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1 Solid State

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

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

(*i*) High temperature (*ii*) Low temperature
(*iii*) High thermal energy (*iv*) Weak cohesive forces

Ans. (*ii*) Low temperature

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

(*i*) Definite and characteristic heat of fusion.
(*ii*) Isotropic nature.
(*iii*) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal.
(*iv*) A true solid

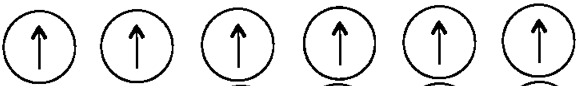
Ans. (*ii*) Isotropic nature.

3. Which of the following is an amorphous solid?

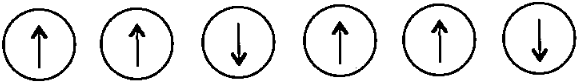
(*i*) Graphite (C) (*ii*) Quartz glass (SiO_2)
(*iii*) Chrome alum (*iv*) Silicon carbide (SiC)

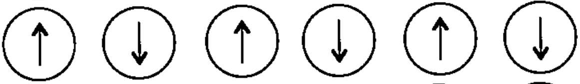
Ans. (*ii*) Quartz glass (SiO_2)

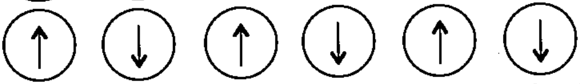
4. Which of the following arrangements shows schematic alignment of magnetic moments of antiferromagnetic substances?

(*i*)


(*ii*)


(*iii*)


(*iv*)


Ans. (*iv*)


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

(*i*) Same in all directions (*ii*) Different in different directions
(*iii*) Cannot be measured (*iv*) Always zero

Ans. (*i*) Same in all directions

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

(*i*) On heating they may become crystalline at certain temperature.

(*ii*) They may become crystalline on keeping for long time.

(*iii*) Amorphous solids can be moulded by heating.

(*iv*) They are anisotropic in nature.

Ans. (*iv*) They are anisotropic in nature.

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

(*i*) a regular arrangement of constituent particles observed over a short distance in the crystal lattice.

(*ii*) a regular arrangement of constituent particles observed over a long distance in the crystal lattice.

(*iii*) same arrangement of constituent particles in different directions.

(*iv*) different arrangement of constituent particles in different directions.

Ans. (*ii*) a regular arrangement of constituent particles observed over a long distance in the crystal lattice.

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

(*i*) london forces (*ii*) dipole-dipole interactions

(*iii*) covalent bonds (*iv*) coulombic forces

Ans. (*i*) London forces

9. Which of the following is a network solid?

(*i*) SO_2 (Solid) (*ii*) I_2

(*iii*) Diamond (*iv*) H_2O (Ice)

Ans. (*iii*) Diamond

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

(A) Mg (s) (B) TiO (s) (C) I_2 (s) (D) H_2O (s)

(*i*) (A) only (*ii*) (B) Only

(*iii*) (C) and (D) (*iv*) (B), (C) and (D)

Ans. (*iii*) (C) and (D)

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

(*i*) Very low value of electrical conductivity in the molten state.

(*ii*) Brittle nature.

(*iii*) Very strong forces of interactions.

(*iv*) Anisotropic nature.

Ans. (*i*) Very low value of electrical conductivity in the molten state.

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

(*i*) lone pair of electrons (*ii*) free valence electrons

(*iii*) cations (*iv*) anions

Ans. (*ii*) free valence electrons

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

(*i*) TiO	(*ii*) SiO_2
(*iii*) TiO_3	(*iv*) MgO

Ans. (*iii*) TiO_3

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

(*i*) SiO_2	(*ii*) MgO
(*iii*) $SO_2(s)$	(*iv*) CrO_2

Ans. (*iv*) CrO_2

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

(*i*) molecule	(*ii*) ion
(*iii*) electron	(*iv*) atom

Ans. (*iii*) electron

16. Graphite cannot be classified as __________.

(*i*) conducting solid	(*ii*) network solid
(*iii*) covalent solid	(*iv*) ionic solid

Ans. (*iv*) ionic solid

17. Cations are present in the interstitial sites in __________.

(*i*) Frenkel defect	(*ii*) Schottky defect
(*iii*) Vacancy defect	(*iv*) Metal deficiency defect

Ans. (*i*) Frenkel defect

18. Schottky defect is observed in crystals when __________.
    (*i*) some cations move from their lattice site to interstitial sites.
    (*ii*) equal number of cations and anions are missing from the lattice.
    (*iii*) some lattice sites are occupied by electrons.
    (*iv*) some impurity is present in the lattice.

Ans. (*ii*) equal number of cations and anions are missing from the lattice.

19. Which of the following is true about the charge acquired by *p*-type semiconductors?
    (*i*) positive (*ii*) neutral
    (*iii*) negative
    (*iv*) depends on concentration of *p* impurity

Ans. (*ii*) neutral

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

(*i*) 2	(*ii*) 1
(*iii*) 3	(*iv*) 5

Ans. (*iv*) 5

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

(*i*) 6	(*ii*) 8
(*iii*) 10	(*iv*) 12

Ans. (*ii*) 8

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

(A) Schottky defect
(B) Frenkel defect
(C) Metal excess defect
(D) Metal deficiency defect

(*i*) (A) and (B)
(*ii*) (C) and (D)
(*iii*) (A) and (B)
(*iv*) (B) and (D)

Ans. (*i*) (A) and (B)

23. In which pair most efficient packing is present?

(*i*) *hcp* and *bcc*
(*ii*) *hcp* and *ccp*
(*iii*) *bcc* and *ccp*
(*iv*) *bcc* and simple cubic cell

Ans. (*ii*) *hcp* and *ccp*

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

(*i*) 74
(*ii*) 68
(*iii*) 32
(*iv*) 26

Ans. (*iii*) 32

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

(*i*) The coordination number is 12.
(*ii*) It has 74% packing efficiency.
(*iii*) Tetrahedral voids of the second layer are covered by the spheres of the third layer.
(*iv*) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer.

Ans. (*iv*) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer.

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

(*i*) Cl^- ion form *fcc* lattice and Na^+ ions occupy all octahedral voids of the unit cell.
(*ii*) Ca^{2+} ions form *fcc* lattice and F^- ions occupy all the eight tetrahedral voids of the unit cell.
(*iii*) O_2^- ions form *fcc* lattice and Na^+ ions occupy all the eight tetrahedral voids of the unit cell.
(*iv*) S^{2-} ions form *fcc* lattice and Zn^{2-} ions go into alternate tetrahedral voids of the unit cell.

Ans. (*i*) Cl^- ion form *fcc* lattice and Na^+ ions occupy all octahedral voids of the unit cell.

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

(*i*) 2
(*ii*) 3
(*iii*) 4
(*iv*) 6

Ans. (*iii*) 4

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28. Which kind of defects are introduced by doping?

(*i*) Dislocation defect	(*ii*) Schottky defect
(*iii*) Frenkel defects	(*iv*) Electronic defects

Ans. (*iv*) Electronic defects

29. Silicon doped with electron-rich impurity forms __________.

(*i*) *p*-type semiconductor	(*ii*) *n*-type semiconductor
(*iii*) intrinsic semiconductor	(*iv*) insulator

Ans. (*ii*) *n*-type semiconductor

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

(*i*) Paramagnetic substances are weakly attracted by magnetic field.

(*ii*) Ferromagnetic substances cannot be magnetised permanently.

(*iii*) The domains in antiferromagnetic substances are oppositely oriented with respect to each other.

(*iv*) Pairing of electrons cancels their magnetic moment in the diamagnetic substances.

Ans. (*ii*) Ferromagnetic substances cannot be magnetised permanently.

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

(*i*) Bigger ions form the close packed structure.

(*ii*) Smaller ions occupy either the tetrahedral or the octahedral voids depending upon their size.

(*iii*) Occupation of all the voids is not necessary.

(*iv*) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions occupying the voids.

Ans. (*iv*) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions occupying the voids.

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

(*i*) all the domains get oriented in the direction of magnetic field.

(*ii*) all the domains get oriented in the direction opposite to the direction of magnetic field.

(*iii*) domains get oriented randomly.

(*iv*) domains are not affected by magnetic field.

Ans. (*i*) all the domains get oriented in the direction of magnetic field.

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

(*i*) *fcc* < *bcc* < simple cubic	(*ii*) *fcc* > *bcc* > simple cubic
(*iii*) *fcc* < *bcc* > simple cubic	(*iv*) *bcc* < *fcc* > simple cubic

Ans. (*ii*) *fcc* > *bcc* > simple cubic

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

(*i*) Frenkel defect	(*ii*) Schottky defect
(*iii*) Non-stoichiometric defect	(*iv*) Simple interstitial defect

Ans. (*i*) Frenkel defect

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35. In the cubic close packing, the unit cell has __________.
   (*i*) 4 tetrahedral voids each of which is shared by four adjacent unit cells.
   (*ii*) 4 tetrahedral voids within the unit cell.
   (*iii*) 8 tetrahedral voids each of the which is shared by four adjacent unit cells.
   (*iv*) 8 tetrahedral voids within the unit cells.

Ans. (*iv*) 8 tetrahedral voids within the unit cells.

36. The edge lengths of the unit cells in terms of the radius of spheres constituting fcc, bcc and simple cubic unit cell are respectively __________.
   (*i*) $2\sqrt{2r}, \frac{4r}{\sqrt{3}}, 2r$ (*ii*) $\frac{4r}{\sqrt{3}}, 2\sqrt{2r}, 2r$
   (*iii*) $2r, 2\sqrt{2r}, \frac{4r}{\sqrt{3}}$ (*iv*) $2r, \frac{4r}{\sqrt{3}}, 2\sqrt{2r}$

Ans. (*i*) $2\sqrt{2r}, \frac{4r}{\sqrt{3}}, 2r$

37. Which of the following represents correct order of conductivity in solids?
   (*i*) $\kappa_{\text{metals}} >> \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
   (*ii*) $\kappa_{\text{metals}} << \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
   (*iii*) $\kappa_{\text{metals}} < \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} = \text{zero}$
   (*iv*) $\kappa_{\text{metals}} < \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} \neq \text{zero}$

Ans. (*i*) $\kappa_{\text{metals}} >> \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note: In the following questions two or more options may be correct.

38. Which of the following is **not** true about the voids formed in 3 dimensional hexagonal close packed structure?
   (*i*) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer.
   (*ii*) All the triangular voids are not covered by the spheres of the second layer.
   (*iii*) 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.
   (*iv*) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer.

Ans. (*iii*) and (*iv*)

39. The value of magnetic moment is zero in the case of antiferromagnetic substances because the domains.
   (*i*) get oriented in the direction of the applied magnetic field.
   (*ii*) get oriented opposite to the direction of applied magnetic field.

(*iii*) are oppositely oriented with respect to each other without the application of magnetic field.

(*iv*) cancel out each other's magnetic moment.

Ans. (*iii*) and (*iv*)

Explanation: Anti ferromagnetic substances: The magnetic moments and domains are oppositely oriented and cancel out each others magnetic moment. Example MnO

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

(*i*) Vacancy defect results in a decrease in the density of the substance.

(*ii*) Interstitial defects results in an increase in the density of the substance.

(*iii*) Impurity defect has no effect on the density of the substance.

(*iv*) Frenkel defect results in an increase in the density of the substance.

Ans. (*iii*) and (*iv*)

Explanation: In impurity defect the ion (usually cation) is dislocated (moved) from its normal lattice site to an interstitial site. So it is also called dislocation defect. It does not change the density of the crystal. It only creates cationic vacancies. Frenkel defect causes vacancy defect at its original site and an interstitial defect at its new location. Thus, it does not change the density of the solid.

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

(*i*) Valence band overlaps with conduction band.

(*ii*) The gap between valence band and conduction band is negligible.

(*iii*) The gap between valence band and conduction band cannot be determined.

(*iv*) Valence band may remain partially filled.

Ans. (*i*), (*ii*) and (*iv*)

Explanation: Gap between valence band and conduction band determines the conductivity of the metal thus all the three options could be correct.

42. Under the influence of electric field, which of the following statements is true about the movement of electrons and holes in a *p*-type semi-conductor?

(*i*) Electron will move towards the positvely charged plate through electron holes.

(*ii*) Holes will appear to be moving towards the negatively charged plate.

(*iii*) Both electrons and holes appear to move towards the positively charged plate.

(*iv*) Movement of electrons is not related to the movement of holes.

Ans. (*i*) and (*ii*)

Explanation: Silicon or Germanium (group – 14) doped with electron deficient impurity (group-13 element like B or Al or Ga) is called *p*-type

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semiconductors. Here conductivity is due to positively charged electron holes.

43. Which of the following statements are true about semiconductors?
   (*i*) Silicon doped with electron rich impurity is a *p*-type semiconductor.
   (*ii*) Silicon doped with an electron rich impurity is an *n*-type semiconductor.
   (*iii*) Delocalised electrons increase the conductivity of doped silicon.
   (*iv*) An electron vacancy increases the conductivity of *n*-type semiconductor.

Ans. (*ii*) and (*iii*)

44. An excess of potassium ions makes KCl crystals appear violet or lilac in colour since ________.
   (*i*) some of the anionic sites are occupied by an unpaired electron.
   (*ii*) some of the anionic sites are occupied by a pair of electrons.
   (*iii*) there are vacancies at some anionic sites.
   (*iv*) F-centres are created which impart colour to the crystals

Ans. (*i*) and (*iv*)

Explanation: The anionic vacancies occupied by unpaired electrons. F-centers impart colour to the crystals (E.g. yellow to NaCl and violet to KCl) due to excitation of these electrons by absorbing energy from the visible light falling on the crystals.

45. The number of tetrahedral voids per unit cell in NaCl crystal is
   (*i*) 4
   (*ii*) 8
   (*iii*) twice the number of octahedral voids.
   (*iv*) four times the number of tetrahedral voids.

Ans. (*ii*) and (*iii*)

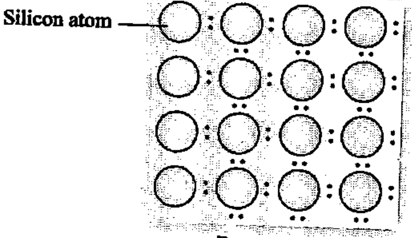
Explanation: NaCl has *fcc* lattice. No. of atoms = 4
No . of octahedral void = 4. No. of tetrahedral void = 2 × 4 = 8

46. Amorphous solid can also be called ________.
   (*i*) pseudo solids
   (*ii*) true solids
   (*iii*) super cooled liquids
   (*iv*) super cooled solids

Ans. (*i*) and (*iii*)

Explanation: It has tendency to flow like liquid.

47. A perfect crystal of silicon (See Figure) is doped with some elements as given in the options. Which of these options show *n*-type semiconductors?



Pure crystal

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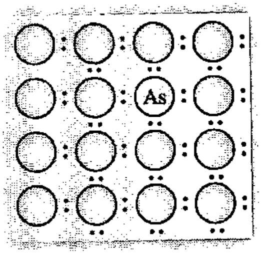
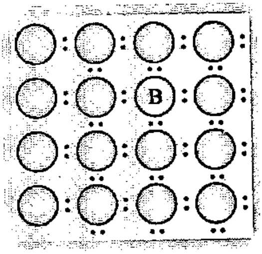
(*i*)



(*ii*)



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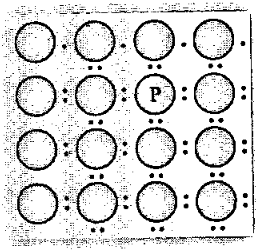
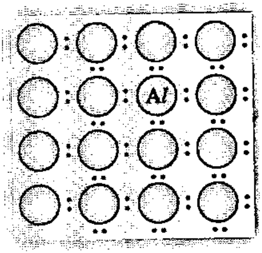


(*iv*)



Ans. (*i*) and (*iii*)

48. Which of the following statements are correct?

(*i*) Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic.

(*ii*) Ferrimagnetic substances do not lose ferrimagnetism on heating and remain ferrimagnetic.

(*iii*) Antiferromagnetic substances have domain structures similar to ferromagnetic substances and their magnetic moments are not cancelled by each other.

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

Ans. (*i*) and (*iv*)

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

(*i*) This is a crystalline solid.

(*ii*) Refractive index is same in all the directions.

(*iii*) This has definite heat of fusion.

(*iv*) This is also called super cooled liquid.

Ans. (*i*) and (*iii*)

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

(*i*) SiC (Silicon carbide) (*ii*) AlN

(*iii*) Diamond (*iv*) I_2

Ans. (*i*), (*ii*) and (*iii*)

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

(*i*) *hcp* (*ii*) *bcc*

(*iii*) simple cubic (*iv*) *fcc*

Ans. (*i*) and (*iv*)

52. Frenkel defect is also known as ________.

(*i*) stoichiometric defect
(*ii*) dislocation defect
(*iii*) impurity defect
(*iv*) non-stoichiometric defect

Ans. (*i*) and (*ii*)

53. Which of the following defects decrease the density?

(*i*) Interstitial defect
(*ii*) Vacancy defect
(*iii*) Frenkel defect
(*iv*) Schottky defect

Ans. (*ii*) and (*iv*)

III. SHORT ANSWER TYPE

54. Why are liquids and gases categorised as fluids?

Ans. The liquids and gases have a property to flow i.e. the molecules can move past and tumble over one another freely. Hence, they have been categorised as fluids.

55. Why are solids incompressible?

Ans. The constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.

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

Ans. Crystals have long range order repeated pattern of arrangement of constitutent 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.

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

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

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 for the loss of positive charge. Eventually there would be less amount of metal as compared to stoichiometric proportion

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

Ans. On heating ZnO loses oxygen according to the following reaction:

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

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

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

Ans. In case of semiconductors, with increase in temperature, more electrons can shift from valence band to conduction band. Hence conductivity increases.

61. Explain why does conductivity of germanium crystals increase on doping with galium.

Ans. On doping germanium with galium some of the positions of lattice of germanium are occupied by galium. Galium atom has only three valence electrons. Therefore, fourth valency of nearby germanium atom is not satisfied. 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 gap, thereby creating a hole in its original position. Under the influence of electric field electron move towards positively charged plates through these holes and conduct electricity. The holes appear to move towards negatively charged plates.

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 atom in *ccp* = x

Number of tetrahedral voids = $2x$

Number of M atoms = $1/3 \times 2x$

N : M = $3x : 2x = 3 : 2$

Formula of the compound = M_2N_3

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

Ans. On heating amorphous substance change to crystalline form at some temperature.This is due to crystallization.

IV. MATCHING TYPE

Note: In the following questions match the items given in Column I with the items given in Column II. In some questions more than one item of Column I and Column II may match.

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

Column I	Column II
(*i*) Simple vacancy defect	(*a*) shown by non-ionic solids and increases density of the solid.
(*ii*) Simple interstitial defect	(*b*) shown by ionic solids and decreases density of the solid.
(*iii*) Frenkel defect	(*c*) shown by non ionic solids and density of the solid decreases
(*iv*) Schottky defect	(*d*) shown by ionic solids and density of he solid remains the same.

Ans. (*i*) → (*c*); (*ii*) → (*a*); (*iii*) → (*d*); (*iv*) → (*b*)

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

Column I	Column II
(*i*) Primitive cubic unit cell	(*a*) Each of the three perpendicular edges compulsorily have the different edge length *i.e*; a≠b≠c.
(*ii*) Body centred cubic unit cell	(*b*) Number of atoms per unit cell is one.
(*iii*) Face centred cubic unit cell	(*c*) Each of the three perpendicular edges compulsorily have the same edge length *i.e*; a = b = c
(*iv*) End centred orthorhombic unit cell	(*d*) In addition to the contribution from unit cell the corner atoms the number of atoms present in a unit cell is one.
	(*e*) In addition to the contribution from the corner atoms the number of atoms present in a unit cell is three.

Ans. (*i*) → (*b*), (*c*); (*ii*) → (*c*), (*d*); (*iii*) → (*c*), (*e*); (*iv*) → (*a*), (*d*)

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

Column I	Column II
(*i*) Impurity defect	(*a*) NaCl with anionic sites called F-centres
(*ii*) Metal excess defect	(*b*) FeO with Fe^{3+}
(*iii*) Metal deficiency defect	(*c*) NaCl with Sr^{2+} and some cationic sites vacant

Ans. (*i*) → (*c*); (*ii*) → (*a*); (*iii*) → (*b*)

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

Column I	Column II
(*i*) Mg in solid state	(*a*) *p*-Type semiconductor
(*ii*) $MgCl_2$ in molten state	(*b*) *n*-Type semiconductor
(*iii*) Silicon with phosphorus	(*c*) Electrolytic conductors
(*iv*) Germanium with boron	(*d*) Electronic conductors

Ans. (*i*) → (*d*); (*ii*) → (*c*); (*iii*) → (*b*); (*iv*) → (*a*)

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

Column I	Column II
(*i*) Square close packing in two dimensions	(*a*) Triangular voids
(*ii*) Hexagonal close packing in two dimensions	(*b*) Pattern of spheres is repeated in every fourth layer
(*iii*) Hexagonal close packing in three dimensions	(*c*) Coordination number 4
(*iv*) Cubic close packing in three dimensions	(*d*) Pattern of sphere is repeated alternate layers

Ans. (*i*) → (*c*); (*ii*) → (*a*); (*iii*) → (*d*); (*iv*) → (*b*)

V. ASSERTION AND REASON TYPE

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(*ii*) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(*iii*) Assertion is correct statement but reason is wrong statement.

(*iv*) Assertion is wrong statement but reason is correct statement.

69. **Assertion:** The total number of atoms present in a simple cubic unit cell is one.

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

Ans. (*i*)

Explanation: In simple cubic unit cell total no. of atoms = $8 \times 1/8 = 1$

70. **Assertion:** Graphite is a good conductor of electricity however diamond belongs to the category of insulators.

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

Ans. (*ii*)

Explanation: In graphite carbon atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between different layers and is free to move which makes graphite a good conductor of electricity. As different layers can slide over each other so it is soft.

In case of diamond C atom is bonded covalently. So it is hard and have very high melting point. It decomposes before melting so act as insulator.

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71. **Assertion:** 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: 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. (*iii*)

Explanation: In *ccp* structure atoms are present at the face centre as well as corner and create octahedral void at each body centre and all the 12 edges of the unit cell which is surrounded by 6 atoms. 4 atoms belong to the same unit cell and 2 belongs to the adjacent unit cell.

72. **Assertion:** The packing efficiency is maximum for the *fcc* structure.
Reason: The cordination number is 12 in *fcc* structures.

Ans. (*ii*)

Explanation: The correct explanation is, in fcc no. of atoms present = 4 and packing efficiency is 74%.

73. **Assertion:** Semiconductors are solids with conductivities in the intermediate range from $10^{-6} - 10^{4}$ ohm^{-1}m^{-1}.
Reason: Intermediate conductivity in semiconductor is due to partially filled valence band.

Ans. (*iii*)

Explanation: Intermediate conductivity in semiconductor is due to small energy gap between valence band and conduction band.

VI. LONG ANSWER TYPE

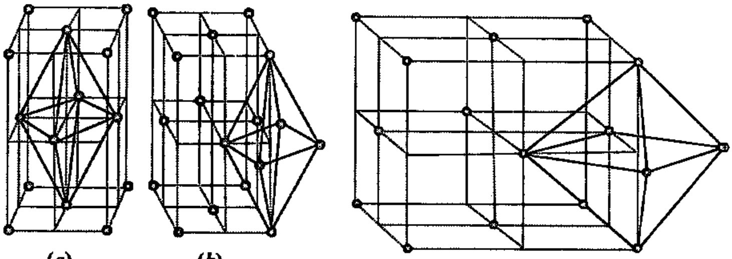
74. With the help of a labelled diagram show that there are four octahedral voids per unit cell in a cubic close packed structure.

Ans. As we know any atom surrounded by six atoms creates an octahedral void. In *fcc* body centre is surrounded by six atoms present at face centre. And hence one octahedral void is present at body centre of each unit cell.

No. of octahedral void at the centre of 12 edge = $\frac{1}{4} \times 12 = 3$

No. of octahedral void at body centre = 1

Total no. of octahedral void in ccp = 3 + 1 = 4



(*a*) (*b*)

Fig. 1 Location of octahedral voids per unit cell of *ccp* or *fcc* lattice (*a*) at the body centre of the cube and (*b*) at the centre of each edge (only one such void is shown).

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

Ans. In *ccp* structure unit cell is divided into 8 small cubes. Each small cube has atoms at alternate corners. In all, each small cube has 4 atoms. When joined to one another, they make a regular tetrahedron. Thus there is one tetrahedral void in each small cube and 8 tetrahedral void in total.

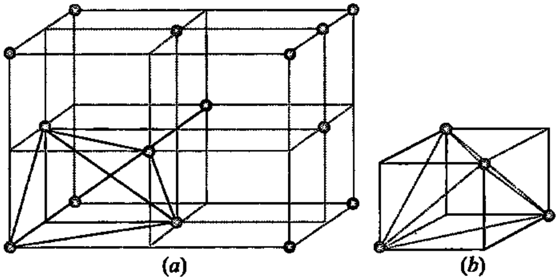


Fig. 2 (*a*) Eight tetrahedral voids per unit cell of ccp structure
(*b*) one tetrahedral void showing the geometry.

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

Ans. For practical use conductivity of a semiconductor is very low conductivity can be increased by adding small impurity ,this process is called doping. Doping can be done with an impurity which is electron rich or electron deficient.

***n*-type semiconductors:** Silicon or Germanium (group – 14) doped with electron rich impurity (group-15 element like P or As) is called n-type semiconductors. Here conductivity is due to the extra electron or delocalized electron.

***p*-type semiconductors:** Silicon or Gemanium (group – 14) doped with electron deficient impurity (group-13 element like B or Al or Ga) is called p-type semiconductors. Here conductivity is due to positively charged electron holes.

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

Ans. Let us consider out of 100 the no. of Fe^{2+} ion in the crystal = x

$Fe^{3+} = 93 - x$

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

$2x + 3(93 - x) = 200$

$2x + 279 - 3x = 200$

$-x = -79$ or $x = 79$

Fraction of $Fe^{2+} = 79/93 = 0.849$

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

❑❑❑

2 Solution

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

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

(*i*) mole fraction (*ii*) parts per million

(*iii*) mass percentage (*iv*) molality

Ans. (*i*)

Explanation: $p = k_H \times$ (According to Henry's law)

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?

(*i*) Sugar crystals in cold water.

(*ii*) Sugar crystals in hot water.

(*iii*) Powdered sugar in cold water.

(*iv*) Powdered sugar in hot water.

Ans. (*iv*)

Explanation: Higher the surface area higher will be the solubility and on increasing the temperature dissolution of sugar will increase since it is an endothermic process.

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

(*i*) less than the rate of crystallisation

(*ii*) greater than the rate of crystallisation

(*iii*) equal to the rate of crystallisation

(*iv*) zero

Ans. (*iii*)

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 _________.

(*i*) saturated (*ii*) supersaturated

(*iii*) unsaturated (*iv*) concentrated

Ans. (*ii*)

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

(*i*) Temperature (*ii*) Nature of solute

(*iii*) Pressure (*iv*) Nature of solvent

Ans. (*iii*) **Explanation:** Solubility of a solid in liquid does not depend upon pressure since solid and liquids are almost incompressible.

6. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to __________.
   (*i*) low temperature
   (*ii*) low atmospheric pressure
   (*iii*) high atmospheric pressure
   (*iv*) both low temperature and high atmospheric pressure

Ans. (*ii*) **Explanation:** At high altitude due to low atmospheric pressure the solubility of oxygen in blood get decreased.

