

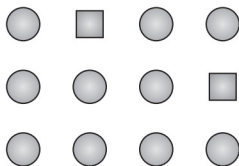
Matching The Columns

Q. 64 Match the defects given in Column I with the statements in given Column II.

	Column I	Column II
A.	Simple vacancy defect	1. Shown by non-ionic solids and increases density of the solid
B.	Simple interstitial defect	2. Shown by ionic solids and decreases density of the solid
C.	Frenkel defect	3. Shown by non-ionic solids and density of the solid decreases
D.	Schottky defect	4. Shown by ionic solids and density of the solid remains the same

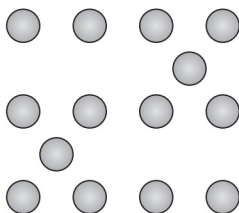
Ans. A. → (3) B. → (1) C. → (4) D. → (2)

A. When some of lattice sites are vacant in any non-ionic solid, the crystal is said to have vacancy defect and due to decrease in number of particles present in crystal lattice the density of crystal decreases.



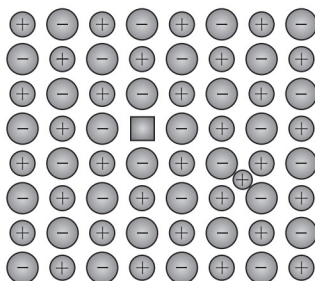
Vacancy defects

B. Simple interstitial defect are shown by non-ionic solids in which constituent particles is displaced from its normal site to an interstitial site. Hence, density of solid increases.



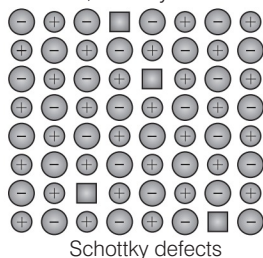
Interstitial defects

C. Frenkel defect is shown by ionic solids in which smaller ions get dislocated from its normal site to its interstitial site which lead to decrease its density.



Frenkel defects

- D. Schottky defect is shown by ionic solids in which equal number of cation and anion get missed from ionic solids and thus, density of solid decreases.



Q. 65 Match the type of unit cell given in Column I with the features given in Column II.

Column I	Column II
A. Primitive cubic unit cell	1. Each of the three perpendicular edges compulsorily have the different edge length <i>i.e.</i> , $a \neq b \neq c$
B. Body centred cubic unit cell	2. Number of atoms per unit cell is one
C. Face centred cubic unit cell	3. Each of the three perpendicular edges compulsorily have the same edge length <i>i.e.</i> , $a = b = c$
D. End centred orthorhombic unit cell	4. In addition to the contribution from the corner atoms the number of atoms present in a unit cell is one
	5. In addition to the contribution from the corner atoms the number of atoms present in a unit cell is three

Ans. A. $\rightarrow (2, 3)$ B. $\rightarrow (3, 4)$ C. $\rightarrow (3, 5)$ D. $\rightarrow (1, 4)$

A. For primitive unit cell, $a = b = c$

Total number of atoms per unit cell = $1/8 \times 8 = 1$

Here, $1/8$ is due to contribution of each atom present at corner.

B. For body centred cubic unit cell, $a = b = c$

This lattice contain atoms at corner as well as body centre. Contribution due to atoms at corner = $1/8 \times 8 = 1$ contribution due to atoms at body centre = 1

C. For face centred unit cell, $a = b = c$

Total constituent ions per unit cell present at corners = $\frac{1}{8} \times 8 = 1$

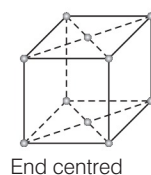
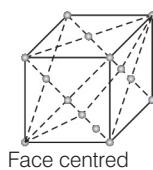
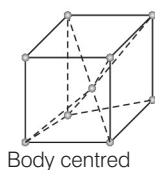
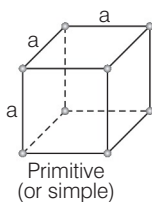
Total constituent ions per unit cell present at face centre = $\frac{1}{2} \times 6 = 3$

D. For end centered orthorhombic unit cell, $a \neq b \neq c$

Total contribution of atoms present at corner = $\frac{1}{8} \times 8 = 1$

Total contribution of atoms present at end centre = $\frac{1}{2} \times 2 = 1$

Hence, other than corner it contain total one atom per unit cell.



Q. 66 Match the types of defect given in Column I with the statement given in Column II.

Column I	Column II
A. Impurity defect	1. NaCl with anionic sites called F-centres
B. Metal excess defect	2. FeO with Fe^{3+}
C. Metal deficiency defect	3. NaCl with Sr^{2+} and some cationic sites vacant

Ans. A. \rightarrow (3) B. \rightarrow (1) C. \rightarrow (2)

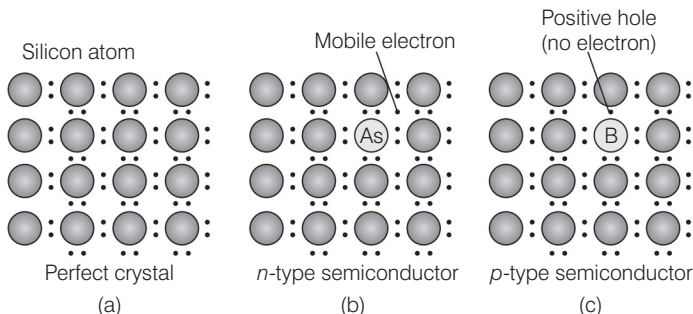
- A. Impurity defect arises due to replacement of one common ion present in any crystal by another uncommon ion.
- B. Metal excess defect is due to missing of cation from ideal ionic solid which lead to create a F-centre generally occupied by unpaired electrons. e.g., NaCl with anionic site.
- C. Metal deficiency defect In FeO, Fe^{3+} exists along with Fe^{2+} which lead to decrease in metal ion(s) so this is a type of metal deficiency defect.

Q. 67 Match the items given in Column I with the items given in Column II.

Column I	Column II
A. Mg in solid state	1. p -type semiconductor
B. MgCl_2 in molten state	2. n -type semiconductor
C. Silicon with phosphorus	3. Electrolytic conductors
D. Germanium with boron	4. Electronic conductors

Ans. A. \rightarrow (4) B. \rightarrow (3) C. \rightarrow (2) D. \rightarrow (1)

- A. Mg in solid state show electronic conductivity due to presence of free electrons hence, they are known as electronic conductors.
- B. MgCl_2 in molten state show electrolytic conductivity due to presence of electrolytes in molten state.
- C. Silicon doped with phosphorus contain one extra electron due to which it shows conductivity under the influence of electric field and known as p -type semiconductor.
- D. Germanium doped with boron contain one hole due to which it shows conductivity under the influence of electric field and known as n -type semiconductor.

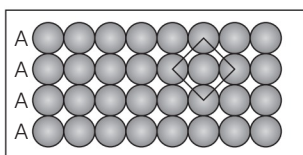


Q. 68 Match the type of packing given in Column I with the items given in Column II.

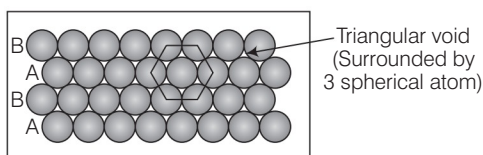
Column I	Column II
A. Square close packing in two dimensions	1. Triangular voids
B. Hexagonal close packing in two dimensions	2. Pattern of spheres is repeated in every fourth layer
C. Hexagonal close packing in three dimensions	3. Coordination number = 4
D. Cubic close packing in three dimensions	4. Pattern of sphere is repeated in alternate layers

Ans. A. → (3) B. → (1) C. → (4) D. → (2)

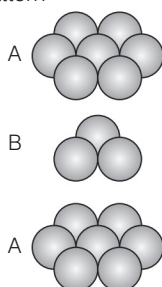
A. Square close packing in two dimensions each sphere have coordination number 4, as shown below



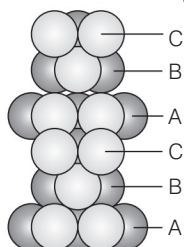
B. Hexagonal close packing in two dimensions each sphere have coordination number 6 as shown below and creates a triangular void



C. Hexagonal close packing in 3 dimensions is a repeated pattern of sphere in alternate layers also known as *ABAB* pattern



D. Cubic close packing in a 3 dimensions is a repeating pattern of sphere in every fourth layer



Assertion and Reason

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.
- (b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
- (c) Assertion is correct statement but Reason is wrong statement.
- (d) Assertion is wrong statement but Reason is correct statement.

Q. 69 Assertion (A) The total number of atoms present in a simple cubic unit cell is one.

Reason (R) Simple cubic unit cell has atoms at its corners, each of which is shared between eight adjacent unit cells.

Ans. (a) In simple cubic unit cell each atom is present at corners having contribution $1/8$.

Hence, total number of atoms present per unit cell in scc is $\frac{1}{8} \times 8 = 1$.

Q. 70 Assertion (A) Graphite is a good conductor of electricity however diamond belongs to the category of insulators.

Reason (R) Graphite is soft in nature on the other hand diamond is very hard and brittle.

Ans. (b) Assertion and Reason both are correct but Reason is not correct explanation of Assertion.

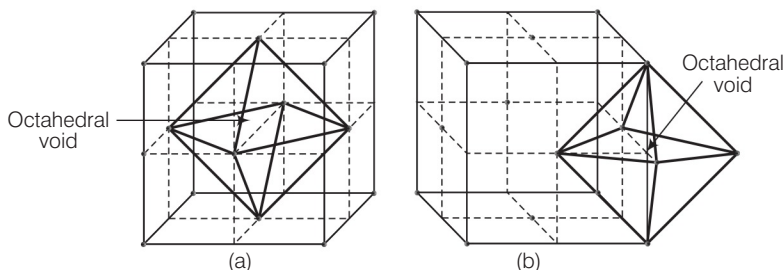
Correct explanation is that graphite have layered structure with free electrons due to which it is a good conductor of electricity. On the other hand, diamond have tetrahedral arrangement with no unpaired electron. Therefore, diamond is hard and brittle but insulator.

Q. 71 Assertion (A) Total number of octahedral voids present in unit cell of cubic close packing including the one that is present at the body centre, is four.

Reason (R) Besides the body centre there is one octahedral void present at the centre of each of the six faces of the unit cell and each of which is shared between two adjacent unit cells.

Ans. (c) Assertion is correct statement but Reason is incorrect statement.

Assertion is true as in ccp atom present at face centre and corner of each unit cell which creates octahedral void at each body centre and all twelve edges of a unit cell as shown below



Correct reason is that beside the body centre there is one octahedral void at centre of each of 12 edges which is surrounded by six atoms.

Out of six atoms four belongs to same unit cell (2 at corner and 2 at face centre) and 2 atoms belongs to adjacent unit cell.

Q. 72 Assertion (A) The packing efficiency is maximum for the fcc structure.

Reason (R) The coordination number is 12 in fcc structures.

Ans. (b) Assertion and Reason both are correct statements but reason is not the correct explanation of Assertion.

Correct reason is that, packing efficiency is maximum for fcc structure because it consists of total four atoms per unit cell. Packing efficiency is maximum in fcc structure which is equal to 74%.

Q. 73 Assertion (A) Semiconductors are solids with conductivities in the intermediate range from $10^{-6} - 10^4 \text{ ohm}^{-1} \text{ m}^{-1}$.

Reason (R) Intermediate conductivity in semiconductor is due to partially filled valence band.

Ans. (c) Assertion is correct statement but reason is incorrect statement.

Semiconductors are solids with conductivities in the intermediate range varie from $10^{-6} - 10^4 \text{ } \Omega^{-1} \text{ m}^{-1}$. Intermediate conductivity is due to small energy gap between valence band and conduction band.

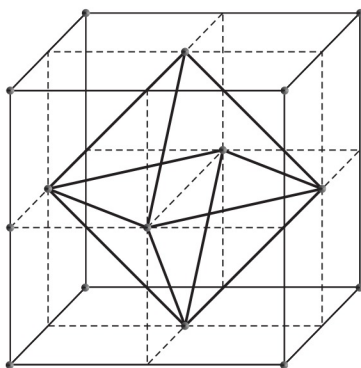
(Also, refer to Q. 60)

Long Answer Type Questions

Q. 74 With the help of a labelled diagram show that there are four octahedral voids per unit cell in a cubic close packed structure.

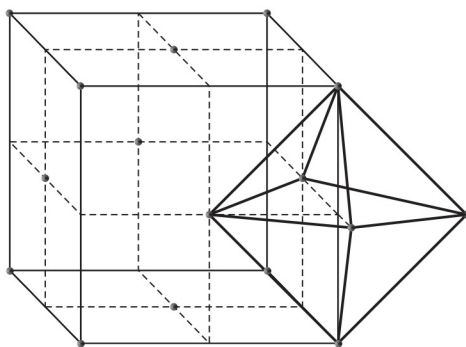
Ans. Cubic close packed structure contains one atom at each of eight corners of a unit cell and one atom at each of six faces which can be represented below

As we know any atom surrounded by six atoms (hard sphere) creates an octahedral void. In case of fcc body centre is surrounded by six identical atoms present at face centre hence, there is a octahedral void at body centre of each unit cell.



Location of octahedral voids per unit cell of ccp or fcc lattice at the body centre of the cube

Beside the body centre there is one octahedral void at centre of each of 12 edge as shown below



Octahedral void at centre of each edge

Since, each void is shared by 4 unit cell. Therefore, contribution of octahedral void to each edge of a unit cell is $\frac{1}{4}$.

Number of octahedral void at centre of 12 edge = $\frac{1}{4} \times 12 = 3$

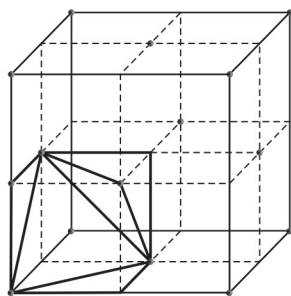
Number of octahedral void at body centre = 1

Therefore, total number of octahedral void at each ccp lattice = $3 + 1 = 4$

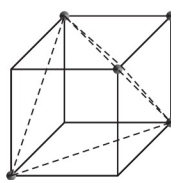
Q. 75 Show that in a cubic close packed structure, eight tetrahedral voids are present per unit cell.

Ans. Cubic close packed structure contains one atom at each corner of a unit cell and at face centre of each unit cell. Each unit cell consists of 8 small cubes.

Each small cube contains 4 atoms at its alternate corner when these atoms are joined to each other lead to creation of a tetrahedral void as shown below



(a)
Eight tetrahedral voids per unit cell of ccp structure



(b)
One tetrahedral void showing the geometry

Since, there are total 8 smaller cubes present at one unit cell and each smaller cube has one tetrahedral void hence, total number of tetrahedral void present in each unit cell is equal to eight.

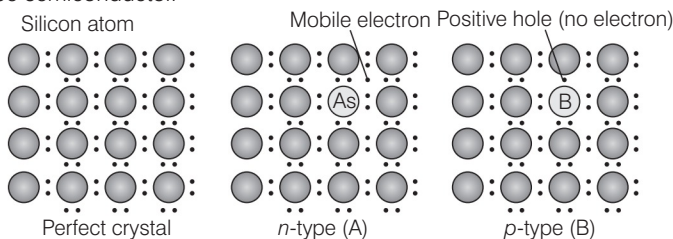
As we know ccp structure has 4 atoms per unit cell. Thus, total number of tetrahedral void in one ccp unit cell is equal to 8.

Q. 76 How does the doping increase the conductivity of semiconductors?

Ans. Conductivity of a semiconductor is too low for practical use. The conductivity of a semiconductor can be increased by adding a suitable amount of impurity to perfect crystal. This process is known as doping. It can be done by adding either of two types of impurity to the crystal.

(A) By adding **electron rich impurities** i.e., group 15 elements to the silicon and germanium of group 14 elements. Out of 4 valence electrons of group 14 elements and 5 valence electrons of group 15 elements, four electrons of each element led to formation of four covalent bonds while the one extra electron of group 15 elements become delocalised.

Thus, increases conductivity of semiconductor. This type of semiconductor is known as *n*-type semiconductor.



Creation of *n*-type and *p*-type semiconductors by doping groups 13 and 15 elements

(B) By adding **electron deficient impurity** i.e., group 14 to the perfect crystal of group 14 elements when group 13 element is doped to group 14 element it lead to create a hole in the ideal crystal which is known as electron hole or electron vacancy.

An electron from the neighbouring atom come and fill the electron hole in doing so an electron from the neighbour leaves an electron hole to its original position. Thus, it increases conductivity of semiconductor. This type of semiconductor is known as *p*-type semiconductor.

Q. 77 A sample of ferrous oxide has actual formula $\text{Fe}_{0.93}\text{O}_{1.00}$. In this sample, what fraction of metal ions are Fe^{2+} ions? What type of non-stoichiometric defect is present in this sample?

💡 Thinking Process

Consider the number of Fe^{2+} and Fe^{3+} ions as x and y then write their sum equal to 0.93. Write another equation in terms of x and y by taking the sum of their total charge equal to 2 [charge on oxygen]. Now using the substitution method. Calculate the value of x and y then calculate fraction of Fe^{2+} ion present in this sample.

Ans. Let the formula of the sample be $(\text{Fe}^{2+})_x (\text{Fe}^{3+})_y \text{O}$

On looking at the given formula of the compound

$$x + y = 0.93 \quad \dots(i)$$

Total positive charge on ferrous and ferric ions should balance the two units of negative charge on oxygen

Therefore, $2x + 3y = 2 \quad \dots(ii)$

$$\Rightarrow x + \frac{3}{2}y = 1 \quad \dots(iii)$$

On subtracting equation (i) from equation (iii) we have

$$\frac{3}{2}y - y = 1 - 0.93$$

$$\Rightarrow \frac{1}{2}y = 0.07$$

$$\Rightarrow y = 0.14$$

On putting the value of y in equation (i), we get

$$x + 0.14 = 0.93$$

$$\Rightarrow x = 0.93 - 0.14$$

$$\Rightarrow x = 0.79$$

$$\text{Fraction of } \text{Fe}^{2+} \text{ ions present in the sample} = \frac{0.79}{0.93} = 0.849$$

Metal deficiency defect is present in the sample because iron is less in amount than that required for stoichiometric composition.

2

Solutions

Multiple Choice Questions (MCQs)

Q. 1 Which of the following units is useful in relating concentration of solution with its vapour pressure?

- (a) Mole fraction
- (b) Parts per million
- (c) Mass percentage
- (d) Molality

Ans. (a) According to Henry's law partial pressure of gas in the solution is proportional to the mole fraction of gas in the solution.

$$p = K_H x$$

where, K_H = Henry's constant

Hence, (a) mole fraction is the correct choice.

Q. 2 On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid?

- (a) Sugar crystals in cold water
- (b) Sugar crystals in hot water
- (c) Powdered sugar in cold water
- (d) Powdered sugar in hot water

💡 Thinking Process

Use the concept of solubility and effect of temperature on solubility to answer this question.

Ans. (d) Dissolution of sugar in water will be most rapid when powdered sugar is dissolved in hot water because powder form can easily insert in the vacancies of liquid particles.

Further dissolution of sugar in water is an endothermic process. Hence, high temperature will favour the dissolution of sugar in water.

Q. 3 At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is

- (a) less than the rate of crystallisation
- (b) greater than the rate of crystallisation
- (c) equal to the rate of crystallisation
- (d) zero

Ans. (c) At equilibrium the rate of dissolution of solid in a volatile liquid solvent is equal to the rate of crystallisation.

Q. 4 A beaker contains a solution of substance 'A'. Precipitation of substance 'A' takes place when small amount of 'A' is added to the solution. The solution is

- (a) saturated
- (b) supersaturated
- (c) unsaturated
- (d) concentrated

💡 Thinking Process

This problem includes concept of saturated, unsaturated, supersaturated and concentrated solution.

Ans. (b) When solute is added to the solution three cases may arise

- (i) It dissolves into solution then solution is unsaturated.
- (ii) It does not dissolve in the solution then solution is known as saturated.
- (iii) When solute get precipitated solution is known as supersaturated solution.

Q. 5 Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does not depend upon

- (a) temperature
- (b) nature of solute
- (c) pressure
- (d) nature of solvent

Ans. (c) Maximum amount of solid that can be dissolved in a specified amount of a given solvent does not depend upon pressure. This is because solid and liquid are highly incompressible and practically remain unaffected by change in pressure.

Q. 6 Low concentration of oxygen in the blood and tissues of people living at high altitude is due to

- (a) low temperature
- (b) low atmospheric pressure
- (c) high atmospheric pressure
- (d) Both low temperature and high atmospheric pressure

Ans. (b) Low concentration of oxygen in the blood and tissues of people living at high altitude is due to low atmospheric pressure. Because at high altitude, the partial pressure of oxygen is less than at the ground level. This decreased atmospheric pressure causes release of oxygen from blood.

Q. 7 Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law?

- (a) Methanol and acetone
- (b) Chloroform and acetone
- (c) Nitric acid and water
- (d) Phenol and aniline

Ans. (a) In pure methanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them.

Therefore, the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules.

On the other hand, other three remaining options will show negative deviation from Raoult's law where the intermolecular attractive forces between the solute-solvent molecules are stronger than those between the solute-solute and solvent-solvent molecules.

Q. 8 Colligative properties depend on

- (a) the nature of the solute particles dissolved in solution
- (b) the number of solute particles in solution
- (c) the physical properties of the solute particles dissolved in solution
- (d) the nature of solvent particles

Ans. (b) Colligative properties depend upon number of solute particles in solution irrespective of their nature. Colligative property is used to determine the molecular mass of particle.

Q. 9 Which of the following aqueous solutions should have the highest boiling point?

- (a) 1.0 M NaOH
- (b) 1.0 M Na₂SO₄
- (c) 1.0 M NH₄NO₃
- (d) 1.0 M KNO₃

Thinking Process

This process includes concept of van't Hoff factor and boiling point. Calculate van't Hoff factor then correlate it with boiling point of solution.

Ans. (b) As we know greater the value of van't Hoff factor higher will be the elevation in boiling point and hence higher will be the boiling point of solution.

Solution	van't Hoff factor (<i>i</i>)
1.0 M NaOH	2
1.0 M Na ₂ SO ₄	3
1.0 M NH ₄ NO ₃	2
1.0 M KNO ₃	2

Hence, 1.0 M Na₂SO₄ has highest value of boiling point.

Q. 10 The unit of ebullioscopic constant is

- (a) K kg mol⁻¹ or K (molality)⁻¹
- (b) mol kg K⁻¹ or K⁻¹ (molality)
- (c) kg mol⁻¹ K⁻¹ or K⁻¹ (molality)⁻¹
- (d) K mol kg⁻¹ or K (molality)

Thinking Process

Write the formula of ebullioscopic constant then put the values of their unit and then calculate unit of ebullioscopic constant.

Ans. (a) As we know from elevation in boiling point that

$$\Delta T_b = K_b m$$

$$K_b = \frac{\Delta T_b}{m}$$

$$\text{Unit of } K_b = \frac{\text{unit of } \Delta T_b}{\text{unit of } m} = \frac{\text{K}}{\text{molality}}$$

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

Q. 11 In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M MgCl₂ solution is

- (a) the same
- (b) about twice
- (c) about three times
- (d) about six times

Thinking Process

Calculate value of van't Hoff factor then correlate it with colligative property of given solution.

Ans. (c) As we know depression in freezing point is directly related to van't Hoff factor (i) according to which greater the value of i greater will be the depression in freezing point.

Solution	i
0.01 M glucose	1
0.01 M MgCl_2	3

Hence, depression in freezing point of glucose is about 3 times of glucose.

Q.12 An unripe mango placed in a concentrated salt solution to prepare pickle shrivels because

- (a) it gains water due to osmosis
- (b) it loses water due to reverse osmosis
- (c) it gains water due to reverse osmosis
- (d) it loses water due to osmosis

Ans. (d) When an unripe mango is placed in a concentrated salt solution to prepare pickle then mango loose water due to osmosis and get shrivel.

Q. 13 At a given temperature, osmotic pressure of a concentrated solution of a substance

- (a) is higher than that of a dilute solution
- (b) is lower than that of a dilute solution
- (c) is same as that of a dilute solution
- (d) cannot be compared with osmotic pressure of dilute solution

Ans. (a) According to definition of osmotic pressure we know that $\pi = CRT$. For concentrated solution C has higher value than dilute solution.
Hence, as concentration of solution increases osmotic pressure will also increase.

Q. 14 Which of the following statements is false?

- (a) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.
- (b) The osmotic pressure of a solution is given by the equation $\pi = CRT$ (where, C is the molarity of the solution)
- (c) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is
 $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{sucrose}$
- (d) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution

Ans. (a) According to definition of depression in freezing point

$$\Delta T_f = K_f m$$

where, K_f = freezing point depression constant, value of K_f depends upon nature of solvent. This is why although the solution have same molality two different solutions of sucrose of same molality prepared in different solvents will have different depression in freezing point.

Q. 15 The values of van't Hoff factors for KCl, NaCl and K_2SO_4 respectively are

..... .

- (a) 2, 2 and 2 (b) 2, 2 and 3 (c) 1, 1 and 2 (d) 1, 1 and 1

Ans. (b) Number of total ions present in the solution is known as van't Hoff factors (i).

Substances	van't Hoff factor (i)
For KCl	2
For NaCl	2
For K_2SO_4	3

Hence, correct choice is (b).

Q. 16 Which of the following statements is false?

- (a) Units of atmospheric pressure and osmotic pressure are the same
 (b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration
 (c) The value of molal depression constant depends on nature of solvent
 (d) Relative lowering of vapour pressure, is a dimensionless quantity

Ans. (b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of higher concentration of solute to lower concentration.

Q. 17 Value of Henry's constant K_H

- (a) increases with increase in temperature
 (b) decreases with increase in temperature
 (c) remains constant
 (d) first increases then decreases

Ans. (a) Value of Henry's constant (K_H) increases with increase in temperature representing the decrease in solubility.

Q. 18 The value of Henry's constant, K_H is

- (a) greater for gases with higher solubility
 (b) greater for gases with lower solubility
 (c) constant for all gases
 (d) not related to the solubility of gases

Ans. (b) According to Henry's law

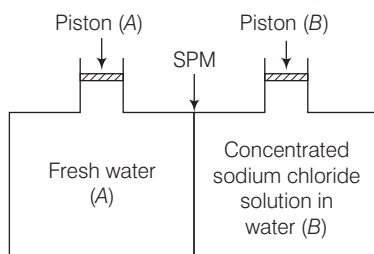
$$p \propto x$$

\Rightarrow

$$p = K_H x$$

As value of K_H rises solubility of gases decreases.

Q. 19 Consider the figure and mark the correct option.



- (a) Water will move from side (A) to side (B) if a pressure lower osmotic pressure is applied on piston (B)
- (b) Water will move from side (B) to side (A) if a pressure greater than osmotic pressure is applied on piston (B)
- (c) Water will move from side (B) to side (A) if a pressure equal to osmotic pressure is applied on piston (B)
- (d) Water will move from side (A) to side (B) if pressure equal to osmotic pressure is applied on piston (A)

Ans. (b) We know that, if a pressure higher than the osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semi-permeable membrane. This process is called reverse osmosis.

Thus, in this case, water will move from side (B) to side (A) if a pressure greater than osmotic pressure is applied on piston (B).

Q. 20 We have three aqueous solutions of NaCl labelled as 'A', 'B' and 'C' with concentrations 0.1 M, 0.01 M and 0.001 M, respectively. The value of van't Hoff factor for these solutions will be in the order

- (a) $i_A < i_B < i_C$
- (b) $i_A > i_B > i_C$
- (c) $i_A = i_B = i_C$
- (d) $i_A < i_B > i_C$

Ans. (b) van't Hoff factor is the measurement of total number of ions present in the solution. Therefore, greater the concentration of solution greater will be its van't Hoff factor.

	Concentration NaCl	
A	0.1 M	On moving top to bottom
B	0.01 M	◆ Concentration decreases
C	0.001 M	◆ Van't Hoff factor(i) decreases

Q. 21 On the basis of information given below mark the correct option.

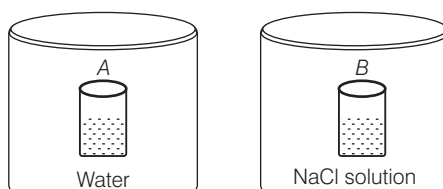
Information

- (i) In bromoethane and chloroethane mixture intermolecular interactions of A—A and B—B type are nearly same as A—B type interactions.
 - (ii) In ethanol and acetone mixture A—A or B—B type intermolecular interactions are stronger than A—B type interactions.
 - (iii) In chloroform and acetone mixture A—A or B—B type intermolecular interactions are weaker than A—B type interactions.
- (a) Solution (ii) and (iii) will follow Raoult's law
 - (b) Solution (i) will follow Raoult's law
 - (c) Solution (ii) will show negative deviation from Raoult's law
 - (d) Solution (iii) will show positive deviation from Raoult's law

Ans. (b) For an ideal solution, the $A-A$ or $B-B$ type intermolecular interaction is near by equal to $A-B$ type interaction. Here, a mixture of bromoethane and chloroethane is an example of ideal solution.

On the other hand chloroform and acetone mixture is an example of non-ideal solution having negative deviation. So, ($A-A$) or ($B-B$) interaction must be stronger than $A-B$ interaction. While ethanol-acetone mixture shows positive deviation due to weaker $A-B$ interaction in comparison to $A-A$ or $A-B$ interaction.

Q. 22 Two beakers of capacity 500 mL were taken. One of these beakers, labelled as "A", was filled with 400 mL water whereas the beaker labelled "B" was filled with 400 mL of 2M solution of NaCl. At the same temperature both the beakers were placed in closed containers of same material and same capacity as shown in figure.



At a given temperature, which of the following statement is correct about the vapour pressure of pure water and that of NaCl solution?

- (a) Vapour pressure in container (A) is more than that in container (B)
- (b) Vapour pressure in container (A) is less than that in container (B)
- (c) Vapour pressure is equal in both the containers
- (d) Vapour pressure in container (B) is twice the vapour pressure in container (A)

Ans. (a) When salt is added to water to make the solution the vapour pressure of solution get decreases. This is due to decrease in surface covered by solvent molecule which lead to decrease in number of solvent molecule escaping from the surface corresponding to pure solvent.

Hence, vapour pressure also get reduces.

Q. 23 If two liquids A and B form minimum boiling azeotrope at some specific composition then

- (a) $A-B$ interactions are stronger than those between $A-A$ or $B-B$
- (b) vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution
- (c) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution
- (d) $A-B$ interactions are weaker than those between $A-A$ or $B-B$

Ans. (a) If two liquids A and B form minimum boiling azeotrope at some specific composition then $A-B$ interactions are weaker than those of $A-A$ and $B-B$. It is due to the fact that in case of positive deviation, we get minimum boiling azeotropes whereas in case of negative deviation we get maximum boiling azeotropes.

Q. 24 4 L of 0.02 M aqueous solution of NaCl was diluted by adding 1 L of water. The molality of the resultant solution is

- (a) 0.004 (b) 0.008 (c) 0.012 (d) 0.016

Thinking Process

To calculate the strength of solution when it is diluted by adding solvent. Write all the given values M_1, V_1, M_2 and V_2 . Then calculate required parameter using formula,

$$M_1 V_1 = M_2 V_2$$

where,

V_1 = volume of solution before dilution

V_2 = volume of solution after dilution

M_1 = strength of solution before dilution

M_2 = strength of solution after dilution

Ans. (d) Given, $M_1 = 0.02\text{ M}$, $V_1 = 4\text{ L}$, $M_2 = ?$, $V_2 = 4\text{ L} + 1\text{ L} = 5\text{ L}$

As we know,

$$M_1 V_1 = M_2 V_2$$

$$0.02 \times 4\text{ L} = M_2 \times 5\text{ L}$$

$$M_2 = \frac{0.08}{5} = 0.016\text{ M}$$

Q. 25 On the basis of information given below mark the correct option.

Information On adding acetone to methanol some of the hydrogen bonds between methanol molecules break.

- (a) At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show positive deviation from Raoult's law
 (b) At specific composition methanol-acetone mixture will form maximum boiling azeotrope and will show positive deviation from Raoult's law
 (c) At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show negative deviation from Raoult's law
 (d) At specific composition methanol-acetone mixture will form maximum boiling azeotrope and will show negative deviation from Raoult's law

Ans. (a) At specific composition methanol- acetone mixture will form minimum boiling azeotrope and will show positive deviation. This is due to weaker A—B interaction than A—A or B—B interaction. i.e., $A-B < A-A$ and $B-B$

Q. 26 K_H value for Ar(g) , $\text{CO}_2\text{(g)}$, HCHO(g) and $\text{CH}_4\text{(g)}$ are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively.

Arrange these gases in the order of their increasing solubility.

- (a) $\text{HCHO} < \text{CH}_4 < \text{CO}_2 < \text{Ar}$ (b) $\text{HCHO} < \text{CO}_2 < \text{CH}_4 < \text{Ar}$
 (c) $\text{Ar} < \text{CO}_2 < \text{CH}_4 < \text{HCHO}$ (d) $\text{Ar} < \text{CH}_4 < \text{CO}_2 < \text{HCHO}$

Thinking Process

Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

Ans. (c) Value of K_H depends upon nature of gases dissolved in water.

Gas	Temperature (K)	$K_H/\text{k bar}$
Ar	298 K	40.3
CO_2	298 K	1.67
CH_4	298 K	0.413
HCHO	298 K	1.83×10^{-5}

Hence, correct order is $\text{Ar} < \text{CO}_2 < \text{CH}_4 < \text{HCHO}$ and correct choice is (c).

Multiple Choice Questions (More Than One Options)

Q. 27 Which of the following factor(s) affect the solubility of a gaseous solute in the fixed volume of liquid solvent?

- (i) Nature of solute
- (ii) Temperature
- (iii) Pressure
- (a) (i) and (iii) at constant T
- (b) (i) and (ii) at constant p
- (c) (ii) and (iii)
- (d) Only (iii)

Ans. (a, b)

Solubility of gaseous solute in the fixed volume of liquid solvent always depends upon nature of solute but it depends upon pressure at constant temperature and depends upon temperature at constant pressure.

Hence, (a) and (b) both are correct.

Q. 28 Intermolecular forces between two benzene molecules are nearly of same strength as those between two toluene molecules. For a mixture of benzene and toluene, which of the following are not true?

- (a) $\Delta_{\text{mix}} H = \text{zero}$
- (b) $\Delta_{\text{mix}} V = \text{zero}$
- (c) These will form minimum boiling azeotrope
- (d) These will not form ideal solution

Ans. (c, d)

The solution which follows Raoult's law is known as ideal solution. For an ideal solution intermolecular forces between two benzene molecules are nearly of same strength as those between two toluene molecules. For an ideal solution

$$\Delta V_{\text{mix}} = 0 \text{ and } \Delta H_{\text{mix}} = 0$$

Thus, the mixture of benzene and toluene is an example of ideal solution. Option (c) is incorrect as minimum boiling azeotropes are formed by non-ideal solution.