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?
   (*i*) Methanol and acetone.
   (*ii*) Chloroform and acetone.
   (*iii*) Nitric acid and water.
   (*iv*) Phenol and aniline.

Ans. (*i*) **Explanation:** A-A interaction is greater than the A-B interaction. Intermolecular hydrogen bonding in methanol is more than methanol and acetone. So, methanol and acetone mixtures will show a positive deviation from Raoult's law.

8. Colligative properties depend on __________.
   (*i*) the nature of the solute particles dissolved in solution.
   (*ii*) the number of solute particles in solution.
   (*iii*) the physical properties of the solute particles dissolved in solution.
   (*iv*) the nature of solvent particles.

Ans. (*ii*)

9. Which of the following aqueous solutions should have the highest boiling point?
   (*i*) 1.0 M NaOH
   (*ii*) 1.0 M Na_2SO_4
   (*iii*) 1.0 M NH_4NO_3
   (*iv*) 1.0 M KNO_3

Ans. (*ii*)

Explanation: In 1.0 M Na_2SO_4 solution $i > 1$. So, the no. of ions dissociated will be more.

10. The unit of ebulioscopic constant is __________.
   (*i*) K kg mol^{-1} or K $(molality)^{-1}$
   (*ii*) mol kg K^{-1} or K^{-1} (molality)
   (*iii*) kg mol^{-1} K^{-1} or $K^{-1}(molality)^{-1}$
   (*iv*) K mol kg^{-1} or K (molality)

Ans. (*i*)

11. In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is __________.
   (*i*) the same
   (*ii*) about twice
   (*iii*) about three times
   (*iv*) about six times

Ans. (*iii*)

Explanation: Depression in freezing point is a colligative property in case of $MgCl_2$ value of van't. Hoff factor will be more. No. of ions dissociated in $MgCl_2 = 3$ that is why depression in freezing point of $MgCl_2$ will be three times.

12. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because ______________.
    (*i*) it gains water due to osmosis.
    (*ii*) it loses water due to reverse osmosis.
    (*iii*) it gains water due to reverse osmosis.
    (*iv*) it loses water due to osmosis.

Ans. (*iv*)

13. At a given temperature, osmotic pressure of a concentrated solution of a substance ______________.
    (*i*) is higher than that at a dilute solution.
    (*ii*) is lower than that of a dilute solution.
    (*iii*) is same as that of a dilute solution.
    (*iv*) cannot be compared with osmotic pressure of dilute solution.

Ans. (*i*)

Explanation: Osmotic pressure is directly proportional to the molar concentration of the solute particle in a solution.

14. Which of the following statements is false?
    (*i*) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.
    (*ii*) The osmotic pressure of a solution is given by the equation π = CRT (where C is the molarity of the solution).
    (*iii*) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is $BaCl_2 > KCl > CH_3COOH >$ sucrose.
    (*iv*) 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. (*i*)

Explanation: $\Delta T_f = k_f m$ (K_f depends on the nature of the solvent)

15. The values of van't Hoff factors for KCl, NaCl and K_2SO_4, respectively, are ______________.
    (*i*) 2, 2 and 2
    (*ii*) 2, 2 and 3
    (*iii*) 1, 1 and 2
    (*iv*) 1, 1 and 1

Ans. (*ii*)

16. Which of the following statements is **false**?
    (*i*) Units of atmospheric pressure and osmotic pressure are the same.
    (*ii*) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration.

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(*iii*) The value of molal depression constant depends on nature of solvent.

(*iv*) Relative lowering of vapour pressure, is a dimensionless quantity.

Ans. (*ii*)

17. Value of Henry's constant K_H ____________.

(*i*) increases with increase in temperature.

(*ii*) decreases with increase in temperature.

(*iii*) remains constant.

(*iv*) first increases then decreases.

Ans. (*i*)

18. The value of Henry's constant K_H is ____________.

(*i*) greater for gases with higher solubility.

(*ii*) greater for gases with lower solubility.

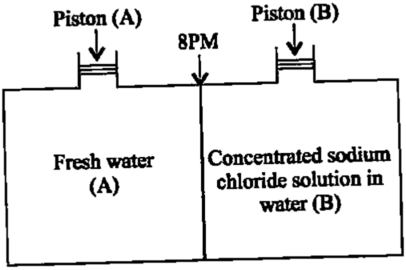
(*iii*) constant for all gases.

(*iv*) not related to the solubility of gases

Ans. (*ii*) greater for gases with lower solubility.

$p = k_H x \quad k_H = p/x$

19. Consider the figure and mark the correct option.



(*i*) water will move from side (A) to side (B) if a pressure lower than osmotic pressure is applied on piston (B).

(*ii*) water will move from side (B) to side (A) if a pressure greater than osmotic pressure is applied on piston (B).

(*iii*) water will move from side (B) to side (A) if a pressure equal to osmotic pressure is applied on piston (B).

(*iv*) water will move from side (A) to side (B) if pressure equal to osmotic pressure is applied on piston (A).

Ans. (*ii*)

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

(*i*) $i_A < i_B < i_C$ (*ii*) $i_A > i_B > i_C$

(*iii*) $i_A = i_B = i_C$ (*iv*) $i_A < i_B > i_C$

Ans. (*ii*)

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

Information:

(A) In bromoethane and chloroethane mixture intermolecular interactions of A–A and B–B type are nearly same as A–B type interactions.

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(B) In ethanol and acetone mixture A–A or B–B type intermolecular interactions are stronger than A–B type interactions.

(C) In chloroform and acetone mixture A–A or B–B type intermolecular interactions are weaker than A–B type interactions.

(*i*) Solution (B) and (C) will follow Raoult's law.

(*ii*) Solution (A) will follow Raoult's law.

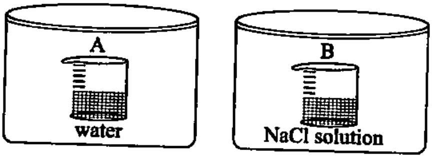
(*iii*) Solution (B) will show negative deviation from Raoult's law.

(*iv*) Solution (C) will show positive deviation from Raoult's law.

Ans. (*ii*)

Explanation: For an ideal solution A-A and B-B interaction should be nearly equal to A-B interaction.

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 2 M solution of NaCl. At the same temperature both the beakers were placed in closed containers of same material and same capacity as shown in Fig. 2.2.



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

(*i*) vapour pressure in container (A) is more than that in container (B).

(*ii*) vapour pressure in container (A) is less than that in container (B).

(*iii*) vapour pressure is equal in both the containers.

(*iv*) vapour pressure in container (B) is twice the vapour pressure in container (A).

Ans. (*i*)

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

(*i*) A–B interactions are stronger than those between A–A or B–B.

(*ii*) vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution.

(*iii*) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution.

(*iv*) A–B interactions are weaker than those between A–A or B–B.

Ans. (*i*)

24. 4L of 0.02 M aqueous solution of NaCl was diluted by adding one litre of water. The molarity of the resultant solution is _______________.

(*i*) 0.004 (*ii*) 0.008

(*iii*) 0.012 (*iv*) 0.016

Ans. (*iv*)

Explanation: Given, $M_1 = 0.02$ M, $V_1 = 4$ L, $M_2 = ?$, $V_2 = 5$ L
$M_1V_1 = M_2V_2 \quad 0.02 \times 4 \text{ L} = M_2 \times 5 \text{ L}$
$M_2 = 0.08/5 = 0.016$M

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.

(*i*) At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show positive deviation from Raoult's law.
(*ii*) At specific composition methanol-acetone mixture forms maximum boiling azeotrope and will show positive deviation from Raoult's law.
(*iii*) At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show negative deviation from Raoult's law.
(*iv*) At specific composition methanol-acetone mixture will form maximum boiling azeotrope and will show negative deviation from Raoult's law.

Ans. (*i*)
Explanation: A-A interaction is more than the A-B interaction.

26. K_H value for Ar(g), CO_2(g), HCHO (g) and CH_4(g) are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively.
Arrange these gases in the order of their increasing solubility.

(*i*) $HCHO < CH_4 < CO_2 < Ar$ (*ii*) $HCHO < CO_2 < CH_4 < Ar$
(*iii*) $Ar < CO_2 < CH_4 < HCHO$ (*iv*) $Ar < CH_4 < CO_2 < HCHO$

Ans. (*iii*)
Explanation: Higher the value of K_H lower will be the solubility of the gas at a given pressure.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note: *In the following questions two or more options may be correct.*

27. Which of the following factor (s) affect the solubility of a gaseous solute in the fixed volume of liquid solvent?
(*a*) nature of solute, (*b*) temperature, (*c*) pressure

(*i*) (*a*) and (*c*) at constant T (*ii*) (*a*) and (*b*) at constant P
(*iii*) (*b*) and (*c*) only (*iv*) (*c*) only

Ans. (*i*) and (*ii*)

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?

(*i*) $\Delta_{mix} H = $ zero
(*ii*) $\Delta_{mix} V = $ zero
(*iii*) These will form minimum boiling azeotrope.
(*iv*) These will not form ideal solution.

Ans. (*iii*) and (*iv*)

Explanation: In a mixture of benzene and toluene strength of the solution will be same and they will form ideal solution according to Raoult's Law.

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

(*i*) It depends on the concentration of a non-electrolyte solute in solution and does not depend on the nature of the solute molecules.
(*ii*) It depends on number of particles of electrolyte solute in solution and does not depend on the nature of the solute particles.
(*iii*) It depends on the concentration of a non-electrolyte solute in solution as well as on the nature of the solute molecules.
(*iv*) It depends on the concentration of an electrolyte or non-electrolyte solute in solution as well as on the nature of solute molecules.

Ans. (*i*) and (*ii*)

Explanation: Clligative property depends on the concentration and as well as numbers of particles. It does not depend on the nature of particles.

30. Van't Hoff factor i is given by the expression ______________.

(*i*) $i = \dfrac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$

(*ii*) $i = \dfrac{\text{Abnormal molar mass}}{\text{Normal molar mass}}$

(*iii*) $i = \dfrac{\text{Observed colligative property}}{\text{Calculated colligative property}}$

(*iv*) $i = \dfrac{\text{Calculated colligative property}}{\text{Observed colligative property}}$

Ans. (*i*) and (*iii*)

31. Isotonic solutions must have the same ______________.

(*i*) solute (*ii*) density
(*iii*) elevation in boiling point (*iv*) depression in freezing point

Ans. (*ii*) and (*iii*)

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

(*i*) Benzene - Toluene (*ii*) Water - Nitric acid
(*iii*) Water - Ethanol (*iv*) *n*-Hexane - *n*-Heptane

Ans. (*ii*) and (*iii*)

Explanation: At particular composition Water-Nitric acid and Water-Ethanol form azeotropic mixture which have same composition in vapour phase and liquid phase.

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33. In isotonic solutions _______________.

(*i*) solute and solvent both are same.

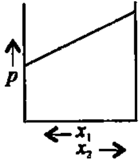
(*ii*) osmotic pressure is same.

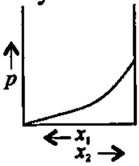
(*iii*) solute and solvent may or may not be same.

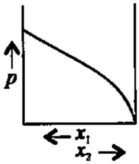
(*iv*) solute is always same solvent may be different.

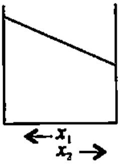
Ans. (*ii*) and (*iii*)

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

(*i*)


(*ii*)


(*iii*)


(*iv*)


Ans. (*i*) and (*iv*)

35. Colligative properties are observed when _____________.

(*i*) a non volatile solid is dissolved in a volatile liquid.

(*ii*) a non volatile liquid is dissolved in another volatile liquid.

(*iii*) a gas is dissolved in non volatile liquid.

(*iv*) a volatile liquid is dissolved in another volatile liquid.

Ans. (*i*) and (*ii*)

III. SHORT ANSWER TYPE

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. This shows that both liquids have form azeotropic mixture at definite composition and boils at same temperature and hence cannot be separated by distillation.

37. Explain why on addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.

Ans. NaCl is a non-volatile solute when it is added to water it decreases, so the vapour pressure and that is why the boiling point of the solution increases. While methyl alcohol is a more volatile liquid water. Therefore addition of methyl alcohol to water increases the total vapour pressure and thus boiling point decreases.

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

Ans. It means that non-polar solute dissolves in non-polar solvent. While polar solute dissolves in polar solvent like ionic salts dissolves in water.

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

Ans. mass percentage, ppm, mole fraction and molality does not depend on temperature as they are dependent on mass of the solute particle. However molarity depends upon volume of the solution which can vary with temperature.

40. What is the significance of Henry's Law constant K^H?

Ans. $P = k^H.x$ (k^H = Henry's law constant). It depends on the nature of gas. Greater the k^H value, the lower will be the solubility and vice versa.

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

Ans. On increasing the temperature solubility of oxygen in water decreases that is why aquatic species are more comfortable in cold water.

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*) According to Henry's law pressure of a gas is directly proportional to solubility. Scuba divers when comes towards surface the pressure gradually decreases. This reduce pressure releases the dissolve gas present in blood and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which is painful and dangerous to life.

(*ii*) At high altitude partial pressure of oxygen is less than that of ground level. This leads to low concentration of oxygen in blood and tissues of people living at high altitude. Low blood oxygen causes weakness and discomfort.

(*b*) When the bottle is opened to air the partial pressure of CO_2 above the solution decreases. As a result, solubility decreases and CO_2 bubbles come out of the bottle.

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

Ans. In a pure liquid the entire surface is occupied by the liquid molecules only.The vapour pressure of the solution is solely from the solvent alone. When a non volatile solute is added to water the fraction of surface covered by the solvent molecule get reduced, and thus the vapour pressure also reduced.

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

Ans. Sprinkling of salt causes depression in freezing point of water which helps in clearing the snow.

45. What is "semipermeable membrane"?

Ans. Continuous sheets or films which contains small pores through which solvent molecules can pass but passage of bigger molecules of solute are hindered.

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

Ans. Cellulose acetate

IV. MATCHING TYPE

Note: *In the following questions match the items given in Column I and Column II.*

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

Column I	Column II
(*i*) Saturated solution	(*a*) Solution having same osmotic pressure at a given temperature as that of given solution.
(*ii*) Binary solution	(*b*) A solution whose osmotic pressure is less than that of another.
(*iii*) Isotonic solution	(*c*) Solution with two components.
(*iv*) Hypotonic solution	(*d*) A solution which contains maximum amount of solute that can be dissolved in a given amount of solvent at a given temperature.
(*v*) Solid solution	(*e*) A solution whose osmotic pressure is more than that of another.
(*vi*) Hypertonic solution	(*f*) A solution in solid phase.

Ans. (*i*) → (*d*) (*ii*) → (*c*) (*iii*) → (*a*)
(*iv*) → (*b*) (*v*) → (*f*) (*vi*) → (*e*)

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

Column I	Column II
(*i*) Soda water	(*a*) A solution of gas in solid
(*ii*) Sugar solution	(*b*) A solution of gas in gas
(*iii*) German silver	(*c*) A solution of solid in liquid
(*iv*) Air	(*d*) A solution of solid in solid
(*v*) Hydrogen gas in palladium	(*e*) A solution of gas in liquid
	(*f*) A solution of liquid in solid

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Ans. (*i*) → (*e*) (*ii*) → (*c*) (*iii*) → (*d*)
(*iv*) → (*b*) (*v*) → (*a*)

49. Match the laws given in Column I with expresions given in Column II.

Column I	Column II
(*i*) Raoult's law	(*a*) $\Delta T_f = K_f m$
(*ii*) Henry's law	(*b*) $\pi = CRT$
(*iii*) Elevation of boiling point	(*c*) $p = x_1 p_1^0 + x_2 p_2^0$
(*iv*) Depression in freezing point	(*d*) $\Delta T_b = K_b m$
(*v*) Osmotic pressure	(*e*) $p = K_H x$

Ans. (*i*) → (*c*) (*ii*) → (*e*) (*iii*) → (*d*)
(*iv*) → (*a*) (*v*) → (*b*)

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

Column I	Column II
(*i*) Mass percentage	(*a*) $\dfrac{\text{Number of moles of the solute component}}{\text{Volume of solution in litres}}$
(*ii*) Volume percentage	(*b*) $\dfrac{\text{Number of moles of the solute component}}{\text{Volume of solution in litres}}$
(*iii*) Mole fraction	(*c*) $\dfrac{\text{Volume of the solute in solution}}{\text{Total volume of solution}} \times 100$
(*iv*) Molality	(*d*) $\dfrac{\text{Number of moles of the solute}}{\text{Mass of solvent in kilograms}} \times 100$
(*v*) Molarity	(*e*) $\dfrac{\text{Number of moles of the solute}}{\text{Mass of solvent in kilograms}}$

Ans. (*i*) → (*d*) (*ii*) → (*c*) (*iii*) → (*b*)
(*iv*) → (*e*) (*v*) → (*a*)

V. ASSERTION AND REASON TYPE

Note: *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.*

(*i*) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(*ii*) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(*iii*) Assertion is correct statement but reason is wrong statement.

(*iv*) Assertion and reason both are incorrect statements.

(*v*) Assertion is wrong statement but reason is correct statement.

51. **Assertion:** Molarity of a solution in liquid state changes with temperature.
Reason: The volume of a solution changes with change in temperature

Ans. (*i*)

Explanation: Molarity = $\frac{\text{No. of moles of solute component}}{\text{Volume of solution in litres}}$. So, on increasing the temperature volume of the solution will increase.

52. **Assertion:** When methyl alcohol is added to water, boiling point of water increases.
Reason : When a volatile solute is added to a volatile solvent elevation in boiling point is observed

Ans. (*iv*)

Explanation: When methyl alcohol is added to water A-B interaction < A-A or B-B interaction that is why it will show positive deviation from Raoult's law and boiling point will decrease.

53. **Assertion :** When NaCl is added to water a depression in freezing point is observed.
Reason: The lowering of vapour pressure of a solution causes depression in freezing point.

Ans. (*i*)

Explanation: On addition of non volatile solute to solution lowering of vapour pressure takes place and it cause depression in freezing point.

54. **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.
Reason : Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.

Ans. (*ii*)

Explanation: Flow of solvent molecule from solvent side to solution side through semipermeable membrane is called osmosis.

VI. LONG ANSWER TYPE

55. Define the following modes of expressing the concentration of a solution. Which of these modes are independent of temperature and why?
(*i*) w/w (mass percentage)
(*ii*) V/V (volume percentage)
(*iii*) w/V (mass by volume percentage)
(*iv*) ppm. (parts per million)
(*v*) *x* (mole fraction)
(*vi*) M (Molarity)
(*vii*) m (Molality)

Ans. (*i*) **Mass percentage (w/w):**

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

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(*ii*) **Volume percentage (v/v):**

$$\text{Volume \% of a component} = \frac{\text{V of the component}}{\text{V of the solution}} \times 100$$

(*iii*) **Mass by volume percentage (w/v):**

$$= \frac{\text{W of solute}}{100\ ml \text{ of solution}} \times 100$$

(*iv*) **1 Parts per million (ppm):**

$$= \frac{\text{No of parts of the component}}{\text{Total number of parts of in the solution}} \times 10^6$$

(*v*) **Mole Fraction (*x*):**

Mole fraction of a component (x) =

$$\frac{\text{No. of moles of the component}}{\text{Total number of moles of all the components}}$$

(*vi*) **Molarity (M):** The no. of moles of solute per litre of solution

(*vii*) **Molality (m):** The no. of moles of solute per kg of solvent

Effect of temperature: mass %, *ppm*, mole fraction and molality do not change with temperature whereas molarity, volume percentage and mass by volume percentage changes with temperature because volume of solution (liquid) changes with temperature.

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.

(*i*) $CHCl_3$ (*l*) and CH_2Cl_2(*l*) (*ii*) NaCl(s) and H_2O (*l*)

Ans. Raoult's law in its general form can be stated as, for any solution, the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction in the solution.

According to Raoult's law for a solution of two volatile liquids,

$P_1 \propto x_1$ and $P_2 \propto x_2$ $P_1 = P_1^0 x_1$ and $P_2 = P_2^0 x_2$

$P = P_1^0 x_1 + P_2^0 x_2$

$$= x_1 P_1^0 + (1 - x_1) P_2^0$$

$$= \left(P_1^0 - P_2^0\right) x_1 + P_2^0$$

P = Total vapour pressure

P_1 = Partial vapour pressure of solvent 1

P_2 = Partial vapour pressure of solvent 2

According to Raoult's law for a solution containing volatile solvent and non- volatile solute. P solvent = P solvent x mole fraction of solvent.

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

Ans. **Ideal solution:** The solution which obey Raoult's law at all concentration and at all temperature *i.e* $P_A = P_{oA.xA}$ $P_B = P_{oB.xB}$

If the intermolecular attractive forces between the solute – solvent (A – B interaction) are nearly equal to those between the solvent – solvent

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(A – A) and solute – solute (B – B) it forms ideal solutions. Enthalpy of mixing, Δmixing H = 0. Volume change on mixing, Δ mixing V = 0. Examples: n - hexane and n-heptane.

Non Ideal solution: The solution which do not obey Raoult's law at all concentration and at all temperature i.e $P_A \neq P_{oAxA}$ $P_B \neq P_{oBxB}$. If the intermolecular attractive forces between the solute – solvent(A – B interaction) are not equal (either stronger or weaker) to those between the solvent – solvent (A – A) and solute – solute (B – B) it forms non-ideal solutions. Enthalpy of mixing, Δ_{mixing} H is not equal to 0. Volume changes on mixing, Δ_{mixing} V is not equal to 0. Example : CS_2 and acetone

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. Azeotropes are binary solutions (liquid mixtures) having the same composition in liquid and vapour phase and it is not possible to separate the components of an azeotrope by fractional distillation. Ethanol - water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution of approx. 95% ethanol by volume of ethanol. This has the same composition in liquid and vapour phase and it is not possible to separate them.

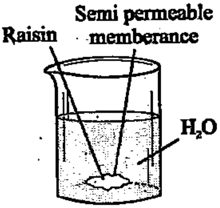
Minimum boiling azeotrope: The non- ideal solutions showing positive deviation form minimum boiling azeotrope at a specific composition. Example; 95% ethanol and 5% water (by volume): Ethanol = 351.3K, Water = 373 K, Azeotrope = 351.1K

Maximum boiling azeotrope: The non-ideal solutions showing negative deviation form maximum boiling azeotrope at a specific composition

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. Phenomenon involved in the above process is known as osmosis.

Osmosis is the process of flow of solvent molecules from pure solvent to the solution through semi permeable membrane. Three applications of osmosis are:



(*i*) Movement of water from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis.

(*ii*) Preservation of meat against bacterial action by adding salt.

(*iii*) Preservation of fruits against bacterial action by adding sugar. Bacterium in canned fruit loses water through the process of osmosis, shrivels and dies.

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60. Discuss biological and industrial importance of osmosis.

Ans. (*i*) Movement of water from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis.

(*ii*) Preservation of meat, fruits and vegetables against bacterial action by adding salt or sugar.

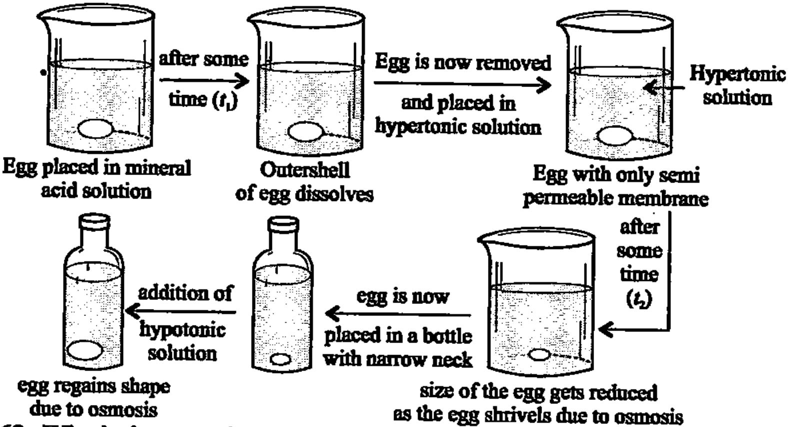
(*iii*) Movement of biomolecules inside and outside of a living cell occurs due to osmosis.

(*iv*) Opening and closing of stomata in plants occur due to osmosis.

(*v*) Reverse osmosis is used for the purification of water in a large scale.

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

Ans. Egg is placed in mineral acid solution → after some time egg is removed and placed in hypertonic solution → after some time size of the egg gets reduced and shrivels due to osmosis → egg is now placed in a bottle with narrow neck → on adding hypotonic solution egg regains shape due to osmosis.



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. When the non volatile solute particles undergo association (E.g.: acetic acid) or dissociation (E.g. electrolytes like KCl, NaCl etc.), the abnormal molar mass is observed.

Van't Hoff factor is defined as I = Normal molar mass/ Abnormal molar mass

Formula to calculate i;

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

Always value is less than unity (i < 1) for association and is greater than unity (i >1) for dissociation.

❑❑❑

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3 Electrochemistry

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

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

   (i) Pt (s) | H_2 (g,0.1 bar) | H^+ (aq.,1 M) || Cu^{2+} (aq.,1M) | Cu

   (ii) Pt (s) | H_2 (g, 1 bar) | H^+ (aq.,1 M) || Cu^{2+} (aq.,2 M) | Cu

   (iii) Pt (s) | H_2 (g, 1 bar) | H^+ (aq.,1 M) || Cu^{2+} (aq.,1 M) | Cu

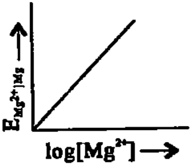
   (iv) Pt (s) | H_2 (g, 1 bar) | H^+ (aq.,0.1 M) || Cu^{2+} (aq.,1 M) | Cu

Ans. (iii)

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

   $E_{Mg^{2+}|Mg} = E^{\ominus}_{Mg^{2+}|Mg} - \frac{0.059}{2} \log \frac{1}{[Mg^{2+}]}$. The graph of $E_{Mg^{2+}|Mg}$ vs log $[Mg^{2+}]$ is

(i)



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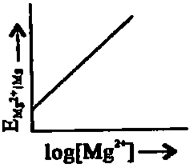

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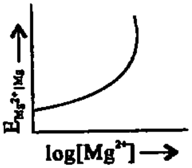
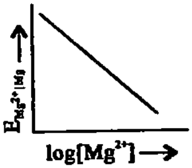


(iv)



Ans. (ii)

3. Which of the following statement is correct?

   (i) E_{Cell} and Δ_rG of cell reaction both are extensive properties.

   (ii) E_{Cell} and Δ_rG of cell reaction both are intensive properties.

   (iii) E_{Cell} is an intensive property while Δ_rG of cell reaction is an extensive property.

   (iv) E_{Cell} is an extensive property while Δ_rG of cell reaction is an intensive property.

Ans. (iii)

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

   (i) Cell potential (ii) Cell emf

   (iii) Potential difference (iv) Cell voltage

Ans. (ii)

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

(*i*) It does not participate in the cell reaction.
(*ii*) It provides surface either for oxidation or for reduction reaction.
(*iii*) It provides surface for conduction of electrons
(*iv*) It provides surface for redox reaction.

Ans. (*iv*)

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

(*i*) $E_{cell} = 0$ (*ii*) $E_{cell} > E_{ext}$
(*iii*) $E_{ext} > E_{cell}$ (*iv*) $E_{cell} = E_{ext}$

Ans. (*iii*)

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

(*i*) Conductivity of solution depends upon size of ions.
(*ii*) Conductivity depends upon viscosiy of solution.
(*iii*) Conductivity does not depend upon solvation of ions present in solution.
(*iv*) Conductivity of solution increases with temperature

Ans. (*iii*)

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

$$E^{\ominus}_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33V \qquad E^{\ominus}_{Cl_2/Cl^-} = 1.36V$$

$$E^{\ominus}_{MnO_4^-/Mn^{2+}} = 1.51V \qquad E^{\ominus}_{Cr^{3+}/Cr} = -0.74V$$

(*i*) Cl^- (*ii*) Cr
(*iii*) Cr^{3+} (*iv*) Mn^{2+}

Ans. (*ii*)

Explanation: Out of four standard reduction potential, chromium has negative value. Hence, it is the stronget reducing agent.

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

(*i*) Cl^- (*ii*) Mn^{2+}
(*iii*) MnO_4^- (*iv*) Cr^{3+}

Ans. (*iii*)

Explanation: Highest positive value of standard reduction potential means strongest oxidising agent. Hence, MnO_4^- is the strongest oxidising agent.

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

(*i*) $Cr^{3+} < Cl^- < Mn^{2+} < Cr$ (*ii*) $Mn^{2+}+ < Cl^- < Cr^{3+} < Cr$
(*iii*) $Cr^{3+} < Cl^- < Cr_2O_7^{2-} < MnO_4^-$ (*iv*) $Mn^{2+} < Cr^{3+} < Cl^- < Cr$

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Ans. (*ii*)

Explanation: Lower the value of standard reduction potential greater will be the reducing power.

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

(*i*) Cl^- (*ii*) Cr^{3+}

(*iii*) Cr (*iv*) Mn^{2+}

Ans. (*iv*)

Explanation: MnO_4^-/Mn^{2+} has highest standard reduction potential hence most stable form among four is Mn^{2+}.

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

(*i*) Cr^{3+} (*ii*) MnO_4^-

(*iii*) $Cr_2O_7^{2-}$ (*iv*) Mn^{2+}

Ans. (*i*)

Explanation: Cr^{3+}/Cr has most negative value of standard reduction potential. Hence, Cr^{3+} is the most stable oxidised species.

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

(*i*) 1F (*ii*) 6F

(*iii*) 3F (*iv*) 2F

Ans. (*iii*)

Explanation: In Al_2O_3 oxidation state of Al is Al^{3+}.

14. The cell constant of a conductivity cell __________.

(*i*) changes with change of electrolyte.

(*ii*) changes with change of concentration of electrolyte.

(*iii*) changes with temperature of electrolyte.

(*iv*) remains constant for a cell.

Ans. (*iv*)

15. While charging the lead storage battery __________.

(*i*) $PbSO_4$ anode is reduced to Pb.

(*ii*) $PbSO_4$ cathode is reduced to Pb.

(*iii*) $PbSO_4$ cathode is oxidised to Pb.

(*iv*) $PbSO_4$ anode is oxidised to PbO_2.

Ans. (*i*)

Explanation: When the lead storage battery is on charging

$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$

16. $\Lambda^0_{m(NH_4OH)}$ is equal to __________.

(*i*) $\Lambda^0_{m(NH_4OH)} + \Lambda^0_{m(NH_4Cl)} - \Lambda^0_{(HCl)}$

(*ii*) $\Lambda^0_{m(NH_4Cl)} + \Lambda^0_{m(NH_4OH)} - \Lambda^0_{(NaCl)}$

(*iii*) $\Lambda^0_{m(NH_4Cl)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{(NaOH)}$

(*iv*) $\Lambda^0_{m(NaOH)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{m(NH_4Cl)}$

Ans. (*ii*)

Explanation: Since we require only sum of molar conductivity of NH_4^+ and OH^-.

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

(*i*) $Na^+ (aq) + e^- \rightarrow Na (s); \quad E^{\ominus}_{Cell} = -2.71V$

(*ii*) $2H_2O (l) \rightarrow O_2(g) + 4H^+ (aq) + 4e^-; \quad E^{\ominus}_{Cell} = 1.23V$

(*iii*) $H^+ (aq) + e^- \rightarrow \frac{1}{2} H_2 (g); \quad E^{\ominus}_{Cell} = 0.00V$

(*iv*) $Cl^- (aq) \rightarrow \frac{1}{2} Cl_2 (g) + e^-; \quad E^{\ominus}_{Cell} = 1.36V$

Ans. (*ii*) and (*iv*)

Explanation: At the anode the following oxidation reactions are possible:

$$Cl^- (aq) \rightarrow \frac{1}{2} Cl_2 (g) + e^-; \quad E^{\ominus}_{Cell} = 1.36V$$

$$2H_2O (l) \rightarrow O_2 (g) + 4H^+(aq) + 4e^-; \quad E^{\ominus}_{Cell} = 1.23V$$

lower value of $E^{\ominus}$ is preferred and therefore, water should get oxidised in preference to $Cl^-(aq)$. However, on account of overpotential of oxygen, reaction $Cl^- (aq) \rightarrow \frac{1}{2} Cl_2 (g) + e^-$ is preferred.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note: In the following questions two or more than two options may be correct.

18. The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that ____________.

(*i*) this redox couple is a stronger reducing agent than the H^+/H_2 couple.

(*ii*) this redox couple is a stronger oxidising agent than H^+/H_2.

(*iii*) Cu can displace H_2 from acid.

(*iv*) Cu cannot displace H_2 from acid.

Ans. (*ii*) and (*iv*)

Explanation: Lower the value of standard reduction potential higher will be the reducing power.

19. $E^{\ominus}_{Cell}$ for some half cell reactions are given below. On the basis of these mark the correct answer.

(*a*) $H^+ (aq) + e^- \rightarrow \frac{1}{2} H_2 (g); \quad E^{\ominus}_{Cell} = 0.00V$

(*b*) $2H_2O (l) \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-; \quad E^{\ominus}_{Cell} = 1.23V$

(*c*) $2SO_4^{2-} (aq) \rightarrow S_2O_8^{2-} (aq) + 2e^-; \quad E^{\ominus}_{Cell} = 1.96 V$

(*i*) In dilute sulphuric acid solution, hydrogen will be reduced at cathode.

(*ii*) In concentrated sulphuric acid solution, water will be oxidised at anode.

(*iii*) In dilute sulphuric acid solution, water will be oxidised at anode.

(*iv*) In dilute sulphuric acid solution, SO_4^{2-} ion will be oxidised to tetrathionate ion at anode.

Ans. (*i*) and (*iii*)

Explanation: In the electrolysis of dil. H_2SO_4 above three reaction takes place.

Oxidation half reaction occurs at anode, lower value of standard reduction potential will be preferred. At cathode hydrogen ion will be converted into hydrogen.

20. $E^{\ominus}_{Cell}$ = 1.1V for Daniel cell. Which of the following expressions are correct description of state of equilibrium in this cell?

(*i*) $1.1 = K_C$

(*ii*) $\frac{2.303\,RT}{2F}\log K_C = 1.1$

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

(*iv*) $\log K_C = 1.1$

Ans. (*ii*) and (*iii*)

Explanation: $\Delta_r G_0 = -2.303\ RT \log K_C$

$$E^{\ominus}_{Cell} = \frac{2.303\,RT}{2F}\log K_C = 1.1$$

21. Conductivity of an electrolytic solution depends on ____________.

(*i*) nature of electrolyte.

(*ii*) concentration of electrolyte.

(*iii*) power of AC source.

(*iv*) distance between the electrodes.

Ans. (*i*) and (*ii*)

Explanation: Conductivity or specific conductance κ (kappa): It is the conductance of solution kept between two electrodes with 1 m^2 area of cross section and distance of 1 m. It is the reciprocal of resistivity (ρ).

$\kappa = 1/\rho$.

S.I unit of $\kappa = Sm^{-1}$

It depends on the nature of the electrolyte and concentration of the electrolyte.

22. $\Lambda^0_{m(H_2O)}$ is equal to

(*i*) $\Lambda^0_{m(HCl)} + \Lambda^0_{m(NaOH)} - \Lambda^0_{m(NaCl)}$

(*ii*) $\Lambda^0_{m(HNO_3)} + \Lambda^0_{m(NaNO_3)} - \Lambda^0_{m(NaOH)}$

(*iii*) $\Lambda^0_{(HNO_3)} + \Lambda^0_{m(NaOH)} - \Lambda^0_{m(NaNO_3)}$

(*iv*) $\Lambda^0_{m(NH_4OH)} + \Lambda^0_{m(HCl)} - \Lambda^0_{m(NH_4Cl)}$

Ans. (*i*) and (*iv*)

Explanation: This problem is based on the concept of Kohlrausch law of independent migration of ions: (Λ^0_m) is the sum of limiting molar conductivities of cation (λ^0_+) and anion (λ^0_-). $\Lambda^0_m = v^+\lambda^0_+ + v^-\lambda^0_-$

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

(*i*) Copper will deposit at cathode.
(*ii*) Copper will deposit at anode.
(*iii*) Oxygen will be released at anode.
(*iv*) Copper will dissolve at anode.

Ans. (*i*) and (*iii*)

Explanation: During electrolysis following reaction takes place at cathode:

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$

Standard electrode potential of Cu^{2+}/Cu is greater than $H^+/\frac{1}{2}H_2$ therefore Cu will deposite at cathode.

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

(*i*) Copper will deposit at cathode.
(*ii*) Copper will dissolve at anode.
(*iii*) Oxygen will be released at anode.
(*iv*) Copper will deposit at anode.

Ans. (*i*) and (*ii*)

25. Conductivity κ, is equal to ____________.

(*i*) $\frac{1}{R}\frac{1}{A}$
(*ii*) $\frac{G^*}{R}$
(*iii*) Λ_m
(*iv*) $\frac{l}{A}$

Ans. (*i*) and (*ii*)

Explanation: $R = \rho L/A \quad 1/\rho = \frac{1}{R}\frac{1}{A}$

Conductivity κ = Conductance (G) × Cell constant (G*)

26. Molar conductivity of ionic solution depends on ____________.

(*i*) temperature
(*ii*) distance between electrodes.
(*iii*) concentration of electrolytes in solution.
(*iv*) surface area of electrodes.

Ans. (*i*) and (*iii*)

Explanation: Λ_m (S cm^2 mol^{-1}) = K

On increasing the temperature molar conductivity increases whereas molar conductivity decreases on increasing the concentration.

27. For the given cell, $Mg|Mg^{2+} \| Cu^{2+}|Cu$

(*i*) Mg is cathode
(*ii*) Cu is cathode

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(*iii*) The cell reaction is $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$

(*iv*) Cu is the oxidising agent

Ans. (*ii*) and (*iii*)

Explanation: Left side of the cell represent oxidation half cell and right side represent reduction half cell.

III. SHORT ANSWER TYPE

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

Ans. No only the difference in potential between two electrode can be measured.

29. Can $E^{\ominus}_{Cell}$ or $\Delta_r G$ for cell reaction ever be equal to zero?

Ans. At equilibrium $G = 0$ $E_{cell} = 0$

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

Ans. $E_{Cell} = 0$ at equilibrium $\Delta_r G = -nF E^{-}_{Cell}$

$\Delta_r G = 0$

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

Ans. A negative *E*.means that the redox couple is a stronger reducing agent than the H^+/H^2 couple.

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. It will be different. According to Faraday's second law, the amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights $\frac{\text{Atomic mass of metal}}{\text{No. of electrons}}$ electrons required to reduce the cation.

Here, for the electrode reactions:

$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

$$Ag^+ + e^- \rightarrow Ag(s)$$

Hence, one mole of Cu^{2+} and Ag^{3+} require 2 mol of electron (2F) and 1 mol of electrons (F_1) respectively.

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

$Cu + 2Ag^+ \rightarrow 2Ag + Cu^{2+}$

Ans. $Cu + 2Ag^+ \rightarrow 2Ag + Cu^{2+}$ cell can be represented is $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$

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. At the anode the following oxidation reactions are possible:

$Cl^-(aq) \rightarrow \frac{1}{2} Cl_2(g) + e^-$

$E^{\ominus}_{Cell} = 1.36$ V

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$2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+ (aq) + 4e^-$

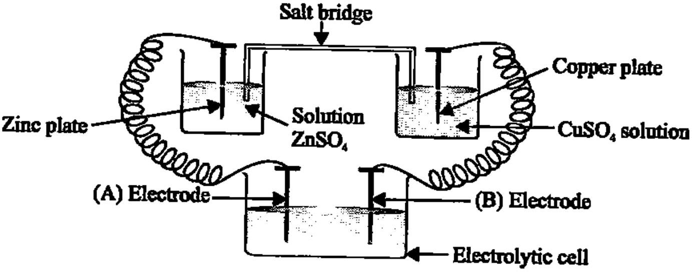
$E^{\ominus}_{Cell} = 1.23\ V$

The reaction at anode with lower value of $E^{\ominus}$ is preferred and therefore, water should get oxidised in preference to $Cl^-(aq)$. However, on account of overpotential of oxygen, oxidation of cl^- is preferred.

35. What is electrode potential?

Ans. A potential difference developing between the electrode and the electrolyte is known as electrode potential.

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 above cell can be represented as Zn | Zn^{2+} || Cu^{2+} | Cu Zinc is oxidized at anode and copper is reduced at cathode.

A has negative polarity and B has positive polarity.

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

Ans. Alternating current is used for measuring the resistance of an electrolytic solution because DC current can change the composition of the solution and the concentration will not remain constant.

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 $E_{cell} = E_{ext}$ current will stop flowing.

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

Ans. As the product of electrolysis NaOH will be formed which will increase the pH of the solution. The net reaction in the electrolysis.

$NaCl\ (aq) + H_2O\ (l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$

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

Ans. Ions are not involved in the overall reaction of the mecury cell. Thus the mercury cell has constant voltage through out the life.

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. 'B' is strong electrolyte. For strong electrolyte Λ_m increases slowly with dilution since the number of ions remains the same only the interionic attraction decrease thus the molar conductivity increases slightly.

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

Ans. pH of the solution remains constant as H^+ remains same during the whole reaction.

At anode: $2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+ + 4e^-$

At cathode: $4H^+ + 4e^- \rightarrow 2H_2\ (g)$

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

Ans. Conductivity always decreases with decrease in concentration for both, weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution.

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

Ans. SHE (standard hydrogen electrode) is used as a reference electrode to measure the standard electrode potential of the other electrode by assigning standard electrode potential of SHE as zero. [$E^0\ H^+$ = zero].

45. Consider a cell given below:

$Cu \mid Cu^{2+} \| Cl^- \mid Cl_2, Pt$.

Write the reactions that occur at anode and cathode.

Ans. Two half cell of the cell reaction can be represented as:

At anode: $Cu \rightarrow Cu^{2+} + 2e^-$

At cathode: $Cl_2 + 2e^- \rightarrow 2Cl^-$

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. $$E_{(cell)} = E^0_{Cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}.$$

E_{cell} will decrease when the concentration of Zn^{2+} increases.

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

Ans. Advantages:

(*a*) High efficiency

(*b*) Continuous source of energy

(*c*) Pollution free.

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. $Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO_4(s) + 2H_2O(l)$
Density of the electrolyte will decrease as water is formed and sulphuric acid is consumed.

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

Ans. **For weak electrolyte(CH_3COOH):** Λ_m increases steeply on dilution due to increase in the number of ions (or the degree of dissociation). For strong electrolytes (CH_3COONa): Λ_m increases as number of ions remains the same but the interionic attraction decreases.

IV. MATCHING TYPE

Note: Match the items of Column I and Column II in the following questions.

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

Column I	Column II
(*i*) Λ_m	(*a*) $S\ cm^{-1}$
(*ii*) E_{Cell}	(*b*) m^{-1}
(*iii*) κ	(*c*) $S\ cm^2\ mol^{-1}$
(*iv*) G^*	(*d*) V

Ans. (*i*) → (*c*) (*ii*) → (*d*)
(*iii*) → (*a*) (*iv*) → (*b*)

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

Column I	Column II
(*i*) Λ_m	(*a*) intensive property
(*ii*) $E^\ominus_{Cell}$	(*b*) depends on number of ions/volume
(*iii*) κ	(*c*) extensive property
(*iv*) $\Delta_r G_{Cell}$	(*d*) increases with dilution

Ans. (*i*) → (*d*) (*ii*) → (*a*)
(*iii*) → (*b*) (*iv*) → (*c*)

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

Column I	Column II
(*i*) Lead storage battery	(*a*) maximum efficiency
(*ii*) Mercury cell	(*b*) prevented by galvanisation
(*iii*) Fuel cell	(*c*) gives steady potential
(*iv*) Rusting	(*d*) Pb is anode, PbO_2 is cathode

Ans. (*i*) → (*d*) (*ii*) → (*c*)
(*iii*) → (*a*) (*iv*) → (*b*)

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

Column I	Column II
(*i*) κ	(*a*) $I \times t$
(*ii*) Λ_m	(*b*) Λ_m/Λ_m^0
(*iii*) α	(*c*) κ/c
(*iv*) Q	(*d*) G^*/R

Ans. (*i*) → (*d*) (*ii*) → (*c*)
(*iii*) → (*b*) (*iv*) → (*a*)

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

Column I	Column II
(*i*) Lechlanche cell	(*a*) cell reaction $2H_2 + O_2 \rightarrow 2H_2O$
(*ii*) Ni–Cd cell	(*b*) does not involve any ion in solution and is used in hearing aids.
(*iii*) Fuel cell	(*c*) rechargeable
(*iv*) Mercury cell	(*d*) reaction at anode, $Zn \rightarrow Zn^{2+} + 2e^-$
	(*e*) converts energy of combustion into electrical energy

Ans. (*i*) → (*d*) (*ii*) → (*c*)
(*iii*) → (*e*) (*iv*) → (*b*)

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

$E^{\ominus}_{F_2/F^-} = 2.87V$, $E^{\ominus}_{Li^+/Li} = -3.5V$, $E^{\ominus}_{Au^{3+}/Au} = 1.4V$, $E^{\ominus}_{Br_2/Br^-} = 1.09V$

Column I	Column II
(*i*) F_2	(*a*) metal is the strongest reducing agent
(*ii*) Li	(*b*) metal ion which is the weakest oxidising agent
(*iii*) Au^{3+}	(*c*) non metal which is the best oxidising agent
(*iv*) Br^-	(*d*) unreactive metal
(*v*) Au	(*e*) anion that can be oxidised by Au^{3+}
(*vi*) Li^+	(*f*) anion which is the weakest reducing agent
(*vii*) F^-	(*g*) metal ion which is an oxidising agent

Ans. (*i*) → (*c*) (*ii*) → (*a*) (*iii*) → (*g*)
(*iv*) → (*e*) (*v*) → (*d*) (*vi*) → (*b*)
(*vii*) → (*f*)

V. ASSERTION AND REASON TYPE

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Both assertion and reason are true and the reason is the correct explanation of assertion.

(*ii*) Both assertion and reason are true and the reason is not the correct explanation of assertion.

(*iii*) Assertion is true but the reason is false.

(*iv*) Both assertion and reason are false.

(*v*) Assertion is false but reason is true.

56. Assertion: Cu is less reactive than hydrogen.

Reason: $E^{\ominus}_{Cu^{2+}/Cu}$ is negative

Ans. (*iii*)

Explanation: Standard electrode potential of $E^{\ominus}_{Cu^{2+}/Cu} = 0.34V$ and $E^{\ominus}_{H^+/H} = 0.00V$. This shows that copper is less reactive than hydrogen.

57. Assertion: E_{Cell} should have a positive value for the cell to function.

Reason: $E_{cathode} < E_{anode}$

Ans. (*iii*)

Explanation: For the cell reaction to be feasible $E_{cathode}$ should be positive. $\Delta_r G^0 = - nF\ E^0$ cell for the value of E^0 cell to be positive $E_{cathode} > E_{anode}$

58. Assertion : Conductivity of all electrolytes decreases on dilution.

Reason : On dilution number of ions per unit volume decreases.

Ans. (*i*)

Explanation: Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution

59. Assertion : Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

Reason : For weak electrolytes degree of dissociation increases with dilution of solution.

Ans. (*i*)

Explanation: For weak electrolyte: Λ_m increases steeply on dilution due to increase in the number of ions (or the degree of dissociation).

60. Assertion : Mercury cell does not give steady potential.

Reason : In the cell reaction, ions are not involved in solution.

Ans. (*v*)

Explanation: Correct assertion is mercury cell gives steady potential.

61. Assertion : Electrolysis of NaCl solution gives chlorine at anode instead of O_2.

Reason : Formation of oxygen at anode requires overvoltage

Ans. (*i*)

Explanation: At the anode the following oxidation reactions are possible:

$$Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-;\ E = 1.36\ V$$

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$2H_2O\,(l) \rightarrow O_2\,(g) + 4H^+(aq) + 4e^-$; E = 1.23 V

Lower value of E_{cell} is preferred but due to overvoltage chlorine is liberated at anode.

62. **Assertion :** For measuring resistance of an ionic solution an AC source is used.

Reason : Concentration of ionic solution will change if DC source is used.

Ans. (*i*)

Explanation: DC current can change the composition of electrolytic solution.

63. **Assertion :** Current stops flowing when $E_{Cell} = 0$.

Reason : Equilibrium of the cell reaction is attained.

Ans. (*i*)

Explanation: At equilibrium $E_{cell} = 0$ and therefore current stops flowing.

64. **Assertion :** $E_{Ag^+/Ag}$ increases with increase in concentration of Ag^+ ions.

Reason : $E_{Ag^+/Ag}$ has a positive value.

Ans. (*ii*)

Explanation: $E_{cell} = E^0_{cell} - 0.059 \log 1/[Ag^+]$ therefore $E_{Ag^+/Ag}$ increases with increase in concentration of Ag^+

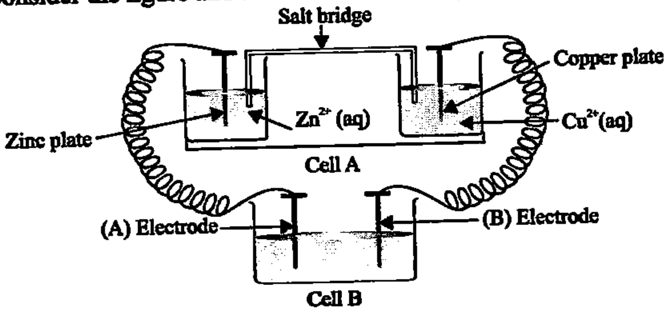
65. **Assertion :** Copper sulphate can be stored in zinc vessel.

Reason : Zinc is less reactive than copper.

Ans. (*iv*)

VI. LONG ANSWER TYPE

66. Consider the figure and answer the following questions.



(*i*) Cell 'A' has $E_{Cell} = 2V$ and Cell 'B' has $E_{Cell} = 1.1V$ 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 $E_{Cell} = 0.5V$ and cell 'B' has $E_{Cell} = 1.1V$ then what will be the reaction at cathode and anode.

Ans. (*i*) Cell 'B' will act as an electrolytic cell following reaction can take place at cathode and anode.

At cathode : $Zn^{2+} + 2e^- \longrightarrow Zn$

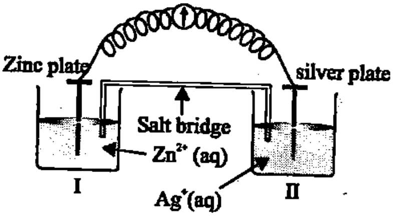
At anode : $Cu \longrightarrow Cu^{2+} + 2e^-$

(*ii*) Now the cell 'B' has higher e.m.f and it will act as an electrochemical cell.

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$

67. Consider the figure 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?

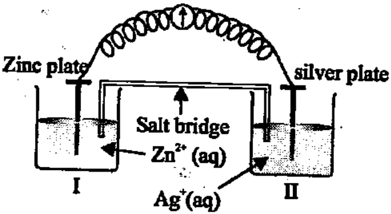
(*iii*) What will happen if salt bridge is removed?

(*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*)



(*ii*) It act as cathode.

(*iii*) Cell will stop functioning.

(*iv*) When equilibrium is attained i.e., $E_{cell} = 0$

(*v*) Concentration of Zn^+ will increase and Ag^+ will decrease.

(*vi*) When $E_{cell} = 0$ (equlibrium is reached), concentration of Zn^{2+} ions Ag^+ ions will not change.

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. The reversible work done by the galvanic cell is equal to decrease in gibbs free energy.

$$\Delta_r G = -nF E_{0\,cell}$$

❑❑❑

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4 Chemical Kinetics

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. The role of a catalyst is to change ____________.
   (*i*) gibbs energy of reaction.
   (*ii*) enthalpy of reaction.
   (*iii*) activation energy of reaction.
   (*iv*) equilibrium constant

Ans. (*iii*)

Explanation: Catalyst can change the activation energy of the reaction by changing the path of the reaction.

2. In the presence of a catalyst, the heat evolved or absorbed during the reaction __________.
   (*i*) increases.
   (*ii*) decreases.
   (*iii*) remains unchanged.
   (*iv*) may increase or decrease.

Ans. (*iii*)

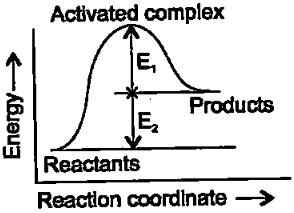
Explanation: Catalyst do not change the stability of the reaction.and thus the heat remains constant.

3. Activation energy of a chemical reaction can be determined by ____________.
   (*i*) determining the rate constant at standard temperature.
   (*ii*) determining the rate constants at two temperatures.
   (*iii*) determining probability of collision.
   (*iv*) using catalyst.

Ans. (*ii*)

Explanation: $\log k_2/k_1 = E_a/2.303[T_2 - T_1/T_1T_2]$ this eq. can be used to calculate the activation energy of the reaction. k_2 and k_1 are the rate constant E_a = activation energy T_1 and T_2 are two different temperature.

4. Consider the figure and mark the correct option.



   (*i*) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.
   (*ii*) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.
   (*iii*) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.
   (*iv*) Activation energy of backward reaction is E_1 and product is more stable than reactant.

Ans. (*i*)

Explanation: The energy required to form the reaction intermediate is clled activation energy.The energy gap between reactant and product molecule = $E_1 + E_2$ some energy is released when complex decomposes to form product.

5. Consider a first order gas phase decomposition reaction given below:

$$A(g) \rightarrow B(g) + C(g)$$

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.

(*i*) $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$ (*ii*) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$

(*iii*) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$ (*iv*) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + x}$

Ans. (*ii*)

Explanation: Let p_A, p_B and p_C are the partial pressures of *A*, *B* and *C* respectively. If *x* atm be the decrease in pressure of *A* at time t and one mole each of *B* and *C* is being formed, the increase in pressure of *B* and *C* will also be *x* atm each.

	$A(g)$	$\rightarrow$	$B(g)$	+	$C(g)$
At $t = 0$	pi atm		0 atm		0 atm
At time t	$(p_i - x)$ atm		x atm		x atm

where, p_i is the initial pressure at time $t = 0$.

$$pt = (p_i - x) + x + x = p_i + x$$

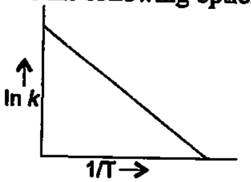
$$x = (p_t - p_i)$$

where, $p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$

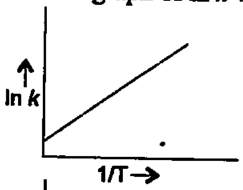
According to the first order reaction rate constant $k = 2.303/t \log \frac{p_i}{2p_i - p_t}$

6. According to Arrhenius equation rate constant *k* is equal to $k = Ae^{-E_a/RT}$. which of the following options represents the graph of ln *k* vs1/T?