Q. 29 Relative lowering of vapour pressure is a colligative property because

- (a) it depends on the concentration of a non-electrolyte solute in solution and does not depend on the nature of the solute molecules
- (b) it depends on number of particles of electrolyte solute in solution and does not depend on the nature of the solute particles
- (c) it depends on the concentration of a non-electrolyte solute in solution as well as on the nature of the solute molecules
- (d) it depends on the concentration of an electrolyte or non-electrolyte solute in solution as well as on the nature of solute molecules

Ans. (a, b)

Relative lowering of vapour pressure is a colligative property because

- (i) It does not depend upon nature of solute.
 - (ii) It depends upon number of solute particles.
 - (iii) It depends upon concentration of non-electrolyte solution.
- Hence, (a) and (b) are correct.

Q. 30 van't Hoff factor (i) is given by the expression

- (a) $i = \frac{\text{normal molar mass}}{\text{abnormal molar mass}}$ (b) $i = \frac{\text{abnormal molar mass}}{\text{normal molar mass}}$
(c) $i = \frac{\text{observed colligative property}}{\text{calculated colligative property}}$ (d) $i = \frac{\text{calculated colligative property}}{\text{observed colligative property}}$

Ans. (a, c)

van't Hoff factor (i) is a measure of extent of association or dissociation of solute particles which can be calculated as

$$i = \frac{\text{normal molar mass}}{\text{abnormal molar mass}} = \frac{\text{observed colligative property}}{\text{calculated colligative property}}$$

Q. 31 Isotonic solutions must have the same

- (a) solute (b) density
(c) elevation in boiling point (d) depression in freezing point

Ans. (c, d)

Isotonic solutions have same osmotic pressure and same concentration. Elevation in boiling point and depression in freezing point are the colligative properties. These two colligative properties depend upon concentration.

As the molar concentration is same for isotonic solutions, so elevation in boiling point and depression in freezing point of isotonic solutions must be same.

Q. 32 Which of the following binary mixtures will have same composition in liquid and vapour phase?

- (a) Benzene-toluene (b) Water-nitric acid
(c) Water-ethanol (d) n -hexane— n -heptane

Ans. (b, c)

Mixtures having same composition in liquid and vapour phase are known as azeotropes. Azeotropes boils at same temperature.

Here, water-nitric acid and water-ethanol mixtures are non-ideal solution. Hence, water-nitric acid and water-ethanol are examples of azeotropes.

While benzene-toluene and n -hexane— n -heptane are examples of ideal solution.

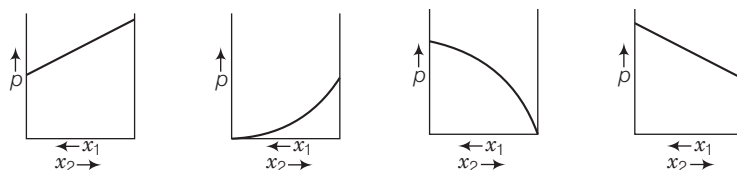
Q. 33 In isotonic solutions

- (a) solute and solvent both are same
(b) osmotic pressure is same
(c) solute and solvent may or may not be same
(d) solute is always same solvent may be different

Ans. (b, c)

The two solutions having same osmotic pressure are known as isotonic solutions. The solute and solvent particles may or may not be same but osmotic pressure must be same.

Q. 34 For a binary ideal liquid solution, the variation in total vapour pressure versus composition of solution is given by which of the curves?



Ans. (a, d)

Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

Q. 35 Colligative properties are observed when

- (a) a non-volatile solid is dissolved in a volatile liquid
- (b) a non-volatile liquid is dissolved in another volatile liquid
- (c) a gas is dissolved in non-volatile liquid
- (d) a volatile liquid is dissolved in another volatile liquid

Ans. (a, b)

When any of one component of binary mixture either solvent or solute is volatile it causes deviation from ideal behaviour and vapour pressure of solution which causes change in colligative property.

Hence, (a) and (b) are correct.

Short Answer Type Questions

Q. 36 Components of a binary mixture of two liquids A and B were being separated by distillation. After some time separation of components stopped and composition of vapour phase became same as that of liquid phase. Both the components started coming in the distillate. Explain why this happened?

Ans. Both the components are appearing in the distillate and composition of liquid and vapour is same. This shows that liquids have formed azeotropic mixture and boils at constant temperature hence cannot be separated at this stage by distillation or fractional distillation. Solution having azeotropic nature show large positive or negative deviation from Raoult's law depending upon intermolecular interaction.

Q. 37 Explain why on addition of 1 mole of NaCl to 1 L of water, the boiling point of water increases, while addition of 1 mole of methyl alcohol to 1 L of water decreases its boiling point.

Ans. NaCl is a non-volatile solute. So, its addition to water lowers the vapour pressure of the water. Hence, boiling point of water (solution) increases. Whereas methyl alcohol is more volatile than water.

So, its addition to water increases the total vapour pressure over the solution. It results in the decrease of boiling point.

Q. 38 Explain the solubility rule “like dissolves like” in terms of intermolecular forces that exist in solutions.

Ans. If the intermolecular interactions are similar in both constituents, *i.e.*, solute and solvent then solute dissolves in the solvent. *e.g.*, polar solutes dissolve in polar solvents and non-polar solutes in non-polar solvents.

Thus, the statement ‘like dissolves like’ proves to be true. *e.g.*, organic compounds dissolve in non-polar organic solvent while polar inorganic compounds (salts) dissolve in polar solvent (water).

Q. 39 Concentration terms such as mass percentage, ppm, mole fraction and molality are independent of temperature, however molarity is a function of temperature. Explain.

💡 Thinking Process

To solve this problem notice the role of temperature in component of concentration term such as volume, mass, number of moles etc.

Ans. Molarity is defined as the number of moles of solute dissolved per litre of a solution. Since, volume depends on temperature and changes with change in temperature, the molarity will also change with change in temperature.

On the other hand, mass does not change with change in temperature, so other concentration terms given in the question also do not do so. Thus, temperature has no effect on the mass but it has significant effect on volume.

Q. 40 What is the significance of Henry’s law constant K_H ?

Ans. According to Henry’s law $p \propto x \Rightarrow p = K_H x$

Higher the value of Henry’s law constant K_H , the lower is the solubility of the gas in a liquid. Thus, the solubility of a gas in the given liquid can be increased by increasing pressure.

Q. 41 Why are aquatic species more comfortable in cold water in comparison to warm water?

Ans. Aquatic species are more comfortable in cold water due to the presence of more oxygen. Solubility of oxygen in water increases with decrease in temperature as solubility of a gas in given liquid decreases with increase in temperature.

Q. 42 (a) Explain the following phenomena with the help of Henry’s law.

(i) Painful condition known as bends.

(ii) Feeling of weakness and discomfort in breathing at high altitude.

(b) Why soda water bottle kept at room temperature fizzes on opening?

Ans. (a) (i) Henry’s law represents a relation between solubility of gases in liquid and pressure. Scuba divers when comes towards surface, the pressure gradually decreases. This reduce pressure releases the dissolve gas present in blood and leads to formation of bubbles of nitrogen in the blood.

This creates a painful condition by blocking capillaries known as blends.

(ii) At high altitude atmospheric pressure is low as compared to surface which causes difficulty in breathing. On that condition we feel weakness and discomfort.

(b) Soda water bottle kept at room temperature fizzes on opening due to different pressure inside and outside the bottle. When the bottle is opened to air, the partial pressure of CO_2 above the solution decreases. As a result, solubility decreases and hence CO_2 bubbles out.

Q. 43 Why is the vapour pressure of an aqueous solution of glucose lower than that of water?

Ans. In pure liquid, the entire surface of liquid is occupied by the molecules of water. When a non-volatile solute, e.g., glucose is dissolved in water, the fraction of surface covered by the solvent molecules gets reduced because some positions are occupied by glucose molecules.

So, number of solvent molecules escaping from the surface is reduced. That is why vapour pressure of aqueous solution of glucose is reduced.

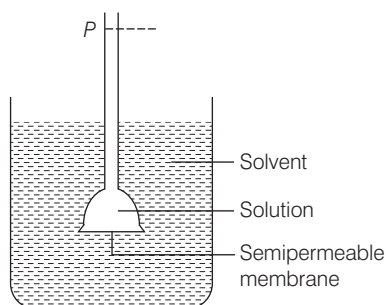
Q. 44 How does sprinkling of salt help in clearing the snow covered roads in hilly areas? Explain the phenomenon involved in the process.

Ans. When salt is spread over snow covered roads, snow starts melting from the surface because depression of freezing point of water takes place due to addition of salt. It helps in clearing of roads.

Hence, the phenomena is depression in freezing point which helps in clearing the snow covered roads in hilly areas.

Q. 45 What is “semipermeable membrane”?

Ans. Continuous sheets or films (natural or synthetic) which contain a network of submicroscopic holes or pores through which small solvent molecules (water etc.) can pass, but solute molecules of bigger size cannot pass are called semipermeable membrane. e.g., cellophane membrane.



Q. 46 Give an example of a material used for making semipermeable membrane for carrying out reverse osmosis.

Ans. Since pressure required for the reverse osmosis is very high, so, a suitable material is used for making semipermeable membrane. It is generally cellulose acetate placed over suitable support.

Matching The Columns

Q. 47 Match the items given in Column I and Column II.

Column I	Column II
A. Saturated solution	1. Solution having same osmotic pressure at a given temperature as that of given solution.
B. Binary solution	2. A solution whose osmotic pressure is less than that of another.
C. Isotonic solution	3. Solution with two components.
D. Hypotonic solution	4. A solution which contains maximum amount of solute that can be dissolved in a given amount of solvent at a given temperature.
E. Solid solution	5. A solution whose osmotic pressure is more than that of another.
F. Hypertonic solution	6. A solution in solid phase.

Ans. A. → (4) B. → (3) C. → (1) D. → (2) E. → (6) F. → (5)

- A. **Saturated solution** A solution which contains maximum amounts of solute that can be dissolved in a given amount of solvent at a given temperature.
- B. **Binary solution** A solution with two components is known as binary solution.
- C. **Isotonic solution** A solution having same osmotic pressure at a given temperature as that of given solution is known as isotonic solution.
- D. **Hypotonic solution** A solution whose osmotic pressure is less than another is known as hypotonic solution.
- E. **Solid solution** A solution in solid phase is known as solid solution.
- F. **Hypertonic solution** A solution whose osmotic pressure is greater than that of another is known as hypertonic solution.

Q. 48 Match the items given in Column I with the type of solutions given in Column II.

Column I	Column II
A. Soda water	1. A solution of gas in solid
B. Sugar solution	2. A solution of gas in gas
C. German silver	3. A solution of solid in liquid
D. Air	4. A solution of solid in solid
E. Hydrogen gas in palladium	5. A solution of gas in liquid
	6. A solution of liquid in solid

Ans. A. → (5) B. → (3) C. → (4) D. → (2) E. → (1)

- A. **Soda water** A solution of gas in liquid. e.g., CO_2 in soft drinks.
- B. **Sugar solution** A solution of solid in liquid in which sugar particles (solid) are dissolved in water (liquid).
- C. **German silver** German silver is an alloy which is a solid solution of solid in solid. It is an alloy of Cu, Zn and Ni.
- D. **Air** A solution of gas in gas. Air is a mixture of various gases.
- E. **Hydrogen gas in palladium** is an example of solution of gas in solid. This is used as an reducing agent.

Q. 49 Match the laws given in Column I with expressions given in Column II.

Column I	Column II
A. Raoult's law	1. $\Delta T_f = K_f m$
B. Henry's law	2. $\pi = CRT$
C. Elevation of boiling point	3. $p = x_1 p_1^\circ + x_2 p_2^\circ$
D. Depression in freezing point	4. $\Delta T_b = K_b m$
E. Osmotic pressure	5. $p = K_H \cdot x$

Ans. A. → (3) B. → (5) C. → (1) D. → (1) E. → (2)

A. **Raoult's law** Mathematical representation of Raoult's law

$$p = x_1 p_1^\circ + x_2 p_2^\circ$$

B. **Henry's law** $p = K_H \cdot x$

C. **Elevation of boiling point** Mathematical representation, $\Delta T_b = K_b \cdot m$

D. **Depression in freezing point** Mathematical representation, $\Delta T_f = K_f \cdot m$

E. **Osmotic pressure** Mathematical representation, $\pi = CRT$.

Q. 50 Match the terms given in Column I with expressions given in Column II.

Column I	Column II
A. Mass percentage	1. $\frac{\text{Number of moles of the solute component}}{\text{Volume of solution in litres}}$
B. Volume percentage	2. $\frac{\text{Number of moles of a component}}{\text{Total number of moles of all the components}}$
C. Mole fraction	3. $\frac{\text{Volume of the solute component in solution}}{\text{Total volume of solution}} \times 100$
D. Molality	4. $\frac{\text{Mass of the solute component in solution}}{\text{Total mass of the solution}} \times 100$
E. Molarity	5. $\frac{\text{Number of moles of the solute components}}{\text{Mass of solvent in kilograms}}$

Ans. A. → (4) B. → (3) C. → (2) D. → (5) E. → (1)

Column I (Concentration terms)	Column II (Mathematical formula)
A. Mass percentage	$\frac{\text{Mass of the solute component in solution}}{\text{Total mass of the solution}} \times 100$
B. Volume percentage	$\frac{\text{Volume of the solute component in solution}}{\text{Total volume of solution}} \times 100$
C. Mole fraction	$\frac{\text{Number of moles of a component}}{\text{Total number of moles of all the components}}$
D. Molality	$\frac{\text{Number of moles of the solute components}}{\text{Mass of solvent in kilograms}}$
E. Molarity	$\frac{\text{Number of moles of the solute component}}{\text{Volume of solution in litres}}$

Assertion and Reason

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion and reason both are incorrect statements.
- (e) Assertion is wrong statement but reason is correct statement.

Q. 51 Assertion (A) Molarity of a solution in liquid state changes with temperature.

Reason (R) The volume of a solution changes with change in temperature.

Ans. (a) Assertion and reason both are correct statements and reason is the correct explanation of assertion.

Volume of solutions is a function of temperature which varies with temperature. Hence, molarity of solution in liquid state changes with temperature.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{volume of solution in litre}}$$

Q. 52 Assertion (A) When methyl alcohol is added to water, boiling point of water increases.

Reason (R) When a volatile solute is added to a volatile solvent elevation in boiling point is observed.

Ans. (d) Assertion is wrong statement but reason is correct statement.

When methyl alcohol is added to water, boiling point of water decreases because when a volatile solute is added to a volatile solvent elevation in boiling point is observed.

Q. 53 Assertion (A) When NaCl is added to water a depression in freezing point is observed.

Reason (R) The lowering of vapour pressure of a solution causes depression in the freezing point.

Ans. (a) Assertion and reason both are correct and reason is correct explanation of assertion. When NaCl is added to water a depression in freezing point is observed. This is due to lowering of vapour pressure of a solution. Lowering of vapour pressure is observed due to intermolecular interaction of solvent-solute particles.

Q. 54 Assertion (A) When a solution is separated from the pure solvent by a semipermeable membrane, the solvent molecules pass through it from pure solvent side to the solution side.

Reason (R) Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.

Ans. (b) Assertion and reason both are correct statements but reason is not the correct explanation of assertion.

When a solution is separated from the pure solvent by a semipermeable membrane, the solvent molecules pass through it from pure solvent side to the solution side. Solvent molecules always flow from lower concentration to higher concentration of solution.

Long Answer Type Questions

Q. 55 Define the following modes of expressing the concentration of a solution? Which of these modes are independent of temperature and why?

- | | |
|-------------------------------------|-----------------------------|
| (a) w/w (mass percentage) | (b) V/V (volume percentage) |
| (c) w/V (mass by volume percentage) | (d) ppm (parts per million) |
| (e) χ (mole fraction) | (f) M (molarity) |
| (g) m (molality) | |

Ans. (a) **w/w** (mass percentage) Mass percentage of a component of a solution can be expressed as

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

Thus, the percentage by mass means the mass of the solute in grams present in 100g of the solution.

(b) **V/V** (volume percentage) is defined as

$$\text{Volume percentage} = \frac{\text{volume of the component}}{\text{total volume of solution}} \times 100$$

Thus, volume percentage means the volume of the liquid solute in cm^3 present in 100 cm^3 of the solution.

(c) **w/V** (mass by volume percentage) = mass of solute dissolved in 100 mL of solution.

(d) **ppm** (parts per million) This parametre is used to express the concentration of very dilute solution.

$$\text{ppm} = \frac{\text{number of parts of component}}{\text{total number of parts of all component of solution}} \times 10^6$$

(e) χ (mole fraction) Mole fraction is an unitless quantity used to determine extent of any particular component present in total solution.

$$\chi = \frac{\text{number of moles of the component}}{\text{total number of moles of all components}}$$

- (f) **M** (molarity) Number of moles of solute dissolved in per litre of solution is known as molarity.

$$M = \frac{\text{number of moles of solute}}{\text{volume of solution in litre}}$$

- (g) **m** (Molality) Molality of any solution can be defined as number of moles of solute dissolved in per kg of solvent.

$$m = \frac{\text{number of moles of solute}}{\text{mass of solvent in kg}}$$

Q. 56 Using Raoult's law explain how the total vapour pressure over the solution is related to mole fraction of components in the following solutions.

- (a) CHCl_3 (l) and CH_2Cl_2 (l) (b) NaCl (s) and H_2O (l)

Ans. According to Raoult's law for any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.

$$p_1 = p_1^\circ x_1$$

- (a) CHCl_3 (l) and CH_2Cl_2 (l) both are volatile components.

Hence, for a binary solution in which both components are volatile liquids, the total pressure will be

$$\begin{aligned} p &= p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ \\ &= x_1 p_1^\circ + (1 - x_1) p_2^\circ = (p_1^\circ - p_2^\circ) x_1 + p_2^\circ \end{aligned}$$

where, p = total vapour pressure

p_1 = partial vapour pressure of component 1

p_2 = partial vapour pressure of component 2

- (b) NaCl (s) and H_2O (l) both are non-volatile components.

Hence, for a solution containing non-volatile solute, the Raoult's law is applicable only to vaporisable component and total vapour pressure can be written as

$$p = p_1 = x_1 p_1^\circ$$

Q. 57 Explain the terms ideal and non-ideal solutions in the light of forces of interactions operating between molecules in liquid solutions.

Ans. The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. For an ideal solution $\Delta V_{\text{mix}} = 0$ and $\Delta H_{\text{mix}} = 0$. The ideal behaviour of the solutions can be explained by considering two components A and B.

In pure components, the intermolecular attractive interactions will be of A—A type and B—B type, whereas in the binary solutions in addition to these two, A—B type of interaction will also be present. If A—A and B—B intermolecular forces are nearly equal to those between A—B, this leads to the formation of ideal solution e.g., solution of *n*-hexane and *n*-heptane.

When a solution does not obey-Raoult's law over the entire range of concentration, then it is called non-ideal solution. The vapour pressure of such a solution is either higher or lower, than that predicted by Raoult's law.

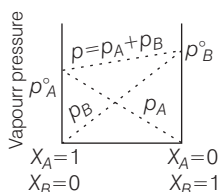
If it is higher, the solution exhibits positive deviation and if it is lower it exhibits negative deviation from Raoult's law. In case of positive deviation, A—B interactions are weaker than those between A—A or B—B. i.e., the attractive forces between solute solvent molecules are weaker than those between solute-solute and solvent-solvent molecules e.g., mixture of ethanol and acetone.

For such solutions $\Delta H_{\text{mixing}} = + \text{ve}$ and $\Delta V_{\text{mixing}} = + \text{ve}$

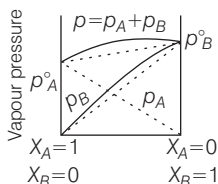
On the other hand, in case of negative deviation the intermolecular attractive forces between A—A and B—B are weaker than those between A—B molecules. Thus, the escaping tendency of A and B types of molecules from the solution becomes less than from the pure liquids i.e., mixture of chloroform and acetone.

For such solution

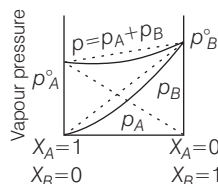
$$\Delta H_{\text{mix}} = - \text{ve and } \Delta V_{\text{mix}} = - \text{ve}$$



Graph for ideal solution



Graph showing +ve deviation



Graph showing -ve deviation

Q. 58 Why is it not possible to obtain pure ethanol by fractional distillation? What general name is given to binary mixtures which show deviation from Raoult's law and whose components cannot be separated by fractional distillation. How many types of such mixtures are there?

Ans. The solution or mixture having same composition in liquid as well as in vapour phase and boils at a constant temperature is known as azeotropes. Due to constant composition it can't be separated by fractional distillation. *There are two types of azeotropes*

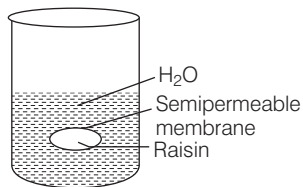
- Minimum boiling azeotropes** Solutions which show large positive deviation from Raoult's law form minimum boiling azeotropes at a specific composition. e.g., ethanol—water mixture
- Maximum boiling azeotropes** Solutions which show large negative deviation from Raoult's law form maximum boiling azeotropes. e.g., solution having composition 68% HNO_3 and 32% water by mass.

Q. 59 When kept in water, raisin swells in size. Name and explain the phenomenon involved with the help of a diagram. Give three applications of the phenomenon.

Ans. This phenomenon is called endo osmosis, i.e., movement of water inside the raisin and shown with the help of diagram as

The process of osmosis is of immense biological as well as industrial important. *It is evident from the following examples.*

- Movement of water from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis.
- Preservation of meat against bacterial action by addition of salt.
- Preservation of fruits against bacterial action by adding sugar. Bacterium in canned fruit loses water through the process of osmosis and become inactive.
- Reverse-osmosis is used in desalination of water.



Q. 60 Discuss biological and industrial applications of osmosis.

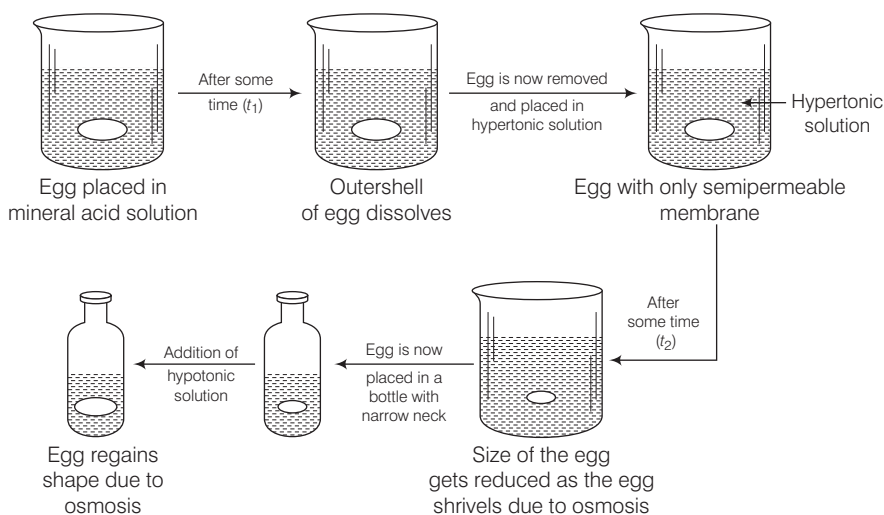
- Ans.**
- In animals, water moves into different parts of the body under the effect of the process of osmosis.
 - Stretching of leaves, flower, etc., is also controlled by osmosis.
 - Osmosis helps in rapid growth of the plants and germination of seeds.
 - Different movements of plants such as opening and closing of flowers etc., are controlled by osmosis.

Q. 61 How can you remove the hard calcium carbonate layer of the egg without damaging its semipermeable membrane? Can this egg be inserted into a bottle with a narrow neck without distorting its shape? Explain the process involved.

Thinking Process

The question can be answered using the concept of solubility, osmosis, reverse-osmosis, hypertonic solution and hypotonic solution.

Ans. When egg is placed in mineral acid solution outershell of egg dissolves. Egg is now removed and placed in hypertonic solution. Size of egg get reduced and egg shrivels due to osmosis. Egg is now placed in a bottle with narrow neck. Finally on adding hypotonic solution egg regain its shape due to osmosis.
Diagrammatically it can be represented as



Q. 62 Why is the mass determined by measuring a colligative property in case of some solutes abnormal? Discuss it with the help of van't Hoff factor.

Ans. Certain compounds when dissolved in suitable solvents either dissociate or associate. e.g., ethanoic acid dimerises in benzene due to H-bonding, while in water, it dissociates and forms ions.

As a result the number of chemical species in solution increases or decreases as compared to the number of chemical species of solute added to form the solution.

Since, the magnitude of colligative property depends on the number of solute particles, it is expected that the molar mass determined on the basis of colligative properties will either higher or lower than the expected value or the normal value and is called abnormal molar mass.

In order to account for the extent of dissociation or association of molecules in solution, van't Hoff introduced a factor, i , known as the van't Hoff factor.

$$i = \frac{\text{expected molar mass}}{\text{abnormal molar mass}} = \frac{\text{observed colligative property}}{\text{calculated colligative property}}$$

$$= \frac{\text{total number of moles of particles after association or dissociation}}{\text{total number of moles of particles before association or dissociation}}$$

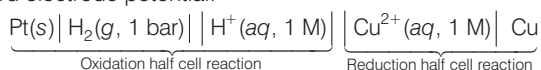
Electrochemistry

Multiple Choice Questions (MCQs)

Q. 1 Which cell will measure standard electrode potential of copper electrode?

- (a) $\text{Pt (s)} \mid \text{H}_2(\text{g}, 0.1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1 \text{ M}) \parallel \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) \mid \text{Cu}$
 (b) $\text{Pt (s)} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1 \text{ M}) \parallel \text{Cu}^{2+}(\text{aq}, 2 \text{ M}) \mid \text{Cu}$
 (c) $\text{Pt (s)} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1 \text{ M}) \parallel \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) \mid \text{Cu}$
 (d) $\text{Pt (s)} \mid \text{H}_2(\text{g}, 0.1 \text{ bar}) \mid \text{H}^+(\text{aq}, 0.1 \text{ M}) \parallel \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) \mid \text{Cu}$

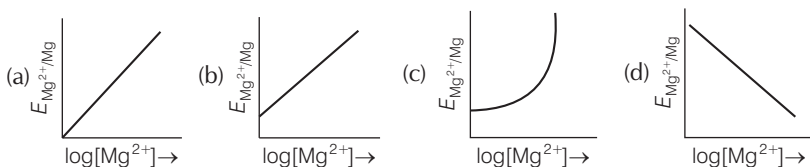
Ans. (c) Standard electrode potential of copper electrode can be calculated by constructing a concentration cell composed of two half cell reactions in which concentration of species on left hand and right hand side are unity. In such case cell potential is equal to standard electrode potential.



Q. 2 Electrode potential for Mg electrode varies according to the equation

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^s - \frac{0.059}{2} \log \frac{1}{[\text{Mg}^{2+}]}$$

vs $\log [\text{Mg}^{2+}]$ is



💡 Thinking Process

This problem includes concept of Nernst equation and its transformation to equation of straight line.

Ans. Electrode potential for Mg electrode varies according to the equation

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Mg}^{2+}]}$$

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} + \frac{0.059}{2} \log [\text{Mg}^{2+}]$$

$$E_{\text{Mg}^{2+}/\text{Mg}} = \frac{0.059}{2} \log [\text{Mg}^{2+}] + E_{\text{Mg}^{2+}/\text{Mg}}^{\circ}$$

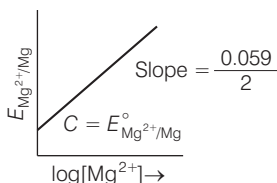
This equation represents equation of straight line. It can be correlated as

$$E_{\text{Mg}^{2+}/\text{Mg}} = \left(\frac{0.059}{2} \right) \log [\text{Mg}^{2+}] + E_{\text{Mg}^{2+}/\text{Mg}}^{\circ}$$

↑
Y
↑
M
↑
X
↑
+ C

So, intercept (C) = $E_{\text{Mg}^{2+}/\text{Mg}}^{\circ}$

Thus, equation can be diagrammatically represented as



Q. 3 Which of the following statement is correct?

- (a) E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties
- (b) E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties
- (c) E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property
- (d) E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property

💡 Thinking Process

This problem is based on thermodynamical concept of intensive and extensive property. During answering this question must keep in mind that intensive property is independent on number of particles and extensive property is dependent on number of particles.

Ans. (c) E_{cell} is an intensive property as it does not depend upon mass of species (number of particles) but $\Delta_r G$ of the cell reaction is an extensive property because this depends upon mass of species (number of particles).

Q. 4 The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called.....

- (a) cell potential
- (b) cell emf
- (c) potential difference
- (d) cell voltage

Ans. (b) Cell emf The difference between the electrode potential of two electrodes when no current is drawn through the cell is called cell emf.

Q. 5 Which of the following statement is not correct about an inert electrode in a cell?

- (a) It does not participate in the cell reaction
- (b) It provides surface either for oxidation or for reduction reaction
- (c) It provides surface for conduction of electrons
- (d) It provides surface for redox reaction

Ans. (d) An inert electrode in a cell provide surface for either oxidation or for reduction reaction by conduction of electrons through its surface but does not participate in the cell reaction.

It does not provide surface for redox reaction.

Q. 6 An electrochemical cell can behave like an electrolytic cell when

- (a) $E_{\text{cell}} = 0$ (b) $E_{\text{cell}} > E_{\text{ext}}$
 (c) $E_{\text{ext}} > E_{\text{cell}}$ (d) $E_{\text{cell}} = E_{\text{ext}}$

Ans. (c) If an external opposite potential is applied on the galvanic cell and increased reaction continues to take place till the opposing voltage reaches the value 1.1 V.

At this stage no current flow through the cell and if there is any further increase in the external potential then reaction starts functioning in opposite direction.

Hence, this works as an electrolytic cell.

Q. 7 Which of the statements about solutions of electrolytes is not correct?

- (a) Conductivity of solution depends upon size of ions
 (b) Conductivity depends upon viscosity of solution
 (c) Conductivity does not depend upon solvation of ions present in solution
 (d) Conductivity of solution increases with temperature

Ans. (c) Solution consists of electrolytes is known as electrolytic solution and conductivity of electrolytic solution depends upon the following factors

- (i) **Size of ions** As ion size increases, ion mobility decreases and conductivity decreases.
 (ii) **Viscosity of solution** Greater the viscosity of the solvent lesser will be the conductivity of the solution.
 (iii) **Solvation of ions** Greater the solvation of ions of an electrolyte lesser will be the electrical conductivity of the solution.
 (iv) **Temperature of medium** Conductivity of solution increases with increase in temperature.

Q. 8 Using the data given below find out the strongest reducing agent.

$$E^{\circ}_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33\text{V}; E^{\circ}_{\text{Cl}_2/\text{Cl}^-} = 1.36\text{V}$$

$$E^{\circ}_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51\text{V}; E^{\circ}_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{V}$$

- (a) Cl^- (b) Cr (c) Cr^{3+} (d) Mn^{2+}

💡 Thinking Process

This problem includes concept of electrochemical series and standard reduction potential of the metal.

Higher the negative value of standard reduction potential, strongest will be the reducing agent.

As value of SRP increases from negative to positive value nature of species changes from reducing to oxidising nature.

Ans. (b) Here, out of given four options standard reduction potential of chromium has highest negative value hence most powerful reducing agent is chromium.

Q. 9 Use the data given in Q. 8 and find out which of the following is the strongest oxidising agent?

- (a) Cl^- (b) Mn^{2+}
(c) MnO_4^- (d) Cr^{3+}

Ans. (c) Higher the positive value of standard reduction potential of metal ion higher will be its oxidising capacity.

Since, $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}}$ has value equal to 1.51 V hence it is the strongest oxidising agent.

Q. 10 Using the data given in Q.8 find out in which option the order of reducing power is correct.

- (a) $\text{Cr}^{3+} < \text{Cl}^- < \text{Mn}^{2+} < \text{Cr}$ (b) $\text{Mn}^{2+} < \text{Cl}^- < \text{Cr}^{3+} < \text{Cr}$
(c) $\text{Cr}^{3+} < \text{Cl}^- < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$ (d) $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Cl}^- < \text{Cr}$

Ans. (b)

Species (ions)	SRP values
Mn^{2+}	1.51 V
Cl^-	1.36 V
Cr^{3+}	1.33 V
Cr	- 0.74 V

On moving top to bottom SRP value decreases from positive to negative value which will increase the reducing capacity. So, the correct option is (b).

Q. 11 Use the data given in Q. 8 and find out the most stable ion in its reduced form.

- (a) Cl^- (b) Cr^{3+} (c) Cr (d) Mn^{2+}

Ans. (d) $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}}$ has +ve value equal to 1.51 V which is highest among given four choices. So, Mn^{2+} is most stable ion in its reduced form.

Q. 12 Use the data of Q. 8 and find out the most stable oxidised species.

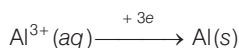
- (a) Cr^{3+} (b) MnO_4^- (c) $\text{Cr}_2\text{O}_7^{2-}$ (d) Mn^{2+}

Ans. (a) $E^\circ_{\text{Cr}^{3+}/\text{Cr}}$ has most -ve value equal to - 0.74 among given four choices. So, Cr^{3+} is the most stable oxidised species.

Q. 13 The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is

- (a) 1 F (b) 6 F (c) 3 F (d) 2 F

Ans. (c) The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is equal to number of electron required to convert Al_2O_3 to Al.



Hence, total 3F is required.

Q. 14 The cell constant of a conductivity cell

- (a) changes with change of electrolyte
- (b) changes with change of concentration of electrolyte
- (c) changes with temperature of electrolyte
- (d) remains constant for a cell

Ans. (d) Cell constant is defined as the ratio of length of object and area of cross section.

$$G = \frac{l}{A}$$

Since, l and A remain constant for any particular object hence value of cell constant always remains constant.

Q. 15 While charging the lead storage battery

- (a) PbSO_4 anode is reduced to Pb
- (b) PbSO_4 cathode is reduced to Pb
- (c) PbSO_4 cathode is oxidised to Pb
- (d) PbSO_4 anode is oxidised to PbO_2

Ans. (a) While charging the lead storage battery the reaction occurring on cell is reversed and PbSO_4 (s) on anode and cathode is converted into Pb and PbO_2 respectively

Hence, option (a) is the correct choice

The electrode reactions are as follows

At cathode $\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$ (Reduction)

At anode $\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2(\text{s}) + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$ (Oxidation)

Overall reaction $2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq.}) + 2\text{SO}_4^{2-}(\text{aq.})$

Q. 16 $\Lambda_m^\circ(\text{NH}_4\text{OH})$ is equal to

- (a) $\Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{NH}_4\text{Cl}) - \Lambda_m^\circ(\text{HCl})$
- (b) $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$
- (c) $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NaOH})$
- (d) $\Lambda_m^\circ(\text{NaOH}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl})$

Thinking Process

This question is based on the concept of Kohlrausch law and can be solved by using the concept involved in calculation of limiting molar conductivity of any salt. According to Kohlrausch law limiting molar conductivity of any salt is equal to sum of limiting molar conductivity of individual molar conductivity of cations and anions of electrolyte.

Ans. (b)

$$\Lambda_m^\circ(\text{NH}_4\text{Cl}) = \Lambda_m^\circ(\text{NH}_4^+) + \Lambda_m^\circ(\text{Cl}^-)$$

$$\Lambda_m^\circ(\text{NaOH}) = \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{OH}^-)$$

$$\Lambda_m^\circ(\text{NaCl}) = \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{Cl}^-)$$

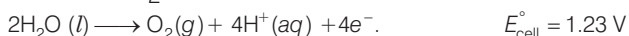
$$\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl}) = \Lambda_m^\circ(\text{NH}_4\text{OH})$$

Hence, option (b) is correct choice.

Q. 17 In the electrolysis of aqueous sodium chloride solution which of the half cell reaction will occur at anode?

- (a) $\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s}); E_{\text{cell}}^{\text{s}} = -2.71 \text{ V}$
- (b) $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-; E_{\text{cell}}^{\text{s}} = -1.23 \text{ V}$
- (c) $\text{H}^+(\text{aq}) + \text{e}^- \longrightarrow \frac{1}{2} \text{H}_2(\text{g}); E_{\text{cell}}^{\text{s}} = 0.00 \text{ V}$
- (d) $\text{Cl}^-(\text{aq}) \longrightarrow \frac{1}{2} \text{Cl}_2(\text{g}) + \text{e}^-; E_{\text{cell}}^{\text{s}} = 1.36 \text{ V}$

Ans. (d) In case of electrolysis of aqueous NaCl oxidation reaction occurs at anode as follows



But due to lower E°_{cell} value water should get oxidised in preference of $\text{Cl}^- (\text{aq})$.

However, the actual reaction taking place in the concentrated solution of NaCl is (d) and not (b) i.e., Cl_2 is produced and not O_2 .

This unexpected result is explained on the basis of the concept of 'overvoltage', i.e., water needs greater voltage for oxidation to O_2 (as it is kinetically slow process) than that needed for oxidation of Cl^- ions to Cl_2 . Thus, the correct option is (d) not (b).

Multiple Choice Questions (More Than One Options)

Q. 18 The positive value of the standard electrode potential of $\text{Cu}^{2+} / \text{Cu}$ indicates that.....

- (a) this redox couple is a stronger reducing agent than the H^+ / H_2 couple
- (b) this redox couple is a stronger oxidising agent than H^+ / H_2
- (c) Cu can displace H_2 from acid
- (d) Cu cannot displace H_2 from acid

Ans. (b, d)

'Lesser the E° value of redox couple higher the reducing power'

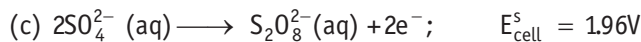
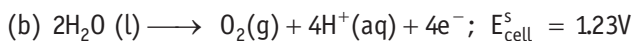
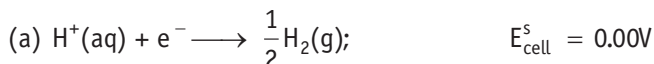


Since, $2\text{H}^+ / \text{H}_2$ has lesser SRP than $\text{Cu}^{2+} / \text{Cu}$ redox couple. Therefore,

- (i) This redox couple is a stronger oxidising agent than H^+ / H_2 .
- (ii) Cu can't displace H_2 from acid.

Hence, (b) and (d) are correct.

Q. 19 E°_{cell} for some half cell reactions are given below. On the basis of these mark the correct answer.

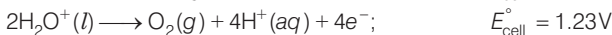


- (a) In dilute sulphuric acid solution, hydrogen will be reduced at cathode
- (b) In concentrated sulphuric acid solution, water will be oxidised at anode
- (c) In dilute sulphuric acid solution, water will be oxidised at anode
- (d) In dilute sulphuric acid solution, SO_4^{2-} ion will be oxidised to tetrathionate ion at anode

Ans. (a, c)

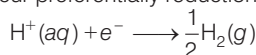
During the electrolysis of dilute sulphuric acid above given three reaction occurs each of which represents particular reaction either oxidation half cell reaction or reduction half cell reaction.

Oxidation half cell reactions occur at anode are as follows



Reaction having lower value of E_{cell}° will undergo faster oxidation.

Hence, oxidation of water occur preferentially reduction half cell reaction occurs at cathode



At cathode

Hence, options (a) and (b) are correct.

Q. 20 $E_{\text{cell}}^\circ = 1.1\text{ V}$ or Daniel cell. Which of the following expressions are correct description of state of equilibrium in this cell?

(a) $1.1 = K_C$

(b) $\frac{2.303RT}{2F} \log K_C = 1.1$

(c) $\log K_C = \frac{2.2}{0.059}$

(d) $\log K_C = 1.1$

Ans. (b, c)

At state of equilibrium

$$\Delta G = -RT \log K$$

$$-nFE^\circ = -RT 2.303 \log K_C$$

$$E^\circ = \frac{+RT 2.303 \log K_C}{+ 2F} \quad (n = 2 \text{ for Daniel cell})$$

\therefore At equilibrium $E^\circ = 1.1$

$$\therefore \frac{2.303RT}{2F} \log K_C = 1.1$$

$$\log K_C = \frac{2.2}{0.059} \quad [\text{on solving}]$$

Hence, options (b) and (c) are the correct choices.

Q. 21 Conductivity of an electrolytic solution depends on

- (a) nature of electrolyte
- (b) concentration of electrolyte
- (c) power of AC source
- (d) distance between the electrodes

Ans. (a, b)

Conductivity of electrolytic solution is due to presence of mobile ions in the solution. This type of conductance is known as ionic conductance. Conductivity of these type of solutions depend upon

- (i) the nature of electrolyte added
- (ii) size of the ion produced and their solvation
- (iii) concentration of electrolyte
- (iv) nature of solvent and its viscosity
- (v) temperature

While power of source or distance between electrodes has no effect on conductivity of electrolyte solution.

Hence, options (a) and (b) are the correct choices.

Q. 22 $\Lambda_m^\circ \text{H}_2\text{O}$ is equal to.....

(a) $\Lambda_m^\circ(\text{HCl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$

(b) $\Lambda_m^\circ(\text{HNO}_3) + \Lambda_m^\circ(\text{NaNO}_3) - \Lambda_m^\circ(\text{NaOH})$

(c) $\Lambda_m^\circ(\text{HNO}_3) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaNO}_3)$

(d) $\Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{HCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl})$

Thinking Process

This problem includes concept of Kohlrausch law and its application in determination of molar conductivity of species. This problem can be solved by following three steps.

(i) Write the molar conductance of each species in terms of sum of their constituent ions.

(ii) Now operate the equation of each option given above by using information provided in the question.

(iii) At last if the sum of molar conductivity remaining constituent ions is equal to the molar conductivity of species asked (here $\Lambda_m^\circ(\text{H}_2\text{O})$) then that will be the correct choice.

Ans. (a, c)

(a)

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

(d)

$$\begin{aligned}\Lambda_m^\circ(\text{NH}_4\text{OH}) &= \Lambda_m^\circ(\text{NH}_4^+) + \Lambda_m^\circ(\text{OH}^-) \\ \Lambda_m^\circ(\text{HCl}) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{Cl}^-) \\ \Lambda_m^\circ(\text{NH}_4\text{Cl}) &= \Lambda_m^\circ(\text{NH}_4^+) + \Lambda_m^\circ(\text{Cl}^-) \\ \hline \Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{HCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl}) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{OH}^-) = \Lambda_m^\circ(\text{H}_2\text{O})\end{aligned}$$

This type of decomposition is not possible due to weak basic strength of NH_4OH . This line will be placed above.

(b)

$$\begin{aligned}\Lambda_m^\circ(\text{HNO}_3) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{NO}_3^-) \\ \Lambda_m^\circ(\text{NaNO}_3) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{NO}_3^-) \\ \Lambda_m^\circ(\text{NaOH}) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{OH}^-) \\ \hline \Lambda_m^\circ(\text{HNO}_3) + \Lambda_m^\circ(\text{NaNO}_3) - \Lambda_m^\circ(\text{NaOH}) &= \Lambda_m^\circ(\text{H}^+) + 2\Lambda_m^\circ(\text{NO}_3^-) - \Lambda_m^\circ(\text{OH}^-)\end{aligned}$$

(b) is incorrect

(c)

$$\begin{aligned}\Lambda_m^\circ(\text{HNO}_3) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{NO}_3^-) \\ \Lambda_m^\circ(\text{NaOH}) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{OH}^-) \\ \Lambda_m^\circ(\text{NaNO}_3) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{NO}_3^-) \\ \hline \Lambda_m^\circ(\text{HNO}_3) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaNO}_3) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{OH}^-) = \Lambda_m^\circ(\text{H}_2\text{O})\end{aligned}$$

Hence, Options (a) and (c) are the correct choices.

Q. 23 What will happen during the electrolysis of aqueous solution of CuSO_4 by using platinum electrodes?

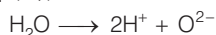
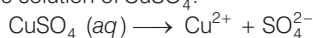
- (a) Copper will deposit at cathode (b) Copper will deposit at anode
(c) Oxygen will be released at anode (d) Copper will dissolve at anode

💡 Thinking Process

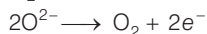
This problem is based on electrolysis of electrolytes.

Ans. (a, c)

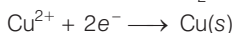
For electrolysis of aqueous solution of CuSO_4 .



At anode



At cathode



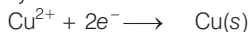
Q. 24 What will happen during the electrolysis of aqueous solution of CuSO_4 in the presence of Cu electrodes?

- (a) Copper will deposit at cathode (b) Copper will dissolve at anode
(c) Oxygen will be released at anode (d) Copper will deposit at anode

Ans. (a, b)

Electrolysis of CuSO_4 can be represented by two half cell reactions these occurring at cathode and anode respectively as

At cathode



At anode



Here, Cu will deposit at cathode while copper will dissolved at anode.

Hence, options (a) and (b) are the correct choices.

Q. 25 Conductivity κ , is equal to.....

(a) $\frac{1}{R} \cdot \frac{l}{A}$

(b) $\frac{G^*}{R}$

(c) Λ_m

(d) $\frac{l}{A}$

Ans. (a, b)

As we know that, conductance is reciprocal of resistance and conductivity is the conductance of 1 cm^3 of substance. Also, conductivity is reciprocal of resistivity.

$$\kappa = \frac{1}{\rho}$$

\therefore

$$R = \rho \cdot \frac{l}{A}$$

$$\rho = \frac{R \cdot A}{l} \Rightarrow \kappa = \frac{1}{\left(\frac{R \cdot A}{l}\right)}$$

$$\kappa = \frac{1}{R} \cdot \frac{l}{A} = \frac{1}{R} \times G^* = \frac{G^*}{R}$$

Hence, options (a) and (b) are the correct choices.

Q. 26 Molar conductivity of ionic solution depends on

- (a) temperature
(b) distance between electrodes
(c) concentration of electrolytes in solution
(d) surface area of electrodes

Ans. (a, c)

Molar conductivity is the conductivity due to ions furnished by one mole of electrolyte in solution. Molar conductivity of ionic solution depends on

(i) **Temperature** Molar conductivity of electrolyte solution increases with increase in temperature.

(iii) **Concentration of electrolytes in solution** As concentration of electrolyte increases, molar conductivity decreases.

$$\therefore \lambda = \frac{\kappa}{C}$$

Q. 27 For the given cell, $\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$

(a) Mg is cathode

(b) Cu is cathode

(c) The cell reaction is $\text{Mg} + \text{Cu}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Cu}$

(d) Cu is the oxidising agent

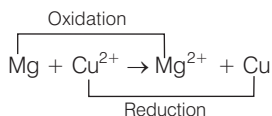
Ans. (b, c)

Left side of cell reaction represents oxidation half cell *i.e.*, oxidation of Mg and right side of cell represents reduction half cell reactions *i.e.*, reduction of copper.

(ii) Cu is reduced and reduction occurs at cathode.

(iii) Mg is oxidised and oxidation occurs at anode.

(iv) whole cell reaction can be written as



Hence, options (b) and (c) both are correct choices.

Short Answer Type Questions

Q. 28 Can absolute electrode potential of an electrode be measured ?

Ans. No, only the difference in potential between two electrodes can be measured. This is due to the reason that oxidation or reduction cannot occur alone. So, when we measure electrode potential of any electrode we have to take a reference electrode.

Q. 29 Can E_{cell}° or $\Delta_r G^{\circ}$ for cell reaction ever be equal to zero ?

Ans. No, otherwise the reaction become non-feasible.

The reaction is feasible only at $E_{\text{cell}}^{\circ} = \text{positive}$ or $\Delta_r G^{\circ} = \text{negative}$.

when $E^{\circ} = \Delta_r G^{\circ} = 0$ the reaction reaches at equilibrium.

Q. 30 Under what condition is $E_{\text{cell}} = 0$ or $\Delta_r G = 0$?

Ans. At the stage of chemical equilibrium in the cell.

$$\begin{aligned} E_{\text{cell}} &= 0 \\ \Delta_r G^{\circ} &= -n F E_{\text{cell}}^{\circ} \\ &= -n \times F \times 0 = 0 \end{aligned}$$

Q. 31 What does the negative sign in the expression $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ mean?

Ans. Greater the negative reactivity of standard reduction potential of metal greater is its reactivity. It means that Zn is more reactive than hydrogen. When zinc electrode will be connected to standard hydrogen electrode, Zn will get oxidised and H^+ will get reduced.

Thus, zinc electrode will be the anode of the cell and hydrogen electrode will be the cathode of the cell.

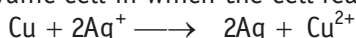
Q. 32 Aqueous copper sulphate solution and aqueous silver nitrate solution are electrolysed by 1 ampere current for 10 minutes in separate electrolytic cells. Will the mass of copper and silver deposited on the cathode be same or different? Explain your answer.

Ans. Different masses of Cu and Ag will be deposited at cathode. According to Faraday's second law of electrolysis amount of different substances liberated by same quantity of electricity passes through electrolyte solution is directly proportional to their chemical equivalent weight.

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

where, E_1 and E_2 have different values depending upon number of electrons required to reduce the metal ion. Thus, masses of Cu and Ag deposited will be different.

Q. 33 Depict the galvanic cell in which the cell reaction is

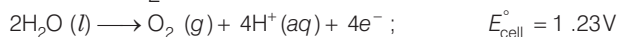
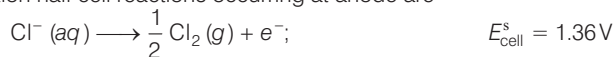


Ans. In a galvanic cell, oxidation half reaction is written on left hand side and reduction half reaction is on right hand side. Salt bridge is represented by parallel lines
 $\text{Cu} \mid \text{Cu}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$.

Q. 34 Value of standard electrode potential for the oxidation of Cl^- ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl^- oxidised at anode instead of water?

Ans. Under the condition of electrolysis of aqueous sodium chloride, oxidation of water at anode requires over potential. So, Cl^- is oxidized at anode instead of water.

Possible oxidation half cell reactions occurring at anode are

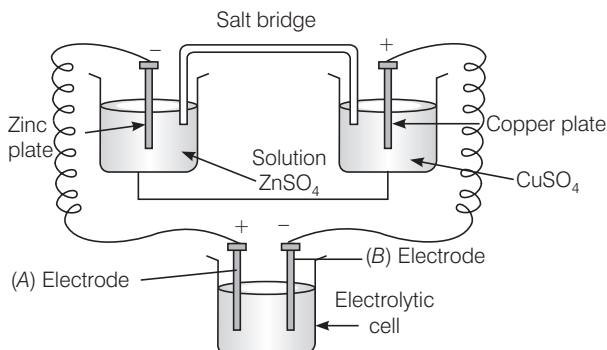


Species having lower E°_{cell} undergo oxidation first than the higher value but oxidation of H_2O to O_2 is kinetically so slow that it needs some overvoltage.

Q. 35 What is electrode potential?

Ans. The potential difference between the electrode and the electrolyte in an electrochemical cell is called electrode potential.

Q. 36 Consider the following diagram in which an electrochemical cell is coupled to an electrolytic cell. What will be the polarity of electrodes 'A' and 'B' in the electrolytic cell?



Ans. The cell drawn above represents electrochemical cell in which two different electrodes are fitted in their respective electrolytic solution and cell drawn at bottom represents electrolytic cell.

Cell representation can be represented as $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$.

Zn is losing electrons which are going towards electrode (A) and copper is accepting electron from electrode B. Hence,

Charge on electrode A = +

Charge on electrode B = -

Q. 37 Why is alternating current used for measuring resistance of an electrolytic solution?

Ans. Alternating current is used in electrolysis so that concentration of ions in the solution remains constant and exact value of resistance is measured.

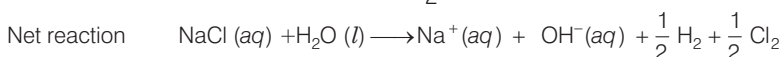
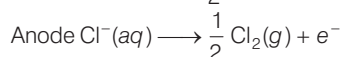
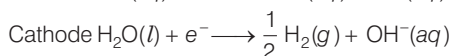
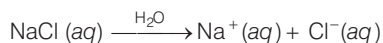
Q. 38 A galvanic cell has electrical potential of 1.1V. If an opposing potential of 1.1V is applied to this cell, what will happen to the cell reaction and current flowing through the cell ?

Ans. When an opposing potential of 1.1V is applied to a galvanic cell having electrical potential of 1.1V then cell reaction stops completely and no current will flow through the cell.

Q. 39 How will the pH of brine (aq NaCl solution) be affected when it is electrolysed?

Ans. The pH of the solution will rise as NaOH is formed in the electrolytic cell.

Chemical reaction occurring at cell when aqueous brine solution is electrolysed are as follows



Q. 40 Unlike dry cell, the mercury cell has a constant cell potential throughout its useful life. Why ?

Ans. Life time of any cell depends upon ions present in cell. Ions are not involved in the overall cell reaction of mercury cell. Hence, mercury cell has a constant cell potential throughout its useful life.

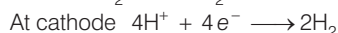
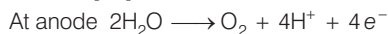
Q. 41 Solutions of two electrolytes A and B are diluted. The Λ_m of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte ? Justify your answer.

Ans. Strong electrolytes dissociate almost completely even on high concentration. Therefore, concentration of such solutions remain almost same on dilution. Electrolyte 'B' is stronger than 'A' because in 'B' the number of ions remains the same on dilution, but only interionic attraction decreases.

Therefore, Λ_m increases only 1.5 times. While in case of weak electrolyte on dilution, number of constituent ions increases.

Q. 42 When acidulated water (dil. H_2SO_4 solution) is electrolysed, with pH of the solution be affected ? Justify your answer.

Ans. Since pH of solution depends upon concentration of H^+ presence in solutions. pH of the solution will not be affected as $[\text{H}^+]$ remains constant.



Q. 43 In an aqueous solution how does specific conductivity of electrolytes change with addition of water?

Ans. Conductivity of solution due to total ions present in per unit volume of solution is known as specific conductivity. Specific conductivity decreases due to decrease in the number of ions per unit volume. We add water to aqueous solution, number of ions present in per unit volume decreases.

Q. 44 Which reference electrode is used to measure the electrode potential of other electrodes?

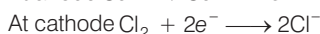
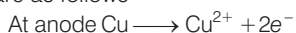
Ans. Standard hydrogen electrode (SHE) is the reference electrode whose electrode potential is taken to be zero. The electrode potential of other electrodes are measured with respect to it .

Q. 45 Consider a cell given below



Write the reactions that occur at anode and cathode.

Ans. Cell reaction represented in the question is composed of two half cell reactions. These reactions are as follows



Copper is getting oxidised at anode. Cl_2 is getting reduced at cathode.

Q. 46 Write the Nernst equation for the cell reaction in the Daniel cell. How will the E_{cell} be affected when concentration of Zn^{2+} ions is increased?

Ans. $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \left[\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}} \right]$$

$$E_{\text{cell}}^{\circ} = E_{\text{cell}} + \frac{0.0591}{2} \log \left[\frac{\text{Cu}^{2+}}{\text{Zn}^{2+}} \right]$$

According to this equation

E_{cell}° is directly dependent on concentration of Cu^{2+} and inversely dependent upon concentration of Zn^{2+} ions.

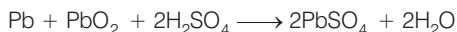
E_{cell} decreases when concentration of Zn^{2+} ions is increased.

Q. 47 What advantage do the fuel cells have over primary and secondary batteries ?

Ans. Primary batteries contain a limited amount of reactants and are discharged when the reactants have been consumed. Secondary batteries can be recharged but it takes a long time. Fuel cell runs continuously as long as the reactants are supplied to it and products are removed continuously.

Q. 48 Write the cell reaction of a lead storage battery when it is discharged. How does the density of the electrolyte change when the battery is discharged?

Ans. When a lead storage battery is discharged then the following cell reaction takes place



Density of electrolyte depends upon number of constituent ions present in per unit volume of electrolyte solution. In this case density of electrolyte decreases as water is formed and sulphuric acid is consumed as the product during discharge of the battery.

Q. 49 Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually?

Ans. In the case of CH_3COOH , which is a weak electrolyte, the number of ions increases on dilution due to an increase in degree of dissociation.



In case of strong electrolyte, the number of ions remains the same but the interionic attraction decreases.

Matching The Columns

Q. 50 Match the terms given in Column I with the units given in Column II.

Column I	Column II
A. Λ_m	1. S cm^{-1}
B. E_{cell}	2. m^{-1}
C. κ	3. $\text{S cm}^2 \text{ mol}^{-1}$
D. G^*	4. V

Ans. A. \rightarrow (3) B. \rightarrow (4) C. \rightarrow (1) D. \rightarrow (2)

Column I	Column II (Unit of parameter)
A. Λ_m	$\text{S cm}^2 \text{ mol}^{-1}$
B. E_{cell}	V
C. κ (conductivity)	S cm^{-1}
D. $G^* = \frac{l}{a}$	m^{-1}

Q. 51 Match the terms given in Column I with the items given in Column II.

Column I	Column II
A. Λ_m	1. Intensive property
B. E_{cell}°	2. Depends on number of ions/volume
C. κ	3. Extensive property
D. $\Delta_r G_{\text{cell}}$	4. Increases with dilution

Ans. A. \rightarrow (4) B. \rightarrow (1) C. \rightarrow (2) D. \rightarrow (3)

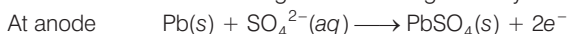
- A. Λ_m (molar conductivity) is the conductivity due to number of ions furnished by one mole of electrolyte. As dilution increases number of ions present in the solution increases hence molar conductivity increases.
- B. E_{cell}° of any atom/ion does not depend upon number of atom/ion, hence E_{cell}° of any atom/ion is an intensive properties.
- C. κ represents specific conductivity which depends upon number of ions present in per unit volume.
- D. $\Delta_r G_{\text{cell}}$ is an extensive property as it depends upon number of particles(species).

Q. 52 Match the items of Column I and Column II.

Column I	Column II
A. Lead storage battery	1. Maximum efficiency
B. Mercury cell	2. Prevented by galvanisation
C. Fuel cell	3. Gives steady potential
D. Rusting	4. Pb is anode, PbO ₂ is cathode

Ans. A. → (4) B. → (3) C. → (1) D. → (2)

A. Chemical reaction occurring on lead storage battery can be represented as



Thus, Pb is anode and PbO₂ is cathode.

B. Mercury cell does not include ions during their function hence produce steady current.

C. Fuel cell has maximum efficiency as they produce energy due to combustion reaction of fuel.

D. Rusting is prevented by corrosion.

Q. 53 Match the items of Column I and Column II.

Column I	Column II
A. κ	1. $I \times t$
B. \wedge_m	2. \wedge_m / \wedge_m^0
C. α	3. $\frac{\kappa}{C}$
D. Q	4. $\frac{G^*}{R}$

Ans. A. → (4) B. → (3) C. → (2) D. → (1)

A. Conductivity (κ) = $\frac{G^*}{R}$

B. Molar conductivity (\wedge_m) = $\frac{\kappa}{C}$

C. Degree of dissociation (α) = $\frac{\wedge_m}{\wedge_m^0}$

D. Charge $Q = I \times t$

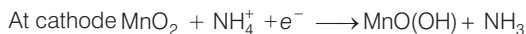
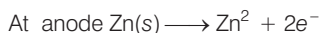
where, Q is the quantity of charge in coulomb when I ampere of current is passed through an electrolyte for t second.

Q. 54 Match the items of Column I and Column II.

Column I	Column II
A. Leclanche cell	1. Cell reaction $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$
B. Ni-Cd cell	2. Does not involve any ion in solution and is used in hearing aids.
C. Fuel cell	3. Rechargeable
D. Mercury cell	4. Reaction at anode, $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$
	5. Converts energy of combustion into electrical energy

Ans. A. → (4) B). → (3) C. → (1, 5) D. → (2)

A. Lechlanche cell The electrode reaction occurs at Lechlanche cell are



B. Ni-Cd cell is rechargeable. So, it has more life time.

C. Fuel cell produces energy due to combustion. So, fuel cell converts energy of combustion into electrical energy e.g., $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$

D. Mercury cell does not involve any ion in solution and is used in hearing aids.

Q. 55 Match the items of Column I and Column II on the basis of data given below

$$\begin{aligned} E_{\text{F}_2/\text{F}^{-}}^{\text{S}} &= 2.87\text{V}, E_{\text{Li}^{+}/\text{Li}}^{\text{S}} = -3.5\text{V}, \\ E_{\text{Au}^{3+}/\text{Au}}^{\text{S}} &= 1.4\text{V}, E_{\text{Br}_2/\text{Br}^{-}}^{\text{S}} = 1.09\text{V} \end{aligned}$$

Column I	Column II
A. F_2	1. Metal is the strongest reducing agent
B. Li	2. Metal ion which is the weakest oxidising agent
C. Au^{3+}	3. Non-metal which is the best oxidising agent
D. Br^{-}	4. Unreactive metal
E. Au	5. Anion that can be oxidised by Au^{3+}
F. Li^{+}	6. Anion which is the weakest reducing agent
G. F^{-}	7. Metal ion which is an oxidising agent

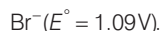
Ans. A. → (3) B. → (1) C. → (7) D. → (5) E. → (4) F. → (2) G. → (6)

A. F_2 is a non-metal and best oxidising agent because SRP of F_2 is + 2.87 V.

B. Li is a metal and strongest reducing agent because SRP of Li is – 3.05 V.

C. Au^{3+} is a metal ion which is an oxidising agent as SRP of Au^{3+} is +1.40 V.

D. Br^{-} is an anion that can be oxidised by Au^{3+} as Au^{3+} ($E^{\circ} = 1.40$) is greater than



E. Au is an unreactive metal.

F. Li^{+} is a metal ion having least value of SRP (– 3.05 V), hence it is the weakest oxidising agent.

G. F^{-} is an anion which is the weakest reducing agent as $\text{F}^{-} / \text{F}_2$ has low oxidation potential (–2.87 V).

Assertion and Reason

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both assertion and reason are true and the reason is the correct explanation of assertion.
- (b) Both assertion and reason are true and reason is not the correct explanation of assertion.
- (c) Assertion is true but the reason is false.
- (d) Both assertion and reason are false.
- (e) Assertion is false but reason is true.

Q. 56 Assertion (A) Cu is less reactive than hydrogen.

Reason (R) $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$ is negative.

Ans. (c) Assertion is true but the reason is false. Electrode potential of Cu^{2+}/Cu is + 0.34V and Electrode potential of $2\text{H}^{+}/\text{H}_2$ is 0.00 V.
Hence, correct reason is due to positive value of Cu^{2+}/Cu it loses electron to H^{+} and get reduced, while H_2 gas evolves out.

Q. 57 Assertion (A) E_{cell} should have a positive value for the cell to function.

Reason (R) $E_{\text{cathode}} < E_{\text{anode}}$

Ans. (c) Assertion is true but the reason is false. Feasibility of chemical reaction depends on Gibbs free energy which is related to E_{cell}° as
$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

When value of E_{cell}° is positive then ΔG° becomes negative. Hence, reaction becomes feasible.
Correct reason is $E_{\text{cathode}} > E_{\text{anode}}$.

Q. 58 Assertion (A) Conductivity of all electrolytes decreases on dilution.

Reason (R) On dilution number of ions per unit volume decreases.

Ans. (a) Both assertion and reason are correct and reason is the correct explanation of assertion.
Since, conductivity depends upon number of ions per unit volume. Therefore, the conductivity of all electrolytes decreases on dilution due to decrease in number of ions per unit volume.

Q. 59 Assertion (A) Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

Reason (R) For weak electrolytes degree of dissociation increases with dilution of solution.

Ans. (a) Assertion and reason are true and the reason is the correct explanation of the assertion.
Molar conductivity of weak electrolytic solution increases on dilution, because as we add excess water to increase the dilution degree of dissociation increases which lead to increase in number of ions in the solution. Thus, Λ_m show a very sharp increase.

Q. 60 Assertion (A) Mercury cell does not give steady potential.
Reason (R) In the cell reaction, ions are not involved in solution.

Ans. (e) Assertion is false but reason is true. Correct assertion is mercury cell gives steady potential.
Reason is correct as ions are not involved in cell reaction.

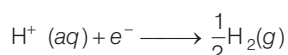
Q. 61 Assertion (A) Electrolysis of NaCl solution gives chlorine at anode instead of O_2 .

Reason (R) Formation of oxygen at anode requires over voltage.

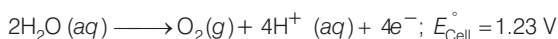
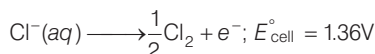
Ans. (a) Both assertion and reason are correct and reason is the correct explanation of assertion.

Explanation Electrolysis of NaCl is represented by following chemical reactions

At cathode



At anode



E_{cell}° for this reaction has lower value but formation of oxygen at anode requires over potential.

Q. 62 Assertion (A) For measuring resistance of an ionic solution an AC source is used.

Reason (R) Concentration of ionic solution will change if DC source is used.

Ans. (a) Both assertion and reason are correct and reason is the correct explanation of assertion.

Concentration of ionic solution changes on using DC current as a source of energy while on passing AC current concentration does not change. Hence, AC source is used for measuring resistance.

Q. 63 Assertion (A) Current stops flowing when $E_{cell} = 0$.

Reason (R) Equilibrium of the cell reaction is attained.

Ans. (a) Both assertion and reason are correct and reason is the correct explanation of assertion.

Current stop flowing when $E_{cell} = 0$

As at $E_{cell} = 0$ reaction reaches the equilibrium.

Q. 64 Assertion (A) $E_{\text{Ag}^+/\text{Ag}}$ increase with increase in concentration of Ag^+ ions.

Reason (R) $E_{\text{Ag}^+/\text{Ag}}$ has a positive value.

Ans. (b) Both assertion and reason are correct but reason is not the correct explanation of assertion.

$$E = E^\circ - \frac{0.0591}{1} \log \frac{1}{[\text{Ag}^+]}$$

$$E = E^\circ + 0.059 \log [\text{Ag}^+]$$

Thus, $E_{\text{Ag}^+/\text{Ag}}$ increases with increase in concentration of Ag^+ .

Q. 65 Assertion (A) Copper sulphate can be stored in zinc vessel.

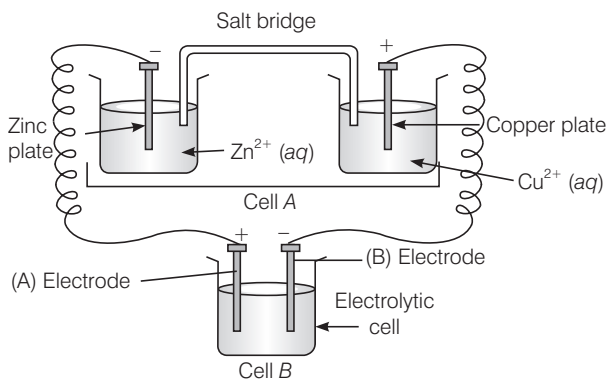
Reason (R) Zinc is less reactive than copper.

Ans. (d) Both assertion and reason are false.

Copper sulphate can't be stored in zinc vessel as zinc is more reactive than copper due to negative value of standard reduction potential of Zn.

Long Answer Type Questions

Q. 66 Consider the figure and answer the following questions.



(i) Cell 'A' has $E_{\text{cell}} = 2\text{V}$ and Cell 'B' has $E_{\text{cell}} = 1.1\text{V}$ which of the two cells 'A' or 'B' will act as an electrolytic cell. Which electrode reactions will occur in this cell?

(ii) If cell 'A' has $E_{\text{cell}} = 0.5\text{V}$ and cell 'B' has $E_{\text{cell}} = 1.1\text{V}$ then what will be the reactions at anode and cathode?

Thinking Process

This problem includes concept of electrochemical cell, electrolytic cell and charge on electrode. To solve this problem identify the charge on each electrode first.

Ans. (i) Cell 'B' will act as electrolytic cell due to its lesser value of emf.

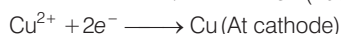
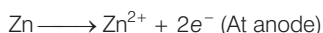
The electrode reactions will be



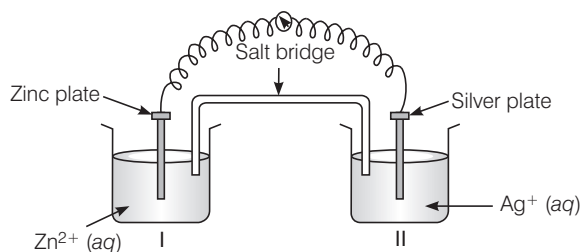
(ii) If cell 'B' has higher emf, it acts as galvanic cell.

Now it will push electrons into cell 'A'

In this case, the reactions will be

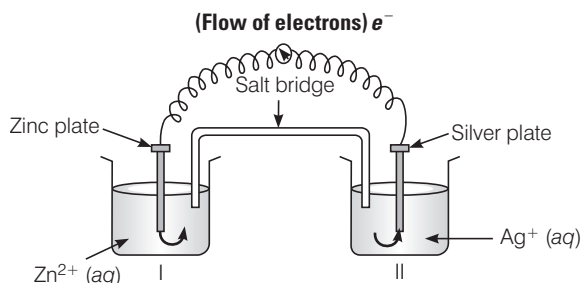


Q. 67 Consider figure from the above question and answer the questions (i) to (vi) given below.



- (i) Redraw the diagram to show the direction of electron flow.
- (ii) Is silver plate the anode or cathode?
- (iii) What will happen if salt bridge is removed?
- (iv) When will the cell stop functioning?
- (v) How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions?
- (vi) How will the concentration of Zn^{2+} ions and Ag^+ ions be affected after the cell becomes 'dead'?

Ans. (i) Electrons move from Zn to Ag as E° is more negative for Zn, so Zn undergoes oxidation and Ag^+ undergoes reduction.



- (ii) Ag is the cathode as it is the site of reduction where Ag^+ takes electrons from medium and deposit at cathode.
- (iii) Cell will stop functioning because cell potential drops to zero. At $E = 0$ reaction reaches equilibrium.

- (iv) When $E_{\text{cell}} = 0$ because at this condition reaction reaches to equilibrium.
- (v) Concentration of Zn^{2+} ions will increase and concentration of Ag^+ ions will decrease because Zn is converted into Zn^{2+} and Ag^+ is converted into Ag.
- (vi) When $E_{\text{cell}} = 0$ equilibrium is reached and concentration of Zn^{2+} ions and Ag^+ will not change.

Q. 68 What is the relationship between Gibbs free energy of the cell reaction in a galvanic cell and the emf of the cell? When will the maximum work be obtained from a galvanic cell?