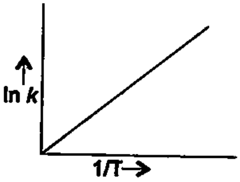
(*i*)



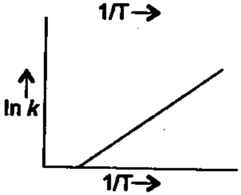
(*ii*)



(*iii*)



(*iv*)



Ans. (*i*)

Explanation: In the Arrhenius equation the factor $k = Ae^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a.

Taking natural logarithm of both sides of equation

$$\ln k = \frac{E_a}{RT} + \ln k$$

The plot of ln k vs $1/T$ gives a straight line according to the equation. Thus, it has been found from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

In graph, slope $= \dfrac{-E_a}{R}$

7. Consider the Arrhenius equation given below and mark the correct option.

$$k = Ae^{-E_a/RT}$$

(*i*) Rate constant increases exponentially with increasing activation energy and decreasing temperature.

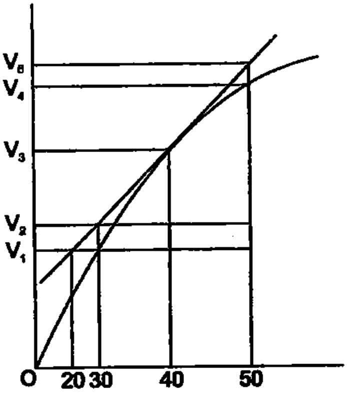
(*ii*) Rate constant decreases exponentially with increasing activation energy and decreasing temperature.

(*iii*) Rate constant increases exponentially with decreasing activation energy and decreasing temperature.

(*iv*) Rate constant increases exponentially with decreasing activation energy and increasing temperature.

Ans. (*iv*)

8. A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in the figure. On the basis of this mark the correct option.



(*i*) Average rate upto 40second is $\dfrac{V_3 - V_2}{40}$

(*ii*) Average rate upto 40 seconds is $\dfrac{V_3 - V_2}{40 - 30}$

(*iii*) Average rate upto 40 seconds is $\dfrac{V_3}{40}$

(*iv*) Average rate upto 40 seconds is $\dfrac{V_3 - V_1}{40 - 20}$

Ans. (*iii*)

Explanation: Average rate for the reaction = $\dfrac{\text{Change in concentration of } H_2}{\text{Change in time}}$

$$= \frac{V_3 - 0}{40 - 0} = \frac{V_3}{40}$$

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9. Which of the following statements is **not** correct about order of a reaction.

(*i*) The order of a reaction can be a fractional number.

(*ii*) Order of a reaction is experimentally determined quantity.

(*iii*) 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.

(*iv*) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression

Ans. (*iii*)

Explanation: The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction. Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

10. Consider the graph given in figure 4.2 (see question no. 8). Which of the following options does **not** show instantaneous rate of reaction at 40th second?

(*i*) $\dfrac{V_5 - V_2}{50-30}$ (*ii*) $\dfrac{V_3 - V_2}{40-30}$

(*iii*) $\dfrac{V_3 - V_2}{40-30}$ (*iv*) $\dfrac{V_3 - V_1}{40-20}$

Ans. (*ii*)

Explanation: The rate of a reaction at a particular moment of time. Average rate expression becomes instantaneous rate expression as $\Delta t \rightarrow 0$ (*i*), (*iii*) and (*iv*) are correct expression of instantaneous rate since small change in volume and small interval of time is taken

11. Which of the following statements is correct?

(*i*) The rate of a reaction decreases with passage of time as the concentration of reactants dereases.

(*ii*) The rate of a reaction is same at any time during the reaction.

(*iii*) The rate of a reaction is independent of temperature change.

(*iv*) The rate of a reaction decreases with increase in concentration of reactant(s).

Ans. (*i*)

Explanation: The rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of:

(*i*) the rate of decrease in concentration of any one of the reactants, or

(*ii*) the rate of increase in concentration of any one of the products.

Concentration of reactant decreases with the passage of time, we can say that the rate is also decreasing. $r = -dx/dt$ (r = rate)

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12. Which of the following expressions is correct for the rate of reaction given below?

$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

(*i*) $\frac{\Delta[Br^-]}{\Delta t} = 5\frac{\Delta[H^+]}{\Delta t}$ (*ii*) $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5}\frac{\Delta[H^+]}{\Delta t}$

(*iii*) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$ (*iv*) $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$

Ans. (*iii*)

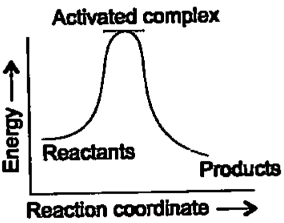
Explanation: For the above equation rate of reaction can be written as

$$r = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

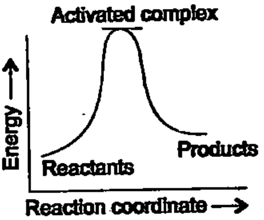
$$\Rightarrow -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} \text{ or } \frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$$

13. Which of the following graphs represents exothermic reaction?

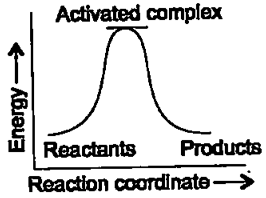
(*a*)



(*b*)



(*c*)



(*i*) (*a*) only (*ii*) (*b*) only

(*iii*) (*c*) only (*iv*) (*a*) and (*b*)

Ans. (*i*) (*a*)

Explanation: For an exothermic reaction activation energy of product should be greater than the reactant.

14. Rate law for the reaction A + 2B → C is found to be

Rate = *k* [A][B]

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be______.

(*i*) the same (*ii*) doubled

(*iii*) quadrupled (*iv*) halved

Ans. (*ii*)

Explanation: From the rate law expression it is clear that the rate w.r.t to B is of first order.

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When the concentration of A is kept constant and the concentration of B gets double than the rate will be twice.

Rate → $R_1 = k[A][B]$ ...(*i*)
Rate → $R_2 = k[A][2B]$ ...(*ii*)
Dividing eq. (*i*) by eq. (*ii*) = $R_2 = 2R_1$

15. Which of the following statements is **incorrect** about the collison theory of chemical reaction?

(*i*) It considers reacting molecules or atoms to be hard spheres and ignores their structural features.
(*ii*) Number of effective collisions determines the rate of reaction.
(*iii*) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation.
(*iv*) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

Ans. (*iii*)

16. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?

(*i*) 1.26×10^{15} s
(*ii*) 2.52×10^{14} s
(*iii*) 2.52×10^{28} s
(*iv*) infinite

Ans. (*iv*)

Explanation: It is impossible to perform 100% of the reaction, whole of the substance never react.

17. Compounds 'A' and 'B' react according to the following chemical equation.

$$A(g) + 2B(g) \rightarrow 2C(g)$$

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 concentraction of [B]/mol L^{-1}	Initial rate of formation 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

(*i*) Rate = $k[A]^2[B]$
(*ii*) Rate = $k[A][B]^2$
(*iii*) Rate = $k[A][B]$
(*iv*) Rate = $k[A]^2[B]^0$

Ans. (*ii*)

Explanation: Rate of experiment = $k[A]^x[B]^y = k[0.30]^x[0.30]^y$
Rate of experiment = $k[0.30]^x[0.60]^y$
Dividing experiment (1) by (2)

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$$\frac{k[0.30]^x[0.30]^y}{k[0.30]^x[0.60]^y} = \frac{0.10}{0.40}$$

$$[1/2]y = 1/4 \text{ or } y = 2$$

Similarly, on dividing rate of experiment (1) by (3)

$$\frac{k[0.30]^x[0.30]^y}{k[0.60]^x[0.30]^y} = \frac{0.10}{0.20}$$

$$[1/2]x = 1/2 \text{ or } x = 1$$

So the rate law expression is Rate $= k[A]\,[B]^2$

18. Which of the following statement is not correct for the catalyst?

(*i*) It catalyses the forward and backward reaction to the same extent.

(*ii*) It alters ΔG of the reaction.

(*iii*) It is a substance that does not change the equilibrium constant of a reaction.

(*iv*) It provides an alternate mechanism by reducing activation energy between reactants and products

Ans. (*ii*)

Explanation: A catalyst does not alter Gibbs energy, (ΔG) of a reaction. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.

19. The value of rate constant of a pseudo first order reaction ________.

(*i*) depends on the concentration of reactants present in small amount.

(*ii*) depends on the concentration of reactants present in excess.

(*iii*) is independent of the concentration of reactants.

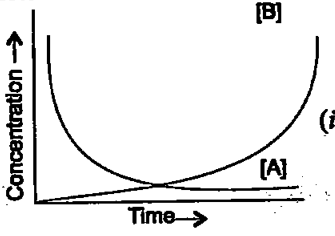
(*iv*) depends only on temperature

Ans. (*ii*)

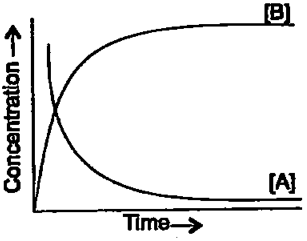
Explanation: The concentration of the reactants that is present in excess does not get altered much during the course of the reaction. Due to this reaction behaves as first order reaction. Such reactions are called pseudo first order reactions. Hence, concentration of reactants present in excess determines rate constant of a pseudo first order reaction.

20. Consider the reaction A → 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?

(*i*)



(*ii*)



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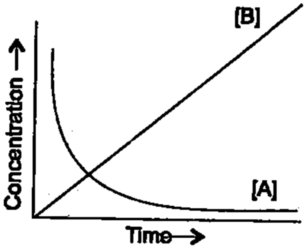
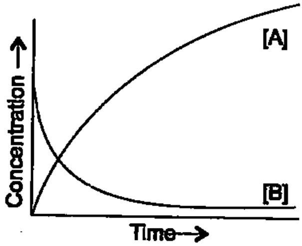
(*iii*)



(*iv*)



Ans. (*ii*)

Explanation: In graph (*ii*) concentration of reactant decreases exponentially with time and the concentration of product increases exponentially with time.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note : In the following questions two or more options may be correct.

21. Rate law cannot be determined from balanced chemical equation if ________.

(*i*) reverse reaction is involved.
(*ii*) it is an elementary reaction.
(*iii*) it is a sequence of elementary reactions.
(*iv*) any of the reactants is in excess

Ans. (*i*), (*iii*) and (*iv*)

Explanation: Rate law can be determined from balanced chemical equation if it is an elementary reaction.

22. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?

(*i*) Order is same as molecularity.
(*ii*) Order is less than the molecularity.
(*iii*) Order is greater than the molecularity.
(*iv*) Molecularity can never be zero.

Ans. (*i*), (*iv*)

Explanation: For a single step reactions, the order and molecularity will be the same.

23. In any unimolecular reaction ____________.

(*i*) only one reacting species is involved in the rate determining step.
(*ii*) the order and the molecularity of slowest step are equal to one.
(*iii*) the molecularity of the reaction is one and order is zero.
(*iv*) both molecularity and order of the reaction are one.

Ans. (*i*) and (*ii*)

Explanation: In an unimolecular reaction only one reacting species are involved in the slowest step or rate determining step.

24. For a complex reaction ____________.

(*i*) order of overall reaction is same as molecularity of the slowest step.

(*ii*) order of overall reaction is less than the molecularity of the slowest step.

(*iii*) order of overall reaction is greater than molecularity of the slowest step.

(*iv*) molecularity of the slowest step is never zero or non interger.

Ans. (*i*) and (*iv*)

Explanation: Order of a complex reaction can be determined experimentally by the slowest step. Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

25. At high pressure the following reaction is zero order.

$$2NH_3(g) \xrightarrow[\text{Platinum catalyst}]{1130\text{K}} N_2(g) + 3H_2(g)$$

Which of the following options are correct for this reaction?

(*i*) Rate of reaction = Rate constant

(*ii*) Rate of the reaction depends on concentration of ammonia.

(*iii*) Rate of decomposition of ammonia will remain constant until ammonia disappears completely.

(*iv*) Further increase in pressure will change the rate of reaction.

Ans. (*i*), (*iii*) and (*iv*)

Explanation: Rate = $k\,[NH_3]^0$ or rate of reaction = rate constant

At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of catalyst making rate of the reaction independent of its concentration.

26. During decomposition of an activated complex

(*i*) energy is always released (*ii*) energy is always absorbed

(*iii*) energy does not change (*iv*) reactants may be formed

Ans. (*i*) and (*iv*)

Explanation: Eenergy required to form an intermediate, called activated complex (C), is known as activation energy (E_a). Some energy is released when the complex decomposes to form product . the entire concentration of activated complex do not convert into product some activated complex may give reactant also.

27. According to Maxwell Boltzmann distribution of energy, __________.

(*i*) the fraction of molecules with most probable kinetic energy decreases at higher temperatures.

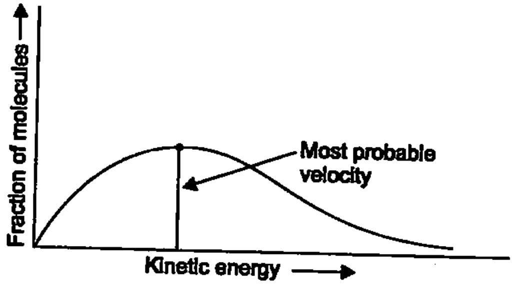
(*ii*) the fraction of molecules with most probable kinetic energy increases at higher temperatures.

(*iii*) most probable kinetic energy increases at higher temperatures.

(*iv*) most probable kinetic energy decreases at higher temperatures.

Ans. (*i*) and (*iii*)

Explanation: Maxwell Boltzmann distributon of energy can be explained by fig.

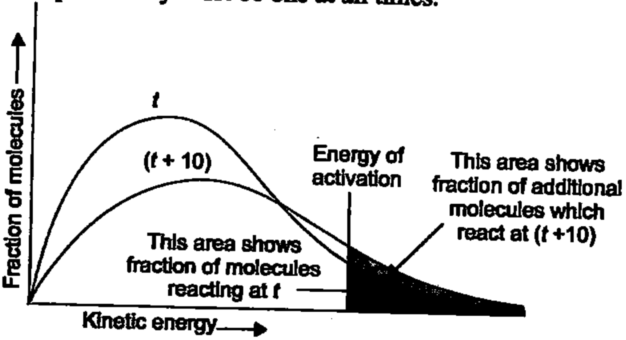


28. In the graph showing Maxwell Boltzman distribution of energy, ________.

(*i*) area under the curve must not change with increase in temperature.
(*ii*) area under the curve increases with increase in temperature.
(*iii*) area under the curve decreases with increase in temperature.
(*iv*) with increase in temperature curve broadens and shifts to the right hand side.

Ans. (*i*) and (*iv*)

Explanation: When the temperature is raised, the maximum of the curve moves to the higher energy value and the curve broadens out, i.e., spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times.



29. Which of the following statements are in accordance with the Arrhenius equation?

(*i*) Rate of a reaction increases with increase in temperature.
(*ii*) Rate of a reaction increases with decrease in activation energy.
(*iii*) Rate constant decreases exponentially with increase in temperature.
(*iv*) Rate of reaction decreases with decrease in activation energy.

Ans. (*i*) and (*ii*)

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Explanation: It has been found from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

30. Mark the **incorrect** statements.

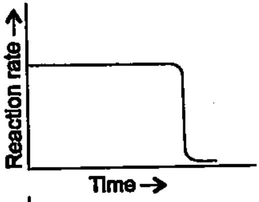
(*i*) Catalyst provides an alternative pathway to reaction mechanism.
(*ii*) Catalyst raises the activation energy.
(*iii*) Catalyst lowers the activation energy.
(*iv*) Catalyst alters enthalpy change of the reaction

Ans. (*ii*) and (*iv*)

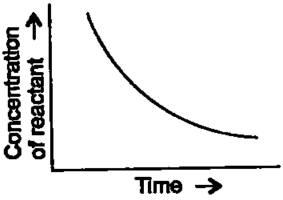
Explanation: Catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.

31. Which of the following graphs is correct for a zero order reaction?

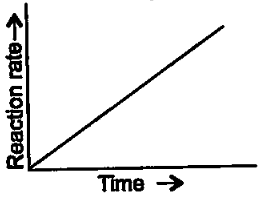
(*i*)



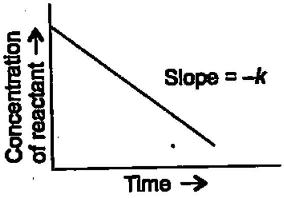
(*ii*)



(*iii*)



(*iv*)



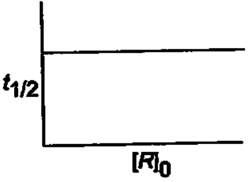
Ans. (*i*) and (*iv*)

Explanation: $k = \frac{[R]_0 - [R]}{t}$ where, k = rate constant for zero order reaction

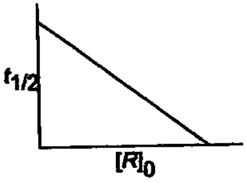
$[R]_0$ = initial concentration of the reactant
$[R]$ = concentration of the reactant at time t'

32. Which of the following graphs is correct for a first order reaction?

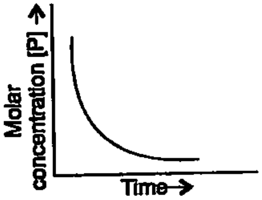
(*i*)



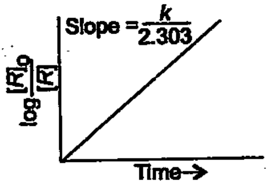
(*ii*)



(*iii*)



(*iv*)



Ans. (*i*) and (*iv*)

Explanation: For first order reaction $K = 2.303/t \log [R]_0/[R]$

$$\text{Slope} = -k/2.303$$

For first order reaction $t_{1/2} = 0.693/k$

Therefore $t_{1/2}$ for first order reaction is independent of the concentration of the reactant.

III. SHORT ANSWER TYPE

33. State a condition under which a bimolecular reaction is kinetically first order reaction.

Ans. Bimolecular reaction becomes kinetically first order or pseudo first order reaction when one of the reactant is in excess w.r.t to other, the rate of reaction depends on one of the reactant only. For example, inversion of cane sugar is a pseudo first order reaction.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

34. Write the rate equation for the reaction 2A + B → C if the order of the reaction is zero.

Ans. The rate law for the above reaction is

$$\text{Rate} = k[A]^0[B]^0$$

35. How can you determine the rate law of the following reaction?

$$2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$$

Ans. Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

We can measure 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.

36. For which type of reactions, order and molecularity have the same value?

Ans. For an elementary reaction order and molecularity have same value.

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.

$$\text{rate } r = k[A]^x \quad \text{...}(i)$$

$$\text{according to equation } 27r = k[3A]^x \quad \text{...}(ii)$$

Dividing eq. (*i*) by eq. (*ii*)

$$\frac{r}{27r} = \frac{k[A]^x}{k[3A]^x}$$

$$1/27 = [1/3]^x$$

$$[1/3]^3 = [1/3]^x \quad x = 3$$

Thus the order of reaction = 3.

38. **Derive an expression to calculate time required for completion of zero order reaction.**

Ans. R → P

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

As any quantity raised to power zero is unity

$$\text{Rate} = \frac{-d[R]}{dt} = k \times 1$$

$$d[R] = -k\,dt$$

Integrating both sides

$$[R] = -kt + I \qquad ...(i)$$

where, I is the constant of integration.

At $t = 0$, the concentration of the reactant $R = [R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation (*i*)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (*i*)

$$[R] = -kt + [R]_0$$

For completion [R] = 0

$$\therefore \qquad t = \frac{[R]_0}{k}$$

39. **For a reaction A + B → Products, the rate law is — Rate = $k[A][B]^{3/2}$. Can the reaction be an elementary reaction? Explain.**

Ans. From the rate law expression it is clear that w.r.t to B is 3/2 and w.r.t to A it is 1.

Thus the order of reaction is 5/2 for an elementary reaction order and molecularity should be same.

Therefore the above reaction cannot be an elementary reaction.

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. If in a reaction large fraction of molecules has energy more than the threshold energy and still the rate of reaction is slow it means there is lack of proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collision.

41. **For a zero order reaction will the molecularity be equal to zero? Explain.**

Ans. Molecularity shows the no. of reactants taking part in a chemical reaction. It can never be zero or a fractional number.

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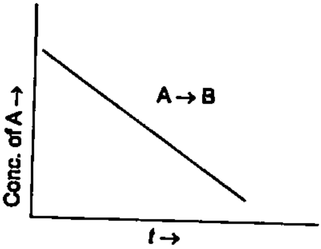
42. For a general reaction A → B, plot of concentration of A vs time is given in the figure. Answer the following question on the basis of this graph.

(*i*) What is the order of the reaction?

(*ii*) What is the slope of the curve?

(*iii*) What are the units of rate constant?



Ans. (*i*) The graph shows that it is a zero order reaction.

(*ii*) $[R] = -kt + [R]^0$ (mathematical expressions of zero order reaction)

slope $= -k$

(*iii*) Rate $= k\,[\text{reactant}]^0$

Or, rate $= k$

$$-\frac{d[R]}{dt} = k \text{ mol L}^{-1}\text{s}^{-1}$$

43. The reaction between $H_2(g)$ and $O_2(g)$ 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. This is because activation energy for the above reaction is very high at room temperature. For the reaction to be feasible it requires breaking of H—H and O—O bonds which is not possible at room temperature.

44. Why does the rate of a reaction increase with rise in temperature?

Ans. Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than E_a and leads to faster rate.

45. Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain.

Ans. Activation energy for combustion of any fuel is very high that is why it could not be possible at room temperature.

46. Why is the probability of reaction with molecularity higher than three very rare?

Ans. Because it is very difficult for more than three molecules to collide effectively with proper orientation.

47. Why does the rate of any reaction generally decreases during the course of the reaction?

Ans. Rate of reaction directly depends on the molar concentration of the reactant with the progress of the reaction concentration of the reactant start decreasing that is why the rate also decreases.

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 into graphite is highly feasible but the reaction is very slow because the activation energy is very high.

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49. Why in the redox titration of $KMnO_4$ vs oxalic acid, we heat oxalic acid solution before starting the titration?

Ans. In a mixture of potassium permanganate ($KMnO_4$) and oxalic acid ($H_2C_2O_4$), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature. Because the rate of reaction increases at high temperature.

50. Why can't molecularity of any reaction be equal to zero?

Ans. Molecularity can be defined as the no. of reactant molecule taking part in a chemical reaction. Without any reactant no product will be formed that is why it cannot be zero.

51. Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

Ans. A complex reaction involves a number of steps that is why molecularity is meaningless for complex reaction. Order of a complex reaction is determined by the slowest step in the reaction mechanism. In elementary reaction number of reactant molecule decide the molecularity of the reaction.

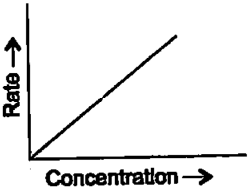
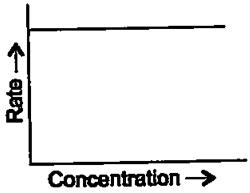
52. Why can we not determine the order of a reaction by taking into consideration the balanced chemical equation?

Ans. In a complex reaction order can not be predicted by balanced chemical equation because the reaction takes place in several steps Which step controls the rate of the overall reaction can be decide by the overall mechanism of the reaction thus the order of a reaction is an experimental quantity.

IV. MATCHING TYPE

Note : In the following questions match the items of Column I with appropriate item given in Column II.

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
(*i*) 	
(*ii*) 	(*a*) Ist order

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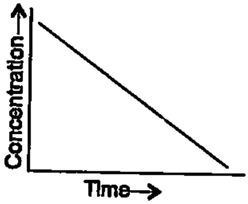
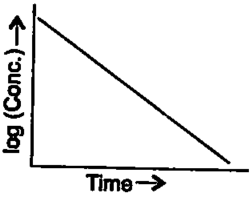
(iii)



(b) Zero order

(iv)



Ans. (i) → (a) (ii) → (b) (iii) → (b) (iv) → (a)

Explanation: For the first order reaction rate of reaction is directly proportional to the concentration of the reactant.

$d[R]/dt \propto [R]$

Hence the graph (i) will be a straight line.

Modifying the integrated rate equation for first order reaction

$k = 2.303/t \ \log [R_0]/[R]$ graph (iv) is of first order reaction.

For zero order reaction rate = $k[R]_0$. Therefore rate is independent of the concentration of reactant.

Therefore graph (ii) is of zero order reaction.

From integrated rate equation of zero order reaction $k = [R_0] - [R]$ thus graph (iii) of zero order reaction.

54. Match the statements given in Column I and Column II.

Column I	Column II
(i) Catalyst alters the rate of reaction	(a) cannot be fraction or zero
(ii) Molecularity	(b) proper orientation is not there always
(iii) Second half life of first order reaction	(c) by lowering the activation energy
(iv) $e^{-E_a/RT}$	(d) is same as the first
(v) Energetically favourable reactions are sometimes slow	(e) total probability is one
(vi) Area under the Maxwell Boltzman curve is constant	(f) refers to the fraction of molecules with energy equal to or greater than activation energy

Ans. (i) → (c) (ii) → (a) (iii) → (d)

(iv) → (f) (v) → (b) (vi) → (e)

Explanation:

(*i*) Catalyst can alter the rate of reaction by lowering the activation energy.

(*ii*) Molcularity is always a whole number it cannot be zero or fraction.

(*iii*) Second half life of first order reaction is also temperature dependent.

(*iv*) In the Arrhenius equation the factor $e - E_a/RT$ correspondes to the fraction of molecules that have kinetic energy greater than E_a.

(*v*) In collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

(*vi*) The area under the Maxwell Boltzmann distribution curve must be constant since total probability must be one at all times.

55. Match the items of Column I and Column II.

Column I	Column II
(*i*) Diamond	(*a*) short interval of time
(*ii*) Instantaneous rate	(*b*) ordinarily rate of conversion is imperceptible
(*iii*) Average rate	(*c*) long duration of time

Ans. (*i*) → (*b*)   (*ii*) → (*a*)   (*iii*) → (*c*)

Explanation: (*i*) Rate of conversion of diamond is imperceptible because it requires high activation energy. (*ii*) Instantaneous rate of a reaction is rate of a reaction at a particular moment of time. (*iii*) Average rate is obtained by dividing the change in concentration of any one of the reactant or product by the time taken for the change i.e., $\Delta x/\Delta t$.

56. Match the items of Column I and Column II.

Column I	Column II
(*i*) Mathematical expression for rate of reaction	(*a*) rate constant
(*ii*) Rate of reaction for zero order reaction is equal to	(*b*) rate law
(*iii*) Units of rate constant for zero order reaction is same as that of	(*c*) order of slowest step
(*iv*) Order of a complex reaction is determined by	(*d*) rate of a reaction

Ans. (*i*) → (*b*)   (*ii*) → (*a*)

(*iii*) → (*d*)   (*iv*) → (*c*)

Explanation:

(*i*) Mathematical expressions for rate of a reaction can be given by rate law.

(*ii*) Rate for zero order reaction : rate = k [reactant]^0 = k (rate constant).

(*iii*) It is very clear from above that unit of rate constant = rate of reaction.

(*iv*) Order of a complex reaction is determined by the slowest step which is known as rate determining step.

V. ASSERTION AND REASON TYPE

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Both assertion and reason are correct and the reason is correct explanation of assertion.

(*ii*) Both assertion and reason are correct but reason does not explain assertion.

(*iii*) Assertion is correct but reason is incorrect.

(*iv*) Both assertion and reason are incorrect.

(*v*) Assertion is incorrect but reason is correct.

57. Assertion : Order of the reaction can be zero or fractional.

Reason : We cannot determine order from balanced chemical equation.

Ans. (*ii*)

Explanation: Assertion is correct as order can be zero or fraction but it can be determined experimentally.

58. Assertion : Order and molecularity are same.

Reason : Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

Ans. (*v*)

Explanation: Order and molecularity can be same only for elementary reaction and it is different for complex reaction.

59. Assertion : The enthalpy of reaction remains constant in the presence of a catalyst.

Reason : A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the different in energy of reactant and product remains the same.

Ans. (*i*)

Explanation: It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier but the enthalpy of reaction remains constant.

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60. **Assertion** : All collision of reactant molecules lead to product formation.
Reason : Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

Ans. (*v*)

Explanation: The collisions in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, leads to the formation of product.

61. **Assertion** : Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.
Reason : Reactant molecules undergo chemical change irrespective of their orientation during collision.

Ans. (*iii*)

Explanation: Rate = $PZ\, e^{E_a/RT}$

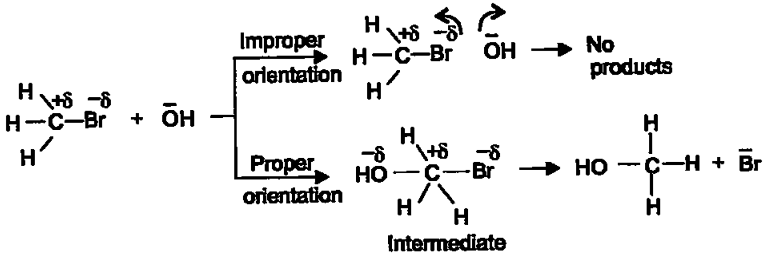
Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

VI. LONG ANSWER TYPE

62. All energetically effective collisions do not result in a chemical change. Explain with the help of an example.

Ans. All energetically effective collisions do not result in a chemical change. For example, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown below:

$$CH_3Br + \bar{O}H \longrightarrow CH_3OH + Br^-$$

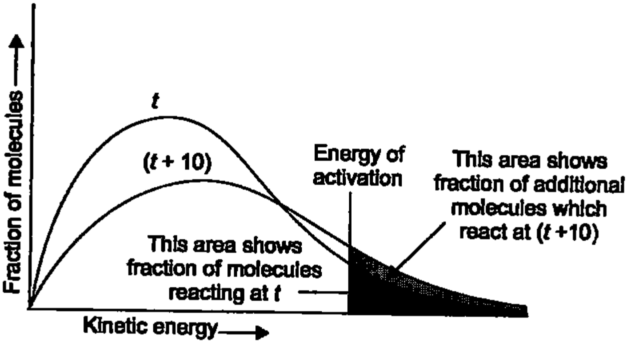


The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

To account for effective collisions, another factor P, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB}e^{-Ea/RT}$$

63. What happens to most probable kinetic energy and the energy of activation with increase in temperature?



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

$$k = Ae^{-E_a/RT}$$

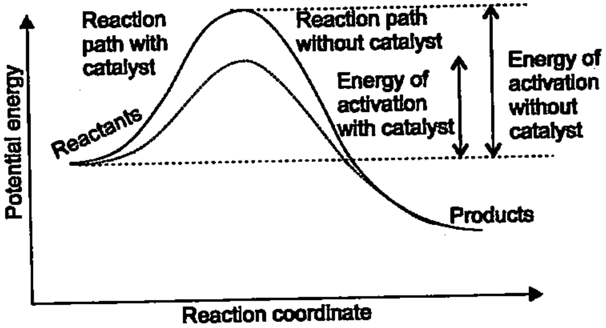
Thus, it also shows an increase with rise in temperature.

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 rate of a reaction without itself undergoing any permanent chemical change. The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy, ΔG of a reaction. Difference in energy between reactants and product is constant.

It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same enthalpy of reaction means difference in energy between reactant and product it will also remain unchanged. It can be shown by



65. Explain the difference between instantaneous rate of a reaction and average rate of a reaction.

Ans. Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur. However, average rate cannot be used to predict the rate of a reaction at a particular instant as it would be constant for the time interval for which it is calculated. So, to express the rate at a particular moment of time we determine the instantaneous rate. It is obtained when we consider the average rate at the smallest time interval say dt (i.e. when Δt approaches zero). Hence, mathematically for an infinitesimally small dt instantaneous rate is given by

$$\text{Average } r_{av} = \Delta x/\Delta t$$

Instantaneous rate $r_{inst} = dx/dt$

66. With the help of an example explain what is meant by pseudo first order reaction.

Ans. **Pseudo first order reaction:** Reaction which appears to be a second order reaction, but actually is first order reaction is called pseudo first order reaction. This condition occur in a chemical reaction between two substances when one reactant is present in large amount. The concentration of reactant present in excess does not get altered much during the course of the reaction. Due to this reaction behaves as first order reaction.

E.g. hydrolysis of esters

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

Rate law for this reaction is ; rate = $k[CH_3COOC_2H_5][H_2O]$

But the concentration of water does not change during the course of the reaction. So; $[H_2O]$ is constant.

Therefore rate = $k_1[CH_3COOC_2H_5]$. Where $k = k[H_2O]$.

The reaction behaves as a first order reaction.

❑❑❑

5 Surface Chemistry

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Which of the following process does not occur at the interface of phases?

   (i) crystallisation (ii) heterogenous catalysis
   (iii) homogeneous catalysis (iv) corrosion

Ans. (iii)

Explanation: In homogeneous catalysis only, the reactant and product are in same phase and composition is uniform throughout.

2. At the equilibrium position in the process of adsorption _________.

   (i) $\Delta H > 0$ (ii) $\Delta H = T\Delta S$
   (iii) $\Delta H > T\Delta S$ (iv) $\Delta H < T\Delta S$

Ans. (ii)

Explanation: At equilibrium $\Delta G = 0$

$$\Delta G = \Delta H - T\Delta S$$

Therefore $\Delta H = T\Delta S$

3. Which of the following interface cannot be obtained?

   (i) liquid-liquid (ii) solid-liquid
   (iii) liquid-gas (iv) gas-gas

Ans. (iv)

Explanation: Because gas-gas forms homogeneous composition.

4. The term 'sorption' stands for _________.

   (i) absorption
   (ii) adsorption
   (iii) both absorption and adsorption
   (iv) desorption

Ans. (iii)

Explanation: When adsorption and absorption occur simultaneously it is known as sorption.

5. Extent of physisorption of a gas increases with _________.

   (i) increase in temperature.
   (ii) decrease in temperature.
   (iii) decrease in surface area of adsorbent.
   (iv) decrease in strength of van der Waals forces

Ans. (ii)

Explanation: Since the adsorption (Solid + Gas $\rightleftharpoons$ Gas/Solid + Heat) process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature as the equilibrium will shift in backward direction. (Le-Chatelier's principle).

6. Extent of adsorption of adsorbate from solution phase increases with __________.

(*i*) increase in amount of adsorbate in solution.
(*ii*) decrease in surface area of adsorbent.
(*iii*) increase in temperature of solution.
(*iv*) decrease in amount of adsorbate in solution.

Ans. (*i*)

Explanation: The extent of adsorption depends on the concentration of the solute in solution as the concentration of adsorbate increases interaction between adsorbate and adsorbent increases thus the extent of adsorption increases.

7. Which one of the following is **not** applicable to the phenomenon of adsorption?

(*i*) $\Delta H > 0$
(*ii*) $\Delta G < 0$
(*iii*) $\Delta S < 0$
(*iv*) $\Delta H < 0$

Ans. (*i*)

Explanation: Since adsorption is an exothermic process ΔH can not be greater than zero.

8. Which of the following is **not** a favourable condition for physical adsorption?

(*i*) high pressure
(*ii*) negative ΔH
(*iii*) higher critical temperature of adsorbate
(*iv*) high temperature

Ans. (*iv*)

Explanation: High temperature is not favourable for physical adsorption since it is an exothermic process.

9. Physical adsorption of a gaseous species may change to chemical adsorption with __________.

(*i*) decrease in temperature
(*ii*) increase in temperature
(*iii*) increase in surface area of adsorbent
(*iv*) decrease in surface area of adsorbent

Ans. (*ii*)

Explanation: on increasing the temperature activation energy of the adsorbate molecule increases. Which can convert physical adsorption into chemisorptions.

10. In physisorption adsorbent does not show specificity for any particular gas because __________.

(*i*) involved van der Waals forces are universal.
(*ii*) gases involved behave like ideal gases.
(*iii*) enthalpy of adsorption is low.
(*iv*) it is a reversible process.

Ans. (*i*)

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11. Which of the following is an example of absorption?
   (*i*) Water on silica gel
   (*ii*) Water on calcium chloride
   (*iii*) Hydrogen on finely divided nickel
   (*iv*) Oxygen on metal surface

Ans. (*ii*)

12. On the basis of a data given below predict which of 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

   (*i*) CO_2 (*ii*) SO_2
   (*iii*) CH_4 (*iv*) H_2

Ans. (*iv*)

Explanation: Lesser the value of critical temp of gases lesser will the force of attraction among molecules and least will be the adsorption.

13. In which of the following reactions heterogenous catalysis is involved?

(*a*) $2SO_2\,(g) + O_2\,(g) \xrightarrow{NO(g)} 2SO_3\,(g)$

(*b*) $2SO_2\,(g) \xrightarrow{Pt(s)} 2SO_3\,(g)$

(*c*) $N_2\,(g) + 3H_2\,(g) \xrightarrow{Fe(s)} 2NH_3\,(g)$

(*d*) $CH_3COOCH_3\,(l) + H_2O\,(l) \xrightarrow{HCl(l)} CH_3COOH\,(aq) + CH_3OH\,(aq)$

   (*i*) (*b*), (*c*) (*ii*) (*b*), (*c*), (*d*)
   (*iii*) (*a*), (*b*), (*c*) (*iv*) (*d*)

Ans. (*i*) (*b*), (*c*)

Explanation: When the reactant and catalyst are in different phase it is known as heterogeneous catalysis.

14. At high concentration of soap in water, soap behaves as ________.
   (*i*) molecular colloid (*ii*) associated colloid
   (*iii*) macromolecular colloid (*iv*) lyophilic colloid

Ans. (*ii*)

Explanation: There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids.

15. Which of the following will show Tyndall effect?
   (*i*) Aqueous solution of soap below critical micelle concentration.
   (*ii*) Aqueous solution of soap above critical micelle concentration.
   (*iii*) Aqueous solution of sodium chloride.
   (*iv*) Aqueous solution of sugar.

Ans. (*ii*)

Explanation: Tyndall effect is the optical property shown by the colloidal particle. Above critical micelle concentration, a solution of soap behave as associated colloid that is why it shows tyndall effect.

16. Method by which lyophobic sol can be protected.

(*i*) By addition of oppositely charged sol.
(*ii*) By addition of an electrolyte.
(*iii*) By addition of lyophilic sol.
(*iv*) By boiling.

Ans. (*iii*)

Explanation: Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect the latter from electrolytes. Lyophilic colloids used for this purpose are called protective colloids.

17. Freshly prepared precipitate sometimes gets converted to colloidal solution by _________.

(*i*) coagulation (*ii*) electrolysis
(*iii*) diffusion (*iv*) peptisation

Ans. (*iv*)

Explanation: Peptisation is the process in which freshly prepared precipitate can be converted into colloidal solution.

18. Which of the following electrolytes will have maximum coagulating value for AgI/Ag^+ sol?

(*i*) Na_2S (*ii*) Na_3PO_4
(*iii*) Na_2SO_4 (*iv*) NaCl

Ans. (*ii*)

Explanation: Higher the value of oppositely charge electrolyte faster will be the rate of coagulation.

19. A colloidal system having a solid subtance as a dispersed phase and a liquid as a dispersion medium is classified as _________.

(*i*) solid sol (*ii*) gel
(*iii*) emulsion (*iv*) sol

Ans. (*iv*)

Explanation: Solid + liquid = sol (here solid is the dispersed phase and liquid is the dispersion medium.)

20. The values of colligative properties of colloidal solution are of small order in comparison to those shown by true solutions of same cocentration because of colloidal particles _________.

(*i*) exhibit enormous surface area.
(*ii*) remain suspended in the dispersion medium
(*iii*) form lyophilic colloids
(*iv*) are comparatively less in number.

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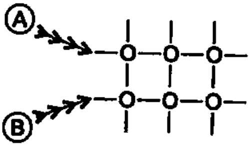
Ans. (*iv*)

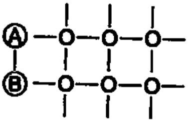
Explanation: Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentration

21. Arrange the following diagrams in correct sequence of steps involved in the mechanism of catalysis, in accordance with modern adsorption theory.

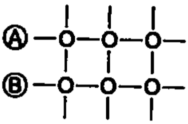
(*a*)



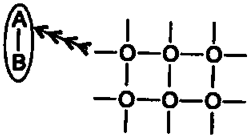
(*b*)



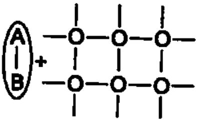
(*c*)



(*d*)



(*e*)



(*i*) $a \rightarrow b \rightarrow c \rightarrow d \rightarrow e$ (*ii*) $a \rightarrow c \rightarrow b \rightarrow d \rightarrow e$

(*iii*) $a \rightarrow c \rightarrow b \rightarrow e \rightarrow d$ (*iv*) $a \rightarrow b \rightarrow c \rightarrow e \rightarrow d$

Ans. (*ii*)

Explanation: Correct sequence of steps involed in catalysis is:

(*i*) → Adsorption of Aand B on surface

(*ii*) → Interaction between Aand B to form intermediate

(*iii*) → Starting of desorption from surface

(*iv*) → Complete desorption from the surface

22. Which of the following process is responsible for the formation of delta at aplace where rivers meet the sea?

(*i*) Emulsification (*ii*) Colloid formation

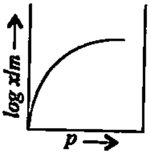
(*iii*) Coagulation (*iv*) Peptisation

Ans. (*iii*)

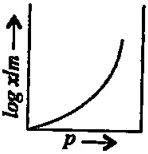
Explanation: River water is a colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

23. Which of the following curves is in accordance with Freundlich adsorption isotherm?

(*i*)



(*ii*)



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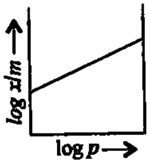
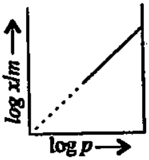
(iii) 

(iv) 

Ans. (*i*)

Explanation: Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

$$x/m = k\,p^{1/n} \quad (n > 1)$$

The adsorption varies directly.

Where x/m = mass of gas adsorbed per unit mass of adsorbent particle

P = Pressure of gas at particular temperature.

24. Which of the following process is **not** responsible for the presence of electric charge on the sol particles?

(*i*) Electron capture by sol particles.

(*ii*) Adsorption of ionic species from solution.

(*iii*) Formation of Helmholtz electrical double layer.

(*iv*) Absorption of ionic species from solution.

Ans. (*iv*)

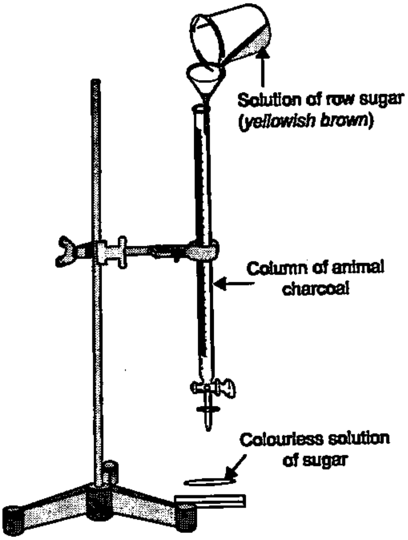
Explanation: The charge on the sol particles is due to one or more reasons, viz.,

(*a*) due to electron capture by sol particles during electrodispersion of metals,

(*b*) due to preferential adsorption of ions from solution and/or

(*c*) due to formulation of electrical double layer.

25. Which of the following phenomenon is applicable to the process shown in the figure?



(*i*) Absorption

(*ii*) Adsorption

(*iii*) Coagulation

(*iv*) Emulsification

Ans. (*ii*)

Explanation: In the figure adsorption of coloured particle from charcoal is shown. Solution of raw sugar is filtered by animal charcoal and yellowish brown colour of raw sugar is adsorbed and filterate is colourless which gives white colour on crystallization.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note: In the following questions two or more options may be correct.

26. Which of the following options are correct?

(*i*) Micelle formation by soap in aqueous solution is possible at all temperatures.

(*ii*) Micelle formation by soap in aqueous solution occurs above a particular concentration.

(*iii*) On dilution of soap solution micelles may revert to individual ions.

(*iv*) Soap solution behaves as a normal strong electrolyte at all concentrations

Ans. (*ii*) and (*iii*)

Explanation: The formation of micelles takes place only above a particular temperature called Kraft temperature (T_k) and above a particular concentration called critical micelle concentration (CMC). On dilution, these colloids revert back to individual ions.

27. Which of the following statements are correct about solid catalyst?

(*i*) Same reactants may give different product by using different catalysts.

(*ii*) Catalyst does not change ΔH of reaction.

(*iii*) Catalyst is required in large quantities to catalyse reactions.

(*iv*) Catalytic activity of a solid catalyst does not depend upon the strength of chemisorption

Ans. (*i*) and (*ii*)

Explanation: Action of a catalyst is highly selective in nature, i.e., a given substance can act as a catalyst only in a particular reaction and not for all the reactions. It means that a substance which acts as a catalyst in one reaction may fail to catalyse another reaction. Catalyst do not change the enthalpy of reaction.

28. Freundlich adsorption isotherm is given by the expression $\frac{x}{m} = k\, p^{\frac{1}{n}}$ which of the following conclusion can be drawn from this expression.

(*i*) When $\frac{1}{n} = 0$, the adsorption is independent of pressure.

(*ii*) When $\frac{1}{n} = 0$, the adsorption is directly proportional to pressure.

(*iii*) When $n = 0$, $\frac{x}{m}$ vs p graph is a line parallel to x-axis.

(*iv*) When $n = 0$, plot of $\frac{x}{m}$ vs p is a curve.

Ans. (*i*) and (*iii*)

Explanation: Freundlich gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

$$\frac{x}{m} = kp^{1/n}$$

If $\frac{1}{n} = 0$; $\frac{x}{m} = k$ extent of adsorption is independent of pressure.

When $n = 0$; $\frac{x}{m} = kp^{\infty}$

$\frac{x}{m}$ vs p is a line parallel to x-axis

29. H_2 gas is adsorbed on activated charcoal to a very little extent in comparison to easily liquefiable gases due to ____________.

(*i*) very strong van der Waal's interaction.

(*ii*) very weak van der Waals forces.

(*iii*) very low critical temperature.

(*iv*) very high critical temperature.

Ans. (*ii*) and (*iii*)

Explanation: H_2 molecule on an activated charcoal is adsorbed to a very little extent in comparison to easily liquefiable gases because it has

(*a*) very weak van der Waals force of attraction

(*b*) very low critical temperature

30. Which of the following statements are correct?

(*i*) Mixing two oppositely charged sols neutralises their charges and stabilises the colloid.

(*ii*) Presence of equal and similar charges on colloidal particles provides stability to the colloids.

(*iii*) Any amount of dispersed liquid can be added to emulsion without destabilising it.

(*iv*) Brownian movement stabilises sols.

Ans. (*ii*) and (*iv*)

Explanation: The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from coalescing or aggregating when they come closer to one another.

The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.

31. An emulsion cannot be broken by __________ and __________.

(*i*) heating

(*ii*) adding more amount of dispersion medium

(*iii*) freezing

(*iv*) adding emulsifying agent

Ans. (*ii*) and (*iv*)

Explanation: Emulsions can be broken into constituent liquids by heating, freezing and centrifuging.

32. Which of the following substances will precipitate the negatively charged emulsions?

(*i*) KCl
(*ii*) glucose
(*iii*) urea
(*iv*) NaCl

Ans. (*i*) and (*iv*)

Explanation: Negatively charged emulsion can be precipitated by oppositely charged electrolyte. Na^+ and K^+ from the electrolyte can neutralize the negatively charge emulsion and precipitate the colloid.

33. Which of the following colloids cannot be coagulated easily?

(*i*) Lyophobic colloids.
(*ii*) Irreversible colloids.
(*iii*) Reversible colloids.
(*iv*) Lyophilic colloids.

Ans. (*iii*) and (*iv*)

Explanation: Sols directly formed by mixing substances like gum, gelatin, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. They are also known as reversible colloid. These sols are very stable and cannot coagulate easily.

34. What happens when a lyophilic sol is added to a lyophobic sol?

(*i*) Lyophobic sol is protected.
(*ii*) Lyophilic sol is protected.
(*iii*) Film of lyophilic sol is formed over lyophobic sol.
(*iv*) Film of lyophobic sol is formed over lyophilic sol.

Ans. (*i*) and (*iii*)

Explanation: Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect the latter from electrolytes. Lyophilic colloids used for this purpose are called protective colloid.

35. Which phenomenon occurs when an electric field is applied to a colloidal solution and electrophoresis is prevented?

(*i*) Reverse osmosis takes place.
(*ii*) Electroosmosis takes place.
(*iii*) Dispersion medium begins to move.
(*iv*) Dispersion medium becomes stationary.

Ans. (*ii*) and (*iii*)

Explanation: When electrophoresis, i.e., 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 electroosmosis.

36. In a reaction, catalyst changes ____________.

(*i*) physically (*ii*) qualitatively
(*iii*) chemically (*iv*) quantitatively

Ans. (*i*) and (*ii*)

Explanation: Substances, which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as catalysts they can undergo physical change.

37. Which of the following phenomenon occurs when a chalk stick is dipped in ink?

(*i*) adsorption of coloured substance
(*ii*) adsorption of solvent
(*iii*) absorption and adsorption both of solvent
(*iv*) absoprtion of solvent

Ans. (*i*) and (*iv*)

Explanation: When a chalk stick is dipped in ink, the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption.

III. SHORT ANSWER TYPE

38. Why is it important to have clean surface in surface studies?

Ans. If the surface is covered by the other gaseous molecule it will not available for the desired molecules. To accomplish surface studies meticulously, it becomes imperative to have a really clean surface.

39. Why is chemisorption referred to as activated adsorption?

Ans. Chemisorption is caused by chemical bond formation. It involves a high energy of activation and is, therefore, often referred to as activated adsorption.

40. What type of solutions are formed on dissolving different concentrations of soap in water?

Ans. Soap solutions at low concentrations behave as normal electrolytes, but after a certain concentration, called critical micelle concentration, exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids.

41. What happens when gelatin is mixed with gold sol?

Ans. Gold sol is a lyophobic colloid it is quite unstable in nature. Gelatin is a lyophilic colloid it stablises the sol and act as protective colloid.

42. How does it become possible to cause artificial rain by spraying silver iodide on the clouds?

Ans. Clouds are aerosols having small droplets of water suspended in air. The rainfall occurs when two oppositely charged clouds meet. Sometimes, it is possible to cause artificial rain by throwing electrifieds and or spraying a sol carrying charge opposite to the one on the clouds. Spraying of silver iodide, an electrolyte, on clouds results in its congulation leading to rain.

43. Gelatin which is a peptide is added in icecreams. What can be its role?

Ans. Gelatin act as a emulsifying agent in the icecreams. The emulsifying agent forms an interfacial film between suspended particles and the medium.

44. What is collodion?

Ans. Collodion is a 4% solution of nitrocellulose in a mixture of alcohol and ether.

45. Why do we add alum to purify water?

Ans. The water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.

46. What happens when electric field is applied to colloidal solution?

Ans. The existence of charge on colloidal particles is confirmed by electrophoresis experiment. When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the charged colloidal particles start moving towards oppositely charged electrode. The movement of colloidal particles under an applied electric potential is called electrophoresis.

47. What causes brownian motion in colloidal dispersion?

Ans. The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.

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. By adding $FeCl_3$ in excess of hot water a positively charged colloid is formed. When excess of sodium chloride is added to the solution negatively charged chloride ions coagulate the positvely charged colloidal solution of $FeCl_3$.

49. How do emulsifying agents stabilise the emulsion?

Ans. The emulsifying agent forms an interfacial film between suspended particles and the medium.

50. Why are some medicines more effective in the colloidal form?

Ans. Most of the medicines are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated.

51. Why does leather get hardened after tanning?

Ans. Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather.

52. How does the precipitation of colloidal smoke take place in Cottrell precipitator?

Ans. Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber.

53. How will you distinguish between dispersed phase and dispersion medium in an emulsion?

Ans. Emulsion can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed, forms a separate layer.

54. On the basis of Hardy-Schulze rule explain why the coagulating power of phosphate is higher than chloride.

Ans. Greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as Hardy-Schulze rule. Phosphate ion has greater charge (–3) than chloride ion (–1), so coagulating power of PO_4^{3-} is more than Cl^-.

55. Why does bleeding stop by rubbing moist alum?

Ans. Blood is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.

56. Why is $Fe(OH)_3$ colloid positively charged, when prepared by adding $FeCl_3$ to hot water?

Ans. If $FeCl_3$ is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of Fe^{3+} ions.

57. Why do physisorption and chemisorption behave differently with rise in temperature?

Ans. Physisorption involves weak vander Waals forces. So, adsorption occurs readily at low temperature and decreases with increasing temperature because vander Waals forces weaken with rise in temperature. Chemisorption increases on increasing the temperature because it involves the formation of chemical bond which requires high energy of activation.

58. What happens when dialysis is prolonged?

Ans. Colloid becomes unstable and coagulation occurs because the traces of electrolyte which is needed for the stabilization of the sol get removed due to prolonged dialysis.

59. Why does the white precipitate of silver halide become coloured in the presence of dye eosin.

Ans. Because the dye eosin get adsorbed on the surface of the precipitate of silver halide.

60. What is the role of activated charcoal in gas mask used in coal mines?

Ans. Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

61. How does a delta form at the meeting place of sea and river?

Ans. River water is a colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

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 is an example of physisorption but when the temperature is increased it changes into chemisorption. Hydrogen molecule dissociate into hydrogen atom and form chemical bond at the surface of the metal.

63. Why is desorption important for a substance to act as good catalyst?

Ans. The reactants must get adsorbed reasonably strongly on to the catalyst to become active. However, they must not get adsorbed so strongly that they are immobilised and other reactants are left with no space on the catalyst's surface.

Desorption is very important so that the surface of the catalyst can be available for the other reactant.

64. What is the role of diffusion in heterogenous catalysis?

Ans. The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis. First step involve in the heterogeneous catalysis is the diffusion of reactant on the surface of catalyst which facilitates adsorption. Second step involves diffusion of reaction products away from the catalyst's surface leaving the surface free for more ractant molecules to get adsorbed and undergo reaction. It is also very important for the whole process of catalysis.

65. How does a solid catalyst enhance the rate of combination of gaseous molecules?

Ans. The surface of the catalyst unlike the inner part of the bulk, has free valencies which provide the seat for chemical forces of attraction. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. Different molecules adsorbed side by side have better chance to react and form new moleculs. This enhances the rate of reaction. Also, adsorption is an exothermic process. The heat released in the process of adsorption is utilised in enhancing the reaction rate.