Ans. If concentration of all reacting species is unity, then $E_{\text{cell}} = E_{\text{cell}}^{\circ}$ and $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$ where, $\Delta_r G^{\circ}$ is standard Gibbs energy of the reaction

$$E_{\text{cell}}^{\circ} = \text{emf of the cell}$$

$$nF = \text{charge passed}$$

If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly.

The reversibly work done by a galvanic cell is equal to decrease in its Gibbs energy.

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

As E_{cell} is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on n .

For reaction, $\text{Zn (s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu (s)}$ in a galvanic cell.

$$\Delta_r G = -2FE_{\text{cell}} \quad [\text{Here, } n = 2]$$

Chemical Kinetics

Multiple Choice Questions (MCQs)

Q. 1 The role of a catalyst is to change

- (a) Gibbs energy of reaction (b) enthalpy of reaction
(c) activation energy of reaction (d) equilibrium constant

Ans. (c) The role of a catalyst is to change the activation energy of reaction. This is done by either increasing or decreasing activation energy of molecule as catalyst are mainly of two types; +ve catalyst and –ve catalyst.

Note Catalyst are of two types one is positive catalyst which increases rate of reaction by decreasing activation energy and another is negative catalyst which decreases rate of reaction by increasing energy of activation.

Q. 2 In the presence of a catalyst, the heat evolved or absorbed during the reaction

- (a) increases (b) decreases
(c) remains unchanged (d) may increase or decrease

Ans. (c) In the presence of catalyst, the heat absorbed, or evolved during the reaction remains unchanged as there is no change in stability of reactant and product.

Q. 3 Activation energy of a chemical reaction can be determined by

- (a) determining the rate constant at standard temperature
(b) determining the rate constant at two temperatures
(c) determining probability of collision
(d) using catalyst

Ans. (b) Activation energy of a chemical reaction is related to rate constant of a reaction at two different temperatures i.e., k_1 and k_2 respectively

$$\ln \left(\frac{k_1}{k_2} \right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where,

E_a = activation energy

T_2 = higher temperature

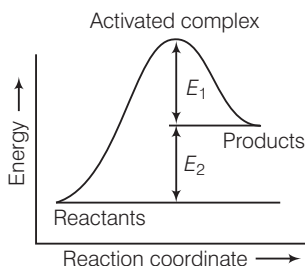
T_1 = lower temperature

k_1 = rate constant at temperature T_1

k_2 = rate constant at temperature T_2

This equation is known as Arrhenius equation.

Q. 4 Consider figure and mark the correct option.



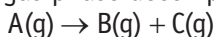
- (a) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant
- (b) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant
- (c) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product
- (d) Activation energy of backward reaction is E_1 and product is more stable than reactant

Ans. (a) Activation energy is the minimum energy required to convert reactant molecules to product molecules. Here, the energy gap between reactants and activated complex is sum of E_1 and E_2 .

$$\therefore \text{Activation energy} = E_1 + E_2$$

Product is less stable than reactant as energy of product is greater than the reactant.

Q. 5 Consider a first order gas phase decomposition reaction given below



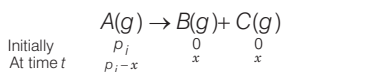
The initial pressure of the system before decomposition of A was p_i . After lapse of time 't' total pressure of the system increased by x units and became ' p_t '. The rate constant k for the reaction is given as

- (a) $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$
- (b) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$
- (c) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$
- (d) $k = \frac{2.303}{t} \log \frac{p_i}{p_i + x}$

💡 Thinking Process

This problem is based on first order rate of reaction. To solve this question determine the value of total pressure then calculate value of x followed by rate constant. where, x = pressure of gas transform to product

Ans. (b)

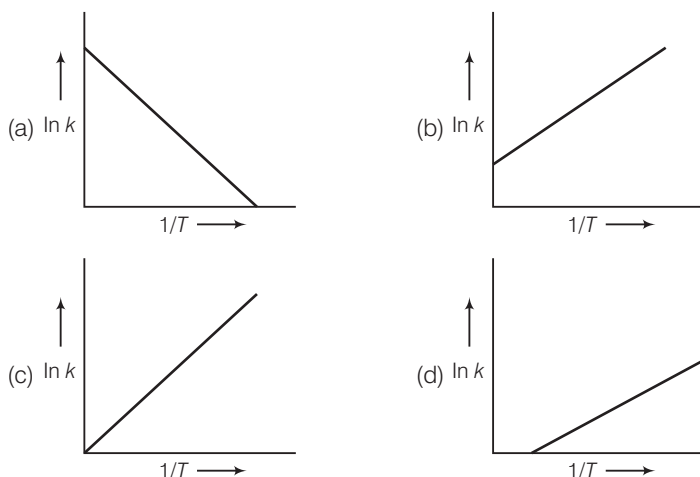


$$p_t = p_i - x + x + x = p_i + x$$

For first order reaction

$$\begin{aligned}
 x &= p_t - p_i \\
 k &= \frac{2.303}{t} \log \frac{p_i}{p_i - x} \\
 &= \frac{2.303}{t} \log \frac{p_i}{p_i - (p_t - p_i)} \\
 &= \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}
 \end{aligned}$$

Q. 6 According to Arrhenius equation rate constant k is equal to $A e^{-E_a/RT}$. Which of the following options represents the graph of $\ln k$ vs $\frac{1}{T}$?



Thinking Process

This problem includes graphical representation of Arrhenius equation. To solve this problem transform the Arrhenius equation into equation of straight line taking $\ln k$ on x -axis and $\frac{1}{T}$ on y -axis

Ans. (a) According to Arrhenius equation, $k = A e^{-E_a/RT}$

Taking log on both side $\ln k = \ln(A e^{-E_a/RT})$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A$$

$$y = m x + c$$

This equation can be related to equation of straight line as shown above.

From the graph, it is very clear that slope of the plot = $-\frac{E_a}{R}$ and intercept = $\ln A$.

Q. 7 Consider the Arrhenius equation given below and mark the correct option.

$$k = A e^{-\frac{E_a}{RT}}$$

- (a) Rate constant increases exponentially with increasing activation energy and decreasing temperature
- (b) Rate constant decreases exponentially with increasing activation energy and decreasing temperature
- (c) Rate constant increases exponentially with decreasing activation energy and decreasing temperature
- (d) Rate constant increases exponentially with decreasing activation energy and increasing temperature

Ans. (d) According to Arrhenius equation $k = A e^{-E_a/RT}$

Here,

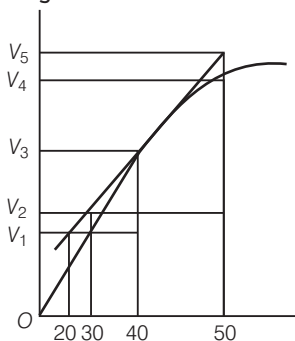
$$k \propto e^{-E_a}$$

$$k \propto e^{-\frac{1}{T}}$$

$$\propto e^T$$

which indicates that as activation energy decreases rate constant increases and as temperature increases rate of reaction increases.

Q. 8 A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in figure. On the basis of this mark the correct option.



- (a) Average rate upto 40 s is $\frac{V_3 - V_2}{40}$ (b) Average rate upto 40 s is $\frac{V_3 - V_2}{40 - 30}$
 (c) Average rate upto 40 s is $\frac{V_3}{40}$ (d) Average rate upto 40 s is $\frac{V_3 - V_1}{40 - 20}$

Ans. (c) $\text{Zn} + \text{Dil. HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2 \uparrow$

$$\text{Average rate of reaction} = \frac{\text{Change in concentration of H}_2}{\text{Change in time}} = \frac{V_3 - 0}{40 - 0} = \frac{V_3}{40}$$

Q. 9 Which of the following statements is not correct about order of a reaction?

- (a) The order of a reaction can be a fractional number
 (b) Order of a reaction is experimentally determined quantity
 (c) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction
 (d) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression

Ans. (c) Out of the given four statements, option (c) is not correct.

Order of Reaction

Order of reaction is equal to the sum of powers of concentration of the reactants in rate law expression.

For any chemical reaction

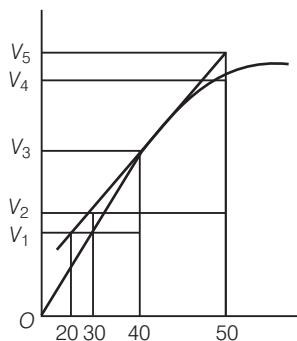


$$\text{Rate} = k [A]^x [B]^y$$

$$\text{Order} = x + y$$

Order of reaction can be a fraction also. Order of reaction is not always equal to sum of the stoichiometric coefficients of reactants in the balanced chemical equation. For a reaction it may or may not be equal to sum of stoichiometric coefficient of reactants.

Q. 10 Consider the graph given in figure. Which of the following options does not show instantaneous rate of reaction at 40s?



- (a) $\frac{V_5 - V_2}{50 - 30}$ (b) $\frac{V_4 - V_2}{50 - 30}$ (c) $\frac{V_3 - V_2}{40 - 30}$ (d) $\frac{V_3 - V_1}{40 - 20}$

Ans. (b) Reaction occurring at smallest time interval is known as instantaneous rate of reaction e.g., instantaneous rate of reaction at 40 s is rate of reaction during a small interval of time close to 40 s. Volume change during a small time interval close to 40 s i.e., 40 – 30 s, 50 – 40 s, 50 – 30 s, 40 – 20 s.

$$\text{Instantaneous rate of reaction} = \frac{\text{Change in volume}}{\text{Time interval close to 40 s}}$$

- (a) $r_{\text{inst}} (20 \text{ s}) = \frac{V_5 - V_2}{50 - 30}$ correct
 (b) $r_{\text{inst}} (20 \text{ s}) = \frac{V_4 - V_3}{50 - 30}$ incorrect, correct is $\frac{V_5 - V_3}{50 - 30}$
 (c) $r_{\text{inst}} (10 \text{ s}) = \frac{V_3 - V_2}{40 - 30}$ correct
 (d) $r_{\text{inst}} (20 \text{ s}) = \frac{V_3 - V_1}{40 - 20}$ correct

Q. 11 Which of the following statements is correct?

- (a) The rate of a reaction decreases with passage of time as the concentration of reactants decreases
 (b) The rate of a reaction is same at any time during the reaction
 (c) The rate of a reaction is independent of temperature change
 (d) The rate of a reaction decreases with increase in concentration of reactant (s)

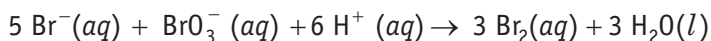
Ans. (a) Rate of reaction is defined as rate of decrease of concentration of any one of reactant with passage of time

$$\text{Rate of reaction} = \frac{\text{Rate of disappearance of reactant}}{\text{Time taken}}$$

$$r = \frac{-dx}{dt}$$

Thus, as the concentration of reactant decreases with passage of time, rate of reaction decreases.

Q. 12 Which of the following expressions is correct for the rate of reaction given below?



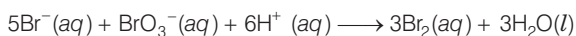
(a) $\frac{\Delta[\text{Br}^-]}{\Delta t} = 5 \frac{\Delta[\text{H}^+]}{\Delta t}$

(b) $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{6}{5} \frac{\Delta[\text{H}^+]}{\Delta t}$

(c) $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$

(d) $\frac{\Delta[\text{Br}^-]}{\Delta t} = 6 \frac{\Delta[\text{H}^+]}{\Delta t}$

Ans. (c) Given, chemical reaction is



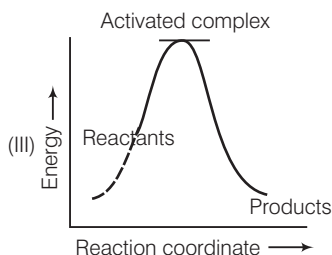
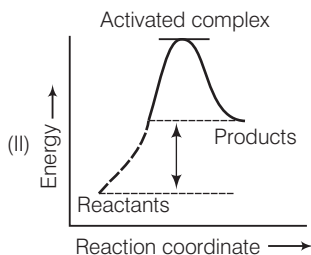
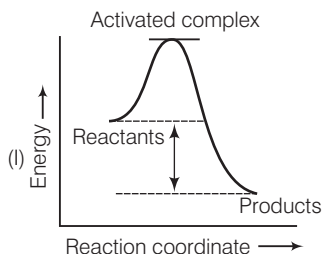
Rate law expression for the above equation can be written as

$$-\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{-1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{+1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t}$$

$$\Rightarrow \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{-5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$$

$$\Rightarrow \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$$

Q. 13 Which of the following graphs represents exothermic reaction?



(a) Only (I)

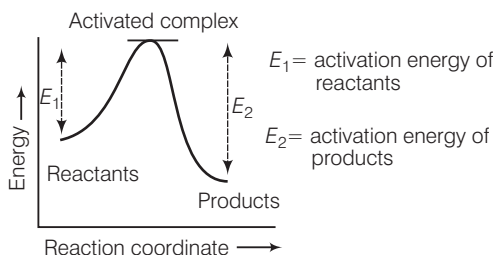
(b) Only (II)

(c) Only (III)

(d) (I) and (II)

Ans. (a) The chemical reaction in which energy is evolved during the reaction is known as exothermic reaction i.e., activation energy of product is greater than activation energy of reactants.

Here, only (I) denotes correct picture of exothermic reaction.



Q. 14 Rate law for the reaction $A + 2B \longrightarrow C$ is found to be

$$\text{Rate} = k[A][B]$$

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be..... .

- (a) the same
- (b) doubled
- (c) quadrupled
- (d) halved

Ans. (b) Rate law can be written as

$$\text{Rate} = k[A][B]$$

Rate of reaction w.r.t B is of first order.

$$R_1 = k[A][B]$$

when concentration of reactant 'B' is doubled then rate (R_2)

$$R_2 = k[A][2B]$$

$$R_2 = 2k[A][B]$$

$$R_2 = 2R_1$$

Therefore; as concentration of B is doubled keeping the concentration of A constant rate of reaction doubles.

Q. 15 Which of the following statements is incorrect about the collision theory of chemical reaction?

- (a) It considers reacting molecules or atoms to be hard spheres and ignores their structural features
- (b) Number of effective collisions determines the rate of reaction
- (c) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation
- (d) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective

Ans. (c) According to the postulates of collision theory there are following necessary conditions for any reaction to occur

- (i) Molecule should collide with sufficient threshold energy.
- (ii) Their orientation must be proper.
- (iii) The collision must be effective.

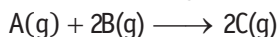
Q. 16 A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?

- (a) 1.26×10^{15} s
- (b) 2.52×10^{14} s
- (c) 2.52×10^{28} s
- (d) Infinite

Ans. (d) The time taken for half the reaction to complete. i.e., the time in which the concentration of a reactant is reduced to half of its original value is called half-life period of the reaction.

But it is impossible to perform 100% of the reaction. Whole of the substance never reacts because in every half-life, 50% of the substance reacts. Hence, time taken for 100% completion of a reaction is infinite.

Q. 17 Compounds 'A' and 'B' react according to the following chemical equation.



Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained. Choose the correct option for the rate equations for this reaction.

Experiment	Initial concentration of [A]/mol L ⁻¹	Initial concentration of [B]/mol L ⁻¹	Initial concentration of [C]/mol L ⁻¹ s ⁻¹
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

(a) Rate = $k[A]^2[B]$

(b) Rate = $k[A][B]^2$

(c) Rate = $k[A][B]$

(d) Rate = $k[A]^2[B]^0$

Ans. (b) Rate of reaction is change in concentration of reactant with respect to time.

$$r = k[A]^x[B]^y$$

$$\frac{\text{Rate of exp.1}}{\text{Rate of exp.2}} = \frac{[0.30]^x [0.30]^y}{[0.30]^x [0.60]^y}$$

$$\frac{0.10}{0.40} = \frac{[0.30]^y}{[0.60]^y}$$

$$\frac{1}{4} = \left[\frac{1}{2} \right]^y$$

$$\frac{1}{4} = \left[\frac{1}{2} \right]^y$$

$$\left[\frac{1}{2} \right]^2 = \left[\frac{1}{2} \right]^y$$

$$y = 2$$

$$\frac{\text{Rate of exp.1}}{\text{Rate of exp.3}} = \frac{[0.30]^x [0.30]^y}{[0.60]^x [0.30]^y}$$

$$\frac{0.10}{0.20} = \left[\frac{0.30}{0.60} \right]^x \left[\frac{0.30}{0.30} \right]^y$$

$$\frac{1}{2} = \left[\frac{1}{2} \right]^x [1]^y$$

$$\frac{1}{2} = \left[\frac{1}{2} \right]^x$$

$$x = 1$$

$$\text{Rate} = k[A]^x [B]^y$$

$$\text{Rate} = k[A]^1 [B]^2$$

i.e.,

∴

Q. 18 Which of the following statement is not correct for the catalyst?

(a) It catalyses the forward and backward reactions to the same extent

(b) It alters ΔG of the reaction

(c) It is a substance that does not change the equilibrium constant of a reaction

(d) It provides an alternate mechanism by reducing activation energy between reactants and products

Ans. (b) *Characteristics of catalyst*

- (a) It catalyses the forward and backward reaction to the same extent as it decreases energy of activation hence, increases the rate of both the reactions.
- (b) Since, reaction quotient is the relation between concentration of reactants and products. Hence, catalyst does not alter Gibbs free energy as it is related to reaction quotient. Thus, Gibbs free energy does not change during the reaction when catalyst is added to it.

$$\Delta G = -RT \ln Q$$

where, Q = reaction quotient

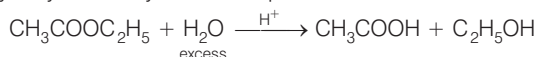
- (c) It doesn't alter equilibrium of reaction as equilibrium constant is also concentration dependent term.
- (d) It provides an alternate mechanism by reducing activation energy between reactants and products.

Q. 19 The value of rate constant of a pseudo first order reaction

- (a) depends on the concentration of reactants present in small amount
- (b) depends on the concentration of reactants present in excess
- (c) is independent of the concentration of reactants
- (d) depends only on temperature

Ans. (a, b) Pseudo first order reaction is a chemical reaction in which rate of reaction depends upon concentration of only one reactant while concentration of another reactant has no effect on rate of reaction.

e.g., hydrolysis of ethyl acetate in presence of excess of water

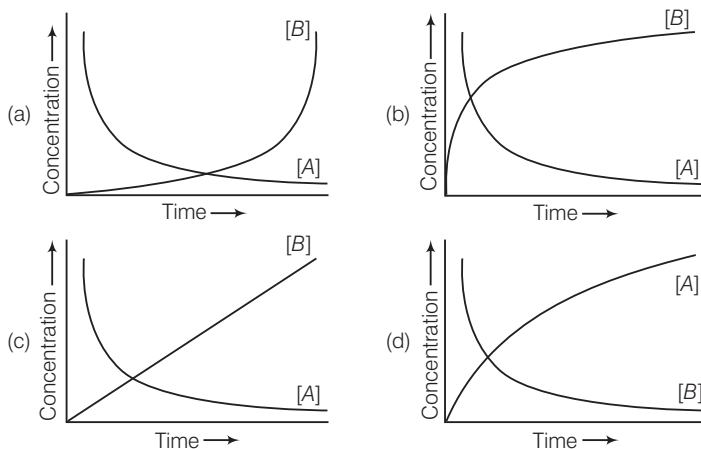


$$r = k [\text{CH}_3\text{COO C}_2\text{H}_5]^2 [\text{H}_2\text{O}]^0$$

Excess $[\text{H}_2\text{O}]$ can cause the independency of reaction on H_2O .

Hence, (a) is the correct choice.

Q. 20 Consider the reaction $\text{A} \longrightarrow \text{B}$. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?



Ans. (b) $A \longrightarrow B$

Concentration of reactants and products varies exponentially w.r.t time.

- (i) Concentration of reactant (here, A) decreases exponentially w.r.t time.
 - (ii) Concentration of product (here, B) increases exponentially w.r.t time
- new line correct graph representing the above reaction is (b).

Multiple Choice Questions (More Than One Options)

Q. 21 Rate law cannot be determined from balanced chemical equation if

- (a) reverse reaction is involved
- (b) it is an elementary reaction
- (c) it is a sequence of elementary reactions
- (d) any of the reactants is in excess

Ans. (a, c, d)

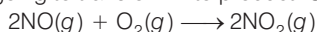
Rate law can be determined from balanced chemical equation if it is an elementary reaction.

Q. 22 Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?

- (a) Order is same as molecularity
- (b) Order is less than the molecularity
- (c) Order is greater than the molecularity
- (d) Molecularity can never be zero

Ans. (a, d)

For a balanced chemical equation of an elementary reaction order is same as molecularity and molecularity can never be zero. If molecularity of a reaction is considered to be zero it mean that no reactant is going to transform into product. Consider a chemical reaction.



Differential rate law expression can be written as

$$\frac{dR}{dt} = k[\text{NO}]^2 [\text{O}_2]$$

Here, molecularity = 3, order = 3

Q. 23 In any unimolecular reaction

- (a) only one reacting species is involved in the rate determining step
- (b) the order and the molecularity of slowest step are equal to one
- (c) the molecularity of the reaction is one and order is zero
- (d) both molecularity and order of the reaction are one

Ans. (a, b)

Since, the reaction is an unimolecular reaction. Hence, in the slowest step *i.e.*, in the rate determining step the only one reacting species is involved. Therefore, order of reaction and molecularity of reaction is equal to one.

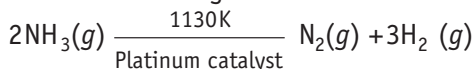
Q. 24 For a complex reaction

- (a) order of overall reaction is same as molecularity of the slowest step
- (b) order of overall reaction is less than the molecularity of the slowest step
- (c) order of overall reaction is greater than molecularity of the slowest step
- (d) molecularity of the slowest step is never zero or non-integer

Ans. (a, d)

- (a) For a complex reaction, order of overall reaction = molecularity of slowest step
As rate of overall reaction depends upon total number of molecules involved in slowest step of the reaction. Hence, molecularity of the slowest step is equal to order of overall reaction.
- (d) Since, the completion of any chemical reaction is not possible in the absence of reactants. Hence, slowest step of any chemical reaction must contain at least one reactant. Thus, molecularity of the slowest step is never zero or non-integer.

Q. 25 At high pressure the following reaction is zero order.



Which of the following options are correct for this reaction?

- (a) Rate of reaction = Rate constant
(b) Rate of the reaction depends on concentration of ammonia
(c) Rate of decomposition of ammonia will remain constant until ammonia disappears completely
(d) Further increase in pressure will change the rate of reaction

Ans. (a, c, d)

Given, chemical reaction is



At very high pressure reaction become independent of concentration of ammonia i.e., zero order reaction

Hence,

$$\text{Rate} = k[\rho_{\text{NH}_3}]^0$$

$$\text{Rate} = k$$

- (a) Rate of reaction = Rate constant
(b) Rate of decomposition of ammonia will remain constant until ammonia disappears completely.
(c) Since, formation of ammonia is a reversible process further increase in pressure will change the rate of reaction. According to Le-Chatelier principle increase in pressure will favour in backward reaction.

Q. 26 During decomposition of an activated complex

- (a) energy is always released (b) energy is always absorbed
(c) energy does not change (d) reactants may be formed

Ans. (a, d)

When the reactant molecules collide each other they lead to formation of an activated complex. It has highest energy among reactants, products and activated complex. When it decomposes to give product, energy is released and stability of product increases.

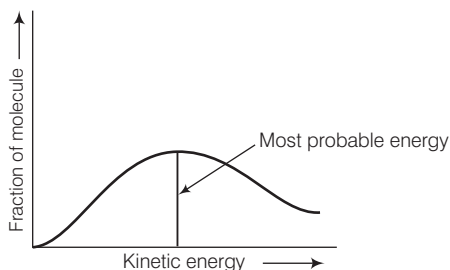
Since, the entire concentration of activated complex do not convert into products while, some activated complex may give reactants also.

Q. 27 According to Maxwell, Boltzmann distribution of energy.....

- (a) the fraction of molecules with most probable kinetic energy decreases at higher temperatures
(b) the fraction of molecules with most probable kinetic energy increases at higher temperatures
(c) most probable kinetic energy increases at higher temperatures
(d) most probable kinetic energy decreases at higher temperatures

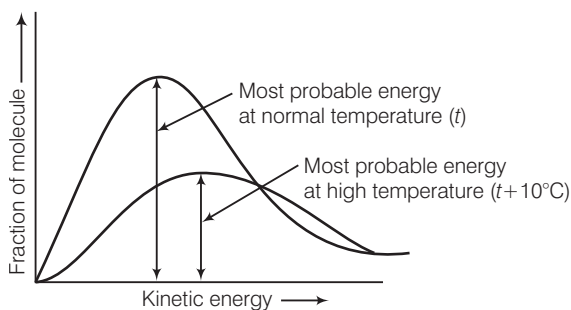
Ans. (a, c)

Distribution of kinetic energy may be described by plotting a graph of fraction of molecules versus kinetic energy.



Kinetic energy of maximum fraction of molecule is known as most probable kinetic energy. It is important to note that with increase of temperature, peak shifts forward but downward. This means that with increase of temperature,

- (i) most probable kinetic energy increases.
- (ii) the fractions of molecules possessing most probable kinetic energy decreases.

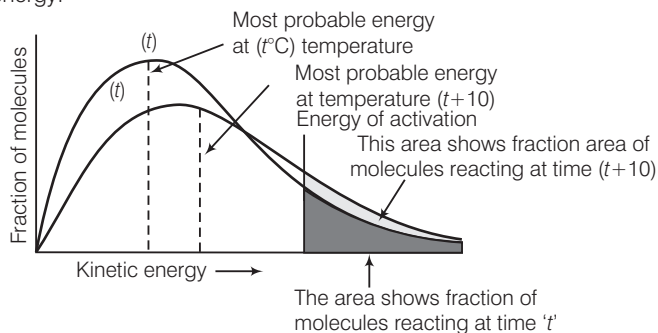


Q. 28 In the graph showing Maxwell, Boltzmann distribution of energy

- (a) area under the curve must not change with increase in temperature
- (b) area under the curve increases with increase in temperature
- (c) area under the curve decreases with increase in temperature
- (d) with increase in temperature curve broadens and shifts to the right hand side

Ans. (a, d)

According to Maxwell Boltzmann distribution curve, area under the curve must not change with increase in temperature. But with increase in temperature curve broadens and shift towards right hand side due to decrease in fraction of molecules having most probable kinetic energy.



Q. 29 Which of the following statements are in accordance with the Arrhenius equation?

- (a) Rate of a reaction increases with increase in temperature
- (b) Rate of a reaction increases with decrease in activation energy
- (c) Rate constant decreases exponentially with increase in temperature
- (d) Rate of reaction decreases with decrease in activation energy

Ans. (a, b)

Arrhenius equation can be written as $k = A.e^{\frac{-E_a}{RT}}$

$k \propto e^{-E_a}$ i.e., rate of reaction increases with decrease in activation energy.

$$k \propto e^{\frac{1}{T}}$$

$k \propto e^T$ i.e., rate of reaction increases with increase in temperature.

Q. 30 Mark the incorrect statements.

- (a) Catalyst provides an alternative pathway to reaction mechanism
- (b) Catalyst raises the activation energy
- (c) Catalyst lowers the activation energy
- (d) Catalyst alters enthalpy change of the reaction

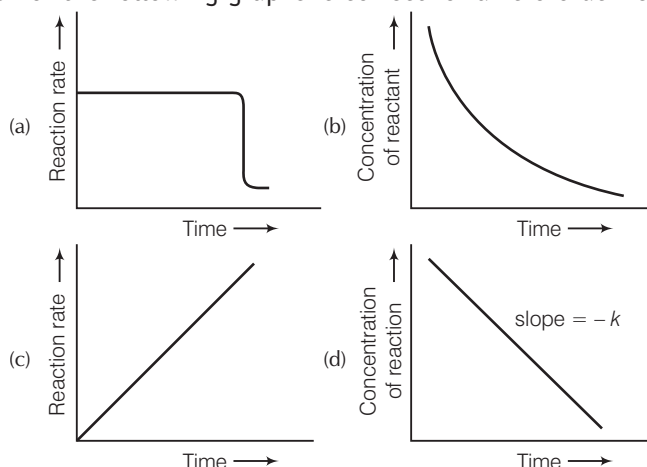
Ans. (b, d)

Function of Catalyst As the catalyst is added to the reaction medium rate of reaction increases by decreasing activation energy of molecule. Hence, it follows an alternative pathway.

Catalyst does not change the enthalpy change of reaction. Energy of reactant and product remain same in both catalysed and uncatalysed reaction.

Hence, (a) and (c) are correct statements.

Q. 31 Which of the following graphs is correct for a zero order reaction?



Thinking Process

This problem includes graphical representation of zero order reaction. To solve this problem.

- (i) Write rate equation of zero order reaction.
- (ii) Transform it into equation of straight line.
- (iii) Transform it into a curve representing rate versus time.

Ans. (a, d)

For a zero order reaction

$$[R] = (-k)t + [R]_0 \quad \dots(i)$$

$$\uparrow \quad \uparrow \quad \uparrow$$

$$y = m \times x + c$$

On comparing with Eq. of straight line

$$y = [R] \text{ concentration}$$

$$x = t \text{ time}$$

$$\text{Slope (m)} = -k \text{ rate constant}$$

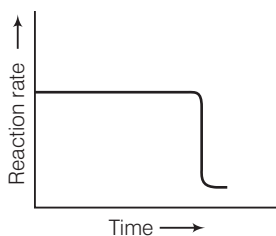
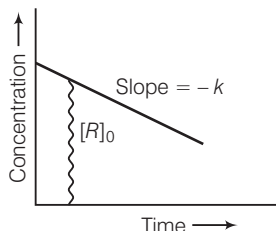
$$\text{Intercept (c)} = [R]_0 \text{ initial concentration}$$

On rearranging Eq. (i)

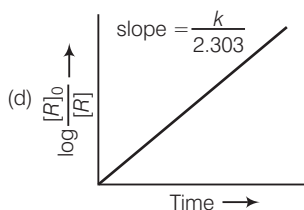
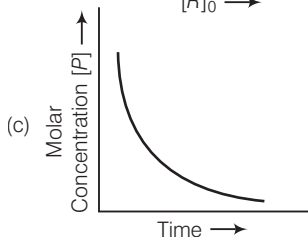
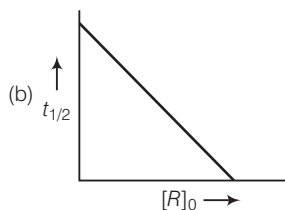
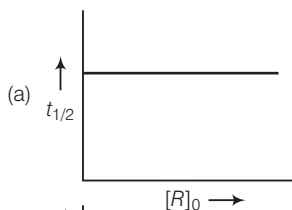
$$\frac{[R] - [R]_0}{t} = -k$$

$$\frac{[R] - [R]_0}{t} = -kt^0$$

$$\text{Rate} \propto t^0$$



Q. 32 Which of the following graphs is correct for a first order reaction?



Ans. (a, d)

For the first order reaction

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\frac{kt}{2.303} = \log \frac{[R]_0}{[R]}$$

$$\log \frac{[R]_0}{[R]} = \left(\frac{k}{2.303} \right) \times t + 0$$

$$\uparrow \quad \uparrow \quad \uparrow \quad \uparrow$$

$$y = m x + c$$

Correct plot of $\log \frac{[R]_0}{[R]}$ can be represented by (d)

where, $\text{slope} = \frac{k}{2.303}$

The time taken for any fraction of the reaction to complete is independent of the initial concentration. Let, us consider it for half of the reaction to complete.

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

For half-life

$$t = t_{1/2} \text{ and } x = \frac{a}{2}$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - \frac{a}{2}}$$

$$t_{1/2} = \frac{2.303}{k} \log 2$$

Half-life time

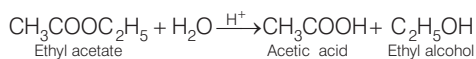
$$t_{1/2} = \frac{0.693}{k}$$

$t_{1/2}$ is independent of initial concentration. Hence, correct plot of $t_{1/2}$ and $[R]_0$ can be represented by a.

Short Answer Type Questions

Q. 33 State a condition under which a bimolecular reaction is kinetically first order reaction.

Ans. Presence of one of the reactants in excess, as in such a condition, its concentration remains constant and rate of such reaction depends upon concentration of one reactant only and reaction is known as pseudo first order reaction e.g., acid catalysed hydrolysis of ethyl acetate.



This reaction is bimolecular but is found to be of first order as experimentally it is observed that rate of reaction depends upon the concentration of ethyl acetate not on water as it is present in excess.

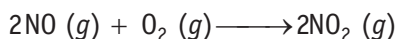
Q. 34 Write the rate equation for the reaction $2A + B \longrightarrow C$ if the order of the reaction is zero.

Ans. For reaction $2A + B \longrightarrow C$ if the rate of reaction is zero then it can be represented as

$$\text{Rate} = k [A]^0 [B]^0 = k$$

i.e., rate of reaction is independent of concentration of A and B.

Q. 35 How can you determine the rate law of the following reaction?



Ans. We can determine the rate of this reaction as a function of initial concentrations either by keeping the concentration of one of the reactants constant and changing the concentration of the other reactant or by changing the concentration of both the reactants. e.g., for the given reaction,

- (i) Keeping $[\text{O}_2]$ constant, if the concentration of NO is doubled, rate is found to become four times. This shows that,

$$\text{Rate} \propto [\text{NO}]^2$$

- (ii) Keeping $[\text{NO}]$ constant, if the concentration of $[\text{O}_2]$ is doubled, rate is also found to become double. This shows that,

$$\text{Rate} \propto [\text{O}_2]$$

Hence, overall rate law will be

$$\text{Rate} = k[\text{NO}]^2 [\text{O}_2]$$

$$\begin{aligned} \text{Rate law expression} \quad -\frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} &= -\frac{\Delta[\text{O}_2]}{\Delta t} \\ &= \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} \end{aligned}$$

Q. 36 For which type of reactions, order and molecularity have the same value?

Ans. If the reaction is elementary reaction then order and molecularity have same value because elementary reaction proceeds in a single step.

Q. 37 In a reaction if the concentration of reactant A is tripled, the rate of reaction becomes twenty seven times. What is the order of the reaction?

Ans. Rate of any elementary reaction can be represented as

$$r = k[A]^n$$

After changing concentration to its triple value $A = 3A$, r becomes $27r$

$$27r = k[3A]^n$$

$$\frac{r}{27r} = \frac{k[A]^n}{k[3A]^n}$$

$$\frac{1}{27} = \left[\frac{1}{3}\right]^n \Rightarrow \left[\frac{1}{3}\right]^3 = \left[\frac{1}{3}\right]^n$$

Hence, $n = 3$

Order of reaction is three.

Q. 38 Derive an expression to calculate time required for completion of zero order reaction.

Ans. For zero order reaction $[R] = [R]_0 - kt$

For completion of the reaction $[R] = 0$

$$\therefore t = \frac{[R]_0}{k}$$

Q. 39 For a reaction $A + B \longrightarrow \text{Products}$, the rate law is $\text{Rate} = k[A][B]^{3/2}$.

Can the reaction be an elementary reaction? Explain.

Ans. During an elementary reaction, the number of atoms or ions colliding to react is referred to as molecularity. Had this been an elementary reaction, the order of reaction with respect to B would have been 1, but in the given rate law it is $\frac{3}{2}$. This indicates that the reaction is not an elementary reaction. Hence, this reaction must be a complex reaction.

Q. 40 For a certain reaction large fraction of molecules has energy more than the threshold energy, yet the rate of reaction is very slow. Why?

Ans. According to collision theory apart from the energy considerations, the colliding molecules should also have proper orientation for effective collision.

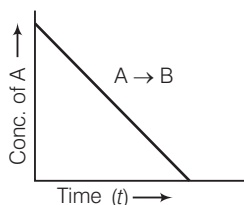
This condition might not be getting fulfilled in the reaction as it shows the number of reactants taking part in a reaction, which can never be zero.

Q. 41 For a zero order reaction will the molecularity be equal to zero? Explain.

Ans. No, the molecularity can never be zero or a fractional number as it shows the number of reactants taking part in a reaction which can never be zero.

Q. 42 For a general reaction $A \rightarrow B$, plot of concentration of A vs time is given in figure. Answer the following questions on the basis of this graph.

- What is the order of the reaction?
- What is the slope of the curve?
- What are the units of rate constant?



Ans. (i) For $A \longrightarrow B$ the given graph shows a zero order reaction. Mathematically represented as

$$[R] = -kt + [R]_0$$

Which is equation of straight line. Hence, reaction is a zero order.

(ii) Slope = $-k$

(iii) Unit of zero order reaction is $\text{mole L}^{-1} \text{s}^{-1}$.

Q. 43 The reaction between $\text{H}_2(g)$ and $\text{O}_2(g)$ is highly feasible yet allowing the gases to stand at room temperature in the same vessel does not lead to the formation of water. Explain.

Ans. Because activation energy of the reaction is very high at room temperature but at high temperature $\text{H}-\text{H}$ and $\text{O}-\text{O}$ bond break and colliding particles cross the energy barrier.

This is why reaction between $\text{H}_2(g)$ and $\text{O}_2(g)$ does not lead to formation of water at room temperature while keeping in the same vessel.

Q. 44 Why does the rate of a reaction increase with rise in temperature?

Ans. At higher temperatures, larger fraction of colliding particles can cross the energy barrier (*i.e.*, the activation energy) which leads to faster rate.

Q. 45 Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain.

Ans. For combustion reactions, activation energy of fuels is very high at room temperature. So, fuels do not burn by themselves at room temperature.

Q. 46 What is the probability of reaction with molecularity higher than three very rare?

Ans. According to collision theory, we know that to complete any chemical reaction there must be effective collision between reactant particles and they must have minimum sufficient energy. The probability of more than three molecules colliding simultaneously is very small. Hence, possibility of molecularity being three is very low.

Q. 47 Why does the rate of any reaction generally decreases during the course of the reaction?

Ans. The rate of a reaction depends on the concentration of the reactants. As the reaction proceeds in forward direction, concentration of reactant decreases and that of products increases. So, the rate of reaction generally decreases during the course of reaction.

Q. 48 Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example.

Ans. Thermodynamically the conversion of diamond to graphite is highly feasible but this reaction is very slow because its activation energy is high.
Hence, thermodynamic feasibility of the reaction alone cannot decide the rate of reaction.

Q. 49 Why in the redox titration of KMnO_4 vs oxalic acid, we heat oxalic acid solution before starting the titration?

Ans. As we know with increase in temperature rate of reaction increases, Hence, we heat oxalic acid solution before starting of titration to increase the rate of decolourisation.

Q. 50 Why can't molecularity of any reaction be equal to zero?

Ans. Molecularity of the reaction is the number of molecules taking part in an elementary step. For this we require at least a single molecule leading to the value of minimum molecularity of one. Hence, molecularity of any reaction can never be equal to zero.

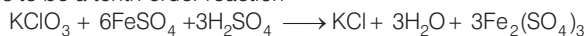
Q. 51 Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

Ans. A complex reaction occurs through a number of steps *i.e.*, elementary reactions. Number of molecules involved in each elementary reaction may be different, *i.e.*, the molecularity of each step may be different. Therefore, it is meaningless to talk of molecularity of the overall complex reaction.

On the other hand, order of complex reaction depends upon the molecularity of the slowest step. Hence, it is not meaningless to talk of the order of a complex reaction.

Q. 52 Why can we not determine the order of a reaction by taking into consideration the balanced chemical equation?

Ans. Balanced chemical equation often leads to incorrect order or rate law. e.g., the following reaction seems to be a tenth order reaction

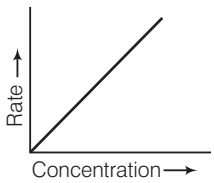
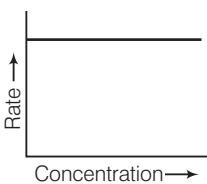
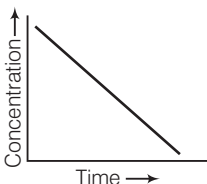
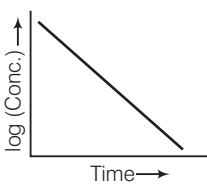


This is actually a second order reaction. Actually the reaction is complex and occurs in several steps. The order of such reaction is determined by the slowest step in the reaction mechanism.

Order is determined experimentally and is confined to the dependence of observed rate of reaction on the concentration of reactants.

Matching The Columns

Q. 53 Match the graph given in Column I with the order of reaction given in Column II. More than one item in Column I may link to the same item of Column II.

Column I		Column II
A.		
B.		1. First order
C.		2. Zero order
D.		

Ans. A. → (1) B. → (2) C. → (2) D. → (1)

For zero order reaction rate equation may be written as

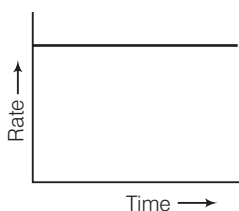
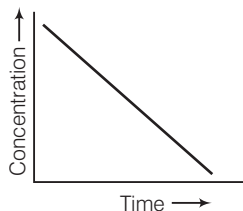
$$[R] = -kt + [R_0] \quad \dots(i)$$

Which denotes a straight line equation similar to $y = mx + c$

On transforming (i)

$$\frac{[R] - [R_0]}{t} = -k$$

$$k = \frac{[R_0] - [R]}{t}$$



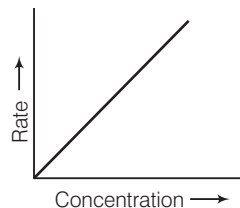
$$k = \text{Rate}$$

$$\text{Rate} = k \cdot [t]^0$$

$$\text{Rate} \propto [t]^0$$

For a first order reaction $\frac{dx}{dt} \propto [\text{concentration}]^1$

∴ Graph between rate and concentration may be drawn as



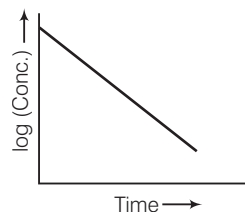
$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\frac{kt}{2.303} = \log \left[\frac{R^0}{R} \right]$$

$$\frac{kt}{2.303} = \log[R]_0 - \log[R]$$

$$\log[R] = \left(\frac{-k}{2.303} \right) t + \log[R]_0$$

Slope Intercept



Q. 54 Match the statements given in Column I and Column II.

Column I	Column II
A. Catalyst alters the rate of reaction	1. Cannot be fraction or zero
B. Molecularity	2. Proper orientation is not there
C. Second half-life of first order reaction	3. By lowering the activation energy
D. $e^{-E_a/RT}$	4. Is same as the first
E. Energetically favourable reactions are sometimes slow	5. Total probability is one
F. Area under the Maxwell, Boltzmann curve is constant	6. Refers to the fraction of molecules with energy equal to or greater than activation energy

Ans. A. → (3) B. → (1) C. → (4) D. → (6) E. → (2) F. → (5)

1. Catalyst alters the rate of reaction by lowering activation energy.
2. Molecularity can't be fraction or zero. If molecularity is zero, then reaction is not possible.
3. Second half-life of first order reaction is same as first because half-life time is temperature independent.
4. $e^{-E_a/RT}$ refers to the fraction of molecules with kinetic energy equal to or greater than activation energy.
5. Energetically favourable reactions are sometimes slow due to improper orientation of molecule cause some ineffective collision of molecules.
6. Area under the Maxwell, Boltzmann curve is constant because total probability of molecule taking part in a chemical reaction is equal to one.

Q. 55 Match the items of Column I and Column II.

Column I	Column II
A. Diamond	1. Short interval of time
B. Instantaneous rate	2. Ordinarily rate of conversion is imperceptible
C. Average rate	3. Long duration of time

Ans. A. → (2) B. → (1) C. → (3)

1. Diamond can't be converted into graphite under ordinary condition.
2. Instantaneous rate of reaction completes at very short span of time.
3. Average rate of reaction occurs to a long duration of time.

Q. 56 Match the items of Column I and Column II.

Column I	Column II
A. Mathematical expression for rate of reaction	1. Rate constant
B. Rate of reaction for zero order reaction is equal to	2. Rate law
C. Units of rate constant for zero order reaction is same as that of	3. Order of slowest step
D. Order of a complex reaction is determined by	4. Rate of reaction

Ans. A. → (2) B → (1) C → (4) D → (3)

1. Mathematical expression for rate of reaction is known as rate law.
2. Rate of reaction for zero order reaction is equal to rate constant

$$r = k[A]^0$$

$$\therefore r = k$$
3. Unit of rate of reaction is same as that of rate of reaction.
4. Order of complex reaction is determined by rate of a reaction, which is slowest.

Assertion and Reason

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both assertion and reason are correct and the reason is correct explanation of assertion.
- (b) Both assertion and reason are correct, but reason does not explain assertion.
- (c) Assertion is correct, but reason is incorrect.
- (d) Both assertion and reason are incorrect.
- (e) Assertion is incorrect, but reason is correct.

Q. 57 Assertion (A) Order of the reaction can be zero or fractional.

Reason (R) We cannot determine order from balanced chemical equation.

Ans. (b) Both assertion and reason are correct, but the reason is not the correct explanation of assertion.

Order of reaction can be zero or fractional as order of reaction is directly related to sum of power of reactants. Reason is a correct statement but not correct explanation.

Q. 58 Assertion (A) Order and molecularity are same.

Reason (R) Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

Ans. (e) Assertion is incorrect and reason is correct.

Order and molecularity may or may not be same as order of reaction is sum of power of reactant which can be determined experimentally. But molecularity is sum of stoichiometric coefficient of rate determining elementary step.

Q. 59 Assertion (A) The enthalpy of reaction remains constant in the presence of a catalyst.

Reason (R) A catalyst participating in the reaction forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.

Ans. (a) Assertion and reason both are correct and reason is the correct explanation of assertion.

Enthalpy of reaction *i.e.*, difference of total enthalpy of reactants and product remains constant in the presence of a catalyst. As a catalyst participating in the reaction forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains same.

Q. 60 Assertion (A) All collision of reactant molecules lead to product formation.

Reason (R) Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

Ans. (e) Assertion is incorrect, but reason is correct.

Correct assertion is "only effective collision lead to formation of product." Reason defines correct meaning of effective collision, and criterion of collision theory for completion of reaction.

Only those collisions in which molecules have correct orientation and sufficient energy lead to formation of product.

- Q. 61** Assertion (A) Rate constant determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.
Reason (R) Reactant molecules undergo chemical change irrespective of their orientation during collision.

Ans. (c) Assertion is correct, but reason is incorrect.

Rate constant determined from Arrhenius equation are fairly accurate for simple and complex molecules because only those molecules which have proper orientation during collision (*i.e.*, effective collision) and sufficient kinetic energy lead the chemical change.

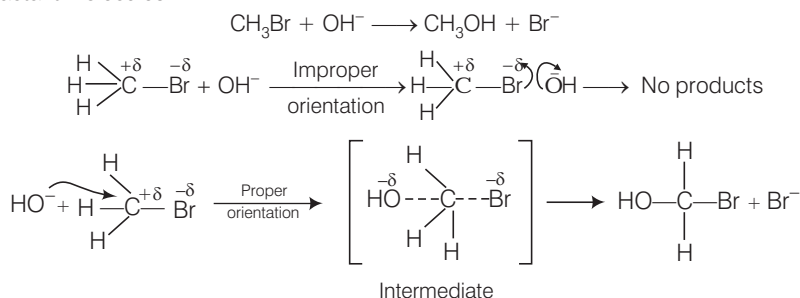
Long Answer Type Questions

- Q. 62** All energetically effective collisions do not result in a chemical change. Explain with the help of an example.

Ans. Only effective collision lead to the formation of products. It means that collisions in which molecules collide with sufficient kinetic energy (called threshold energy = activation energy + energy possessed by reacting species).

And proper orientation lead to a chemical change because it facilitates the breaking of old bonds between (reactant) molecules and formation of the new ones *i.e.*, in products.

e.g., formation of methanol from bromomethane depends upon the orientation of the reactant molecules.



The proper orientation of reactant molecules leads to bond formation whereas improper orientation makes them simply back and no products are formed.

To account for effective collisions, another factor P (probability or steric factor) is introduced
 $K = PZ_{AB}e^{-E_a/RT}$.

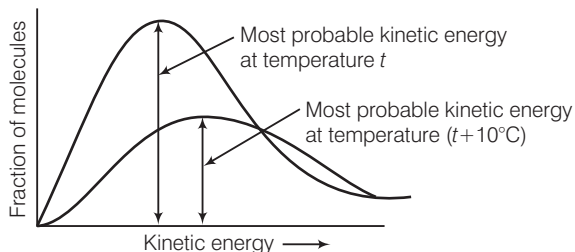
- Q. 63** What happens to most probable kinetic energy and the energy of activation with increase in temperature?

Ans. Kinetic energy is directly proportional to the absolute temperature and the number of molecules possessing higher energies increases with increase in temperature, *i.e.*, most probable kinetic energy increases with increase in temperature.

Energy of activation is related to temperature by the following Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Thus, it also shows an increase with rise in temperature.



Q. 64 Describe how does the enthalpy of reaction remain unchanged when a catalyst is used in the reaction?

Ans. A catalyst is a substance which increases the speed of a reaction without itself undergoing any chemical change.

According to "intermediate complex formation theory" reactants first combine with the catalyst to form an intermediate complex which is short-lived and decomposes to form the products and regenerating the catalyst.

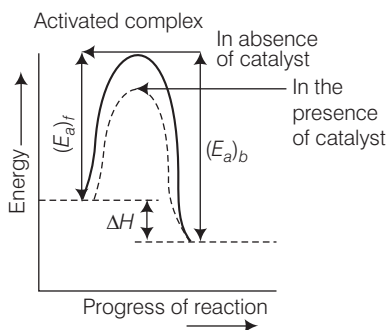
The intermediate formed has much lower potential energy than the intermediate complex formed between the reactants in the absence of the catalyst.

Thus, the presence of catalyst lowers the potential energy barrier and the reaction follows a new alternate pathway which require less activation energy.

We know that, lower the activation energy, faster is the reaction because more reactant molecules can cross the energy barrier and change into products.

Enthalpy, ΔH is a state function. Enthalpy of reaction, i.e., difference in energy between reactants and product is constant, which is clear from potential energy diagram.

Potential energy diagram of catalysed reaction is given as



Q. 65 Explain the difference between instantaneous rate of a reaction and average rate of a reaction.

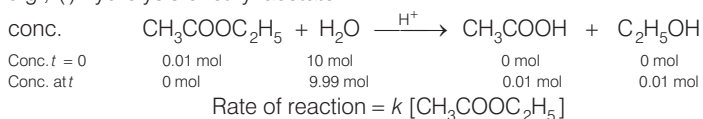
Ans. The difference between instantaneous rate of reaction and average rate of a reaction are as below

Instantaneous rate of reaction	Average rate of reaction
(i) It occurs within a short span of time.	It occurs during a long interval of time.
(ii) It can't be calculated for multistep reaction.	It can be calculated for multistep reaction.
(iii) It can be calculated for elementary reaction.	It can be calculated for elementary reaction.

Q. 66 With the help of an example explain what is meant by pseudo first order reaction.

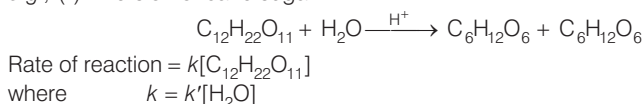
Ans. A reaction in which one reactant is present in large amount and its concentration does not get altered during the course of the reaction, behaves as first order reaction. Such reaction is called pseudo first order reaction.

e.g., (i) hydrolysis of ethyl acetate



where, $k = k' [\text{H}_2\text{O}]$

e.g., (ii) inversion of cane sugar



Surface Chemistry

Multiple Choice Questions (MCQs)

Q. 1 Which of the following process does not occur at the interface of phases?

- (a) Crystallisation (b) Heterogeneous catalysis
(c) Homogeneous catalysis (d) Corrosion

Ans. (c) Homogeneous catalysis does not occur at the interface of phases as in case of homogeneous catalysis reactant and catalyst have same phase and their distribution is uniform throughout.

Q. 2 At the equilibrium position in the process of adsorption

- (a) $\Delta H > 0$ (b) $\Delta H = T\Delta S$ (c) $\Delta H > T\Delta S$ (d) $\Delta H < T\Delta S$

Ans. (b) As we know that, at equilibrium $\Delta G = 0$

$$\Delta H - T\Delta S = 0$$

$$\Delta H = T\Delta S$$

Hence, at equilibrium enthalpy change is equal to product of temperature and entropy change.

Q. 3 Which of the following interface cannot be obtained?

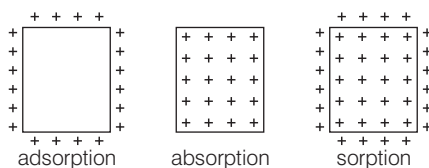
- (a) Liquid-liquid (b) Solid-liquid
(c) Liquid-gas (d) Gas-gas

Ans. (d) Gas-gas interface can not be obtained as they are completely miscible in nature. e.g., air is a mixture of various gases such as, O_2 , N_2 , CO_2 etc.

Q. 4 The term 'sorption' stands for

- (a) absorption (b) adsorption
(c) Both absorption and adsorption (d) desorption

Ans. (c) Sorption stands for both absorption and adsorption. We can understand this by using following figures



Q. 5 Extent of physisorption of a gas increases with

- (a) increase in temperature
- (b) decrease in temperature
- (c) decrease in surface area of adsorbent
- (d) decrease in strength of van der Waals' forces

Ans. (b) Extent of physisorption of a gas increases with decrease in temperature. Because in physisorption particles are held to the surface by weak van der Waals' force of attraction hence on increasing temperature they get desorbed easily.

Q. 6 Extent of adsorption of adsorbate from solution phase increases with

- (a) increase in amount of adsorbate in solution
- (b) decrease in surface area of adsorbent
- (c) increase in temperature of solution
- (d) decrease in amount of adsorbate in solution

Ans. (a) Extent of adsorption of adsorbate from solution phase increases with increase in amount of adsorbate in solution. As amount of adsorbate in the solution increases interaction of adsorbate with adsorbent increases which lead to increase in extent of adsorption.

Q. 7 Which one of the following is not applicable to the phenomenon of adsorption?

- (a) $\Delta H > 0$
- (b) $\Delta G < 0$
- (c) $\Delta S < 0$
- (d) $\Delta H < 0$

Ans. (a) For phenomenon of adsorption $\Delta H < 0$, i.e., enthalpy change during phenomenon of adsorption is negative because during adsorption, there is always a decrease in residual forces of the surface which lead to decrease in surface energy which appears as heat.

So, adsorption is an exothermic process and $\Delta H < 0$.

Q. 8 Which of the following is not a favourable condition for physical adsorption?

- (a) High pressure
- (b) Negative ΔH
- (c) Higher critical temperature of adsorbate
- (d) High temperature

Ans. (d) Physisorption is a process in which adsorbate get adsorbed on the adsorbent surface by weak van der Waals' force of attraction. On increasing temperature the interaction between adsorbate and adsorbent becomes weak and adsorbate particles get desorbed.

Q. 9 Physical adsorption of a gaseous species may change to chemical adsorption with

- (a) decrease in temperature
- (b) increase in temperature
- (c) increase in surface area of adsorbent
- (d) decrease in surface area of adsorbent

Ans. (b) On increasing temperature physisorption changes to chemisorption. As temperature increases, energy of activation of adsorbate particles increases which lead to formation of chemical bond between adsorbate and adsorbent.

Hence, physisorption transform into chemisorption.

Q. 10 In physisorption adsorbent does not show specificity for any particular gas because

- (a) involved van der Waals' forces are universal
- (b) gases involved behave like ideal gases
- (c) enthalpy of adsorption is low
- (d) it is a reversible process

Ans. (a) In physisorption adsorbent does not show specificity for any particular gas because involved van der Waals' forces are universal. It means extent of van der Waals' interaction between adsorbate and adsorbent is constant for all gases.

Q. 11 Which of the following is an example of absorption?

- (a) Water on silica gel
- (b) Water on calcium chloride
- (c) Hydrogen on finely divided nickel
- (d) Oxygen on metal surface

Ans. (b) Absorption means penetration of adsorbate molecules into the bulk of the adsorbent e.g., water on calcium chloride. When water is spread over calcium chloride, water get penetrate into bulk of the calcium chloride.

Q. 12 On the basis of data given below predict which of the following gases shows least adsorption on a definite amount of charcoal?

Gas	CO ₂	SO ₂	CH ₄	H ₂
Critical temp./K	304	630	190	33

(a) CO₂

(b) SO₂

(c) CH₄

(d) H₂

Thinking Process

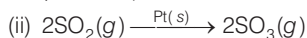
*This problem includes concept of extent of conjugation and critical temperature.
Extent of adsorption is directly related to critical temperature of gases.*

Ans. (d) Lesser the value of critical temperature of gases lesser will be the extent of adsorption. Here H₂ has lowest value of critical temperature, i.e., 33.
Hence, hydrogen gas shows least adsorption on a definite amount of charcoal.

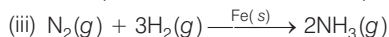
Q. 13 In which of the following reactions heterogeneous catalysis is involved?

- (i) $2\text{SO}_2(g) + \text{O}_2(g) \xrightarrow{\text{NO}(g)} 2\text{SO}_3(g)$
 - (ii) $2\text{SO}_2(g) \xrightarrow{\text{Pt}(s)} 2\text{SO}_3(g)$
 - (iii) $\text{N}_2(g) + 3\text{H}_2(g) \xrightarrow{\text{Fe}(s)} 2\text{NH}_3(g)$
 - (iv) $\text{CH}_3\text{COOCH}_3(l) + \text{H}_2\text{O}(l) \xrightarrow{\text{HCl}(l)} \text{CH}_3\text{COOH}(aq) + \text{CH}_3\text{OH}(aq)$
- (a) (ii), (iii) (b) (ii), (iii) and (iv) (c) (i), (ii) and (iii) (d) (iv)

Ans. (c) (i) Reaction in which catalyst is in different phase than other (reactants and products) is known as heterogeneous catalysis.



Here, reactant SO₂ and product SO₃ are in gaseous phase while platinum is in solid phase. So, this reaction represents a heterogeneous catalysis.



Similarly, here N₂ and H₂ reactants are in gaseous phase while NH₃ is in solid phase. Whereas in other reactions catalyst is in same phase with reactant(s) and product(s).

Q. 14 At high concentration of soap in water, soap behaves as

- (a) molecular colloid
- (b) associated colloid
- (c) macromolecular colloid
- (d) lyophilic colloid

Ans. (b) **Associated colloid** At high concentration of soap in water, soap particles present in the solution get associated around and lead to formation of associated colloid.

Q. 15 Which of the following will show Tyndall effect?

- (a) Aqueous solution of soap below critical micelle concentration
- (b) Aqueous solution of soap above critical micelle concentration
- (c) Aqueous solution of sodium chloride
- (d) Aqueous solution of sugar

Ans. (b) Aqueous solution of soap above critical micelle concentration lead to formation of colloidal solution. Tyndall effect is a characteristic of colloidal solution in which colloidal particles show a coloured appearance when sunlight is passes through it and seen from the perpendicular side.

Q. 16 Method by which lyophobic sol can be protected.

- (a) By addition of oppositely charged sol
- (b) By addition of an electrolyte
- (c) By addition of lyophilic sol
- (d) By boiling

Ans. (c) Lyophobic sol can be protected by addition of lyophilic sol. As lyophobic sols are readily precipitated on addition of small amount of electrolytes or shaking, or heating hence they are made stable by adding lyophilic sol which stabilises the lyophobic sols.

Q. 17 Freshly prepared precipitate sometimes gets converted to colloidal solution by

- (a) coagulation
- (b) electrolysis
- (c) diffusion
- (d) peptisation

Ans. (d) Freshly prepared precipitate sometimes gets converted to colloidal solution by peptisation. Peptisation is a process in which by addition of a suitable peptising agent precipitate gets converted into colloidal solution.

Q. 18 Which of the following electrolytes will have maximum coagulating value for Ag/Ag^+ sol?

- (a) Na_2S
- (b) Na_3PO_4
- (c) Na_2SO_4
- (d) NaCl

🔑 Thinking Process

This problem includes concept of Hardy-Schulze law. According to which higher charge on oppositely charge ion of electrolyte decide the coagulating power of colloid.

Ans. (b) According to Hardy-Schulze law, greater the charge on anion greater will be its coagulating power.

Electrolytes	Anionic part	Charge on anion
Na_2S	S^{2-}	2
Na_3PO_4	PO_4^{3-}	3
Na_2SO_4	SO_4^{2-}	2
NaCl	Cl^-	1

Here, PO_4^{3-} have highest charge. Hence, PO_4^{3-} have highest coagulating power.

Q. 19 A colloidal system having a solid substance as a dispersed phase and a liquid as a dispersion medium is classified as

- (a) solid sol (b) gel (c) emulsion (d) sol

Ans. (d) Sol is a colloidal system in which solid substance is a dispersed phase and a liquid is a dispersion medium. *e.g.*, paint, cell fluids etc.

In paints solid colouring particles are dissolved in liquid dispersion medium.

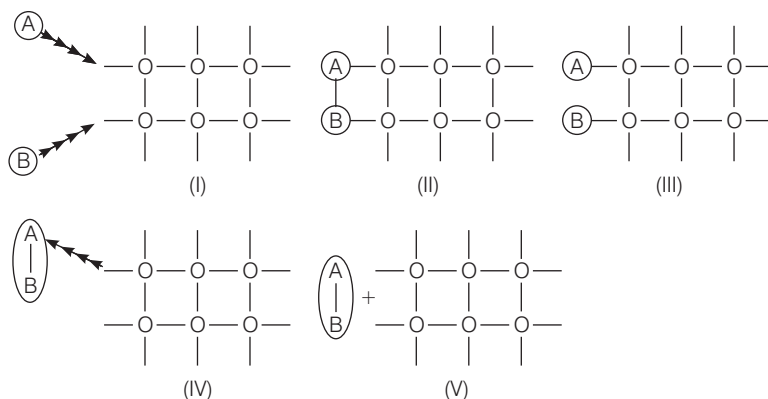
Q. 20 The values of colligative properties of colloidal solution are of small order in comparison to those shown by true solutions of same concentration because of colloidal particles

- (a) exhibit enormous surface area
(b) remain suspended in the dispersion medium
(c) form lyophilic colloids
(d) are comparatively less in number

Ans. (d) The value of colligative properties of colloidal solution are of small order in comparison to those of true solution of same concentration because of colloidal particles are comparatively less in number.

This is due to slight large size of colloidal particles in comparison to particles present in true solution. Size of colloidal particles is in between 1 nm to 1000 nm.

Q. 21 Arrange the following diagrams in correct sequence of steps involved in the mechanism of catalysis, in accordance with modern adsorption theory.



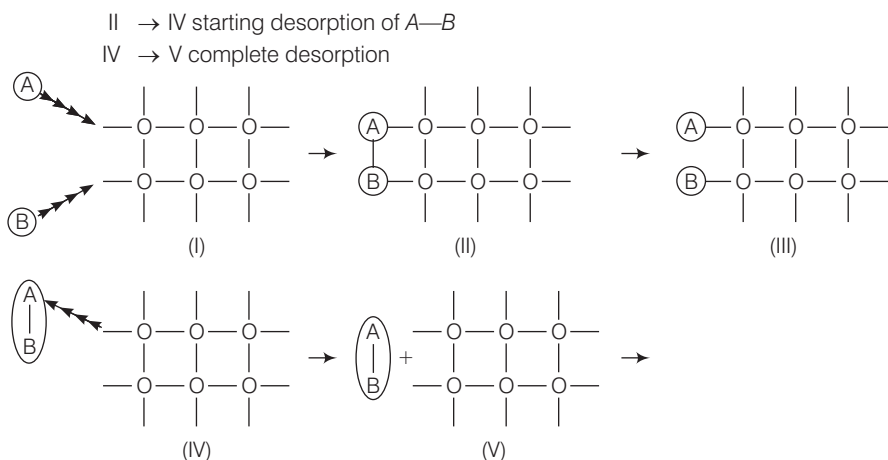
- (a) I \rightarrow II \rightarrow III \rightarrow IV \rightarrow V
(b) I \rightarrow III \rightarrow II \rightarrow IV \rightarrow V
(c) I \rightarrow III \rightarrow II \rightarrow V \rightarrow IV
(d) I \rightarrow II \rightarrow III \rightarrow V \rightarrow IV

Ans. (b) Correct sequence is I \rightarrow III \rightarrow II \rightarrow IV \rightarrow V

Each transformation denotes a meaningful process as follows

I \rightarrow adsorption of A and B on surface

III \rightarrow II interaction between A and B to form intermediate

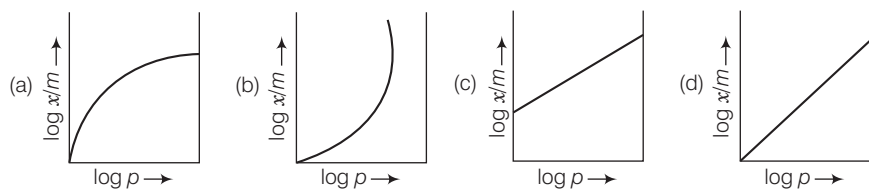


Q. 22 Which of the following process is responsible for the formation of delta at a place where rivers meet the sea?

- (a) Emulsification (b) Colloid formation
 (c) Coagulation (d) Peptisation

Ans. (c) River water is a colloidal solution of clay and sea. Water contains various electrolytes. When river water comes in contact with sea water, then the electrolytes present in sea water coagulate the suspended colloidal particles which ultimately settle down at the point of contact.

Q. 23 Which of the following curves is in according with Freundlich adsorption isotherm?



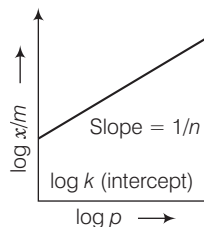
Ans. (c) According to the Freundlich adsorption isotherm

$$\frac{x}{m} = kp^n$$

Taking log on both side $\log \frac{x}{m} = \left(\frac{1}{n}\right) \log p + \log k$

$$\begin{array}{ccccccc} \uparrow & & \uparrow & & \uparrow & & \uparrow \\ Y & = & m & & x & + & C \end{array}$$

On comparing it with equation of straight line and drawing the graph $\log \frac{x}{m}$ versus $\log p$, we get a straight line with intercept $\log k$ and slope of the straight line gives the value of $\frac{1}{n}$.



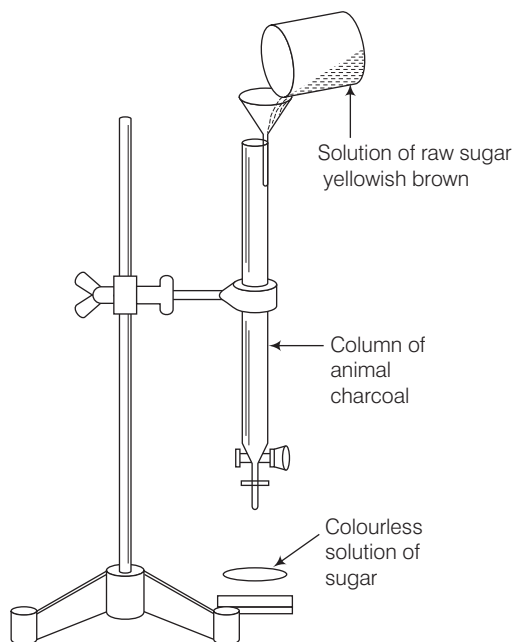
Q. 24 Which of the following process is not responsible for the presence of electric charge on the sol particles?

- (a) Electron capture by sol particles
- (b) Adsorption of ionic species from solution
- (c) Formation of Helmholtz electrical double layer
- (d) Absorption of ionic species from solution

Ans. (d) Absorption of ionic species from solution is not responsible for the presence of electric charge on the sol particles. *Charge on the sol particles is due to*

- (i) electrons capture by sol particles during electro dispersion of metal.
- (ii) preferential adsorption of ionic species from solution.
- (iii) formation of Helmholtz electrical double layer.

Q. 25 Which of the following phenomenon is applicable to the process shown in the figure?



- (a) Absorption
- (b) Adsorption
- (c) Coagulation
- (d) Emulsification

Ans. (b) Above figure represent adsorption of yellowish brown colour of raw sugar by animal charcoal.

Here, aqueous solution of raw sugar is filtered by using animal charcoal. Yellowish brown colour of raw sugar is adsorbed and filtrate is colourless which gives white colour on crystallisation. Hence, this phenomenon is adsorption.

Multiple Choice Questions (More Than One Options)

Q. 26 Which of the following options are correct?

- (a) Micelle formation by soap in aqueous solution is possible at all temperatures
- (b) Micelle formation by soap in aqueous solution occurs above a particular concentration
- (c) On dilution of soap solution micelles may revert to individual ions
- (d) Soap solution behaves as a normal strong electrolyte at all concentrations

💡 Thinking Process

This problem is based on concept of micelle formation and CMC (critical micelle concentration).

Ans. (b, c)

Micelle formation Some substances at low concentration behaves as a normal electrolytes but at higher concentration exhibit colloidal behaviour due to formation of micelles.

CMC (Critical Micelle Concentration) The concentration above which it behaves as a micelle known as critical micelle concentration (CMC).

e.g., soap solution in aqueous solution above particular concentration (called CMC = $10^{-4} - 10^3 \text{ mol L}^{-1}$) forms soap micelles.

On dilution soap solution behaves as a normal electrolyte and after adding excess of water intermolecular force of attraction between the soap particles decreases and soap solution micelles may revert to individual ions.

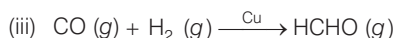
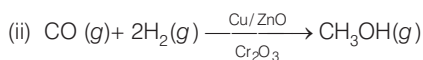
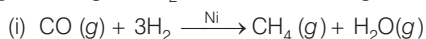
Q. 27 Which of the following statements are correct about solid catalyst?

- (a) Same reactants may give different products by using different catalysts
- (b) Catalyst does not change ΔH of reaction
- (c) Catalyst is required in large quantities to catalyse reactions
- (d) Catalytic activity of a solid catalyst does not depend upon the strength of chemisorption

Ans. (a, b)

(a) Same reactants may give different products by using different catalysts as different catalysts have different specific functions to mold the reaction towards specific product.

e.g., starting with H_2 and CO , and using different catalysts, we get different products.



(b) Catalyst does not change ΔH of reaction as ΔH of reaction is difference between enthalpy of reactants and products. So, it does not change during catalysed reaction.