66. Do the vital functions of the body such as digestion get affected during fever? Explain your answer.

Ans. The rate of an enzyme reaction is maximum at a definite temperature, called the optimum temperature. On either side of the optimum temperature, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298-310 K. Human body temperature being 310 K is suited for enzyme-catalysed reactions. Therefore during fever, catalytic activity of the enzyme may get affected.

IV. MATCHING TYPE

Note: Match the items of Column I and Column II in the following questions:

67. Method of information of solution is given in Column I. Match it with the type of solution given in Column II.

Column I	Column II
(*i*) Sulphur vapours passed through cold water	(*a*) Normal electrolyte solution
(*ii*) Soap mixed with water above critical micelle concentration	(*b*) Molecular colloids
(*iii*) White of egg whipped with water	(*c*) Associated colloid
(*iv*) Soap mixed with water below critical micelle concentration	(*d*) Macro molecular colloids

Ans. (*i*) → (*b*) (*ii*) → (*c*) (*iii*) → (*d*) (*iv*) → (*a*)

Explanation:

(*i*) By passing vapours of sulphur through cold water sulphur sol can be prepared which is a molecular colloid.

(*ii*) When soap is mixed with water above critical micelle concentration forms associated colloid.

(*iii*) White of egg whipped with water forms macromolecular colloid.

(*iv*) Soap mixed with water below critical micelle concentration behave as normal electrolyte.

68. Match the statement given in Column I with the phenomenon gives in Column II.

Column I	Column II
(*i*) Dispersion medium moves in an electric field	(*a*) Osmosis
(*ii*) Solvent molecules pass through semi permeable membrane towards solvent side	(*b*) Electrophoresis
(*iii*) Movement of charged colloidal particles under the influence of applied electric potential towards oppositely charged electrodes	(*c*) Electroosmosis
(*iv*) Solvent molecules pass through semi permeable membranes towards solution side	(*d*) Reverse osmosis

Ans. (*i*) → (*c*) (*ii*) → (*d*) (*iii*) → (*b*) (*iv*) → (*a*)

Explanation:

(*i*) When electrophoresis, i.e., 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 Electroosmosis.

(*ii*) Solvent molecules pass through semi-permeable membrane towards solvent side is termed as reverse osmosis.

(*iii*) When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode. The movement of colloidal particles under an applied electric potential is called electrophoresis.

(*iv*) Solvent molecules pass through semipermeable membrane towards solution side is termed as osmosis.

69. Match the items given in Column I and Column II.

Column I	Column II
(*i*) Protective colloid	(*a*) $FeCl_3$ + NaOH
(*ii*) Liquid-liquid colloid	(*b*) Lyophilic colloids
(*iii*) Positively charged colloid	(*c*) Emulsion
(*iv*) Negatively charged colloid	(*d*) $FeCl_3$ + hot wataer

Ans. (*i*) → (*b*) (*ii*) → (*c*) (*iii*) → (*d*) (*iv*) → (*a*)

Explanation:

(*i*) Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect the colloid.

(*ii*) If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called emulsion.

(*iii*) If $FeCl_3$ is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of Fe^{3+} ions.

(*iv*) When ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of OH^- ions.

70. Match the types of colloidal systems given in Column I with the name given in Column II.

Column I	Column II
(*i*) Solid in liquid	(*a*) Foam
(*ii*) Liquid in solid	(*b*) Sol
(*iii*) Liquid in liquid	(*c*) Gel
(*iv*) Gas in liquid	(*d*) Emulsion

Ans. (*i*) → (*b*) (*ii*) → (*c*) (*iii*) → (*d*) (*iv*) → (*a*)

Explanation:

S. No.	Dispersed phase	Dispersion medium	colloid
(*i*)	solid	liquid	sol
(*ii*)	liquid	solid	gel
(*iii*)	liquid	liquid	emulsion
(*iv*)	gas	liquid	foam

71. Match the items of Column I and Column II.

Column I	Column II
(*i*) Dialysis	(*a*) Cleansing action of soap
(*ii*) Peptisation	(*b*) Coagulation
(*iii*) Emulsification	(*c*) Colloidal sol formation
(*iv*) Electrophoresis	(*d*) Purification

Ans. (*i*) → (*d*) (*ii*) → (*c*) (*iii*) → (*a*) (*iv*) → (*b*)

Explanation:

(*i*) **Dialysis:** process used for the purification of colloid.

(*ii*) **Peptisation:** Peptisation may be defined as the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of small amount of electrolyte.

(*iii*) **Emulsification:** Process of cleansing of oil and dirt from soap by emulsification.

(*iv*) **Electrophoresis:** The movement of colloidal particles under an applied electric potential is called electrophoresis.

72. Match the items of Column I and Column II.

Column I	Column II
(*i*) Butter	(*a*) dispersion of liquid in liquid
(*ii*) Pumice stone	(*b*) dispersion of solid in liquid
(*iii*) Milk	(*c*) dispersion of gas in solid
(*iv*) Paints	(*d*) dispersion of liquid in solid

Ans. (*i*) → (*d*) (*ii*) → (*c*) (*iii*) → (*a*) (*iv*) → (*b*)

Explanation:

Dispersed phase	Dispersion medium	Ex: colloidal solution
solid	liquid	butter
gas	solid	Pumice stone
liquid	liquid	milk
solid	liquid	paint

V. ASSERTION AND REASON TYPE

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are correct and the reason is correct explanation of assertion.

(*ii*) Assertion and reason both are correct but reason does not explain Assertion.

(*iii*) Assertion is correct but reason is incorrect.

(*iv*) Both assertion and reason are incorrect.

(*v*) Assertion is incorrect but reason is correct.

73. Assertion : An ordinary filter paper impregnated with collodion solution stops the flow of colloidal particles.

Reason : Pore size of the filter paper becomes more than the size of colloidal particle.

Ans. (*iii*)

Explanation: Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with collodion solution to stop the flow of colloidal particles.

74. Assertion : Colloidal solutions show colligative properties.

Reason : Colloidal particles are large in size.

Ans. (*i*)

Explanation: Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentration.

75. Assertion : Colloidal solutions do not show brownian motion.

Reason : Brownian motion is responsible for stability of sols.

Ans. (*v*)

Explanation: Colloidal particle shows Brownian movement.The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.

76. Assertion : Coagulation power of Al^{3+} is more than Na^+.

Reason : Greater the valency of the flocculating ion added, greater is its power to cause precipitation (Hardy Schulze rule).

Ans. (*i*)

Explanation: The greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as Hardy-Schulze rule. In the coagulation of a negative sol, the flocculating power is in the order: $Al^{3+} > Ba^{2+} > Na^+$.

77. Assertion : Detergents with low CMC are more economical to use.

Reason : Cleansing action of detergents involves the formation of micelles. These are formed when the concentration of detergents becomes equal to CMC.

Ans. (*i*)

Explanation: Detergents with low CMC are more economical to use as they involves the formation of micelle which is used for cleaning of oil and dirt from our cloth. Micelle formation takes place when the concentration of detergent become equal to CMC.

VI. LONG ANSWER TYPE

78. What is the role of adsorption in heterogenous catalysis?

Ans. In heterogeneous catalysis reactants are generally in gas phase and catalyst are in solid phase. The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst to become active. However, they must not get adsorbed so strongly that they are immobilised and other reactants are left with no space on the catalyst's surface for adsorption. It has been found that for hydrogenation reaction, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by groups 7-9 elements of the periodic table. Catalyst also direct a reaction to yield a particular product. For example, starting with H_2 and CO, and using different catalysts, we get different products.

79. What are the applications of adsorption in chemical analysis?

Ans. (*i*) **Separation of inert gases:** Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

(*ii*) **Adsorption indicators:** Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at end point.

(*iii*) **Chromatographic analysis:** Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and and industrial fields.

80. What is the role of adsorption in froth floatation process used especially for concentration of sulphide ores?

Ans. This method has been in use for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. To it, collectors and froth stabilisers are added. Collectors (e.g., pine oils, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilisers (e. g., cresols, aniline) stabilise the froth.

81. What do you understand by shape selective catalysis? Why are zeolites good shape selective catalysts?

Ans. The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolites are good shape-selective catalysts because of their honeycomb-like structures. They are aluminosilicates with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si framework. The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites. They are found in nature as well as synthesised for catalytic selectivity. Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation.

❑❑❑

6 General Principles and Processes of Isolation of Elements

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. In the extraction of chlorine by electrolysis of brine ____________.
   - (*i*) oxidation of Cl^- ion to chlorine gas occurs.
   - (*ii*) reduction of Cl^- ion to chlorine gas occurs.
   - (*iii*) For overall reaction $\Delta G^\ominus$ has negative value.
   - (*iv*) a displacement reaction takes place.

Ans. (*i*)

Explanation: $2H_2O(l) + 2Cl^-(aq) \rightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$
The $\Delta G^\ominus$ for this reaction is + 422 kJ. When it is converted to $E^\ominus$ (using $\Delta G^\ominus = -nE^\ominus F$), we get $E^\ominus = -2.2$ V. Naturally, it will require an external e.m.f. that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions. Thus, Cl_2 is obtained by electrolysis giving out H_2 and aqueous NaOH as byproducts. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH.

2. When copper ore is mixed with silica, in a reverberatory furnace copper matte is produced. The copper matte contains ____________.
   - (*i*) sulphides of copper (II) and iron (II)
   - (*ii*) sulphides of copper (II) and iron (III)
   - (*iii*) sulphides of copper (I) and iron (II)
   - (*iv*) sulphides of copper (I) and iron (III)

Ans. (*iii*)

Explanation: the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte. This contains Cu_2S and FeS.

$$FeO + SiO_2 \rightarrow FeSiO_3 \text{ (slag)}$$

3. Which of the following reactions is an example of autoreduction?
   - (*i*) $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$
   - (*ii*) $Cu_2O + C \rightarrow 2Cu + CO$
   - (*iii*) $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$
   - (*iv*) $Cu_2O + \frac{1}{2}Cu_2S \rightarrow 3Cu + \frac{1}{2}SO_2$

Ans. (*iv*)

Explanation: In this reaction copper (I) oxide is reduced by copper (I) sulphide. Here copper is reduced by itself hence this process is known as autoreduction.

4. A number of elements are available in earth's crust but most abundant elements are ________.

(*i*) Al and Fe
(*ii*) Al and Cu
(*iii*) Fe and Cu
(*iv*) Cu and Ag

Ans. (*i*)

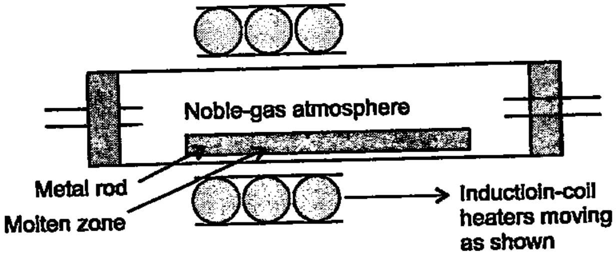
Explanation: Among metals, aluminium is the third most abundant element in earth's crust (8.3% approx. by weight). It is a major component of many igneous minerals including mica and clays. Iron is the second most abundant metal in the earth's crust.

5. Zone refining is based on the principle that ________.

(*i*) impurities of low boiling metals can be separated by distillation.
(*ii*) impurities are more soluble in molten metal than in solid metal.
(*iii*) different components of a mixture are differently adsorbed on an adosrbent.
(*iv*) vapours of volatile compound can be decomposed in pure metal.

Ans. (*ii*)

Explanation: In zone refining method a circular mobile heater is fixed at one end of a rod of the impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone (See given Fig.).



6. In the extraction of copper from its sulphide ore, the metal is formed by the reduction of Cu_2O with

(*i*) FeS
(*ii*) CO
(*iii*) Cu_2S
(*iv*) SO_2

Ans. (*iii*)

Explanation: $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called blister copper.

7. Brine is electrolysed by using inert electrodes. The reaction at anode is ________.

(*i*) $Cl^-(aq.) \rightarrow \frac{1}{2}Cl_2(g) + e^-$; $E^{\ominus}_{Cell} = 1.36V$

(*ii*) $2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$; $E^{\ominus}_{Cell} = 1.23V$

(*iii*) $Na^+(aq.) + e^- \rightarrow Na(s)$; $E^{\ominus}_{Cell} = 2.71V$

(*iv*) $H^+(aq.) + e^- \rightarrow \frac{1}{2}H_2(g)$; $E^{\ominus}_{Cell} = 0.00V$

Ans. (*i*)

Explanation: The reaction at anode with lower value of $E^{\ominus}_{Cell}$ is preferred but due to overvoltage oxygen cannot be obtained in this process.

8. In the metallurgy of aluminium ________.

(*i*) Al^{3+} is oxidised to Al (s).

(*ii*) graphide anode is oxidised to carbon monoxide and carbon dioxide.

(*iii*) oxidation state of oxygen changes in the reaction at anode.

(*iv*) oxidation state of oxygen changes in the overall reaction involved in the process.

Ans. (*ii*)

Explanation: $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

This process of electrolysis is widely known as Hall-Heroult process. Thus electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2.

9. Electrolytic refining is used to purify which of the following metals?

(*i*) Cu and Zn (*ii*) Ge and Si

(*iii*) Zr and Ti (*iv*) Zn and Hg

Ans. (*i*)

Explanation: Zinc and copper can be purified by electrolytic method. In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal.

The more basic metal remains in the solution and the less basic ones go to the anode mud.

10. Extraction of gold and silver involves leaching the metal with CN– ion. The metal is recovered by ________.

(*i*) displacement of metal by some other metal from the complex ion.

(*ii*) roasting of metal complex.

(*iii*) calcination followed by roasting.

(*iv*) thermal decomposition of metal complex.

Ans. (*i*)

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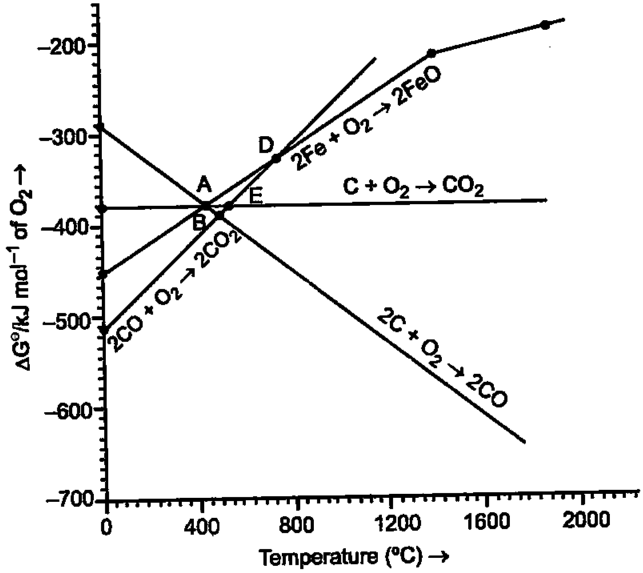
Explanation: Extraction of gold and silver involves leaching the metal with CN^-. This is also an oxidation reaction ($Ag \rightarrow Ag^+$ or $Au \rightarrow Au^+$). The metal is later recovered by displacement method.

$4Au(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$

$2[Au(CN)_2]^-(aq) + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]_2^-(aq)$

Note: Answer the questions 11-13 on the basis of figure.



11. Choose the correct option of temperature at which carbon reduces FeO to iron and produces CO.
    (*i*) Below temperature at point A.
    (*ii*) Approximately at the temperature corresponding to point A.
    (*iii*) Above temperature at point A but below temperature at point D.
    (*iv*) Above temperature at point A.

Ans. (*iv*)

Explanation: At temperatures above point A, the C, CO line comes below the Fe, FeO line [$\Delta G_{(C,\ CO)} < \Delta G_{(Fe,\ FeO)}$]. So in this range, coke will be reducing the FeO and will itself be oxidised to CO.

12. Below point 'A' FeO can ____________.
    (*i*) be reduced by carbon monoxide only.
    (*ii*) be reduced by both carbon monoxide and carbon.
    (*iii*) be reduced by carbon only.
    (*iv*) not be reduced by both carbon and carbon monoxide.

Ans. (*i*)

Explanation: Below the point A, Gibbs free energy change for the formation of CO_2 from CO has lower value than Gibb's free energy change for the formation of FeO. $\Delta G_{(Fe, FeO)}$. Hence FeO will be reduced by CO only below point A.

13. For the reduction of FeO at the temperature corresponding to point D, which of the following statements is correct?
    (*i*) ΔG value for the overall reduction reaction with carbon monoxide is zero.
    (*ii*) ΔG value for the overall reduction reaction with a mixture of 1 mol carbon and 1 mol oxygen is positive.
    (*iii*) ΔG value for the overall reduction reaction with a mixture of 2 mol carbon and 1 mol oxygen will be positive.
    (*iv*) ΔG value for the overall reduction reaction with carbon monoxide is negative.

Ans. (*i*)

Explanation: At point D, ΔG curve for the formation of CO_2 from CO and FeO from Fe intersect each other therefore, overall reduction of FeO with CO is zero.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note: In the following questions two or more options may be correct.

14. At the temperature corresponding to which of the points in Fig. 6.1, FeO will be reduced to Fe by coupling the reaction $2FeO \rightarrow 2Fe + O_2$ with all of the following reactions?
    (*a*) $C + O_2 \rightarrow CO_2$ (*b*) $2C + O_2 \rightarrow 2CO$ and (*c*) $2CO + O_2 \rightarrow 2CO_2$
    (*i*) Point A (*ii*) Point B
    (*iii*) Point D (*iv*) Point E

Ans. (*ii*) and (*iv*)

Explanation: Below the point B and E, FeO will be reduced to Fe by all the three reactions shown above $\Delta G_{(C, CO)}$, $\Delta G_{(C, CO_2)}$, $\Delta G_{(CO, CO_2)}$ lie below $\Delta G_{(Fe, FeO)}$ curve at point B and E.

15. Which of the following options are correct?
    (*i*) Cast iron is obtained by remelting pig iron with scrap iron and coke using hot air blast.
    (*ii*) In extraction of silver, silver is extracted as cationic complex.
    (*iii*) Nickel is purified by zone refining.
    (*iv*) Zr and Ti are purified by van Arkel method.

Ans. (*i*) and (*iv*)

Explanation: Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast.

→ van Arkel method is used for the refining of Zr and Ti

The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:

$$Zr + 2I_2 \rightarrow ZrI_4$$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$$ZrI_4 \rightarrow Zr + 2I_2$$

16. In the extraction of aluminium by Hall-Heroult process, purified Al_2O_3 is mixed with CaF_2 to
   (*i*) lower the melting point of Al_2O_3.
   (*ii*) increase the conductivity of molten mixture.
   (*iii*) reduce Al^{3+} into Al(s).
   (*iv*) acts as catalyst.

Ans. (*i*) and (*ii*)

Explanation: In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mix and brings conductivity.

17. Which of the following statements is correct about the role of substances added in the froth floation process?
   (*i*) Collectors enhance the non-wettability of the mineral particles.
   (*ii*) Collectors enhance the wettability of gangue particles.
   (*iii*) By using depressants in the process two sulphide ores can be separated.
   (*iv*) Froth stabilisers decrease wettability of gangue.

Ans. (*i*) and (*iii*)

Explanation: In froth floatation process, a suspension of the powdered ore is made with water. To it, collectors and froth stabilisers are added. Collectors (e.g., pine oils, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilisers (e.g., cresols, aniline) stabilise the froth.

18. In the Froth Floatation process, zinc sulphide and lead sulphide can be separated by ____________.
   (*i*) using collectors.
   (*ii*) adjusting the proportion of oil to water.
   (*iii*) using depressant.
   (*iv*) using froth stabilisers.

Ans. (*ii*) and (*iii*)

Explanation: In froth floatation process it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants'. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN.

19. Common impurities present in bauxite are ____________.

(*i*) CuO (*ii*) ZnO

(*iii*) Fe_2O_3 (*iv*) SiO_2

Ans. (*iii*) and (*iv*)

Explanaion: The principal ore of aluminium, bauxite, usually contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities.

20. Which of the following ores are concentrated by froth floation?

(*i*) Haematite (*ii*) Galena

(*iii*) Copper pyrites (*iv*) Magnetite

Ans. (*ii*) and (*iii*)

Explanaion: Froth floatation method → is generally used for sulphide ore. Here galena (PbS) and copperpyrites ($CuFeS_2$) are sulphide ores.

21. Which of the following reactions occur during calcination?

(*i*) $CaCO_3 \rightarrow CaO + CO_2$

(*ii*) $2FeS_2 + \frac{11}{2} O_2 \rightarrow Fe_2O_3 + 4SO_2$

(*iii*) $Al_2O_3.x\,H_2O \rightarrow Al_2O_3 + x\,H_2O$

(*iv*) $ZnS + \frac{3}{2} O_2 \rightarrow ZnO + SO_2$

Ans. (*i*) and (*iii*)

Explanation: Calcinaton involves heating when the volatile matter escapes leaving behind the metal oxide. It is generally done in absence of air.

22. For the metallurgical process of which of the ores calcined ore can be reduced by carbon?

(*i*) haematite (*ii*) calamine

(*iii*) iron pyrites (*iv*) sphalerite

Ans. (*i*) and (*ii*)

Explanation: In metallurgical process the oxide ore can be reduced by carbon. Iron pyrite and sphalerite are sulphide ores that cannot be reduced by carbon.

23. The main reactions occurring in blast furnace during extraction of iron from haematite are ____________.

(*i*) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

(*ii*) $FeO + SiO_2 \rightarrow FeSiO_3$

(*iii*) $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

(*iv*) $CaO + SiO_2 \rightarrow CaSiO_3$

Ans. (*i*) and (*iv*)

Explanation:

(*i*) It is the carbon monoxide which is the main reducing agent in the furnace.

(*ii*) This is an endothermic reaction, absorbing heat from the furnace. It is therefore important not to add too much limestone because it would otherwise cool the furnace. Calcium Oxide is a basic oxide and reacts with acidic oxides such as Silicon dioxide present in the rock. Calcium oxide reacts with silicon dioxide to give calcium silicate.

24. In which of the following method of purification, metal is converted to its volatile compound which is decomposed to give pure metal?

(*i*) heating with stream of carbon monoxide.

(*ii*) heating with iodine.

(*iii*) liquation. (*iv*) distillation.

Ans. (*i*) and (*ii*)

Explanation: In vapour phase refining method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal.

Mond process for refining Nickel: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl.

$$Ni + 4CO \xrightarrow{330-350\ K} Ni(CO)_4$$

The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal:

$$Ni(CO)_4 \xrightarrow{450-470\ K} Ni + 4CO$$

The metal iodide being more covalent, volatilises:

$$Zr + 2I_2 \rightarrow ZrI_4$$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800 K. The pure metal is thus deposited on the filament.

$$ZrI_4 \rightarrow Zr + 2I_2$$

25. Which of the following statements are correct?

(*i*) A depressant prevents certain type of particle to come to the froth.

(*ii*) Copper matte contains Cu_2S and ZnS.

(*iii*) The solidified copper obtained from reverberatory furnace has blistered appearance due to evolution of SO_2 during the extraction.

(*iv*) Zinc can be extracted by self-reduction.

Ans. (*i*) and (*iii*)

Explanation:

(*i*) → depressant prevents certain type of particle to come to the froth for example, in case of an ore containing ZnS and PbS, the depressant used is NaCN.

(*ii*) → Copper matte contains Cu_2S and FeS.

(*iii*) → The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called blister copper.

(*iv*) → Zinc can be extracted from ZnO by reducing it with carbon.

26. In the extraction of chlorine from brine __________.

(*i*) $\Delta G^\ominus$ for the overall reaction is negative.

(*ii*) $\Delta G^\ominus$ for the overall reaction is positive.

(*iii*) $E^\ominus$ for overall reaction has negative value.

(*iv*) $E^\ominus$ for overall reaction has positive value.

Ans. (*ii*) and (*iii*)

Explanation: Extraction of chlorine from brine (chlorine is abundant in sea water as common salt).

$2Cl^-(aq) + 2H_2O(l) \rightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$

$\Delta G^\ominus$ for the reaction is 422 kJ. When it is converted to $E^\ominus$ (using $\Delta G^\ominus = -nE^\ominus F$), we get $E^\ominus = -2.2$ V. Naturally, it will require an external emf that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions.

III. SHORT ANSWER TYPE

27. Why is an external emf of more than 2.2 V required for the extraction of Cl_2 from brine?

Ans. Extraction of chlorine from brine (chlorine is abundant in sea water as common salt).

$$2Cl^-(aq) + 2H_2O(l) \rightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$$

$\Delta G^\ominus$ for this reaction is $+422$ kJ.

When it is converted to $E^\ominus$ (using $\Delta G^\ominus = -nE^\ominus F$), we get $E^\ominus = -2.2$ V. Naturally, it will require an external emf that is greater than 2.2 V.

28. At temperatures above 1073 K coke can be used to reduce FeO to Fe. How can you justify this reduction with Ellingham diagram?

Ans. At temperatures above 1073 K (approx.), the C,CO line comes below the Fe,FeO line [$\Delta G_{(C, CO)} < \Delta G_{(Fe, FeO)}$]. So in this range, coke will be reducing the FeO and will itself be oxidised to CO.

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. Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

Limestone is added as flux silicon, sulphur and phosphorus are oxidised and passed into the slag. The metal is removed and freed from the slag by passing through rollers.

30. How is copper extracted from low grade copper ores?

Ans. Copper is extracted by hydrometallurgy from low grade copper ores. It is leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2.

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$$

31. Write two basic requirements for refining of a metal by Mond process and by van Arkel Method.

Ans. Two basic requirements for both processes are:

(*i*) The metal should form a volatile compound with an available reagent.

(*ii*) The volatile compound should be easily decomposable, so that the recovery of metal is easy.

32. **Although carbon and hydrogen are better reducing agents but they are not used to reduce metallic oxides at high temperatures. Why?**

Ans. Carbon and hydrogen are not used to reduce metallic oxides at high temperatures as they react with metal at high temperature to form carbides and hydrides respectively.

33. **How do we separate two sulphide ores by Froth Floatation Method? Explain with an example.**

Ans. It is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants'. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively forms complex with ZnS prevents it from coming to the froth but allows PbS to come with the froth.

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. Haematite ore is used to line the furnace. This haematite oxidises carbon to carbon monoxide:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

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. Compound 'B' is more readily adsorbed on column. Since compound A is eluted in preference to B.

36. **Why is sulphide ore of copper heated in a furnace after mixing with silica?**

Ans. The sulphide ore of copper contains iron oxide as impurity. So, it is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte. This contains Cu_2S and FeS.

$$FeO + SiO_2 \rightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

Copper matte is then charged into silica lined convertor.

37. **Why are sulphide ores converted to oxide before reduction?**

Ans. Sulphide ores are very difficult to reduce while metal oxide can be reduced easily.

38. **Which method is used for refining Zr and Ti? Explain with equation.**

Ans. van Arkel method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti.

The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises.

$$Zr + 2I_2 \rightarrow ZrI_4$$

Metal iodide electrically heated to about 1800 K. The pure metal is thus deposited on the filament.

$$ZrI_4 \rightarrow Zr + 2I_2$$

39. What should be the considerations during the extraction of metals by electrochemical method?

Ans. For the reduction of molten metal electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$$\Delta G^\ominus = -nE^\ominus F$$

Here n is the number of electrons and $E^\ominus$ is the electrode potential of the redox couple formed in the system. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two $E^\ominus$ values corresponds to a positive $E^\ominus$ and consequently negative $\Delta G^\ominus$ in equation , then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,

$$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$$

40. What is the role of flux in metallurgical processes?

Ans. Flux is used to remove gangue particle from the ore and it also make the molten mass more conducting.