Q. 28 Freundlich adsorption isotherm is given by the expression $\frac{x}{m} = kp^{\frac{1}{n}}$

Which of the following conclusions can be drawn from this expression?

- (a) When $\frac{1}{n} = 0$, the adsorption is independent of pressure
- (b) When $\frac{1}{n} = 0$, the adsorption is directly proportional to pressure
- (c) When $n = 0$, $\frac{x}{m}$ vs p graph is a line parallel to x-axis
- (d) When $n = 0$, plot of $\frac{x}{m}$ vs p is a curve

Thinking Process

To solve this problem follow steps given below.

Write Freundlich equation and transform it into different form depending upon value of n then choose the correct answer.

Ans. (a, c)

According to Freundlich adsorption isotherm

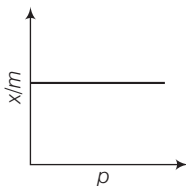
$$\frac{x}{m} \propto p^{\frac{1}{n}} \Rightarrow \frac{x}{m} = kp^{\frac{1}{n}}$$

- (a) At $\frac{1}{n} = 0$ this equation becomes $\frac{x}{m} = kp^0 = k$

Extent of adsorption is independent of pressure.

- (c) At $x = 0$, $\frac{x}{m} = kp^0 = kp^\infty$

Hence, $\frac{x}{m}$ vs p graph can be plotted as



Q. 29 H_2 gas is adsorbed on activated charcoal to a very little extent in comparison to easily liquefiable gases due to

- (a) very strong van der Waals' interaction
- (b) very weak van der Waals' forces
- (c) very low critical temperature
- (d) very high critical temperature

Ans. (b, c)

H_2 gas is adsorbed on activated charcoal to a very little extent in comparison to easily liquefiable gases due to

- (i) very low van der Waals' forces and
- (ii) very low critical temperature equal to 33 K.

Q. 30 Which of the following statements are correct?

- (a) Mixing two oppositely charged sols neutralises their charges and stabilises the colloid
- (b) Presence of equal and similar charges on colloidal particles provides stability to the colloids
- (c) Any amount of dispersed liquid can be added to emulsion without destabilising it
- (d) Brownian movement stabilises sols

Ans. (b, d)

Presence of equal and similar charges on colloidal particles provides stability to colloids as repulsive forces between charge particles having same charge prevent them from colliding when they come closer to each other.

Q. 31 An emulsion cannot be broken by and

- (a) heating
- (b) adding more amount of dispersion medium
- (c) freezing
- (d) adding emulsifying agent

Ans. (b, d)

Emulsions are liquid-liquid colloidal system. They can't be broken by adding more amount of dispersion medium and adding emulsifying agent as on adding more amount of dispersion medium they become dilute and on adding emulsifying agent they get stabilised.

Q. 32 Which of the following substances will precipitate the negatively charged emulsions?

- (a) KCl
- (b) Glucose
- (c) Urea
- (d) NaCl

Ans. (a, d)

The droplets present in emulsion have negative charge. It can be precipitated by adding electrolyte such as KCl, NaCl etc. Since, glucose and urea do not produce ions on dissolving in water.

Hence, they are non-electrolyte and do not precipitate the negatively charged emulsion.

Q. 33 Which of the following colloids cannot be coagulated easily?

- (a) Lyophobic colloids
- (b) Irreversible colloids
- (c) Reversible colloids
- (d) Lyophilic colloids

Ans. (c, d)

Lyophilic colloids (liquid loving colloids) which are also known as reversible colloid can't be coagulated easily. The stability of these colloids are due to

- (i) charge on colloidal particles and
- (ii) solvation of colloidal particles.

Q. 34 What happens when a Lyophilic sol is added to a Lyophobic sol?

- (a) Lyophobic sol is protected
- (b) Lyophilic sol is protected
- (c) Film of lyophilic sol is formed over lyophobic sol
- (d) Film of lyophobic sol is formed over lyophilic sol

Ans. (a, c)

Lyophobic sol is unstable in nature when lyophilic sol is added to lyophobic sol then lyophobic sol is protected because a film of lyophilic sol is formed over lyophobic sol.

Hence, (a) and (c) are correct.

Q. 35 Which phenomenon occurs when an electric field is applied to a colloidal solution and electrophoresis is prevented?

- (a) Reverse osmosis takes place
- (b) Electroosmosis takes place
- (c) Dispersion medium begins to move
- (d) Dispersion medium becomes stationary

💡 Thinking Process

This problem is based on concept of electroosmosis. It can be solved by knowing the exact meaning of electroosmosis

Ans. (b, c)

The movement of colloidal particles under an applied electric potential is called electrophoresis. When this movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed as electroosmosis.

Q. 36 In a reaction, catalyst changes

- (a) physically
- (b) qualitatively
- (c) chemically
- (d) quantitatively

Ans. (a, b)

In a reaction catalyst changes physically and qualitatively as it is unaltered during the reaction and remain quantitatively intact after completion of reaction and chemically does not change.

Q. 37 Which of the following phenomenon occurs when a chalk stick is dipped in ink?

- (a) Adsorption of coloured substance
- (b) Adsorption of solvent
- (c) Absorption and adsorption both of solvent
- (d) Absorption of solvent

Ans. (a, d)

When a chalk stick is dipped in ink absorption as well as adsorption both occurs. Adsorption of coloured substance and absorption of solvent takes place.

Short Answer Type Questions

Q. 38 Why is it important to have clean surface in surface studies?

Ans. It facilitates the adsorption of desired species. If surface is covered by the gases of air then it will not be available for adsorption of desired gases. So, it is very important to have clean surface in surface studies *i.e.*, study of surface chemistry.

Q. 39 Why is chemisorption referred to as activated adsorption?

Ans. Chemisorption referred to as activated adsorption as it involves chemical bond formation between reactant and adsorbent molecules. Formation of chemical bond requires high activation energy. So, it is activated on increasing temperature.

Q. 40 What type of solutions are formed on dissolving different concentrations of soap in water?

Ans. At lower concentration, soap behaves as a normal solution of electrolyte in water. However, after a certain concentration, called critical micelle concentration, colloidal solution is formed due to aggregation of colloidal particles.

CMC for soap solution is 10^{-4} to 10^{-3} mol L⁻¹.

Q. 41 What happens when gelatin is mixed with gold sol?

Ans. Gold sol is a solvent repelling sol *i.e.*, a lyophobic sol and unstable in nature. Addition of gelatin stabilises the gold sol because gelatin forms lyophilic sol and act as a protective colloid.

Q. 42 How does it become possible to cause artificial rain by spraying silver iodide on the clouds?

Ans. As we know artificial rainfall occurs when oppositely charged clouds meets. Since, clouds are colloidal in nature and carry charge. Spray of silver iodide, an electrolyte from aeroplane results in coagulation of colloidal water particles leading to rain. Sometimes electrified sand is also used for this purpose.

Q. 43 Gelatin which is a peptide is added in ice-creams. What can be its role?

Ans. Emulsifying agent is added to emulsion to stabilise the emulsion. Emulsifying agent form a layer between suspended particles and the medium and hence stabilises the emulsion. Ice cream (emulsion) is stabilised by emulsifying agent like gelatin.

Q. 44 What is collodion?

Ans. 4% solution of nitrocellulose in a mixture of alcohol and ether is called collodion.

Q. 45 Why do we add alum to purify water?

Ans. We add alum to purify water as alum coagulates the colloidal impurities present in water, so that these impurities get settle down and remove by decantation or filtration. Thus, water gets purified by adding alum to water.

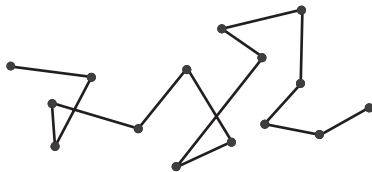
Q. 46 What happens when electric field is applied to colloidal solution?

Ans. When electric potential is applied to colloidal solution, the colloidal particles move towards one or other electrode. Positively charged particles move towards the cathode while negatively charged particles move towards the anode.

The movement of colloidal particles under an applied electric potential is called electrophoresis. When electrophoresis is prevented by some means, then the dispersion medium begins to move in an electric field. This phenomenon is termed as electroosmosis.

Q. 47 What causes Brownian motion in colloidal dispersion?

Ans. Brownian movement may be defined as continuous *zig-zag* movement of colloidal particles in a colloidal sol. A state of continuous *zig-zag* motion of colloidal particles appears to be in view due to unbalanced bombardment of the particles of dispersed phase by molecules of dispersion medium. This Brownian movement stabilises the sol.



Q. 48 A colloid is formed by adding FeCl_3 in excess of hot water. What will happen if excess sodium chloride is added to this colloid?

Ans. Positively charged ions coagulate the negatively charged sol and negatively charged ion coagulate the positively charged sol. Positively charged sol of hydrated ferric oxide is formed when FeCl_3 is added in excess of hot water. On adding excess of NaCl to this sol, negatively charged Cl^- ions coagulate the positively charged sol of hydrated ferric oxide.

Q. 49 How do emulsifying agents stabilise the emulsion?

Ans. Emulsifying agents stabilise the emulsion by forming an interfacial layer between suspended particles and the dispersion medium. e.g., gelatin is added to ice cream to stabilise it.

Q. 50 Why are some medicines more effective in the colloidal form?

Ans. Some medicines are more effective in colloidal form because they have large surface area so easily assimilated in the body.

Q. 51 Why does leather get hardened after tanning?

Ans. Animal hide is colloidal in nature and has positively charged particles. When it is soaked in tanin (negatively charged), a colloid, it results in mutual coagulation and gets hardened. Thus, leather get hardened after tanning.

Q. 52 How does the precipitation of colloidal smoke take place in Cottrell precipitator?

Ans. In Cottrell precipitator, smoke particles (charged) are passed through a chamber containing plates with charge opposite to the smoke particles, smoke particles lose their charge on the plates and get precipitated.

Q. 53 How will you distinguish between dispersed phase and dispersion medium in an emulsion?

Ans. To distinguish between dispersed phase and dispersion medium we increase the concentration of any one dispersion medium or dispersed phase then notice the change.

When dispersion medium is added to an emulsion, it gets diluted to any extent. But on adding dispersed phase it forms a separate layer, if added in excess.

Q. 54 On the basis of Hardy-schulze rule explain why the coagulating power of phosphate is higher than chloride?

Ans. Minimum quantity of an electrolyte required to cause precipitation of a sol is called its coagulating value. Greater the charge on flocculating ion and smaller is the amount of electrolyte required for precipitation, higher is the coagulating power of coagulating ion (Hardy-Schulze Law).

Phosphate ion bear – 3 charge while chloride ion carries only –1 charge and due to high charge phosphate ion has high coagulating power than that of chloride ion.

Q. 55 Why does bleeding stop by rubbing moist alum?

Ans. Blood is a colloidal sol. When we rub the injured part with moist alum then coagulation of blood takes place. Hence, main reason is coagulation, which stops the bleeding.

Q. 56 Why is Fe(OH)_3 colloid positively charged, when prepared by adding Fe(OH)_3 to hot water?

Ans. Charge on sol is decided by adsorption of ions present in medium. Adsorption of positively charged Fe^{3+} ions takes place by the sol of hydrated ferric oxide. Thus, Fe(OH)_3 colloid has positive charge when prepared by adding Fe(OH)_3 to hot water.

Q. 57 Why do physisorption and chemisorption behave differently with rise in temperature?

Ans. Behaviour of physisorption and chemisorption on increase in temperature can be explained on the basis of nature of forces present to bind their particles. Physisorption involves weak van der Waals' forces which weakens with increase in temperature.

Chemisorption involves formation of chemical bond which requires activation energy hence, it is favoured by rise in temperature.

Q. 58 What happens when dialysis is prolonged?

Ans. Traces of electrolyte which stabilises the colloids is removed completely making the colloid unstable. So, coagulation occurs on prolonged dialysis.

Q. 59 Why does the white precipitate of silver halide become coloured in the presence of dye eosin?

Ans. White coloured precipitate of silver halide becomes coloured in the presence of dye eosin because dye eosin (coloured) gets adsorbed on the surface of silver halide precipitate.

Q. 60 What is the role of activated charcoal in gas mask used in coal mines?

Ans. Role of activated charcoal in gas mask can be explained on the basis of adsorption. Activated charcoal adsorbs various poisonous gases on its surface present in coal mines.

Q. 61 How does a delta form at the meeting place of sea and river water?

Ans. Formation of delta at the meeting place of sea and river water is due to coagulation. River water (colloid of sea water + clay) has many dissolved electrolytes. The place where river meets sea is the site for coagulation. Deposition of coagulated clay results in delta formation.

Q. 62 Give an example where physisorption changes to chemisorption with rise in temperature. Explain the reason for change.

Ans. Adsorption of H_2 on finely divided nickel (physisorption) involves weak van der Waals' forces. When temperature is increased, hydrogen molecules dissociate into hydrogen atoms, form chemical bonds with the metal atoms at the surface (chemisorption).

Q. 63 Why is desorption important for a substance to act as good catalyst?

Ans. Desorption is important for a substance to act as a good catalyst so that after the reaction, the products formed on the surface separate out (desorbed) to create free surface again for other reactant molecules to approach the surface and react.

If desorption does not occur then other reactants are left with no space on the catalysts surface for adsorption and reaction will stop.

Q. 64 What is the role of diffusion in heterogeneous catalyst?

Ans. Diffusion of gas molecules occur at the surface of catalyst (solid) followed by adsorption. In the same way, the product formed diffuse from the surface of the catalyst leaving the surface free for more reactant molecules to get adsorbed and undergo reaction.

Q. 65 How does a solid catalyst enhance the rate of combination of gaseous molecules?

Ans. When gaseous molecules come in contact with the surface of a solid catalyst, a weak chemical bond is formed between the surface (catalyst) molecules and reactant (gas) molecules. Thus, concentration of reactant molecules increases at the surface.

The rate of reaction increases by adsorption of different molecules side by side facilitating the chemical reaction. Adsorption, being exothermic also help in increasing the rate of reaction (chemisorption increases with rise in temperature).

Q. 66 Do the vital functions of the body such as digestion get affected during fever? Explain your answer.

Ans. The optimum temperature range for enzymatic activity is 298-310 K, *i.e.*, enzymes are inactive beyond this temperature range (high or low).

Thus, during fever (temperature >310 K) the activity of enzymes may be affected.

Matching The Columns

Q. 67 Method of formation of solution is given in Column I. Match it with the type of solution given in Column II.

Column I	Column II
A. Sulphur vapours passed through cold water.	1. Normal electrolyte solution
B. Soap mixed with water above critical micelle concentration.	2. Molecular colloids
C. White of egg whipped with water.	3. Associated colloid
D. Soap mixed with water below critical micelle concentration.	4. Macromolecular colloids

Ans. A. → (2) **B.** → (3) **C.** → (4) **D.** → (1)

- A. When sulphur vapours passed through cold water it leads to formation of molecular colloids.
- B. When soap is mixed with water above critical micelle concentration it lead to formation of associated colloids.
- C. White of egg whipped with water is an example of macromolecular colloids in which high molecular mass proteneous molecule acts as a colloidal particle.
- D. Soap mixed with water below critical micelle concentration is known as normal electrolyte solution.

Q. 68 Match the statement given in Column I with the phenomenon given in Column II.

Column I	Column II
A. Dispersion medium moves in an electric field.	1. Osmosis
B. Solvent molecules pass through semipermeable membrane towards solvent side.	2. Electrophoresis
C. Movement of charged colloidal particles under the influence of applied electric potential towards oppositely charged electrodes.	3. Electroosmosis
D. Solvent molecules pass through semipermeable membranes towards solution side.	4. Reverse-osmosis

Ans. A. → (3) **B.** → (4) **C.** → (2) **D.** → (1)

- A. Dispersion medium moves in an electric field is known as electroosmosis.
- B. Solvent molecules pass through semipermeable membrane towards solvent side is known as reverse-osmosis.
- C. Movement of charged colloidal particles under the influence of applied electric potential towards oppositely charge electrodes is known as electrophoresis.
- D. Solvent molecules pass through semipermeable membranes towards solution side is known as osmosis.

Q. 69 Match the items given in Column I and Column II.

Column I	Column II
A. Protective colloid	1. $\text{FeCl}_3 + \text{NaOH}$
B. Liquid-liquid colloid	2. Lyophilic colloids
C. Positively charged colloid	3. Emulsion
D. Negatively charged colloid	4. $\text{FeCl}_3 + \text{hot water}$

Ans. A. → (2) **B.** → (3) **C.** → (4) **D.** → (1)

- A. Lyophobic colloid (solvent hating colloid) are readily protected by small amount of electrolyte. These colloids are also stabilised by addition of lyophilic colloids which makes a protective layer around lyophobic sol. Hence, lyophilic sol are known as protective colloid.
- B. Liquid-liquid colloid is also known as emulsion if they are partially miscible or immiscible liquids.
- C. When FeCl_3 is added to hot water it lead to the formation of positively charged colloid.
- D. When NaOH is added to FeCl_3 it lead to the formation of negatively charged colloid.

Q. 70 Match the types of colloidal systems given in Column I with the name given in Column II.

Column I	Column II
A. Solid in liquid	1. Foam
B. Liquid in solid	2. Sol
C. Liquid in liquid	3. Gel
D. Gas in liquid	4. Emulsion

Ans. A. → (2) B. → (3) C. → (4) D. → (1)

Colloids are classified on the basis of types of dispersed phase and dispersion medium.

Dispersed phase	Dispersion medium	Name
A. Solid in	Liquid	Sol
B. Liquid in	Solid	Gel
C. Liquid in	Liquid	Emulsion
D. Gas in	Liquid	Foam

Q. 71 Match the items of Column I and Column II.

Column I	Column II
A. Dialysis	1. Cleansing action of soap
B. Peptisation	2. Coagulation
C. Emulsification	3. Colloidal sol formation
D. Electrophoresis	4. Purification

Ans. A. → (4) B. → (3) C. → (1) D. → (2)

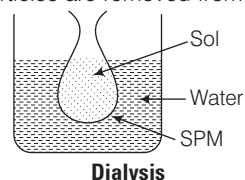
A. Purification of colloid can be done by dialysis in which ions/particles are removed from solution through semipermeable membrane.

B. Peptisation is a process in which when small quantity of electrolyte (peptising agent) is added to precipitate. It leads to formation of colloidal solution.

C. The process of removing of oily or greasy dirt from the cloth is done by emulsification.

D. Process of setting of colloidal particle is called coagulation.

Electrophoresis is a process in which on applying electric potential to the electrodes dipped in sol, the oppositely charged particles of colloidal solution move towards oppositely charged electrodes, get discharged and precipitated.



Q. 72 Match the items of Column I and Column II.

Column I	Column II
A. Butter	1. Dispersion of liquid in liquid
B. Pumice stone	2. Dispersion of solid in liquid
C. Milk	3. Dispersion of gas in solid
D. Paints	4. Dispersion of liquid in solid

Ans. A. → (4) B. → (3) C. → (1) D. → (2)

A. Butter is an example of dispersion of liquid in solid.

B. Pumice stone is an example of dispersion of gas in solid in which gas bubbles are peared within solid particles.

C. Milk is a dispersion of liquid in liquid in which fats and protein are dissolved in milk.

D. Paint is an example of solid in liquid.

Assertion and Reason

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct and the reason is correct explanation of assertion.
- (b) Assertion and reason both are correct but reason does not explain assertion.
- (c) Assertion is correct, but reason is incorrect.
- (d) Both assertion and reason are incorrect.
- (e) Assertion is incorrect, but reason is correct.

Q. 73 Assertion (A) An ordinary filter paper impregnated with collodion solution stops the flow of colloidal particles.

Reason (R) Pore size of the filter paper becomes more than the size of colloidal particle.

Ans. (c) Assertion is correct, but reason is wrong.

An ordinary filter paper impregnated with collodion solution stops the flow of colloidal particles because pore size of the filter paper becomes smaller than the size of colloidal particles.

Q. 74 Assertion (A) Colloidal solution show colligative properties.

Reason (R) Colloidal particles are large in size.

Ans. (b) Assertion and reason both are correct, but reason does not explain assertion.

Colloidal solutions show colligative properties as colloidal particles have large size so colloidal particles have small value of colligative properties because number of particles are small in comparison to normal solution.

Q. 75 Assertion (A) Colloidal solutions do not show Brownian motion.

Reason (R) Brownian motion is responsible for stability of sols.

Ans. (e) Assertion is incorrect, but reason is correct.

Colloidal solutions show Brownian motion and this Brownian motion is responsible for stability of sols.

Q. 76 Assertion (A) Coagulation power of Al^{3+} is more than Na^+ .

Reason (R) Greater the valency of the flocculating ion added, greater is its power to cause precipitation (Hardy–Schulze rule) .

Ans. (a) Assertion and reason both are correct and reason is correct explanation of assertion.

According to Hardy–Schulze law greater the charge/valency on flocculating ion added greater will be its power to cause precipitation.

Coagulating power \propto Valency of flocculating ion

Q. 77 Assertion (A) Detergents with low CMC are more economical to use.

Reason (R) Cleansing action of detergents involves the formation of micelles. These are formed when the concentration of detergents becomes equal to CMC.

Ans. (a) Assertion and reason both are correct and reason is correct explanation of assertion.

Detergents with low CMC are more economic to use as cleansing action of detergents involves the formation of micelles. These are formed when the concentration of detergent becomes equal to CMC. If CMC has lower value then it will form CMC easily and readily.

Long Answer Type Questions

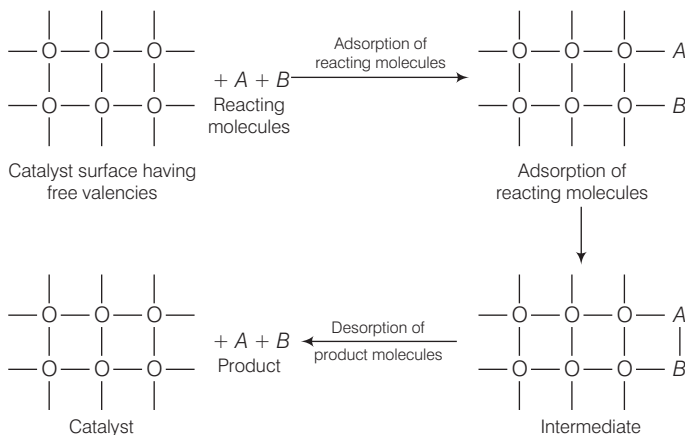
Q. 78 What is the role of adsorption in heterogeneous catalysis?

Ans. Catalyst is used to increase rate of reaction. Heterogeneous catalyst is used to increase rate of reaction in which catalyst is not in phase with reactants and products.

Role of adsorption in heterogeneous catalysis are

- (i) Diffusion of reactants to the surface of the catalyst.
- (ii) Reactants are adsorbed on the catalyst surface.
- (iii) Occurrence of chemical reaction at catalyst surface.
- (iv) Desorption.
- (v) Diffusion of reaction products away from the catalysts surface.

e.g.,



Role of adsorption in heterogeneous catalysis

Q. 79 What are the applications of adsorption in chemical analysis?

Ans. There are various applications of adsorption in chemical analysis.

Some of which are as follows

- (i) **In thin layer chromatography** The lower adsorbing particles comes out readily while another having higher adsorbing tendency comes out later. On this basis compounds are separated or analysed.
- (ii) **In adsorption indicators** Surface of certain precipitate has an ability to adsorb some dyes to produce a characteristic colour e.g., AgX adsorbs eosin dye and thereby producing a characteristic colour at the end point.
- (iii) **In qualitative analysis** Specific material has specific adsorption tendency so particular ion can be identified very easily.
- (iv) **In the separation of inert gases** Different inert gases are adsorbed to different extents at different temperatures on coconut charcoal. This forms the basis of their separation from a mixture.

Q. 80 What is the role of adsorption in froth floatation process used especially for concentration of sulphide ores?

Ans. In froth floatation process sulphide ore is shaken with pine oil and water, the ore particles are adsorbed on froth that floats and the gangue particles settle down in tank. Thus, role of adsorption in froth floatation process can be understood as following processes.

- (i) Adsorption of pine oil on sulphide ore particles.
- (ii) Formation of emulsion takes place.
- (iii) Froth is formed along with ore particles.
- (iv) Mechanism of the functioning of shape selective catalysis.
As sulphide are extracted using froth floatation method therefore, only sulphide ore particles will show these type of adsorbing tendency.

Q. 81 What do you understand by shape selective catalysis? Why are zeolites good shape selective catalysts?

Ans. The catalytic reaction which depends upon pore structure of catalyst and the size of the reactant and product molecules is known as shape selective catalysts. Zeolites are good shape selective catalyst because of honey comb like structure.

- (i) They are microporous aluminosilicates with Al—O—Si framework and general formula $M_{x/n} [(AlO_2)_x (SiO_2)_y] mH_2O$
- (ii) The reactions taking place in zeolites depend upon the size and shape of the reactant and product molecules as well as upon the pores and cavities of the zeolites.
- (iii) Zeolites are widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. They are also used for removing permanent hardness of water.
- (iv) e.g., ZSM-5 is a catalyst used in petroleum industry



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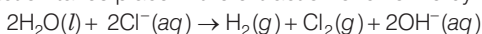
General Principle and Processes of Isolation of Elements

Multiple Choice Questions (MCQs)

Q. 1 In the extraction of chlorine by electrolysis of brine

- (a) oxidation of Cl^- ion to chlorine gas occurs
- (b) reduction of Cl^- ion to chlorine gas occurs
- (c) for overall reaction ΔG° has negative value
- (d) a displacement reaction takes place

Ans. (a) Following reaction takes place in the extraction of chlorine by electrolysis



From the above reaction it is very clear that the oxidation of Cl^- ion to chlorine gas occurs. Thus, option (a) is the correct answer.

$\Delta^\circ G$ for this reaction is +422kJ. Therefore, thermodynamically reaction is not feasible. We know that

$$\Delta^\circ G = -nFE^\circ$$

By using this equation value of E° can be calculated. Thus,

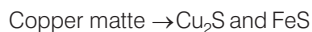
$$E^\circ = -\frac{\Delta G^\circ}{nF} = -2.2V$$

Therefore, for the occurrence of this reaction, external potential (emf) greater than 2.2V is required. Due to this fact (c) is not the correct option.

Q. 2 When copper ore is mixed with silica, in a reverberatory furnace copper matte is produced. The copper matte contains

- (a) sulphides of copper (II) and iron (II)
- (b) sulphides of copper (II) and iron (III)
- (c) sulphides of copper (I) and iron (II)
- (d) sulphides of copper (I) and iron (III)

Ans. (c) When copper ore is mixed with silica in a reverberatory furnace copper matte is produced. The copper matte contains sulphide of copper (I) and iron (II).



Q.3 Which of the following reactions is an example of autoredution?

- (a) $\text{Fe}_3\text{O}_4 + 4\text{CO} \longrightarrow 3\text{Fe} + 4\text{CO}_2$
- (b) $\text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO}$
- (c) $\text{Cu}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Fe}^{2+}(\text{aq})$
- (d) $\text{Cu}_2\text{O} + \frac{1}{2}\text{Cu}_2\text{S} \longrightarrow 3\text{Cu} + \frac{1}{2}\text{SO}_2$

Ans. (d) $\text{Cu}_2\text{O} + \frac{1}{2}\text{Cu}_2\text{S} \longrightarrow 3\text{Cu} + \frac{1}{2}\text{SO}_2$

This reaction includes reduction of copper (I) oxide by copper (I) sulphide. In this process, copper is reduced by itself hence this process is known as autoredution and the solidified copper. So, obtained is known as blister copper.

Q. 4 A number of elements are available in earth's crust but most abundant elements are

- | | |
|---------------|---------------|
| (a) Al and Fe | (b) Al and Cu |
| (c) Fe and Cu | (d) Cu and Ag |

Ans. (a) Among a number of elements which are available in earth crust, the most abundant elements are aluminium and iron. Aluminium is third most abundant element in earth crust. *i.e.*, 8.3% by weight while iron present in earth crust with 4.2% by weight. Copper and silver are also found in earth crust but their abundance percentage is low.

Q. 5 Zone refining is based on the principle that

- (a) impurities of low boiling metals can be separated by distillation.
- (b) impurities are more soluble in molten metal than in solid metal.
- (c) different components of a mixture are differently adsorbed on an adsorbent.
- (d) vapours of volatile compound can be decomposed in pure metal.

Ans. (b) Zone refining is based on the principle that the impurities are more soluble in molten state than in solid state of the metal. A circular mobile heater fixed at one end of impure metal rod. The molten zone moves along with heater which is moved forward.

As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into adjacent molten zone. The process is repeated several times and the heater is moved in the same direction.

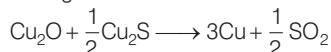
At one end, impurities get concentrated. This end is cut off. *e.g.*, germanium, silicon, gallium etc., are refined by this method.

Q. 6 In the extraction of copper from its sulphide ore, the metal is formed by the reduction of Cu_2O with

- (a) FeS (b) CO
(c) Cu_2S (d) SO_2

Ans. (c) In the extraction of copper from its sulphide ore, the metal is formed by the reduction of Cu_2O with Cu_2S . This reaction completes with the process of autoreduction.

Chemical reaction occurring in this reaction is as follows

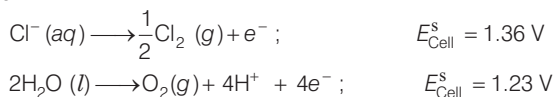


In this process, copper appears as blister copper.

Q. 7 Brine is electrolysed by using inert electrodes. The reaction at anode is

- (a) $\text{Cl}^- (\text{aq}) \rightarrow \frac{1}{2}\text{Cl}_2 (\text{g}) + \text{e}^-$; $E_{\text{Cell}}^{\text{s}} = 1.36 \text{ V}$
(b) $2\text{H}_2\text{O} (\text{l}) \rightarrow \text{O}_2 (\text{g}) + 4\text{H}^+ + 4\text{e}^-$; $E_{\text{Cell}}^{\text{s}} = 1.23 \text{ V}$
(c) $\text{Na}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Na} (\text{s})$; $E_{\text{Cell}}^{\text{s}} = 2.71 \text{ V}$
(d) $\text{H}^+ (\text{aq}) + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 (\text{g})$; $E_{\text{Cell}}^{\text{s}} = 0.00 \text{ V}$

Ans. (a) Brine is electrolysed by using inert electrodes. The possible reactions occurring at anode are



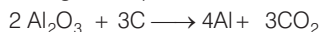
The reaction at anode with lower value of E° is preferred and therefore water should get oxidised in preference to $\text{Cl}^- (\text{aq})$. However, Cl_2 is produced instead of O_2 . This unexpected result is explained on the basis of the fact that water needs greater voltage for oxidation to O_2 (as it is kinetically slow process) than that needed for oxidation of Cl^- ions to Cl_2 .

Q. 8 In the metallurgy of aluminium

- (a) Al^{3+} is oxidised to $\text{Al} (\text{s})$.
(b) graphite anode is oxidised to carbon monoxide and carbon dioxide.
(c) oxidation state of oxygen changes in the reaction at anode.
(d) oxidation state of oxygen changes in the overall reaction involved in the process.

Ans. (b) In the metallurgy of aluminium, electrolysis is performed in a steel vessel with lining of carbon acts as cathode and graphite acts as anode. During this process graphite anode is oxidised to CO and CO_2 .

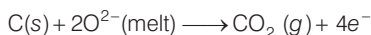
Chemical reaction occurring in this process is as follows



This process is known as Hall - Heroult process. The electrolytic reactions are

At cathode $\text{Al}^{3+} (\text{melt}) + 3\text{e}^- \longrightarrow \text{Al} (\text{l})$

At anode $\text{C} (\text{s}) + \text{O}^{2-} (\text{melt}) \longrightarrow \text{CO} (\text{g}) + 2\text{e}^-$



Q. 9 Electrolytic refining is used to purify which of the following metals?

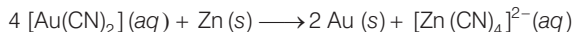
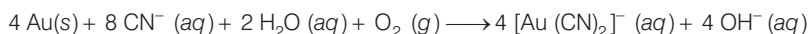
- (a) Cu and Zn (b) Ge and Si (c) Zr and Ti (d) Zn and Hg

Ans. (a) Copper and zinc are two metals which are generally purified by using electrolyte refining. In this process, impure metal is used as anode and pure metal is used as a cathode. Impurities from the blister copper or impure zinc deposit as anode mud.

Q. 10 Extraction of gold and silver involves leaching the metal with CN^- ion. The metal is recovered by

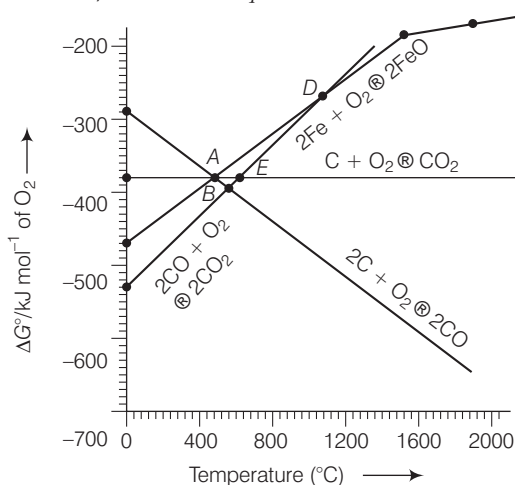
- (a) displacement of metal by some other metal from the complex ion.
 (b) roasting of metal complex.
 (c) calcination followed by roasting.
 (d) thermal decomposition of metal complex.

Ans. (a) Extraction of gold and silver involves leaching the metal with CN^- ion. The metal is recovered by displacement of metal by some other metal from the complex ion. This is an oxidation reaction.



Here, Zn acts as a reducing agent.

Direction (Q. Nos. 11-13) Answer the questions on the basis of figure



Q. 11 Choose the correct option of temperature at which carbon reduces FeO to iron and produces CO .

- (a) Below temperature at point A
 (b) Approximately at the temperature corresponding to point A
 (c) Above temperature at point A but below temperature at point D
 (d) Above temperature at point A

Thinking Process

This problem is based on concept of Ellingham diagram which relates Gibbs free energy of reaction and temperature. The point above which greater the negative value of formation of compound is observed, compound will form at that temperature. At a particular temperature compound having higher negative value of Gibbs free energy will be formed first.

Ans. (d) In the figure shown above point A

$$\Delta_f G^\circ_{(\text{C}, \text{CO})} < \Delta_f G^\circ_{(\text{Fe}, \text{FeO})}$$

Therefore, above point A, C reduces FeO to Fe forming carbon monoxide. Hence, reduction of FeO by carbon occurs above point A only.

Q. 12 Below point 'A' FeO can

- (a) be reduced by carbon monoxide only.
- (b) be reduced by both carbon monoxide and carbon.
- (c) be reduced by carbon only.
- (d) not be reduced by both carbon and carbon monoxide.

Ans. (a) Below point A Gibbs free energy change for the formation of CO_2 from CO ($\Delta G^\circ_{\text{CO}, \text{CO}_2}$) has lower value (more negative value) than Gibbs free energy change for the formation of FeO ($\Delta G^\circ_{\text{Fe}, \text{FeO}}$). Hence, FeO will be reduced by CO only below point A.

Q. 13 For the reduction of FeO at the temperature corresponding to point D, which of the following statements is correct?

- (a) ΔG value for the overall reduction reaction with carbon monoxide is zero.
- (b) ΔG value for the overall reduction reaction with a mixture of 1 mol carbon and 1 mol oxygen is positive.
- (c) ΔG value for the overall reduction reaction with a mixture of 2 mol carbon and 1 mol oxygen will be positive.
- (d) ΔG value for the overall reduction reaction with carbon monoxide is negative.

Ans. (a) At point D, ΔG curve for formation of CO_2 from CO and FeO from Fe intersect each other therefore, overall reduction of FeO with CO is zero.
Hence, (a) is the correct choice.

Multiple Choice Questions (More Than One Options)

Q. 14 At the temperature corresponding to which of the points in Fig. FeO will be reduced to Fe by coupling the reaction $2\text{FeO} \longrightarrow 2\text{Fe} + \text{O}_2$ with all of the following reactions?

1. $\text{C} + \text{O} \longrightarrow \text{CO}_2$
2. $2\text{C} + \text{O}_2 \longrightarrow 2\text{CO}$
3. $2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$

- (a) Point A (b) Point B (c) Point D (d) Point E

Ans. (b, d)

Below point B and E, FeO will be reduced to Fe by all the three reactions shown above in the question. $\Delta G^\circ_{(\text{C}, \text{CO}_2)}$, $\Delta G^\circ_{(\text{C}, \text{CO})}$, $\Delta G^\circ_{(\text{CO}, \text{CO}_2)}$ lie below $\Delta_f G^\circ_{(\text{Fe}, \text{FeO})}$ curve at point B and E. Therefore, FeO will be reduced by all three reactions.
Hence, options (b) and (d) are correct choice.

Q. 15 Which of the following options are correct?

- (a) Cast iron is obtained by remelting pig iron with scrap iron and coke using hot air blast.
- (b) In extraction of silver, silver is extracted as cationic complex.
- (c) Nickel is purified by zone refining.
- (d) Zr and Ti are purified by van Arkel method.

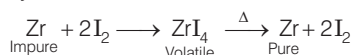
💡 Thinking Process

This process is based on concept of purification techniques and formation of cast iron.

Ans. (a, d)

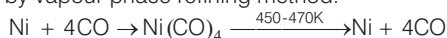
Correct statements are

- (a) Cast iron is obtained by remelting pig iron with scarp iron and coke using hot air blast.
- (d) Zr and Ti are purified by van Arkel method as



(b) and (c) can be correctly stated as

- (b) In extraction of silver, silver is extracted as anionic complex $[\text{Ag}(\text{CN})_2]^-$
- (c) Nickel is purified by vapour phase refining method.



Q. 16 In the extraction of aluminium by Hall-Heroult process, purified Al_2O_3 is mixed with CaF_2 to

- (a) lower the melting point of Al_2O_3
- (b) increase the conductivity of molten mixture.
- (c) reduce Al^{3+} into $\text{Al}(\text{s})$
- (d) acts as catalyst

💡 Thinking Process

This problem is based on extraction of aluminium using Hall-Heroult process.

Ans. (a, b)

In the metallurgy of aluminium Al_2O_3 is mixed with Na_3AlF_6 and CaF_2 which causes following affects.

- (i) Lower the melting point of Al_2O_3
- (ii) Increase the conductivity of molten mixture

Q. 17 Which of the following statements is correct about the role of substances added in the froth floatation process?

- (a) Collectors enhance the non-wettability of the mineral particles.
- (b) Collectors enhance the wettability of gangue particles.
- (c) By using depressants in the process two sulphide ores can be separated.
- (d) Froth stabilisers decrease wettability of gangue.

💡 Thinking Process

This problem is based on the method involved in froth floatation method and function of collector and depressants.

Ans. (a, c)

Froth floatation process is used to extract metal from sulphide ore. This method utilises collectors and depressants whose functions are as follows

- (i) Collectors enhance the non-wettability of the mineral particles.
- (ii) By using depressants in the process two sulphide ores can be separated. e.g., sodium cyanide is used as a depressant to separate lead sulphide ore from zinc sulphide ore.

Q. 18 In the froth floatation process, zinc sulphide and lead sulphide can be separated by

- (a) using collectors (b) adjusting the proportion of oil to water
(c) using depressant stabilisers (d) using froth

Ans. (b, c)

Froth floatation method is used to extract metal from sulphide ore. ZnS and PbS can be separated by using depressant and adjusting the proportion of oil to water. Depressant used for this purpose is NaCN. It selectively prevents ZnS from coming to the froth.

Hence, (b) and (c) are correct choices.

Q. 19 Common impurities present in bauxite are

- (a) CuO (b) ZnO (c) Fe₂O₃ (d) SiO₂

Ans. (c, d)

Bauxite is an ore of aluminium which contains Fe₂O₃ and SiO₂ as common impurities.

Q. 20 Which of the following ores are concentrated by froth floatation?

- (a) Haematite (b) Galena (c) Copper pyrites (d) Magnetite

Ans. (b, c)

Haematite (Fe₂O₃) and magnetite (Fe₃O₄) are oxide ores while galena (PbS) and copper pyrites (CuFeS₂) are sulphide ores. As we know sulphide ores are extracted by using froth floatation method. Hence, (b) and (c) are the correct choices.

Q. 21 Which of the following reactions occur during calcination?

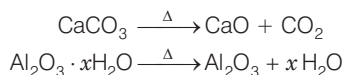
- (a) $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
(b) $2\text{FeS}_2 + \frac{11}{2} \text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_2$
(c) $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} \longrightarrow \text{Al}_2\text{O}_3 + x\text{H}_2\text{O}$
(d) $\text{ZnS} + \frac{3}{2} \text{O}_2 \longrightarrow \text{ZnO} + \text{SO}_2$

🔍 Thinking Process

This process is based on concept of calcination.

Ans. (a, c)

Calcination involves heating of the ore below its melting point in the absence of air or in limited supply of air. Oxygen containing ores like oxide, hydroxides and carbonates are calcined. Thus, the following reactions occur during calcination.



Q. 22 For the metallurgical process of which of the ores calcined ore can be reduced by carbon?

- (a) Haematite (b) Calamine (c) Iron pyrites (d) Sphalerite

Ans. (a, b)

In the metallurgical process, the oxide ores are reduced by carbon. Sulphide ore cannot be reduced by carbon. Here, haematite (Fe₂O₃) and calamine (ZnO) are oxide ores of iron and zinc respectively while iron pyrites (FeS₂) and sphalerite (ZnS) are sulphide ores of iron and zinc respectively.

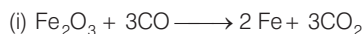
Therefore, haematite and calamine can be reduced by carbon.

Q.23 The main reactions occurring in blast furnace during extraction of iron from haematite ore

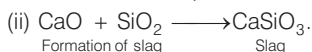
- (a) $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$
- (b) $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$
- (c) $\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$
- (d) $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$

Ans. (a, d)

In extraction of iron from haematite ore following reactions take place.



This reaction represents reduction of Fe_2O_3 to Fe.



Formation of slag

Slag

Q. 24 In which of the following method of purification, metal is converted to its volatile compound which is decomposed to give pure metal?

- (a) Heating with stream of carbon monoxide
- (b) Heating with iodine
- (c) Liquation
- (d) Distillation

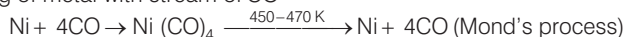
💡 Thinking Process

This problem is based on purification of metal using vapour phase refining method.

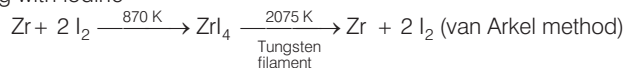
Ans. (a, b)

Vapour phase refining method includes

- (i) Heating of metal with stream of CO



- (ii) Heating with iodine



Q. 25 Which of the following statements are correct?

- (a) A depressant prevents certain type of particle to come to the froth.
- (b) Copper matte contains Cu_2S and ZnS .
- (c) The solidified copper obtained from reverberatory furnace has blistered appearance due to evolution of SO_2 during the extraction.
- (d) Zinc can be extracted by self-reduction.

Ans. (a, c)

Correct statements are

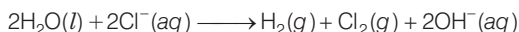
- (i) A depressant prevents certain type of particle to come to the froth. e.g., NaCN is added as a depressant during separation of PbS and ZnS .
- (ii) The solidified copper obtained from reverberatory furnace has blistered appearance due to evolution of SO_2 during the extraction.
- (b) and (d) are incorrect statements, and can be correctly stated as
- (iii) Copper matte contains Cu_2S and FeS .
- (iv) Zinc can be extracted by reduction of ZnO with carbon.

Q. 26 In the extraction of chlorine from brine

- (a) ΔG° for the overall reaction is negative.
- (b) ΔG° for the overall reaction is positive.
- (c) E° for the overall reaction has negative value.
- (d) E° for the overall reaction has positive value.

Ans. (b, c)

Electrolysis of brine solution is used to extract chlorine. Overall chemical reaction occurring in this process and value of ΔG° can be shown as



For the given reaction, value of ΔG° is 422 kJ

Using $\Delta G^\circ = -nFE^\circ$, the value of $E^\circ = E^\circ - 2.2\text{V}$.

Therefore, ΔG° for the overall reaction is positive and E° has negative value.

Short Answer Type Questions

Q. 27 Why is an external emf of more than 2.2V required for the extraction of Cl_2 from brine?

Ans. $2\text{Cl}^-(aq) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{OH}^-(aq) + \text{H}_2(g) + \text{Cl}_2(g)$

For the given reaction, value of ΔG° is + 422 kJ.

Using $\Delta G^\circ = -nFE^\circ$, the value of $E^\circ = -2.2\text{V}$.

Therefore, an external emf greater than 2.2 V is required for the extraction of Cl_2 from brine.

Q. 28 At temperature above 1073 K, coke can be used to reduce FeO to Fe. How can you justify this reduction with Ellingham diagram?

Ans. Using Ellingham diagram, we observe that at temperature greater than 1073 K; $\Delta G_{(\text{C}, \text{CO})} < \Delta G_{(\text{Fe}, \text{FeO})}$. We know that according to Ellingham diagram, compound having lower $\Delta_r G^\circ$ undergo its formation.

Hence, coke can reduce FeO to Fe.

Q. 29 Wrought iron is the purest form of iron. Write a reaction used for the preparation of wrought iron from cast iron. How can the impurities of sulphur, silicon and phosphorus be removed from cast iron?

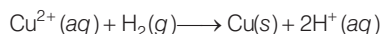
Ans. (a)
$$\underset{\text{Haematite lining}}{\text{Fe}_2\text{O}_3} + \underset{\substack{\text{Impurities} \\ \text{(present in cast iron)}}}{3\text{C}} \longrightarrow \underset{\substack{\text{Wrought} \\ \text{iron}}}{2\text{Fe}} + 3\text{CO}$$

This reaction takes place in reverberatory furnace lined with haematite.

- (b) The haematite oxidises S to SO_2 , Si to SiO_2 and P to P_4O_{10} . Sometimes limestone is added as flux. Impurities of S, Si and P oxidise and pass into slag. The metal is removed and freed from slag by passing through rollers.

Q. 30 How is copper extracted from low grade copper ores?

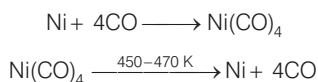
Ans. Copper is extracted from low grade copper ore using hydrometallurgy method. For this purpose, ore is leached out using bacteria. The solution containing Cu^{2+} is treated with scrap iron and H_2 .



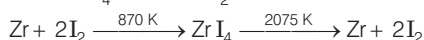
Q. 31 Write two basic requirements for refining of a metal by Mond's process and by van Arkel Method.

Ans. Two basic requirements are

- (i) Metal should form volatile compound with available reagent.
- (ii) The volatile compound should be easily decomposable so that it can be recovered easily.
 - (a) **Mond's process** includes conversion of Ni to $\text{Ni}(\text{CO})_4$ and then decomposition of $\text{Ni}(\text{CO})_4$ to Ni.



- (b) **van Arkel method** includes conversion of Zr to volatile ZrI_4 and then decomposition of ZrI_4 to Zr and I_2 .



Q. 32 Although carbon and hydrogen are better reducing agents but they are not used to reduce metallic oxides at high temperatures. Why?

Ans. Because at high temperatures, carbon and hydrogen react with metals to form carbides and hydrides respectively. So, carbon and hydrogen are not better reducing agents to reduce metallic oxide.

Q. 33 How do we separate two sulphide ores by froth floatation method? Explain with an example.

Ans. Two sulphide ores can be separated by adjusting the proportion of oil and water or by using depressants, e.g., if an ore contains ZnS and PbS both, a depressant NaCN is added during froth floatation. It forms a complex with ZnS and prevents it from coming into froth. PbS comes into the froth and thus separated.

Q. 34 The purest form of iron is prepared by oxidising impurities from cast iron in a reverberatory furnace. Which iron ore is used to line the furnace? Explain by giving reaction.

Ans. (a) Haematite (Fe_2O_3) ore is used to line the furnace.

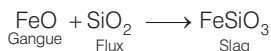


Q. 35 The mixture of compounds A and B is passed through a column of Al_2O_3 by using alcohol as eluant. Compound A is eluted in preference to compound B. Which of the compounds A or B, is more readily adsorbed on the column?

Ans. Compounds which are adsorbed to the more extent comes out later while the another one which absorbed to the less extent comes out readily. Since, compound 'A' comes out before compound 'B', the compound 'B' is more readily adsorbed on the column.

Q. 36 Why is sulphide ore of copper heated in a furnace after mixing with silica?

Ans. Silica (flux) being an acidic flux removes the impurities of iron oxide the basic impurity, by reacting with it. Thus, iron silicate (slag) is formed.



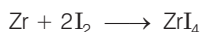
Q. 37 Why are sulphide ores converted to oxide before reduction?

Ans. This is because oxides are reduced to metals easily while sulphides are not. So, sulphide ores are converted to oxide before reduction.

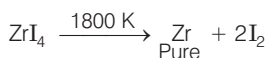
Q. 38 Which method is used for refining Zr and Ti? Explain with equation.

Ans. Zr and Ti are refined by van Arkel method. It involves 2 steps

(a) **Formation of iodide** e.g., zirconium



(b) **Decomposition of iodide**



Q. 39 What should be the considerations during the extraction of metals by electrochemical method?

Ans. During extraction of metals by electrochemical method the following two points must be considered

- Reactivity of metals** If the metals are quite reactive and are expected to react with water then the metals should be extracted by the electrolysis of their purified molten ore rather than their aqueous solution.
- Suitability of electrodes** The electrodes selected should not react with the product of electrolysis. If at all they react, then the electrodes must be made up of a material which is quite cheap since their periodic replacement should not increase the cost of the process.

Q. 40 What is the role of flux in metallurgical processes?

Ans. *Role of flux in metallurgical process*

- Flux is used to remove the gangue by combining with it. Thus, slag formation takes place.
- It makes the molten mass more conducting.

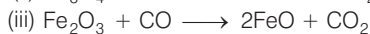
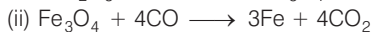
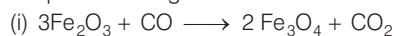
Q. 41 How are metals used as semiconductors refined? What is the principle of the method used like germanium, silicon etc?

Ans. Metals of high grade like germanium, silicon etc., used as semiconductors are refined by zone refining method.

Principle This method is based upon the principle that impurities are more soluble in molten state of metal than in solid state.

Q. 42 Write down the reactions taking place in blast furnace related to the metallurgy of iron in the temperature range 500-800 K.

Ans. Chemical reactions occurring in blast furnace related to the metallurgy of iron in the temperature range 500-800 K are

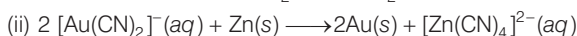
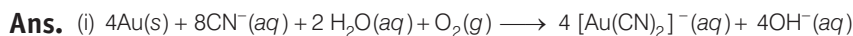


Q. 43 Give two requirements for vapour phase refining.

Ans. Two requirements for vapour phase refining are

- (i) The metal should form a volatile compound with an available reagent.
- (ii) The volatile compound should be easily recovered by decomposition.

Q. 44 Write the chemical reactions involved in the extraction of gold by cyanide process. Also give the role of zinc in the extraction.



Zinc acts as a reducing agent in this reaction.

Matching The Columns

Q. 45 Match the items of Column I with items of Column II and assign the correct code.

Column I	Column II
A. Pendulum	1. Chrome steel
B. Malachite	2. Nickel steel
C. Calamine	3. Na_3AlF_6
D. Cryolite	4. $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
	5. ZnCO_3

Codes

A	B	C	D
(a) 1	2	3	4
(c) 2	3	4	5

A	B	C	D
(b) 2	4	5	3
(d) 4	5	3	2

Ans. (b) A. \rightarrow (2) B. \rightarrow (4) C. \rightarrow (5) D. \rightarrow (3)

A. Pendulum is made up of nickel steel.

B. Molecular formula of malachite is $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$.

C. Molecular formula of calamine is ZnCO_3 .

D. Molecular formula of cryolite is Na_3AlF_6 .

Q. 46 Match the items of Column I with the items of Column II and assign the correct code.

Column I	Column II
A. Coloured bands	1. Zone refining
B. Impure metal to volatile complex	2. Fractional distillation
C. Purification of Ge and Si	3. Mond's process
D. Purification of mercury	4. Chromatography
	5. Liquation

Codes

A B C D
 (a) 1 2 4 5
 (c) 3 4 2 1

A B C D
 (b) 4 3 1 2
 (d) 5 4 3 2

Ans. (b) A. → (4) B. → (3) C. → (1) D. → (2)

- A. Coloured bands are observed in chromatography.
 B. Impure metal is converted to volatile complex by using Mond's process.
 C. Purification of Ge and Si are purified by zone refining method.
 D. Purification of mercury is done by fractional distillation.

Q. 47 Match items of Column I with the items of Column II and assign the correct code.

Column I	Column II
A. Cyanide process	1. Ultrapure Ge
B. Froth floatation process	2. Dressing of ZnS
C. Electrolytic reduction	3. Extraction of Al
D. Zone refining	4. Extraction of Au
	5. Purification of Ni

Codes

A B C D
 (a) 4 2 3 1
 (c) 1 2 3 4

A B C D
 (b) 2 3 1 5
 (d) 3 4 5 1

Ans. (a) A. → (4) B. → (2) C. → (3) D. → (1)

- A. Cyanide process is used for extraction of Au through formation of anionic complex $[\text{Au}(\text{CN})_2]^-$.
 B. Froth floatation process is used for dressing of ZnS.
 C. Electrolytic reduction method is used for extraction of aluminium. Graphite electrode is used for this purpose.
 D. Zone-refining is used for purification of Ge.

Q. 48 Match the items of Column I with the items of Column II and assign the correct code.

Column I	Column II
A. Sapphire	1. Al_2O_3
B. Sphalerite	2. NaCN
C. Depressant	3. Co
D. Corundum	4. ZnS
	5. Fe_2O_3

Codes

A B C D

(a) 3 4 2 1

(c) 2 3 4 5

A B C D

(b) 5 4 3 2

(d) 1 2 3 4

Ans. (a) A. \rightarrow (3) B. \rightarrow (4) C. \rightarrow (2) D. \rightarrow (1)

A. Sapphire is a gemstone which contain Co.

B. Molecular formula of sphalerite is ZnS.

C. NaCN is used as a depressant in froth floatation method.

D. Molecular formula of corundum is Al_2O_3 .

Q.49 Match the items of Column I with items of Column II and assign the correct code.

Column I	Column II
A. Blistered Cu	1. Aluminium
B. Blast furnace	2. $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$
C. Reverberatory furnace	3. Iron
D. Hall-Heroult process	4. $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$
	5. $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$

Codes

A B C D

(a) 2 3 4 1

(c) 5 4 3 2

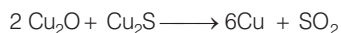
A B C D

(b) 1 2 3 5

(d) 4 5 3 2

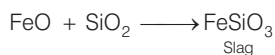
Ans. (a) A. \rightarrow (2) B. \rightarrow (3) C. \rightarrow (4) D. \rightarrow (1)

A. Blistered Cu can be prepared by means of following chemical reaction



B. Iron is extracted by using blast furnace.

C. In reverberatory furnace formation of slag occurs as



D. Hall-Heroult process is used for extraction of aluminium.

Assertion and Reason

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both assertion and reason are true and reason is the correct explanation of assertion.
- (b) Both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) Assertion is true but reason is false.
- (d) Assertion is false but reason is true.
- (e) Assertion and reason both are wrong.

Q. 50 Assertion (A) Nickel can be purified by Mond's process.

Reason (R) $\text{Ni}(\text{CO})_4$ is a volatile compound which decomposes at 460 K to give pure Ni.

Ans. (a) Both assertion and reason are true and reason is the correct explanation of assertion.

Nickel can be purified by Mond's process in which formation of a volatile compound $\text{Ni}(\text{CO})_4$ takes place which further decomposes to Ni at 460K.

Q. 51 Assertion (A) Zirconium can be purified by van Arkel method.

Reason (R) ZrI_4 is volatile and decomposes at 1800K.

Ans. (a) Both assertion and reason are true and reason is the correct explanation of assertion.

Zirconium can be purified by van Arkel method which include formation of volatile ZrI_4 which decomposes at 1800 K to Zr.

Q. 52 Assertion (A) Sulphide ores are concentrated by froth floatation method.

Reason (R) Cresols stabilise the froth in froth floatation method.

Ans. (b) Both assertion and reason are true but reason is not the correct explanation of assertion.

Sulphide ores are concentrated by froth floatation method. Sulphide ore particles are preferentially wetted by oil, become lighter and rise to the surface along with the froth while gangue particles are preferentially wetted by water, become heavier and thus settle down at the bottom of the tank and cresols stabilise the froth in froth floatation method.

Formation of froth is main reason for extraction of metal. Metal ore comes out along with froth.

Q. 53 Assertion (A) Zone refining method is very useful for producing semiconductors.

Reason (R) Semiconductors are of high purity.

Ans. (b) Both assertion and reason are true but reason is not the correct explanation of assertion.

Zone refining method is very useful for producing semiconductors of high purity as in this process pure metal crystallises while impurities pass on into adjacent molten zone when impure metal rod is heated.

Q. 54 Assertion (A) Hydrometallurgy involves dissolving the ore in a suitable reagent followed by precipitation by a more electropositive metal.

Reason (R) Copper is extracted by hydrometallurgy.

Ans. (b) Assertion and reason both are correct but reason is not the correct explanation of assertion.

Hydrometallurgy involves dissolving the ore in suitable reagent followed by precipitation with the help of more electropositive metal in which pure metal is get replaced by more electropositive metal.

Long Answer Type Questions

Q. 55 Explain the following

- CO_2 is a better reducing agent below 710 K whereas CO is a better reducing agent above 710 K.
- Generally sulphide ores are converted into oxides before reduction.
- Silica is added to the sulphide ore of copper in the reverberatory furnace.
- Carbon and hydrogen are not used as reducing agents at high temperatures.
- Vapour phase refining method is used for the purification of Ti.

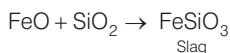
💡 Thinking Process

This problem is based on concept of Ellingham diagrams and purification of metal.

Ans. (a) As shown in Ellingham diagram which relates Gibbs free energy and temperature at below 710 K.

$\Delta G_{(\text{C}, \text{CO}_2)} < \Delta G_{(\text{C}, \text{CO})}$ So, CO_2 is a better reducing agent than CO while above 710K it becomes a very good reducing agent.

- Generally, sulphide ores are converted to oxides before reduction as reduction of oxides can easily be done using C or CO depending upon metal ore and temperature.
- Silica is a flux added to the sulphide ore of copper in the reverberatory furnace leading to the formation of slag



- Carbon and hydrogen are not used as reducing agents at high temperature. At high temperature carbon and hydrogen readily form their carbides and hydrides respectively.
- Vapour phase refining method is used for the purification of Ti as



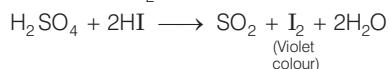
p -Block Elements

Multiple Choice Questions (MCQs)

Q. 1 On addition of conc. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodide salt, violet fumes come out. This is because

- (a) H_2SO_4 reduces HI to I_2 (b) HI is of violet colour
(c) HI gets oxidised to I_2 (d) HI changes to HIO_3

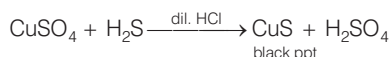
Ans. (c) Hydrogen iodide (HI) is more stronger oxidising agent than H_2SO_4 . So, it reduces H_2SO_4 to SO_2 and itself oxidises to I_2 . Colour of I_2 is violet hence on adding conc. H_2SO_4 to HI, it gets oxidised to I_2 .



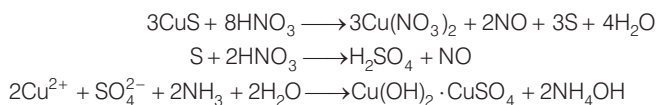
Q. 2 In qualitative analysis when H_2S is passed through an aqueous solution of salt acidified with dil. HCl, a black precipitate is obtained. On boiling the precipitate with dil. HNO_3 , it forms a solution of blue colour. Addition of excess of aqueous solution of ammonia to this solution gives

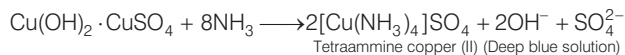
- (a) deep blue precipitate of $\text{Cu}(\text{OH})_2$
(b) deep blue solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$
(c) deep blue solution of $\text{Cu}(\text{NO}_3)_2$
(d) deep blue solution of $\text{Cu}(\text{OH})_2 \cdot \text{Cu}(\text{NO}_3)_2$

Ans. (b) In qualitative analysis when H_2S is passed through an aqueous solution of salt acidified with dil. HCl a black ppt. of CuS is obtained.



On boiling CuS with dil. HNO_3 it forms a blue coloured solution and the following reactions occur

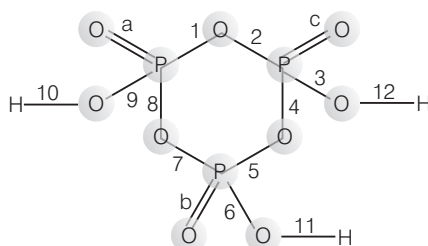




Q. 3 In a cyclotrimetaphosphoric acid molecule, how many single and double bonds are present?

- (a) 3 double bonds; 9 single bonds
- (b) 6 double bonds; 6 single bonds
- (c) 3 double bonds; 12 single bonds
- (d) Zero double bond; 12 single bonds

Ans. (c) Cyclotrimetaphosphoric acid contains three double bonds and 9 single bonds as shown below



Cyclotrimetaphosphoric acid (HPO₃)₃

a, b, c are three π bonds and numerics 1 to 12 are sigma (σ) bonds.

Q. 4 Which of the following elements can be involved in $p\pi - d\pi$ bonding?

- (a) Carbon
- (b) Nitrogen
- (c) Phosphorus
- (d) Boron

Ans. (c) Among given four elements *i.e.*, carbon, nitrogen, phosphorus and boron. Only phosphorus has vacant *d*-orbit so only phosphorus has ability to form $p\pi - d\pi$ bonding.

Q. 5 Which of the following pairs of ions are isoelectronic and isostructural?

- (a) CO_3^{2-} , NO_3^-
- (b) ClO_3^- , CO_3^{2-}
- (c) SO_3^{2-} , NO_3^-
- (d) ClO_3^- , SO_3^{2-}

Ans. (a) Compounds having same value of total number of electrons are known as isoelectronic.

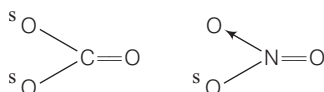
For CO_3^{2-}

$$\begin{aligned} \text{Total number of electrons} &= 6 + 8 \times 3 + 2 \\ &= 6 + 24 + 2 \\ &= 32 \end{aligned}$$

For NO_3^-

$$\begin{aligned} \text{Total number of electrons} &= 7 + 8 \times 3 + 1 \\ &= 7 + 25 \\ &= 32 \end{aligned}$$

Hence, CO_3^{2-} and NO_3^- are isoelectronic. These two ions have similar structure so they are isostructural.



Both have triangular planar structure as in both the species carbon and nitrogen are sp^2 hybridised. Hence, (a) is the correct choice.

Q. 6 Affinity for hydrogen decreases in the group from fluorine to iodine. Which of the halogen acids should have highest bond dissociation enthalpy?

- (a) HF (b) HCl (c) HBr (d) HI

Ans. (a) HF
HCl
HBr
HI

On moving top to bottom

- Size of halogen atom increases
- H-X bond length increases
- Bond dissociation enthalpy decreases

Q. 7 Bond dissociation enthalpy of E—H (E= element) bonds is given below. Which of the compounds will act as strongest reducing agent?

Compound	NH ₃	PH ₃	AsH ₃	SbH ₃
$\Delta_{\text{diss}} (E-H) / \text{kJ mol}^{-1}$	389	322	297	255

- (a) NH₃ (b) PH₃ (c) AsH₃ (d) SbH₃

Ans. (d) On moving top to bottom, size of central atom increases. Bond length of X—H bond increases and bond dissociation energy decreases. Hence, reducing nature increases.

NH₃
PH₃
AsH₃
SbH₃

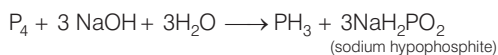
- Bond length increases
- Bond dissociation energy decreases
- Reducing character increases

Hence, SbH₃ is act as strongest reducing agent among these.

Q. 8 On heating with concentrated NaOH solution in an inert atmosphere of CO₂, white phosphorus gives a gas. Which of the following statement is incorrect about the gas?

- (a) It is highly poisonous and has smell like rotten fish
(b) It's solution in water decomposes in the presence of light
(c) It is more basic than NH₃
(d) It is less basic than NH₃

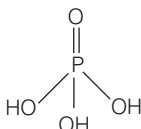
Ans. (c) White phosphorous on reaction with NaOH solution in the presence of inert atmosphere of CO₂ it produces phosphine gas which is less basic than NH₃.



Q. 9 Which of the following acids forms three series of salts?

- (a) H₃PO₂ (b) H₃BO₃ (c) H₃PO₄ (d) H₃PO₃

Ans. (c) Structure of H₃PO₄ is



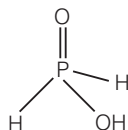
H₃PO₄ has 3—OH groups i.e., has three ionisable H-atoms and hence forms three series of salts. These three possible series of salts for H₃PO₄ are as follows



Q. 10 Strong reducing behaviour of H_3PO_2 is due to

- (a) low oxidation state of phosphorus
- (b) presence of two —OH groups and one P—H bond
- (c) presence of one —OH group and two P—H bonds
- (d) high electron gain enthalpy of phosphorus

Ans. (c) Strong reducing behaviour of H_3PO_2 is due to presence of two P—H bonds and one P—OH bond

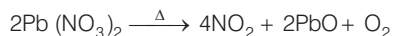


**Hypophosphorous following
(Monobasic)**

Q. 11 On heating lead nitrate forms oxides of nitrogen and lead. The oxides formed are

- (a) N_2O , PbO
- (b) NO_2 , PbO
- (c) NO , PbO
- (d) NO , PbO_2

Ans. (b) On heating lead nitrate it produces brown coloured nitrogen dioxide (NO_2) and lead (II) oxide.



Q. 12 Which of the following elements does not show allotropy?

- (a) Nitrogen
- (b) Bismuth
- (c) Antimony
- (d) Arsenic

Ans. (a) Nitrogen does not show allotropy due to its weak N—N single bond. Therefore, ability of nitrogen to form polymeric structure or more than one structure or form become less. Hence, nitrogen does not show allotropy.

Q. 13 Maximum covalency of nitrogen is

- (a) 3
- (b) 5
- (c) 4
- (d) 6

Ans. (c) Maximum covalency of nitrogen is 4 in which one electron is made available by s-orbital and 3 electrons are made available by p orbitals. Hence, total four electrons are available for bonding.

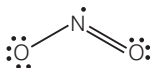
Q. 14 Which of the following statements is wrong?

- (a) Single N—N bond is stronger than the single P—P bond.
- (b) PH_3 can act as a ligand in the formation of coordination compound with transition elements.
- (c) NO_2 is paramagnetic in nature.
- (d) Covalency of nitrogen in N_2O_5 is four.

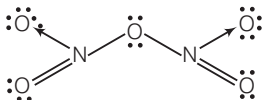
Ans. (a) True statement is that single N—N bond is weaker than the single P—P bond. This is why phosphorous show allotropy but nitrogen does not.

- (i) PH_3 acts as a ligand in the formation of coordination compound due to presence of lone pair of electrons.

- (ii) NO_2 is paramagnetic in nature due to presence of one unpaired electron.
Structure of NO_2 is



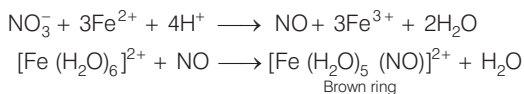
- (iii) Covalency of nitrogen in N_2O_5 is 4.



Q. 15 A brown ring is formed in the ring test for NO_3^- ion. It is due to the formation of

- (a) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ (b) $\text{FeSO}_4 \cdot \text{NO}_2$
(c) $[\text{Fe}(\text{H}_2\text{O})_4(\text{NO})_2]^{2+}$ (d) $\text{FeSO}_4 \cdot \text{HNO}_3$

Ans. (a) When freshly prepared solution of FeSO_4 is added in a solution containing NO_3^- ion, it leads to formation of a brown coloured complex. This is known as brown ring test of nitrate.



Q. 16 Elements of group- 15 form compounds in +5 oxidation state. However, bismuth forms only one well characterised compound in +5 oxidation state. The compound is

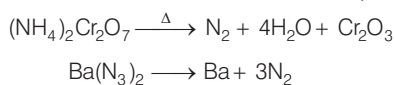
- (a) Bi_2O_5 (b) BiF_5
(c) BiCl_5 (d) Bi_2S_5

Ans. (b) Stability of + 5 oxidation state decreases top to bottom and + 3 oxidation state increases top to bottom due to inert pair effect. Meanwhile compound having + 5 oxidation state of Bi is BiF_5 . It is due to smaller size and high electronegativity of fluorine.

Q. 17 On heating ammonium dichromate and barium azide separately we get

- (a) N_2 in both cases
(b) N_2 with ammonium dichromate and NO with barium azide
(c) N_2O with ammonium dichromate and N_2 with barium azide
(d) N_2O with ammonium dichromate and NO_2 with barium azide

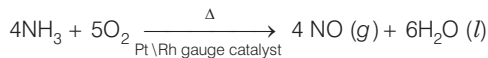
Ans. (a) On heating ammonium dichromate and barium azide it produces N_2 gas separately.



Q. 18 In the preparation of HNO_3 , we get NO gas by catalytic oxidation of ammonia. The moles of NO produced by the oxidation of two moles of NH_3 will be

- (a) 2 (b) 3 (c) 4 (d) 6

Ans. (a) Two moles of NH_3 will produce 2 moles of NO on catalytic oxidation of ammonia in preparation of nitric acid.