41. How are metals used as semiconductors refined? What is the principle of the method used?

Ans. Zone refining method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated.

42. Write down the reactions taking place in Blast furnace related to the metallurgy of iron in the temperature range 500–800 K .

Ans. At 500 – 800 K (lower temperature range in the blast furnace):

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$
$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$

43. Give two requirements for vapour phase refining.

Ans. The 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 decomposable, so that the recovery is easy.

44. Write the chemical reactions involved in the extraction of gold by cyanide process. Also give the role of zinc in the extraction.

Ans. Extraction of gold and silver involves leaching the metal with CN^-. This is also an oxidation reaction.

$$(Ag \rightarrow Ag^+ \text{ or } Au \rightarrow Au^+).$$

The metal is later recovered by displacement method.

$$4Au(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

$$2[Au(CN)_2]^-(aq) + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$$

In this reaction zinc acts as a reducing agent.

IV. MATCHING TYPE

Note : Match the items given in Column I and Column II in the following questions:

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)	$CuCO_3.Cu(OH)_2$
		(5)	$ZnCO_3$

Code :

(*i*) A (1) B (2) C (3) D (4) (*ii*) A (2) B (4) C (5) D (3)

(*iii*) A (2) B (3) C (4) D (5) (*iv*) A (4) B (5) C (3) D (2)

Ans. (*ii*)

Explanation:

A. Pendulum is made up of nickel steel

B. Malachite – $CuCO_3Cu(OH)_2$

C. Calamine – $ZnCO_3$

D. Cryolyte – Na_3AlF_6

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 Process
(D)	Purification of mercury	(4)	Chromatography
		(5)	Liquation

Code :

(*i*) A (1) B (2) C (4) D (5)   (*ii*) A (4) B (3) C (1) D (2)

(*iii*) A (3) B (4) C (2) D (1)   (*iv*) A (5) B (4) C (3) D (2)

Ans. (*ii*)

Explanation:

A. Coloured bands are observed in chromatography.

B. Monds process is used to convert impure metal into volatile complex compound.

C. Ge and Si can be purified by zone refining method.

D. Distillation is done for low boiling metal like mercury.

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

Code :

(*i*) A (4) B (2) C (3) D (1)   (*ii*) A (2) B (3) C (1) D (5)

(*iii*) A (1) B (2) C (3) D (4)   (*iv*) A (3) B (4) C (5) D (1)

Ans. (*i*)

Explanation:

A. For the extraction of Au, cyanide process is used.

B. Froth floatation process is used for sulphide ore like for ZnS.

C. Electrolytic reduction can be used for the extraction of Al.

D. Zone refining is used for ultrapure Ge.

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

Code :

(*i*) A (3) B (4) C (2) D (1)   (*ii*) A (5) B (4) C (3) D (2)

(*iii*) A (2) B (3) C (4) D (5)   (*iv*) A (1) B (2) C (3) D (4)

Ans. (*i*)

Explanation:

A. Sapphire is a gemstone containing Co

B. Sphalerite single is ZnS

C. NaCN is used as depressant

D. Al_2O_3 is known as corundum

49. Match the items of Column I with items of Column II and assign the correct code :

Column I		Column II	
(A)	Blisterred Cu	(1)	Aluminium
(B)	Blast furnace	(2)	$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$
(C)	Reverberatory furnace	(3)	Iron
(D)	Hall-Heroult process	(4)	$FeO + SiO_2 \rightarrow FeSiO_3$
		(5)	$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

Code :

(*i*) A (2) B (3) C (4) D (1) (*ii*) A (1) B (2) C (3) D (5)

(*iii*) A (5) B (4) C (3) D (2) (*iv*) A (4) B (5) C (3) D (2)

Ans. (*i*)

Explanation:

A. → $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$ (6.40)
The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called blister copper.

B. Iron is extracted from blast furnace

C. → The ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte.

$$FeO + SiO_2 \rightarrow FeSiO_3$$

D. → Hall-Heroult process single is used for the extraction of Al.

V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Both assertion and reason are true and reason is the correct explanation of assertion.

(*ii*) Both assertion and reason are true but reason is not the correct explanation of assertion.

(*iii*) Assertion is true but reason is false.

(*iv*) Assertion is false but reason is true.

(*v*) Assertion and reason both are wrong.

50. **Assertion** : Nickel can be purified by Mond process.

Reason : Ni $(CO)_4$ is a volatile compound which decomposes at 460K to give pure Ni.

Ans. (*i*)

Explanation: Nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl which on further decomposition gives pure Ni. This process is called Mond process.

$$Ni + 4CO \xrightarrow{330-450\,K} Ni(CO)_4$$

$$Ni(CO)_4 \xrightarrow{450-470\,K} Ni + 4CO$$

51. **Assertion** : Zirconium can be purificed by van Arkel method.

Reason : ZrI_4 is volatile and decomposes at 1800 K.

Ans. (*i*)

Explanation: van Arkel method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises and then decomposes at 1800 K to given pure Zr.

$$Zr + 2I_2 \rightarrow ZrI_4$$

$$ZrI_4 \xrightarrow{1800\,K} Zr + 2I_2$$

52. **Assertion** : Sulphide ores are concentrated by Froth Flotation method.

Reason : Cresols stabilise the froth in Froth Flotation method.

Ans. (*ii*)

Explanation: Sulphide ores are concentrated by froth floatation process. This process is used for removing gangue from sulphide ore.

53. **Assertion** : Zone refining method is very useful for producing semiconductors.

Reason : Semiconductors are of high purity.

Ans. (*ii*)

Explanation: Zone refining method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium

54. **Assertion** : Hydrometallurgy involves dissolving the ore in a suitable reagent followed by precipitation by a more electropositive metal.

Reason : Copper is extracted by hydrometallurgy.

Ans. (*ii*)

Explanation: Copper is extracted by hydrometallurgy from low grade ore. Hydrometallurgy involves dissolving the ore in suitable reagent followed by precipitation in this method more electropositive metal is used by which pure metal can be displaced.

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VI. LONG ANSWER TYPE

55. Explain the following:

(*a*) CO_2 is a better reducing agent below 710 K whereas CO is a better reducing agent above 710 K.

(*b*) Generally sulphide ores are converted into oxides before reduction.

(*c*) Silica is added to the sulphide ore of copper in the reverberatory furnace.

(*d*) Carbon and hydrogen are not used as reducing agents at high temperatures.

(*e*) Vapour phase refining method is used for the purification of Ti.

Ans. (*a*) From Ellingham diagram it is clear that above 710 K $\Delta G_{(C, CO2)} < \Delta G_{(C, CO)}$. So CO_2 is better reducing agent below 710 K whereas CO is better reducing agent above 710 K.

(*b*) Sulphide ores are difficult to reduce that is why it is converted into oxide before reduction.

(*c*) Sulphide ore of copper contains iron oxide as impurity. So the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte.

(*d*) At high temperature carbon and hydrogen reacts with metal to form metal carbides and hydrides respectively.

(*e*) Ti can form volatile compound (I_1I_4) with the iodine and the compound is easily decomposible to give extra pure Ti. So the recovery is easy.

❑❑❑

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7 THE p-BLOCK ELEMENTS

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

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

   (*i*) H_2SO_4 reduces HI to I_2 (*ii*) HI is of violet colour
   (*iii*) HI gets oxidised to I_2 (*iv*) HI changes to HIO_3

Ans. (*iii*)

Explanation: When iodide salt reacts with H_2SO_4, HI is formed which is a strong reducing agent. It reduces H_2SO_4 to SO_2 and itself get oxidised to I_2.

$$H_2SO_4 + 2HI \rightarrow SO_2 + \underset{\text{(Violet colour)}}{I_2} + 2H_2O$$

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 _________.

   (*i*) deep blue precipitate of $Cu(OH)_2$
   (*ii*) deep blue solution of $[Cu(NH_3)_4]^{2+}$
   (*iii*) deep blue solution of $Cu(NO_3)_2$
   (*iv*) deep blue solution of $Cu(OH)_2 . Cu(NO_3)_2$

Ans. (*ii*)

Explanation: When H_2S is passed through acidified solution of salt with dil. HCl black ppt is formed.

$$CuSO_4 + H_2S \xrightarrow{\text{dil HCl}} \underset{\text{Black ppt}}{CuS\downarrow} + H_2SO_4$$

On boiling CuS with dil. HNO_3 it forms blue coloured solution and the following reaction occur

$$3CuS + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$

$$S + 2HNO_3 \rightarrow H_2SO_4 + NO$$

$$2Cu^{2+} + SO_4^{2-} + 2NH_3 + 2H_2O \rightarrow Cu(OH)_2 . CuSO_4 + 2NH_4OH$$

$$Cu(OH)_2 . CuSO_4 + 8NH_3 \rightarrow \underset{\substack{\text{Tetramine copper (II)} \\ \text{Deep blue solution}}}{2[Cu(NH_3)_4]SO_4} + 2OH^- + SO_4^{2-}$$

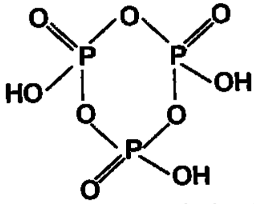
3. In a cyclotrimetaphosphoric acid molecule, how many single and double bonds are present?

   (*i*) 3 double bonds; 9 single bonds
   (*ii*) 6 double bonds; 6 single bonds

(*iii*) 3 double bonds; 12 single bonds
(*iv*) Zero double bonds; 12 single bonds

Ans. (*i*)

Explanation: Structure of Cyclotrimetaphosphoric acid



(Cyclotrimetaphosphoric acid)
3-double bonds, 9-single bonds

4. Which of the following elements can be involved in pπ–dπ bonding?

(*i*) Carbon
(*ii*) Nitrogen
(*iii*) Phosphorus
(*iv*) Boron

Ans. (*iii*)

Explanation: Among four choices only phosphorous has vacant *d*-orbital

5. Which of the following pairs of ions are isoelectronic and isostructural?

(*i*) CO_3^{2-}, NO_3^-
(*ii*) ClO_3^-, CO_3^{2-}
(*iii*) SO_3^{2-}, NO_3^-
(*iv*) ClO_3^-, SO_3^{2-}

Ans. (*i*)

Explanation: No. of electron in both the molecule is = 32
Both has similar structure that is triangular planar.

6. Affinity for hydrogen decreases in the group from fluorine to iodine. Which of the halogen acids should have highest bond dissociation enthalpy?

(*i*) HF
(*ii*) HCl
(*iii*) HBr
(*iv*) HI

Ans. (*i*)

Explanation: On moving down the group atomic radii increases and bond dissociation enthalpy increases. So the highest bond dissociation enthalpy is of HF.

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
Δ_{diss} (E—H)/kJ mol–1	389	322	297	255

(*i*) NH_3
(*ii*) PH_3
(*iii*) AsH_3
(*iv*) SbH_3

Ans. (*iv*)

Explanation: On moving down the group size of the central atom increases *i.e.* bond length increases and bond dissociation enthalpy decreases.

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8. On heating with concentrated NaOH solution in an inert atmosphere of CO_2, white phosphorus gives a gas. Which of the following statement is **incorrect** about the gas?

(*i*) It is highly poisonous and has smell like rotten fish.
(*ii*) It's solution in water decomposes in the presence of light.
(*iii*) It is more basic than NH_3.
(*iv*) It is less basic than NH_3.

Ans. (*iii*)

White phosphorous is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3.

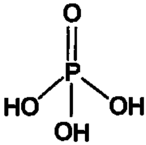
$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

9. Which of the following acids forms three series of salts?

(*i*) H_3PO_2	(*ii*) H_3BO_3
(*iii*) H_3PO_4	(*iv*) H_3PO_3

Ans. (*iii*)

Explanation: Structure of



H_3PO_4 has 3-OH groups i.e. has three ionisable H-atoms and hence forms three series of salts i.e., NaH_2PO_4, Na_2HPO_4, and Na_3PO_4.

10. Strong reducing behaviour of H_3PO_2 is due to

(*i*) Low oxidation state of phosphorus
(*ii*) Presence of two–OH groups and one P–H bond
(*iii*) Presence of one–OH group and two P–H bonds
(*iv*) High electron gain enthalpy of phosphorus

Ans. (*iii*)

Explanation: In H_3PO_2, two H atoms are bonded directly to P atom which imparts reducing character to the acid.

11. On heating lead nitrate forms oxides of nitrogen and lead. The oxides formed are ______.

(*i*) N_2O, PbO	(*ii*) NO_2, PbO
(*iii*) NO, PbO	(*iv*) NO, PbO_2

Ans. (*ii*)

Explanation: $2PbNO_3 \rightarrow 2PbO + 4NO_2 + O_2$

12. Which of the following elements does not show allotropy?

(*i*) Nitrogen	(*ii*) Bismuth
(*iii*) Antimony	(*iv*) Arsenic

Ans. (*i*)

Explanation: The single N—N bond is weak because of high inter-electronic repulsion of the non-bonding electrons, owing to the

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small bond length. As a result the catenation tendency is weaker in nitrogen that is why it does not show allotropy.

13. Maximum covalency of nitrogen is ______________.

(*i*) 3
(*ii*) 5
(*iii*) 4
(*iv*) 6

Ans. (*iii*)

Explanation: The electronic configuration of nitrogen is ns^2np^3. Nitrogen is restricted to the maximum covalency of 4 since only four (one *s* and three *p*) orbitals are available for bonding.

14. Which of the following statements is wrong?

(*i*) Single N–N bond is stronger than the single P–P bond.
(*ii*) PH_3 can act as a ligand in the formation of coordination compound with transition elements.
(*iii*) NO_2 is paramagnetic in nature.
(*iv*) Covalency of nitrogen in N_2O_5 is four.

Ans. (*i*)

Explanation: N—N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length.

15. A brown ring is formed in the ring test for NO_3^- ion. It is due to the formation of

(*i*) $[Fe(H_2O)_5(NO)]^{2+}$
(*ii*) $FeSO_4.NO_2$
(*iii*) $[Fe(H_2O)_4(NO)_2]^{2+}$
(*iv*) $FeSO_4.HNO_3$

Ans. (*i*)

Explanation: When freshly prepared solution of $FeSO_4$ is added in a solution containing NO_3^- ion, it leads to the formation of brown coloured complex.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow O + 3Fe^{2+} + 2H_2O$$

$$[Fe(H_2O)6]^{2+} + NO \rightarrow \underset{\text{Brownish}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

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

(*i*) Bi_2O_5
(*ii*) BiF_5
(*iii*) $BiCl_5$
(*iv*) Bi_2S_5

Ans. (*ii*)

Explanation: Stability of +5 state decreases from top to bottom but because of high electronegativity and smaller size of fluorine bismuth can exist in this form.

17. On heating ammonium dichromate and barium azide separately we get

(*i*) N_2 in both cases
(*ii*) N_2 with ammonium dichromate and NO with barium azide

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(*iii*) N_2O with ammonium dichromate and N_2 with barium azide
(*iv*) N_2O with ammonium dichromate and NO_2 with barium azide

Ans. (*i*)

Explanation: On heating ammonium dichromate and barium azide separately we get N_2 gas in both cases.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$$

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

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 ______.

(*i*) 2   (*ii*) 3
(*iii*) 4   (*iv*) 6

Ans. (*i*)

Explanation: $4NH_3 + 5O_2 \xrightarrow[Pt]{\Delta} 4NO(g) + 6H_2O$

Hence, from above equation, oxidation of 2 moles of ammonia will produce 2 moles of NO.

19. The oxidation state of central atom in the anion of compound NaH_2PO_2 will be ______.

(*i*) +3   (*ii*) +5
(*iii*) +1   (*iv*) –3

Ans. (*iii*)

Explanation: Oxidation state of NaH_2PO_2

$$\overset{+1}{Na}\,\overset{+1}{H_2}\,\overset{n}{P}\overset{-2}{O_2}$$

$$+1 + 2\times + 1 + x + 2 \times -2 = 0$$

$$+3 + x - 4 = 0$$

$$x - 1 = 0$$

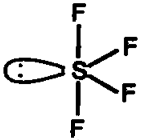
$$x = +1$$

20. Which of the following is not tetrahedral in shape?

(*i*) NH_4^+ (*ii*) $SiCl_4$
(*iii*) SF_4 (*iv*) SO_4^{2-}

Ans. (*iii*)

Explanation:



It has trigonal bipyramidal geometry having sp^3d hybridisation.

21. Which of the following are peroxoacids of sulphur?

(*i*) H_2SO_5 and $H_2S_2O_8$ (*ii*) H_2SO_5 and $H_2S_2O_7$
(*iii*) $H_2S_2O_7$ and $H_2S_2O_8$ (*iv*) $H_2S_2O_6$ and $H_2S_2O_7$

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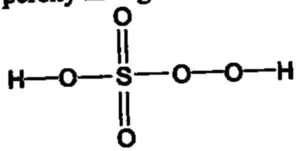
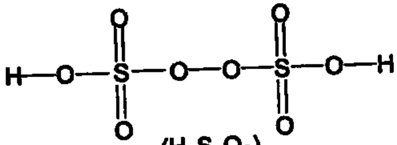
Ans. (*i*)

Explanation: Peroxoacids of sulphur must contain —O—O— or peroxy linkage.



$$\mathrm{H-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-H}$$

(H_2SO_5)



$$\mathrm{H-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-H}$$

($H_2S_2O_8$)

22. Hot conc. H_2SO_4 acts as moderately strong oxidising agent. It oxidises both metals and nonmetals. Which of the following element is oxidised by conc. H_2SO_4 into two gaseous products?

(*i*) Cu
(*ii*) S
(*iii*) C
(*iv*) Zn

Ans. (*iii*)

Explanation: Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2. C is oxidised into two gaseous products.

$$C + 2H_2SO_4(\text{conc.}) \rightarrow CO_2 + 2SO_2 + 2\,H_2O$$

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 ________.

(*i*) – 3 to +3
(*ii*) – 3 to 0
(*iii*) – 3 to +5
(*iv*) 0 to – 3

Ans. (*i*)

Explanation:

$$\underset{\text{(Black)}}{MnO_2} + 4HCl \rightarrow MnCl_2 + 2H_2O + \underset{\substack{\text{greenish}\\ \text{yellow gas}}}{Cl_2}$$

$$\overset{-3}{N}H_3 + 3Cl_2 \rightarrow \overset{+3}{N}Cl_3 + 3HCl$$

Hence oxidation state of nitrogen changes from –3 to +3.

24. In the preparation of compounds of Xe, Bartlett had taken $O_2^+ PtF_6^-$ as a base compound. This is because

(*i*) both O_2 and Xe have same size.
(*ii*) both O_2 and Xe have same electron gain enthalpy.
(*iii*) both O_2 and Xe have almost same ionisation enthalpy.
(*iv*) both Xe and O_2 are gases.

Ans. (*iii*)

Explanation: Neil Bartlett, then observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+ PtF_6^-$.

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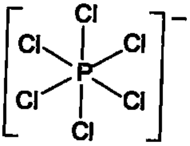
He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol^{-1}) was almost identical with that of xenon (1170 kJ mol^{-1}).

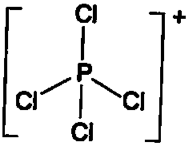
25. In solid state PCl_5 is a ________.
    (*i*) covalent solid
    (*ii*) octahedral structure
    (*iii*) ionic solid with $[PCl_6]^+$ octahedral and $[PCl_4]^-$ tetrahedra
    (*iv*) ionic solid with $[PCl_4]^+$ tetrahedral and $[PCl_6]^-$ octahedra

Ans. (*iv*)

Explanation:



$[PCl_6]^-$
Octahedral



$[PCl_4]^+$
tetrahedral

In solid state PCl_5 exist as an ionic solid with $[PCl_4]^+$ tetrahedral and $[PCl_6]^-$ octahedral.

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 EV potential $E^\ominus$/V	$E^\ominus$=1.19V	$E^\ominus$=1.65V	$E^\ominus$=1.74V

(*i*) $ClO_4^- > IO_4^- > BrO_4^-$ (*ii*) $IO_4^- > BrO_4^- > ClO_4^-$
(*iii*) $BrO_4^- > IO_4^- > ClO_4^-$ (*iv*) $BrO_4^- > ClO_4^- > IO_4^-$

Ans. (*iii*)

Explanation: Higher the standard reduction potential higher will be the oxidizing power.

27. Which of the following is isoelectronic pair?
    (*i*) ICl_2, ClO_2 (*ii*) BrO_2^-, BrF_2^+
    (*iii*) ClO_2, BrF (*iv*) CN^-, O_3

Ans. (*ii*)

Explanation: Isoelectronic species means no. of electron is same.

BrO_2^- (no. of electron) = 35 + 16 + 1 = 52

BrF_2^+ (no. of electron) = 35 + 17 = 52

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note : In the following questions two or more options may be correct.

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 ________.
    (*i*) 0 to +5 (*ii*) 0 to +3
    (*iii*) 0 to −1 (*iv*) 0 to +1

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Ans. (*i*) and (*iii*)

Explanation: $6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

When chlorine gas is passed through hot NaOH solution it produces NaCl and $NaClO_3$. Thus oxidation state of chlorine changes from 0 to –1 and 0 to +5 respectively.

29. Which of the following options are not in accordance with the property mentioned against them?

(*i*) $F_2 > Cl_2 > Br_2 > I_2$	Oxidising power.
(*ii*) $MI > MBr > MCl > MF$	Ionic character of metal halide.
(*iii*) $F_2 > Cl_2 > Br_2 > I_2$	Bond dissociation enthalpy.
(*iv*) $HI < HBr < HCl < HF$	Hydrogen-halogen bond strength.

Ans. (*ii*) and (*iii*)

Explanation: $MI < MBr < MCl < MF$ this is the correct order of ionic metal halide.

The correct order of bond dissociation enthalpy is $Cl_2 > Br_2 > F_2 > I_2$

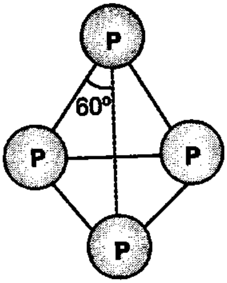
Due to electronic repulsion among lone-pairs in F_2 molecule.

30. Which of the following is correct for P_4 molecule of white phosphorus?

(*i*) It has 6 lone pairs of electrons.
(*ii*) It has six P–P single bonds.
(*iii*) It has three P–P single bonds.
(*iv*) It has four lone pairs of electrons.

Ans. (*ii*) and (*iv*)

Explanation:



It has four lone pairs of electrons at each p-atom

It has six p-p single bond.

31. Which of the following statements are correct?

(*i*) Among halogens, radius ratio between iodine and fluorine is maximum.
(*ii*) Leaving F—F bond, all halogens have weaker X—X bond than X—X' bond in interhalogens.
(*iii*) Among interhalogen compounds maximum number of atoms are present in iodine fluoride.
(*iv*) Interhalogen compounds are more reactive than halogen compounds.

Ans. (*i*), (*iii*) and (*iv*)

Explanation: (*i*) Among group 17 elements radius ratio of iodine and fluorine is maximum because size of iodine is largest and fluorine is smallest in the group.

(*ii*) The correct statement is inter halogen compounds are more reactive than halogens (except fluorine). This is because X—X' bond in interhalogens is weaker than X—X bond in halogens except F—F.

(*iii*) As the ratio between radii of X and X' increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum.

(*iv*) Interhalogen compounds are more reactive than halogens (except fluorine). This is because X—X' bond in interhalogens is weaker than X—X' bond in halogens.

32. Which of the following statements are correct for SO_2 gas?
   (*i*) It acts as bleaching agent in moist conditions.
   (*ii*) It's molecule has linear geometry.
   (*iii*) It's dilute solution is used as disinfectant.
   (*iv*) It can be prepared by the reaction of dilute H_2SO_4 with metal sulphide.

Ans. (*i*) and (*iii*)

Explanation: SO_2 is used in bleaching of wool and silk and as an anti-chlor, disinfectant and preservative.

33. Which of the following statements are correct?
   (*i*) All the three N—O bond lengths in HNO_3 are equal.
   (*ii*) All P—Cl bond lengths in PCl_5 molecule in gaseous state are equal.
   (*iii*) P_4 molecule in white phohsphorus have angular strain therefore white phosphorus is very reactive.
   (*iv*) PCl is ionic in solid state in which cation is tetrahedral and anion is octahedral.

Ans. (*iii*) and (*iv*)

Explanation: (*i*) All the three N-O bond length in HNO_3 are not equal

(*ii*) In gaseous phase all P—Cl bond lengths in PCl_5 molecule are not equal.

(*iii*) White phosphorus is more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule.

(*iv*) Solid state it exists as an ionic solid, $[PCl_4]^+ [PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ octahedral.

34. Which of the following orders are correct as per the properties mentioned against each?
   (*i*) $As_2O_3 < SiO_2 < P_2O_3 < SO_2$ Acid strength.
   (*ii*) $AsH_3 < PH_3 < NH_3$ Enthalpy of vapourisation.
   (*iii*) $S < O < Cl < F$ More negative electron gain enthalpy.
   (*iv*) $H_2O > H_2S > H_2Se > H_2Te$ Thermal stability.

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Ans. (*i*) and (*iv*)

Explanation: (*i*) $As_2O_3 < SiO_2 < P_2O_3 < SO_2$

Order of acid strength

(*ii*) Correct order of enthalpy of vaporization is $AsH_3 > PH_3 > NH_3$

(*iii*) Correct order of more negative electron gain enthalpy $S < O < F < Cl$

(*iv*) Order of thermal stability —$H_2O > H_2S > H_2Se > H_2Te$

35. Which of the following statements are correct?

(*i*) S–S bond is present in $H_2S_2O_6$.

(*ii*) In peroxosulphuric acid (H_2SO_5) sulphur is in +6 oxidation state.

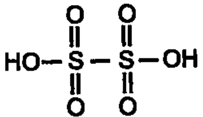
(*iii*) Iron powder along with Al_2O_3 and K_2O is used as a catalyst in the preparation of NH_3 by Haber's process.

(*iv*) Change in enthalpy is positive for the preparation of SO_3 by catalytic oxidation of SO_2.

Ans. (*i*) and (*ii*)

Explanation:

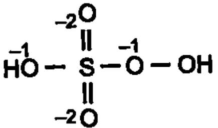
(*i*)



$$\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

It contains one S—S bond.

(*ii*)



$$\mathrm{\overset{-1}{HO}-\overset{\overset{-2O}{\|}}{\underset{\underset{-2O}{\|}}{S}}-\overset{-1}{O}-OH}$$

Oxidation state of S = +6.

(*iii*) Iron oxide with K_2O and Al_2O_3 is used to increase the rate of attainment of equilibrium in Haber's process.

(*iv*) Change in enthalpy is negative for the preparation of SO_3 by catalytic oxidation of SO_2.

36. In which of the following reactions conc. H_2SO_4 is used as an oxidising reagent?

(*i*) $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

(*ii*) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

(*iii*) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

(*iv*) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

Ans. (*ii*) and (*iii*)

Explanation: Among the above four (*ii*) and (*iii*) represent the oxidizing behaviour of H_2SO_4. In (*ii*) reaction it oxidizes HI and itself reduces to SO_2 oxidation state of central atom sulphur decreases from +6 to +4. In (*iii*) it oxidizes copper and itself get reduced to SO_2.