Q. 19 The oxidation state of central atom in the anion of compound NaH_2PO_2 will be

- (a) + 3 (b) + 5 (c) + 1 (d) - 3

Ans. (c) Let oxidation state of P in NaH_2PO_2 is x .

$$1 + 2 \times 1 + x + 2 \times -2 = 0$$

$$1 + 2 + x - 4 = 0$$

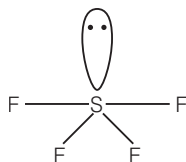
$$+ x - 1 = 0$$

$$x = + 1$$

Q. 20 Which of the following is not tetrahedral in shape?

- (a) NH_4^+ (b) SiCl_4 (c) SF_4 (d) SO_4^{2-}

Ans. (c) SF_4 has sea-saw shaped as shown below

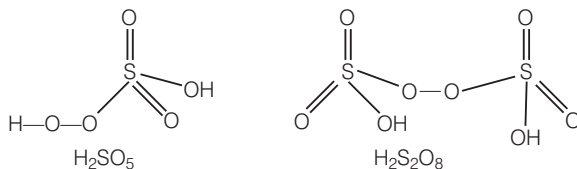


It has trigonal bipyramidal geometry having sp^3d hybridisation.

Q. 21 Which of the following are peroxyacids of sulphur?

- (a) H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_8$ (b) H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_7$
(c) $\text{H}_2\text{S}_2\text{O}_7$ and $\text{H}_2\text{S}_2\text{O}_8$ (d) $\text{H}_2\text{S}_2\text{O}_6$ and $\text{H}_2\text{S}_2\text{O}_7$

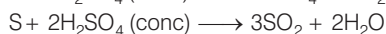
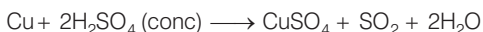
Ans. (a) Peroxyacids of sulphur must contain one —O—O— bond as shown below



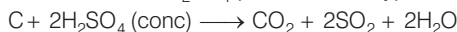
Q. 22 Hot conc. H_2SO_4 acts as moderately strong oxidising agent. It oxidises both metals and non-metals. Which of the following element is oxidised by conc. H_2SO_4 into two gaseous products?

- (a) Cu (b) S (c) C (d) Zn

Ans. (c) H_2SO_4 is a moderately strong oxidising agent which oxidises both metals and non-metals as shown below



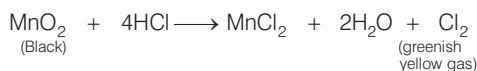
While carbon on oxidation with H_2SO_4 produces two types of oxides CO_2 and SO_2 .



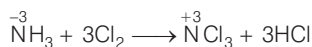
Q. 23 A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH_3 an unstable trihalide is formed. In this process the oxidation state of nitrogen changes from

- (a) -3 to $+3$ (b) -3 to 0
(c) -3 to $+5$ (d) 0 to -3

Ans. (a) Black coloured compound MnO_2 reacts with HCl to produce greenish yellow coloured gas of Cl_2



Cl_2 on further treatment with NH_3 produces NCl_3 .



NH_3 (-3) changes to NCl_3 ($+3$) in the above reaction. Hence, (a) is the correct choice.

Q. 24 In the preparation of compounds of Xe, Bartlett had taken $\text{O}_2^+ \text{Pt F}_6^-$ as a base compound. This is because

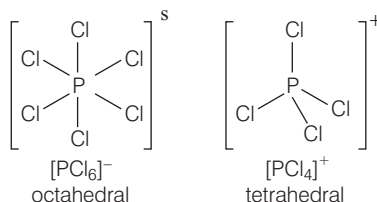
- (a) both O_2 and Xe have same size.
(b) both O_2 and Xe have same electron gain enthalpy.
(c) both O_2 and Xe have almost same ionisation enthalpy.
(d) both Xe and O_2 are gases.

Ans. (c) Bartlett had taken $\text{O}_2^+ \text{Pt F}_6^-$ as a base compound because O_2 and Xe both have almost same ionisation enthalpy. The ionisation enthalpies of noble gases are the highest in their respective periods due to their stable electronic configurations.

Q. 25 In solid state PCl_5 is a

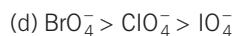
- (a) covalent solid
(b) octahedral structure
(c) ionic solid with $[\text{PCl}_6]^+$ octahedral and $[\text{PCl}_4]^-$ tetrahedral
(d) ionic solid with $[\text{PCl}_4]^+$ tetrahedral and $[\text{PCl}_6]^-$ octahedral

Ans. (d) In solid state PCl_5 exists as an ionic solid with $[\text{PCl}_4]^+$ tetrahedral and $[\text{PCl}_6]^-$ octahedral.



Q. 26 Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power.

Ion	ClO_4^-	IO_4^-	BrO_4^-
Reduction potential E°/V	$E^\circ = 1.19 \text{ V}$	$E^\circ = 1.65 \text{ V}$	$E^\circ = 1.74 \text{ V}$



Thinking Process

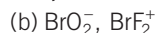
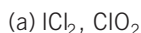
This problem is based on concept of standard reduction potential of species and oxidising property.

Ans. (c) Greater the SRP value of species higher will be its oxidising power.

Species	E°_{cell}	
ClO_4^-	1.19V	<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;">↓</div> <div>SRP of species increases. Oxidising power increase.</div> </div>
IO_4^-	1.65V	
BrO_4^-	1.74V	

Here, SRP = standard reduction potential.

Q. 27 Which of the following is isoelectronic pair?



Ans. (b) Isoelectronic pair have same number of electrons

	BrO_2^-	BrF_2^+
Total number of electrons	$= 35 + 2 \times 8 + 1 = 52$	$= 35 + 9 \times 2 - 1 = 52$

Hence, (b) is the correct choice, while in another cases this value is not equal.

ICl_2	ClO_2
$53 + 2 \times 17 = 87$	$17 + 16 = 33$
ClO_2	BrF
$17 + 16 = 33$	$35 + 9 = 44$
CN^-	O_3
$= 6 + 7 + 1 = 14$	$= 8 \times 3 = 24$

Hence, only (b) is the correct choice.

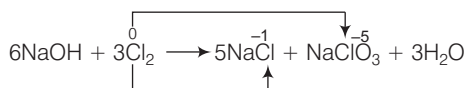
Multiple Choice Questions (More Than One Options)

Q. 28 If chlorine gas is passed through hot **NaOH** solution, two changes are observed in the oxidation number of chlorine during the reaction. These are and

- (a) 0 to +5 (b) 0 to +3 (c) 0 to -1 (d) 0 to +1

Ans. (a, c)

When chlorine gas is passed through hot NaOH solution it produces NaCl and NaClO₃.



Oxidation state varies from 0 to -1 and 0 to +5.

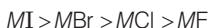
Hence, (a) and (c) are correct choices.

Q. 29 Which of the following options are not in accordance with the property mentioned against them?

- (a) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ Oxidising power
 (b) $\text{MI} > \text{MBr} > \text{MCl} > \text{MF}$ Ionic character of metal halide
 (c) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ Bond dissociation enthalpy
 (d) $\text{HI} < \text{HBr} < \text{HCl} < \text{HF}$ Hydrogen-halogen bond strength

Ans. (b, c)

$\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ As ability to gain electron increases oxidising property increases. Here, F is the most electronegative element having highest value of SRP hence it has highest oxidising power.

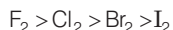


This is the incorrect order of ionic character of metal halide.

Correct order can be written as



As electronegativity difference between metal and halogen increases ionic character increases.



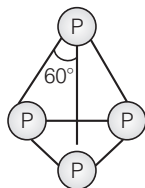
This is incorrect order of bond dissociation energy. Correct order is $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$ due to electronic repulsion among lone pairs in F_2 molecule.

Q. 30 Which of the following is correct for P_4 molecule of white phosphorus?

- (a) It has 6 lone pairs of electrons (b) It has six P — P single bonds
 (c) It has three P — P single bonds (d) It has four lone pairs of electrons

Ans. (b, d)

Structure of P_4 molecule can be represented as



It has total four lone pairs of electrons situated at each P-atom.

It has six P—P single bond.

Q. 31 Which of the following statements are correct?

- (a) Among halogens, radius ratio between iodine and fluorine is maximum.
- (b) Leaving F — F bond, all halogens have weaker X — X bond than X — X' bond in interhalogens.
- (c) Among interhalogen compounds maximum number of atoms are present in iodine fluoride.
- (d) Interhalogen compounds are more reactive than halogen compounds.

Ans. (a, c, d)

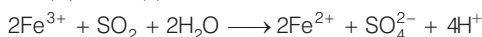
- (a) Among halogens, radius ratio between iodine and fluorine is maximum because iodine has maximum radius and fluorine has minimum radius.
- (b) It can be correctly stated as in general interhalogen compounds are more reactive than halogen. This is because X — X' bond in interhalogen is weaker than X — X bond in halogens except F—F bond.
- (c) Among interhalogen compounds maximum number of atoms are present in iodine fluoride because radius ratio of iodine and fluorine has maximum value.
- (d) Interhalogen compounds are more reactive than halogen due to weaker X — X' bond as compared to X — X of halogen compounds.

Q. 32 Which of the following statements are correct for SO₂ gas?

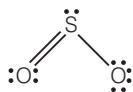
- (a) It acts as bleaching agent in moist conditions.
- (b) Its molecule has linear geometry.
- (c) Its dilute solution is used as disinfectant.
- (d) It can be prepared by the reaction of dilute H₂SO₄ with metal sulphide.

Ans. (a, c)

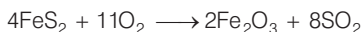
- (a) In moist condition SO₂ gas acts as a bleaching agent.
e.g., it converts Fe (III) to Fe (II) ion and decolourises acidified KMnO₄ (VII).



- (b) is incorrect it has bent structure.



- (c) Its dilute solution is used as a disinfectant.
- (d) It can be prepared by the reaction of O₂ with sulphide ore,



while metal on treatment with H₂SO₄ produces H₂S.

Hence, options (a) and (c) are correct choices.

Q. 33 Which of the following statements are correct?

- (a) All the three N — O bond lengths in HNO₃ are equal.
- (b) All P — Cl bond lengths in PCl₅ molecule in gaseous state are equal
- (c) P₄ molecule in white phosphorus have angular strain therefore white phosphorus is very reactive
- (d) PCl₅ is ionic in solid state in which cation is tetrahedral and anion is octahedral.

Ans. (c, d)

- (a) All the three N—O bond lengths in HNO_3 are not equal.
- (b) All P—Cl bond lengths in PCl_5 molecule in gaseous state are not equal. Axial bond is longer than equatorial bond.
- (c) P_4 molecule in white phosphorous have angular strain therefore white phosphorous is very reactive.
- (d) PCl_5 is ionic in solid state in which cation is tetrahedral and anion is octahedral.

Cation — $[\text{PCl}_4]^+$

Anion — $[\text{PCl}_6]^-$

Q. 34 Which of the following orders are correct as per the properties mentioned against each?

(a) $\text{As}_2\text{O}_3 < \text{SiO}_2 < \text{P}_2\text{O}_3 < \text{SO}_2$

Acid strength.

(b) $\text{AsH}_3 < \text{PH}_3 < \text{NH}_3$

Enthalpy of vaporisation.

(c) $\text{S} < \text{O} < \text{Cl} < \text{F}$

More negative electron gain enthalpy.

(d) $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

Thermal stability.

Ans. (a, d)

(a) $\xrightarrow[\text{acidic strength increases}]{\text{As}_2\text{O}_3 < \text{SiO}_2 < \text{P}_2\text{O}_3 < \text{SO}_2}$

(b) Correct order is $\xleftarrow[\text{enthalpy of vaporisation}]{\text{AsH}_3 > \text{PH}_3 > \text{NH}_3}$

(c) $\text{S} < \text{O} < \text{Cl} < \text{F}$ More negative electron gain enthalpy

(d) $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$ Thermal stability decreases on moving top to bottom due to increase in its bond length.

Q. 35 Which of the following statements are correct?

(a) S—S bond is present in $\text{H}_2\text{S}_2\text{O}_6$

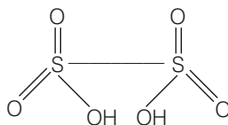
(b) In peroxosulphuric acid (H_2SO_5) sulphur is in + 6 oxidation state

(c) Iron powder along with Al_2O_3 and K_2O is used as a catalyst in the preparation of NH_3 by Haber's process

(d) Change in enthalpy is positive for the preparation of SO_3 by catalytic oxidation of SO_2

Ans. (a, b)

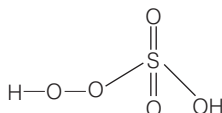
(a) Structure of $\text{H}_2\text{S}_2\text{O}_6$ is as shown below



It contains one S—S bond.

(b) In peroxosulphuric acid (H_2SO_5) sulphur is in + 6 oxidation state.

Structure of H_2SO_5 is



Let oxidation state of S = x

$$2 \times (+1) + x + 3 \times (-2) + 2 \times (-1) = 0$$

$$x - 6 = 0$$

$$x = 6$$

- (c) During preparation of ammonia, iron oxide with small amount of K_2O and Al_2O_3 is used as a catalyst to increase the rate of attainment of equilibrium.
- (d) Change in enthalpy is negative for preparation of SO_3 by catalytic oxidation of SO_2 .

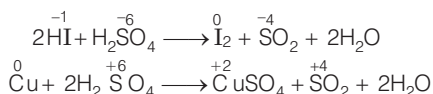
Q. 36 In which of the following reactions conc. H_2SO_4 is used as an oxidising reagent?

- (a) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$
- (b) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
- (c) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
- (d) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

Ans. (b, c)

In the above given four reactions, (b) and (c) represent oxidising behaviour of H_2SO_4 . As we know that oxidising agent reduces itself as oxidation state of central atom decreases.

Here,



Q. 37 Which of the following statements are true?

- (a) Only type of interactions between particles of noble gases are due to weak dispersion forces.
- (b) Ionisation enthalpy of molecular oxygen is very close to that of xenon.
- (c) Hydrolysis of XeF_6 is a redox reaction.
- (d) Xenon fluorides are not reactive.

Ans. (a, b)

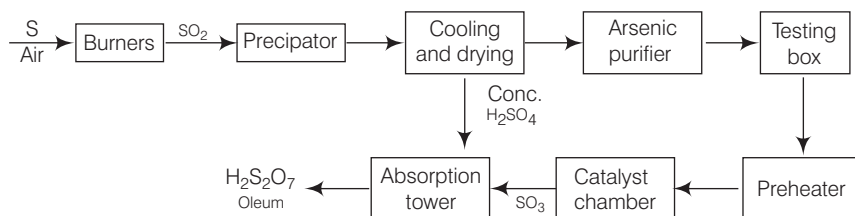
- (a) Only one type of interactions between particles of noble gases are due to weak dispersion forces.
- (b) Ionisation enthalpy of molecular oxygen is very close to that of xenon. This is the reason for the formation of xenon oxides.
- (c) Hydrolysis of XeF_6 ($\overset{+6}{Xe}\overset{-1}{F}_6 + 3\overset{+1}{H_2}\overset{-2}{O} \longrightarrow \overset{+6}{Xe}\overset{-2}{O}_3 + 3\overset{+1}{H}\overset{-1}{F}$) is not a redox reaction.
- (d) Xenon fluorides are highly reactive hydrolysis readily even by traces of water.

Short Answer Type Questions

Q. 38 In the preparation of H_2SO_4 by Contact process, why is SO_3 not absorbed directly in water to form H_2SO_4 ?

Ans. In Contact process SO_3 is not absorbed directly in water to form H_2SO_4 because the reaction is highly exothermic, acid mist is formed. Hence, the reaction becomes difficult to handle.

Note

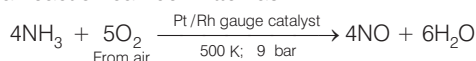


Flow chart of Contact process

Q. 39 Write a balanced chemical equation for the reaction showing catalytic oxidation of NH_3 by atmospheric oxygen.

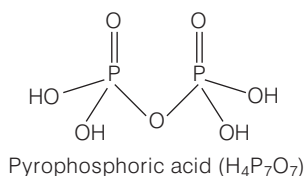
Ans. Ammonia (NH_3) on catalytic oxidation by atmospheric oxygen in presence of Rh/Pt gauge at 500K under pressure of 9 bar produces nitrous oxide.

Balanced chemical reaction can be written as



Q. 40 Write the structure of pyrophosphoric acid.

Ans. Molecular formula of pyrophosphoric acid is $\text{H}_4\text{P}_2\text{O}_7$ and its structure is as follows

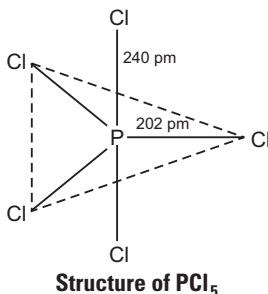


Q. 41 PH_3 forms bubbles when passed slowly in water but NH_3 dissolves. Explain why?

Ans. Dissolution of NH_3 and PH_3 in water can be explained on the basis of H-bonding. NH_3 forms H-bond with water so it is soluble but PH_3 does not form H-bond with water so it remains as gas and forms bubble in water.

Q. 42 In PCl_5 , phosphorus is in sp^3d hybridised state but all its five bonds are not equivalent. Justify your answer with reason.

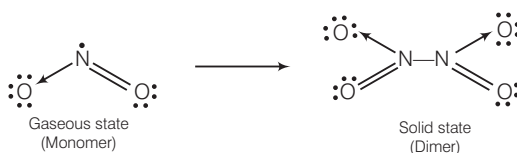
Ans. It has trigonal bipyramidal geometry, in which two Cl atoms occupy axial position while three occupy equatorial positions. All five P—Cl bonds are not identical. There are two types of bond lengths (i) Axial bond lengths (ii) Equatorial bond lengths



Thus, difference in bond length is due to fact that axial bond pairs suffer more repulsion as compared to equatorial bond pairs.

Q. 43 Why is nitric oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic?

Ans. In gaseous state, NO_2 exists as a monomer which has one unpaired electron but in solid state, it dimerises to N_2O_4 so no unpaired electron left. Therefore, NO_2 is paramagnetic in gaseous state but diamagnetic in solid state.

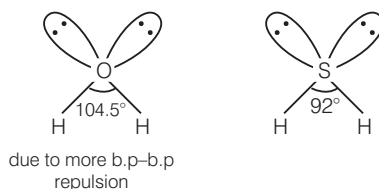


Q. 44 Give one reason to explain why ClF_3 exists but FCl_3 does not exist?

Ans. Existence of ClF_3 and FCl_3 can be explained on the basis of size of central atom. Because fluorine is more electronegative as compared to chlorine and has smaller size. Thus, one large Cl atom can accommodate three smaller F atoms but reverse is not true.

Q. 45 Out of H_2O and H_2S , which one has higher bond angle and why?

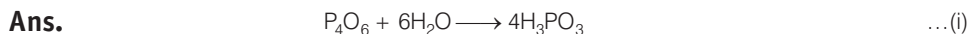
Ans. Bond angle of H_2O ($\text{H}—\text{O}—\text{H} = 104.5^\circ$) is larger than that of H_2S ($\text{H}—\text{S}—\text{H} = 92^\circ$) because oxygen is more electronegative than sulphur therefore, bond pair electron of O—H bond will be closer to oxygen and there will be more bond pair—bond pair repulsion between bond pairs of two O—H bonds.



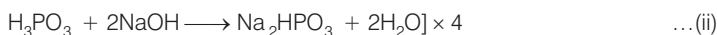
- Q. 51** P_4O_6 reacts with water according to equation $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$. Calculate the volume of 0.1 M NaOH solution required to neutralise the acid formed by dissolving 1.1 g of P_4O_6 in H_2O .

Thinking Process

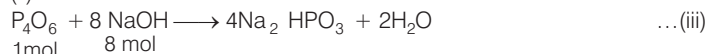
This problem includes conceptual mixing of chemical properties of oxides of phosphorus, mole concept and stoichiometry.



Neutralisation



Adding Eqs. (i) and (ii)



Number of moles of P_4O_6 ,

$$n = \frac{m}{M} = \frac{1.1}{220} = \frac{1}{200} \text{ mol}$$

(Molar mass of P_4O_6 = $(4 \times 31) + (6 \times 16) = 220$)

\therefore Product formed by 1 mole of P_4O_6 is neutralised by 8 moles NaOH

\therefore Product formed by $\frac{1}{200}$ moles of P_4O_6 will be neutralised by NaOH

$$= 8 \times \frac{1}{200} = \frac{8}{200} \text{ mole NaOH}$$

Given, Molarity of NaOH = 0.1 M = 0.1 mol/L

$$\text{Molarity} = \frac{\text{Number of moles}}{\text{Volume in litres}}$$

$$\text{Volume} = \frac{\text{Number of moles}}{\text{Molarity}} = \frac{8}{200} \times \frac{1}{0.1} = 0.4 \text{ L or } 400 \text{ mL}$$

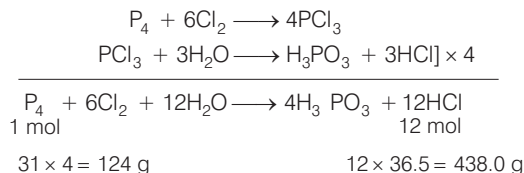
\therefore 400 mL NaOH is required.

- Q. 52** White phosphorus reacts with chlorine and the product hydrolyses in the presence of water. Calculate the mass of HCl obtained by the hydrolysis of the product formed by the reaction of 62 g of white phosphorus with chlorine in the presence of water.

Thinking Process

This problem is based on concept of chemical reaction of phosphorus and stoichiometry. Write balanced chemical reaction and then calculate the amount of HCl produced.

Ans. Equations for the reactions



\therefore 124 g of white phosphorus produces HCl = 438 g

\therefore 62 g of white phosphorus will produces

$$HCl = \frac{438}{124} \times 62 = 219.0 \text{ g HCl}$$

Q. 53 Name three oxoacids of nitrogen. Write the disproportionation reaction of that oxoacid of nitrogen in which nitrogen is in + 3 oxidation state.

Ans. Three oxoacids of nitrogen having oxidation state + 3 are

- (a) HNO_2 , nitrous acid
- (b) HNO_3 , nitric acid
- (c) Hyponitrous acid, $\text{H}_2\text{N}_2\text{O}_2$

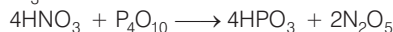
In HNO_2 , N is in + 3 oxidation state

Disproportionation reaction

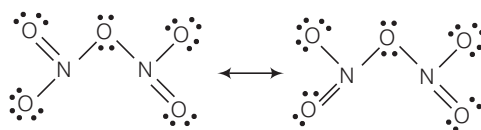


Q. 54 Nitric acid forms an oxide of nitrogen on reaction with P_4O_{10} . Write the reaction involved. Also write the resonating structures of the oxide of nitrogen formed.

Ans. P_4O_{10} being a dehydrating agent, on reaction with HNO_3 removes a molecule of water and forms anhydride of HNO_3 .



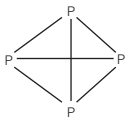
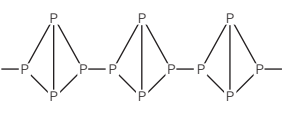
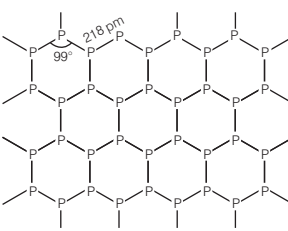
Resonating structures of N_2O_5 are



Q. 55 (i) white phosphorus (ii) red phosphorus and (iii) black phosphorus. Write the difference between white red and black phosphorus on the basis of their structure and reactivity.

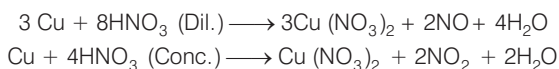
Phosphorus has three allotropic forms —

Ans.

White phosphorus	Red phosphorus	Black phosphorus
1. It is less stable form of P	More stable than white P.	It is most stable form of P
2. It is highly reactive. 	Less reactive than white P. 	It is least reactive. 
3. It has regular tetrahedron structure.	It has polymeric structure.	It has a layered structure.

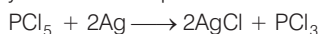
Q. 56 Give an example to show the effect of concentration of nitric acid on the formation of oxidation product.

Ans. Effect of concentration of nitric acid on the formation of oxidation product can be understood by its reaction with conc HNO_3 . Dilute and concentrated nitric acid give different oxidation products on reaction with copper metal.

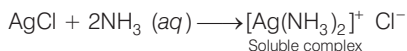


Q. 57 PCl_5 reacts with finely divided silver on heating and a white silver salt is obtained, which dissolves on adding excess aqueous NH_3 solution. Write the reactions involved to explain what happens.

Ans. PCl_5 on reaction with finely divided silver produced silver halide.

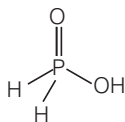


AgCl on further reaction with aqueous ammonia solution produces a soluble complex of $[\text{Ag}(\text{NH}_3)_2]^+ \text{Cl}^-$



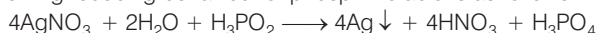
Q. 58 Phosphorus forms a number of oxoacids. Out of these oxoacids, phosphinic acid has strong reducing property. Write its structure and also write a reaction showing its reducing behaviour.

Ans. Among various forms of oxoacids, phosphinic acid has stronger reducing property.



Structure of phosphinic acid

Reaction showing reducing behaviour of phosphinic acid is as follows



Matching The Columns

Q. 59 Match the compounds given in Column I with the hybridisation and shape given in Column II and mark the correct option.

Column I	Column II
A. XeF_6	1. sp^3d^3 -distorted octahedral
B. XeO_3	2. sp^3d^2 -square planar
C. XeOF_4	3. sp^3 -pyramidal
D. XeF_4	4. sp^3d^2 -square pyramidal

Codes

A B C D
 (a) 1 3 4 2
 (c) 4 3 1 2

A B C D
 (b) 1 2 4 3
 (d) 4 1 2 3

Ans. (a) A. → (1) B. → (3) C. → (4) D. → (2)

S. No.	Compound	Hybridisation
A.		sp^3d^3 -distorted octahedral
B.		sp^3 -pyramidal
C.		sp^3d^2 -square pyramidal
D.		sp^3d^2 -square planar

Q. 60 Match the formulas of oxides given in Column I with the type of oxide given in Column II and mark the correct option.

Column I	Column II
A. Pb_3O_4	1. Neutral oxide
B. N_2O	2. Acidic oxide
C. Mn_2O_7	3. Basic oxide
D. Bi_2O_3	4. Mixed oxide

Codes

A	B	C	D
(a) 1	2	3	4
(c) 3	2	4	1

A	B	C	D
(b) 4	1	2	3
(d) 4	3	1	2

Ans. (b) A. → (4) B. → (1) C. → (2) D. → (3)

	Formulas of the compound	Type of oxide
A.	Pb_3O_4 ($PbO \cdot Pb_2O_3$)	Mixed oxide
B.	N_2O	Neutral oxide
C.	Mn_2O_7	Acidic oxide
D.	Bi_2O_3	Basic oxide

Mn_2O_7 on dissolution in water produces acidic solution.

Bi_2O_3 on dissolution in water produces basic solution.

Q. 61 Match the items of Columns I and II and mark the correct option.

Column I	Column II
A. H_2SO_4	1. Highest electron gain enthalpy
B. CCl_3NO_2	2. Chalcogen
C. Cl_2	3. Tear gas
D. Sulphur	4. Storage batteries

Codes

A B C D
 (a) 4 3 1 2
 (c) 4 1 2 3

A B C D
 (b) 3 4 1 2
 (d) 2 1 3 4

Ans. (a) A. \rightarrow (4) B. \rightarrow (3) C. \rightarrow (1) D. \rightarrow (2)

A. H_2SO_4 is used in storage batteries.

B. CCl_3NO_2 is known as tear gas.

C. Cl_2 has highest electron gain enthalpy.

D. Sulphur is a member of chalcogen *i.e.*, ore producing elements.

Q. 62 Match the species given in Column I with the shape given in Column II and mark the correct option.

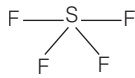

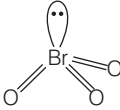
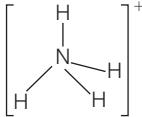
Column I	Column II
A. SF_4	1. Tetrahedral
B. BrF_3	2. Pyramidal
C. BrO_3^-	3. Sea-saw shaped
D. NH_4^+	4. Bent T-shaped

Codes

A B C D
 (a) 3 2 1 4
 (c) 1 2 3 4

A B C D
 (b) 3 4 2 1
 (d) 1 4 3 2

Ans. (b) A. \rightarrow (3) B. \rightarrow (4) C. \rightarrow (2) D. \rightarrow (1)

	Species	Shape	Structure
A.	SF_4	Sea-saw shaped	
B.	BrF_3	Bent T-shaped	
C.	BrO_3^-	Pyramidal	
D.	NH_4^+	Tetrahedral	

Q. 63 Match the items of Columns I and II and mark the correct option.

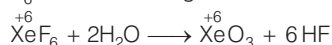
Column I	Column II
A. Its partial hydrolysis does not change oxidation state of central atom.	1. He
B. It is used in modern diving apparatus.	2. XeF_6
C. It is used to provide inert atmosphere for filling electrical bulbs.	3. XeF_4
D. Its central atom is in sp^3d^2 hybridisation.	4. Ar

Codes

A	B	C	D	A	B	C	D
(a) 1	4	2	3	(b) 1	2	3	4
(c) 2	1	4	3	(d) 1	3	2	4

Ans. (c) A. \rightarrow (2) B. \rightarrow (1) C. \rightarrow (4) D. \rightarrow (3)

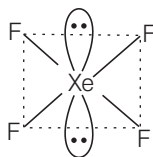
(A) Partial hydrolysis of XeF_6 does not change oxidation state of central atom.



(B) He is used in modern diving apparatus.

(C) Ar is used to provide inert atmosphere for filling electrical bulbs

(D) Central atom (Xe) of XeF_4 is in sp^3d^2 hybridisation.



Square planar geometry

Assertion and Reason

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- Both Assertion and Reason are correct statements, and Reason is the correct explanation of the Assertion.
- Both Assertion and Reason are correct statements, and Reason is not the correct explanation of the Assertion.
- Assertion is correct, but Reason is wrong statement.
- Assertion is wrong but Reason is correct statement.
- Both Assertion and Reason are wrong statements.

Q. 64 Assertion (A) N_2 is less reactive than P_4 .

Reason (R) Nitrogen has more electron gain enthalpy than phosphorus.

Ans. (c) Assertion is true, but reason is false.

N_2 is less reactive than P_4 due to high value of bond dissociation energy which is due to presence of triple bond between two N-atoms of N_2 molecule.

Q. 65 Assertion (A) HNO_3 makes iron passive.

Reason (R) HNO_3 forms a protective layer of ferric nitrate on the surface of iron.

Ans. (c) Assertion is true, but reason is false.

HNO_3 makes iron passive due to formation of passive form of oxide on the surface. Hence, Fe does not dissolve in conc HNO_3 solution.

Q. 66 Assertion (A) HI cannot be prepared by the reaction of KI with concentrated H_2SO_4 .

Reason (R) HI has lowest H—X bond strength among halogen acids.

Ans. (b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

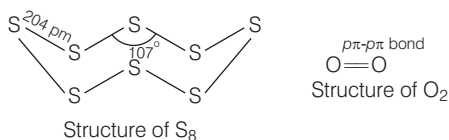
HI cannot be prepared by the reaction of KI with concentrated H_2SO_4 because HI is converted into I_2 on reaction with H_2SO_4 .

Q. 67 Assertion (A) Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2 .

Reason (R) Oxygen forms $p\pi - p\pi$ multiple bond due to small size and small bond length but $p\pi - p\pi$ bonding is not possible in sulphur.

Ans. (a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2 , because oxygen forms $p\pi - p\pi$ multiple bond due to its small size and small bond length. But $p\pi - p\pi$ bonding is not possible in sulphur due to its bigger size as compared to oxygen.

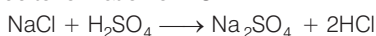


Q. 68 Assertion (A) $NaCl$ reacts with concentrated H_2SO_4 to give colourless fumes with pungent smell. But on adding MnO_2 the fumes become greenish yellow.

Reason (R) MnO_2 oxidises HCl to chlorine gas which is greenish yellow.

Ans. (a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

$NaCl$ reacts with concentrated H_2SO_4 to give colourless fumes with pungent smell. Pungent smell is due to formation of HCl .



But on adding MnO_2 the fumes become greenish yellow due to formation of chlorine gas.

Q. 69 Assertion (A) SF_6 cannot be hydrolysed but SF_4 can be.

Reason (R) Six F-atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6 .

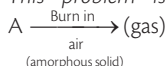
Ans. (a) Assertion and reason both are true and reason is the correct explanation of assertion. SF_4 can be hydrolysed but SF_6 can not because six F-atoms in SF_6 prevent the attack of H_2O on sulphur atoms of SF_6 .

Long Answer Type Questions

Q. 70 An amorphous solid "A" burns in air to form a gas "B" which turns lime water milky. The gas is also produced as a by-product during roasting of sulphide ore. This gas decolourises acidified aqueous KMnO_4 solution and reduces Fe^{3+} to Fe^{2+} . Identify the solid "A" and the gas "B" and write the reactions involved.

Thinking Process

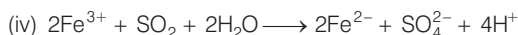
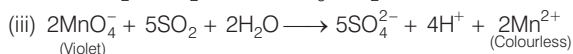
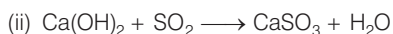
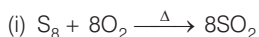
This problem is based on concept of properties of sulphur and its oxide.



Amorphous solid A gives B is a gas which turns lime water milky and also produced as a by product during roasting of sulphide ore. This gas decolourises acidified aqueous KMnO_4 solution and reduces Fe^{3+} to Fe^{2+} . Hence, compound B (g) must be SO_2 .

Ans. Since, the by-product of roasting of sulphide ore is SO_2 , so A is S_8 'A' = S_8 ; 'B' = SO_2

Reactions



Q. 71 On heating lead (II) nitrate gives a brown gas "A". The gas "A" on cooling changes to colourless solid "B". Solid "B" on heating with NO changes to a blue solid 'C'. Identify 'A', 'B' and 'C' and also write reactions involved and draw the structures of 'B' and 'C'.

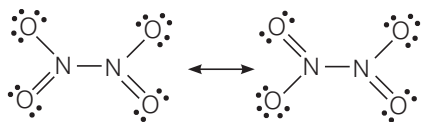
Thinking Process

This problem is based on preparation and properties of NO_2 .

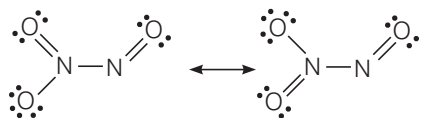
Ans. $\text{Pb(NO}_3)_2$ on heating produces a brown coloured gas which may be NO_2 . Since, on reaction with N_2O_4 and on heating it produces N_2O_3 and N_2O_4 respectively.

Structures

(i) N_2O_4

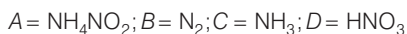


(ii) N_2O_3



Q. 72 On heating compound (A) gives a gas (B) which is a constituent of air. This gas when treated with 3 moles of hydrogen (H_2) in the presence of a catalyst gives another gas (C) which is basic in nature. Gas C on further oxidation in moist condition gives a compound (D) which is a part of acid rain. Identify compounds (A) to (D) and also give necessary equations of all the steps involved.

Ans. The main constituents of air are nitrogen (78%) and oxygen (21%). Only N_2 reacts with three moles of H_2 in the presence of a catalyst to give NH_3 (ammonia) which is a gas having basic nature. On oxidation, NH_3 gives NO_2 which is a part of acid rain. So, the compounds A to D are as



Reactions involved can be given, as