37. Which of the following statements are true?

(*i*) Only type of interactions between particles of noble gases are due to weak dispersion forces.

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(*ii*) Ionisation enthalpy of molecular oxygen is very close to that of xenon.
(*iii*) Hydrolysis of XeF_6 is a redox reaction.
(*iv*) Xenon fluorides are not reactive.

Ans. (*i*) and (*ii*)

Explanation:

(*i*) Attraction in noble gases is due to weak dispersion force.
(*ii*) Ionisation enthalpy of molecular oxygen is very close to that of xenon.
(*iii*) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$ hydrolysis of XeF_6 is not a redox reaction.
(*iv*) Xenon fluorides are reactive in nature.

III. SHORT ANSWER TYPE

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?

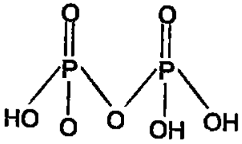
Ans. In contact process SO_3 is not absorbed directly in water to form H_2SO_4 because the reaction is highly exothermic and the reaction forms a corrosive aerosol that is very difficult to separate.

39. Write a balanced chemical equation for the reaction showing catalytic oxidation of NH_3 by atmospheric oxygen.

Ans. $4NH_3 + 5O_2 \xrightarrow[\text{500 k, 9 bar}]{\text{Pt/Rh gauge catalyst}} 4NO + 6H_2O$

40. Write the structure of pyrophosphoric acid.

Ans. **Structure of pyrophosphoric acid:**



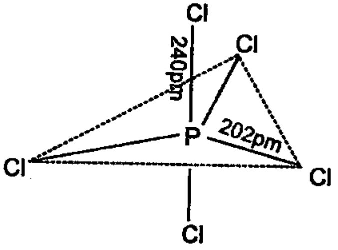
$(H_4P_2O_7)$

41. PH_3 forms bubbles when passed slowly in water but NH_3 dissolves. Explain why?

Ans. Because of H-bonding NH_3 dissolves in water whereas in PH_3 there is lack of H-bonding that is why it remains as gas and form bubbles in water.

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. In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.



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43. Why is nitric oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic?

Ans. NO has 11 valence electrons. It is impossible for them all to be paired, and hence this is an odd number of valence electron and thus the gas is paramagnetic. It is diamagnetic in liquid and solid states, because the molecule dimerises to convert into stable N_2O_4 molecule with even numbers of electrons.

44. Give reason to explain why ClF_3 exists but FCl_3 does not exist.

Ans. Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX', XX_3', XX_5' and XX_7' where X is a larger size halogen and X′ is a smaller size halogen. Fluorine is smallest in size due to high electronegativity therefore it cannot form FCl_3 whereas reverse is true.

45. Out of H_2O and H_2S, which one has higher bond angle and why?

Ans. As size of oxygen is small and due to its high electronegativity than sulphur O—H bond becomes more closer and bond pair-bond pair repulsion will be more. So, H_2O has higher bond angle than H_2S.

46. SF_6 is known but SCl_6 is not. Why?

Ans. Due to small size of fluorine, sulphur can accommodate 6 'F' atom around it. Chlorine is comparatively larger in size therefore because of interionic repulsion with chlorine SCl_6 is not known.

47. On reaction with C_{12}, phosphorus forms two types of halides 'A' and 'B'. Halide A is yellowish-white powder but halide 'B' is colourless oily liquid. Identify A and B and write the formulas of their hydrolysis products.

Ans. Halide 'A' is PCl_5 and 'B' is PCl_3 their hydrolysis reaction are as follows:

$$\underset{\text{(A)}}{PCl_5} + H_2O \rightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

$$\underset{\text{(B)}}{PCl_3} + H_2O \rightarrow H_3PO_3 + 3HCl$$

48. In the ring test of NO_3^- ion, Fe^{2+} ion reduces nitrate ion to nitric oxide, which combines with $Fe^{2+}(aq)$ ion to form brown complex. Write the reactions involved in the formation of brown ring.

Ans.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$

$$\underset{\text{(brown)}}{[Fe(H_2O)_6]^{2+}} + NO \rightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

49. Explain why the stability of oxoacids of chlorine increases in the order given below:

$$HClO < HClO_2 < HClO_3 < HClO_4$$

Ans. The more oxygen atom that are bonded with the oxoacids the electrons will be pulled away from the O—H bond, and the more this bond will be weakend. Thus $HClO_4$ requires the least energy to break the O—H bond and form H^+. Hence $HClO_4$ is the strongest acid, and the order of stability is $HClO < HClO_2 < HClO_3 < HClO_4$.

50. Explain why ozone is thermodynamically less stable than oxygen.

Ans. Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen.

51. P_4O_6 reacts with water according to equation $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$. 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.

Ans. $$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3 \qquad ...(i)$$

For neutralisation

$$4 \times H_3PO_3 + 2NaOH \rightarrow Na_2HPO_3 + 2H_2O \qquad ...(ii)$$

Adding eq. (*i*) and (*ii*)

$$P_4O_6 + 8\ NaOH \rightarrow 4Na_2HPO_3 + 2H_2O$$

P_4O_6 (mol. mass) = $(4 \times 31 + 16 \times 6) = 220$

Number of moles of

$$P_4O_6 = \frac{\text{Given mass}}{\text{Molar mass}} = \frac{1.1}{220}$$

∵ Product formed by $\frac{1.1}{220}$ of P_4O_6 will be neutralised by 8 moles of NaOH.

∴ Product formed by $\frac{1.1}{220}$ of P_4O_6 will be neutralised by NaOH.

$$P_4O_6 = 8 \times = \frac{1.1}{220} = \frac{8.8}{220} \text{ mol NaOH}$$

Given molarity of NaOH in 1L = 0.1 M

$$\text{Molarity} = \frac{\text{No. of moles}}{\text{Volume in litres}}$$

$$\text{Volume} = \frac{\text{No. of moles}}{\text{Molarity}}$$

$$= \frac{8.8}{220} \times \frac{1}{0.1} = 0.4\text{L}$$

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.

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Ans. $P_4 + 6Cl_2 \rightarrow 4PCl_3$ ...(*i*)

$\left. PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl \right\} \times 4$ ...(*ii*)

On adding eq. (*i*) and (*ii*)

$$\begin{array}{rcl} P_4 + 6Cl_2 & \rightarrow & \cancel{4PCl_3} \\ \cancel{4PCl_3} + 12H_2O & \rightarrow & 4H_3PO_3 + 12HCl \\ \hline P_4 + 6Cl_2 + 12H_2O & \rightarrow & 4H_3PO_3 + 12HCl \end{array}$$

$31 \times 4 = 124$ g $\qquad$ $12 \times 36.5 = 438.0$ g

∵ 124 g white phosphorous produces 438g of HCl.

∴ 62 g white phosphorous will produce HCl.

$$\frac{438}{124} \times 62 = 219.0 \text{ g HCl}$$

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 are:

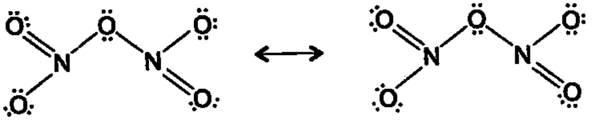
(*i*)	HNO_3	(Nitric acid)
(*ii*)	HNO_2	(Nitrous acid)
(*iii*)	$H_2N_2O_2$	(Hyponitrous acid)

$$3HNO_2 \xrightarrow{\text{disproportionation}} HNO_3 + H_2O + 2NO$$

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.

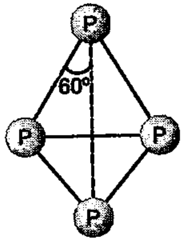
Ans. $4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$

Resonating structure of N_2O_5 are

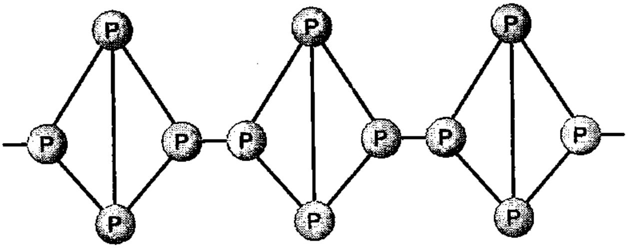


55. Phosphorus has three allotropic forms — (*i*) white phosphorus (*ii*) red phosphorus and (*iii*) black phosphorus. Write the difference between white and red phosphorus on the basis of their structure and reactivity.

Ans.



White phosphorus



Red phosphorus

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White phosphorus is more reactive than red phosphorus because white P exists as discrete P_4 molecules. In red P several P_4 tetrahedra molecules are linked to formed polymeric chain.

Black phosphorus is the most stable form of phosphorus it is least reactive among all the allotropic form of phosphorus.

56. Give an example to show the effect of concentration of nitric acid on the formation of oxidation product.

Ans. Nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

For an example

$$Cu + 8HNO_3(\text{dil.}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3(\text{conc.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

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. Finely divided metals on heating with PCl_5 give corresponding chlorides.

$$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$$

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+Cl^-(aq)$$

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.

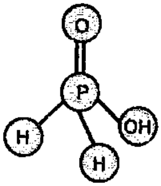
Ans. Hypophosphorus acid also known as phosphinic acid is a good reducing agent as it contains two P–H bonds and reduces, for example, $AgNO_3$ to metallic silver.

$$4AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$$

In the structure of phosphinic acid there is $P{=}O = 1$

$P{-}OH = 1$

$P{-}H$ bond $= 2$



IV. MATCHING TYPE

Note : Match the items of Column I and Column II in the following questions.

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

Ans. (*i*)

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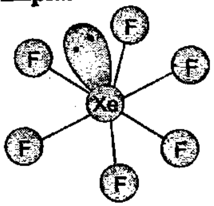
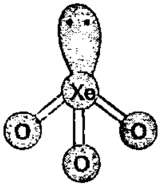
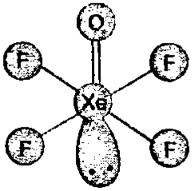
Explanation:



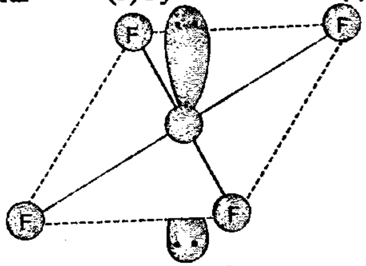
(*a*) Distorted octahedral



(*b*) Pyramidal



(*c*) Square pyramidal



(*d*) Square planar

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

Code :

(*i*) A (1)	B (2)	C (3)	D (4)
(*ii*) A (4)	B (1)	C (2)	D (3)
(*iii*) A (3)	B (2)	C (4)	D (1)
(*iv*) A (4)	B (3)	C (1)	D (2)

Ans. (*ii*)

Explanation:

A. Pb_3O_4 is a mixed oxide.
B. N_2O is a neutral oxide.
C. Mn_2O_7 is a acidic oxide.
D. Bi_2O_3 is basic oxide.

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

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Code :

(*i*) A (4) B (3) C (1) D (2)
(*ii*) A (3) B (4) C (1) D (2)
(*iii*) A (4) B (1) C (2) D (3)
(*iv*) A (2) B (1) C (3) D (4)

Ans. (*i*)

Explanation:

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 also called as chalcogen.

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

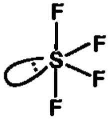
Code :

(*i*) A (3) B (2) C (1) D (4)
(*ii*) A (3) B (4) C (2) D (1)
(*iii*) A (1) B (2) C (3) D (4)
(*iv*) A (1) B (4) C (3) D (2)

Ans. (*ii*)

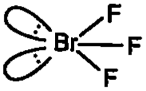
Explanation:

A. SF_4



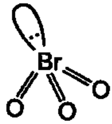
(See Saw Shaped)

B. BrF_3



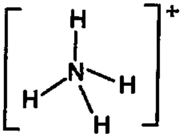
(Bent-shaped)

C. BrO_3^-



(Pyramidal)

D. NH_4^+



(Tetrahedrak)

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

Code :

(*i*) A (1)	B (4)	C (2)	D (3)
(*ii*) A (1)	B (2)	C (3)	D (4)
(*iii*) A (2)	B (1)	C (4)	D (3)
(*iv*) A (1)	B (3)	C (2)	D (4)

Ans. (*iii*)

Explanation: A→Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$XeF_6 + H_2O \rightarrow XeOF_4 + 2\,HF$

$XeF_6 + 2\,H_2O \rightarrow XeO_2F_2 + 4HF$

We can see that oxidation state of central atom Xe remains unchanged.

B. He is used in modern diving apparatus

C. Ar is used to provide inert atmosphere for filling electrical bulbs

D. XeF_4 has Sp^3d^2 hybridization (4-bond pair and 2-lone pair)

V. ASSERTION AND REASON TYPE

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(*ii*) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(*iii*) Assertion is correct, but reason is wrong statement.

(*iv*) Assertion is wrong but reason is correct statement.

(*v*) Both assertion and reason are wrong statements

64. Assertion : N_2 is less reactive than P_4.
Reason : Nitrogen has more electron gain enthalpy than phosphorus.

Ans. (*iii*) Assertion is correct, but reason is wrong statement.

Explanation: N_2 is less reactive than P_4 molecule this is so, because nitrogen has very high bond dissociation enthalpy because of triple bond between two nitrogen atom which is not the case with phosphorus.

65. Assertion : HNO_3 makes iron passive.
Reason : HNO_3 forms a protective layer of ferric nitrate on the surface of iron.

Ans. (*iii*)

Explanation: HNO_3 makes iron passive . HNO_3 forms a protective layer of oxides on the surface of iron.

66. **Assertion** : HI cannot be prepared by the reaction of KI with concentrated H_2SO_4

Reason : HI has lowest H–X bond strength among halogen acids.

Ans. (*ii*)

Explanation: HI cannot be prepared by the reaction of KI with concentrated H_2SO_4 because HI formed is converted to I_2.

67. **Assertion** : Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2.

Reason : 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. (*i*)

Explanation: Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2. 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 due to its larger atomic size than oxygen.

68. **Assertion** : 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 : MnO_2 oxidises HCl to chlorine gas which is greenish yellow.

Ans. (*i*)

Explanation: NaCl reacts with concentrated H_2SO_4 to give colourless fumes with pungent smell. But on adding MnO_2 the fumes become greenish yellow. MnO_2 oxidises HCl to chlorine gas which is greenish yellow .

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ (fumes of HCl is colourless)

By heating manganese dioxide with concentrated hydrochloric acid.

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

69. **Assertion** : SF_6 cannot be hydrolysed but SF_4 can be.

Reason : Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6.

Ans. (*i*)

Explanation: SF_6 do not hydrolysed as it is in its maximum valency of six and it is insoluble in water. SF_4 can be hydrolyse as follows:

$SF_4 + 2H_2O \rightarrow SO_2 + 4HF$

VI. LONG ANSWER TYPE

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.

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Ans. An amorphous solid 'A' is S_8 it react with air to form B (SO_2(g)) which is a by-product of roasting of sulphide ore.

$$S_8 + 8O_2 \xrightarrow[\text{Heat}]{} 8SO_2$$

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2Fe^{2+}$$

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'.

Ans. Lead nitrate on heating produces brown gas 'A'

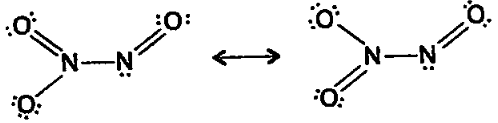
$$Pb(NO_3)_2 \xrightarrow[673k]{\Delta} 2PbO + \underset{\substack{A \\ \text{(Brown colour)}}}{4NO_2}$$

Brown gas NO_2 is unstable on cooling it dimerises to colourless solid N_2O_4

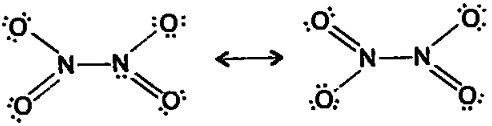
$$2NO_2 \underset{\Delta}{\overset{\text{On cooling}}{\rightleftharpoons}} \underset{\substack{B \\ \text{(Colourless solid)}}}{N_2O_4}$$

$$2NO + N_2O_4 \rightarrow \underset{\substack{C \\ \text{(Blue solid)}}}{2N_2O_3}$$

Structure of N_2O_3



Structure of N_2O_4



72. On heating compound (A) gives a gas (B) which is a constituent of air. This gas when treated with 3 mol 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. $\underset{\text{'A'}}{NH_4NO_2} \rightarrow \underset{\text{'B'}}{N_2} + 2H_2O$

N_2 with 3 moles of H_2 in presence of catalyst form NH_3 gas which is basic in nature.

$N_2 + 3H_2 \rightarrow \underset{(C)}{2NH_3}$

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

$4NO + O_2 \rightarrow 2NO_2$

$3NO_2 + H_2O \rightarrow \underset{(D)}{2HNO_3} + NO$

❑❑❑

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8

The d- and f- Block Elements

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Electronic configuration of a transition element X in +3 oxidation state is $[Ar]3d^5$. What is its atomic number?

(*i*) 25 (*ii*) 26

(*iii*) 27 (*iv*) 24

Ans. (*ii*)

Explanation: Electronic configuration of element X = $[Ar]3d^{5+}$ oxidation state = $18 + 5 + 3 = 26$.

2. The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of the following is correct?

(*i*) Cu(II) is more stable

(*ii*) Cu(II) is less stable

(*iii*) Cu(I) and Cu(II) are equally stable

(*iv*) Stability of Cu(I) and Cu(II) depends on nature of copper salts

Ans. (*i*)

Explanation: The stability of $Cu^{2+}(aq)$ rather than $Cu^{+}(aq)$ is due to the much more negative $\Delta_{hyd}H^{\ominus}$ of $Cu^{2+}(aq)$ than Cu^{+}, which more than compensates for the second ionisation enthalpy of Cu.

3. Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

(*i*) Fe

(*ii*) Ni

(*iii*) Co

(*iv*) Cu

Ans. (*iv*)

Explanation: On moving across the period in the periodic table the atomic radii of the element decreases towards right that is why density increases towards right in a period.

4. Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?

(*i*) Ag_2SO_4 (*ii*) CuF_2

(*iii*) ZnF_2 (*iv*) Cu_2Cl_2

Ans. (*ii*)

Explanation: Here copper is in +2 states in which Cu contains one unpaired electron. Hence it produce colour in solid state.

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5. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following:

(*i*) Mn_2O_7　　(*ii*) MnO_2
(*iii*) $MnSO_4$　　(*iv*) Mn_2O_3

Ans. (*i*)

Explanation: $KMnO_4$ reacts with conc. H_2SO_4 as:

$$2KMnO_4 + 2H_2SO_4 \rightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

Mn_2O_7 is highly explosive in nature.

6. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.

(*i*) $3d^7$　　(*ii*) $3d^5$
(*iii*) $3d^8$　　(*iv*) $3d^2$

Ans. (*ii*)

Explanation: Greater the no. of unpaired electrons higher will be the magnetic moment.

$\mu = \sqrt{n(n+2)}$ where n is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM).

Where n = no. of unpaired electron

That is why $3d^5$ has maximum magnetic moment due to maximum no. of unpaired electrons.

7. Which of the following oxidation state is common for all lanthanoids?

(*i*) +2　　(*ii*) +3
(*iii*) +4　　(*iv*) +5

Ans. (*ii*)

Explanation: In the lanthanoids, La(II) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled *f* subshell.

8. Which of the following reactions are disproportionation reactions?

(*a*) $Cu^+ \rightarrow Cu^{2+} + Cu$
(*b*) $3MnO_4^- + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$
(*c*) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
(*d*) $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$

(*i*) (*a*), (*b*)　　(*ii*) (*a*), (*b*), (*c*)
(*iii*) (*b*), (*c*), (*d*)　　(*iv*) (*a*), (*d*)

Ans. (*i*)

Explanation: Copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

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In a disproportionation reaction an element is simultaneously oxidized and reduced.

9. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because

   (*i*) CO_2 is formed as the product.

   (*ii*) Reaction is exothermic.

   (*iii*) MnO_4^- catalyses the reaction.

   (*iv*) Mn^{2+} acts as autocatalyst

Ans. (*iv*)

Explanation: Oxalate ion is oxidized to CO_2 by acidified $KMnO_4$.

$$2\,MnO_4 + 5C_2O_4^{2-} + 16\,H^+ \rightarrow 2Mn^{2+} + 2CO_2 + 8H_2O$$

In acid medium

$$\underset{\text{(Pink)}}{MnO_4^-} + 8H^+ + 5e^- \rightarrow \underset{\text{(colourless)}}{Mn^{2+}} + 4H_2O$$

Mn^{2+} formed in the reaction act as autocatalyst.

10. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?

   (*i*) U

   (*ii*) Np

   (*iii*) Tm

   (*iv*) Fm

Ans. (*iii*)

Explanation: Tm (thulium) atomic no. = 69 belongs to Lanthanoids (4*f*) series.

11. $KMnO_4$ acts as an oxidising agent in acidic medium. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution is

   (*i*) $\frac{2}{5}$

   (*ii*) $\frac{3}{5}$

   (*iii*) $\frac{4}{5}$

   (*iv*) $\frac{1}{5}$

Ans. (*i*)

Explanation: Hydrogen sulphide is oxidised, sulphur being precipitated:

$$H_2S \rightarrow 2H^+ + S^{2-}$$

$$5S^{2-} + 2MnO^{-4} + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$$

It is clear from the above reaction that 5 moles of sulphide ions needs 2 moles of permanganate ion therefore one mole of sulphide ion require $\frac{2}{5}$ moles of permanganate ion.

12. Which of the following is amphoteric oxide?

   Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4

   (*i*) V_2O_5, Cr_2O_3

   (*ii*) Mn_2O_7, CrO_3

   (*iii*) CrO, V_2O_5

   (*iv*) V_2O_5, V_2O_4

Ans. (*i*)

Explanation: Since they react with acid as well as base.

13. Gadolinium belongs to 4*f* series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?

(*i*) [Xe] $4f^7 5d^1 6s^2$
(*ii*) [Xe] $4f^6 5d^2 6s^2$
(*iii*) [Xe] $4f^8 6d^2$
(*iv*) [Xe] $4f^9 5s^1$

Ans. (*i*)

Explanation: Gadolinium belongs to 4*f* series it has atomic no. = 64. It has extra stability due to half-filled 4*f* sub shell.

14. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?

(*i*) They have high melting points in comparison to pure metals.
(*ii*) They are very hard.
(*iii*) They retain metallic conductivity.
(*iv*) They are chemically very reactive

Ans. (*iv*)

Explanation: Following are the principal properties of interstitial compounds:

(*i*) They have high melting points, higher than those of pure metals.
(*ii*) They are very hard, some borides approach diamond in hardness.
(*iii*) They retain metallic conductivity.
(*iv*) They are chemically inert.

15. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is ____________.

(*i*) 2.87 B.M.
(*ii*) 3.87 B.M.
(*iii*) 3.47 B.M.
(*iv*) 3.57 B.M

Ans. (*ii*)

Explanation: Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula.

The magnetic moment μ is given by the formula

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

for $Cr^{3+} = 3d^3$ the magnetic moment = $\sqrt{3(3+2)} = \sqrt{15} = 3.87\,\text{BM}$

16. $KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to ____________.

(*i*) I_2 (*ii*) IO^-

(*iii*) IO_3^- (*iv*) IO_4^-

Ans. (*iii*)

Explanation: Iodide ion in neutral or faintly alkaline solutions converts iodide to iodate:

$$2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$$

17. Which of the following statements is **not** correct?

(*i*) Copper liberates hydrogen from acids.

(*ii*) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.

(*iii*) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution.

(*iv*) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution.

Ans. (*i*)

Explanation: Cu, having a positive $E^\ominus = +1.34$ V accounts for its inability to liberate H_2 from acids.

18. When acidified $K_2Cr_2O_7$ solution is added to Sn^{2+} salts then Sn^{2+} changes to

(*i*) Sn (*ii*) Sn^{3+}

(*iii*) Sn^{4+} (*iv*) Sn^+

Ans. (*iii*)

Thus, acidified potassium dichromate will oxidise tin(II) to tin(IV)

Explanation: $Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

19. Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7 (Mn_2O_7) because __________

(*i*) fluorine is more electronegative than oxygen.

(*ii*) fluorine does not possess d-orbitals.

(*iii*) fluorine stabilises lower oxidation state.

(*iv*) in covalent compounds fluorine can form single bond only while oxygen forms double bond.

Ans. (*iv*)

Explanation: Manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7 (Mn_2O_7) because in covalent compounds fluorine can form single bond only while oxygen forms double bond. Oxygen has ability to form multiple bonds.

20. Although Zirconium belongs to 4d transition series and Hafnium to 5*d* transition series even then they show similar physical and chemical properties because__________.

(*i*) both belong to *d*-block.

(*ii*) both have same number of electrons.

(*iii*) both have similar atomic radius.

(*iv*) both belong to the same group of the periodic table.

Ans. (*iii*)

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Explanation: The almost identical radii of Zr (160 pm) and H*f*(159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the similar physical and chemical properties.

21. Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium?

(*i*) Both HCl and $KMnO_4$ act as oxidising agents.
(*ii*) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent
(*iii*) $KMnO_4$ is a weaker oxidising agent than HCl.
(*iv*) $KMnO_4$ acts as a reducing agent in the presence of HCl.

Ans. (*ii*)

Explanation: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine .

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note: In the following questions two or more options may be correct.

22. Generally transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compounds are coloured?

(*i*) $KMnO_4$
(*ii*) $Ce(SO_4)_2$
(*iii*) $TiCl_4$
(*iv*) Cu_2Cl_2

Ans. (*i*) and (*ii*)

Explanation: It is due to charge transfer. In MnO_4^- an electron is momentarily transferred from O to the metal, thus momentarily O^{2-} is changed to O^- and reducing the oxidation state of the metal from Mn (VII) to Mn (VI).

23. Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?

(*i*) Co^{2+}
(*ii*) Cr^{2+}
(*iii*) Mn^{2+}
(*iv*) Cr^{3+}

Ans. (*i*) and (*iv*)

Explanation: Co^{2+} = [Ar]$3d^7$ no. of unpaired electrons = 3
Cr^{2+} = [Ar]$3d^4$ no. of unpaired electrons = 4
Mn^{2+} = [Ar]$3d^5$ no. of unpaired electrons = 5
Cr^{3+} = [Ar]d^3 no. of unpaired electrons = 3

We can see that Co^{2+} and Cr^{3+} have same no. of unpaired electrons i.e. = 3.

24. In the form of dichromate, Cr (VI) is a strong oxidising agent in acidic medium but Mo (VI) in MoO_3 and W (VI) in WO_3 are not because ________.

(*i*) Cr (VI) is more stable than Mo(VI) and W(VI).
(*ii*) Mo (VI) and W(VI) are more stable than Cr(VI).
(*iii*) Higher oxidation states of heavier members of group-6 of transition series are more stable.

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(*iv*) Lower oxidation states of heavier members of group-6 of transition series are more stable.

Ans. (*ii*) and (*iii*)

Explanation: In the groups of d-block element higher oxidation states are favourable by heavier element. For example in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

25. Which of the following actinoids show oxidation states upto +7?

(*i*) Am
(*ii*) Pu
(*iii*) U
(*iv*) Np

Ans. (*ii*) and (*iv*)

Explanation: Oxidation states of the actinoids are as follows:

(*i*) Americium (Z = 95)
Electronic configuration = $[R_n]^5f^7 6d^0 7s^2$
Oxidation states = +3, +4, +5, +6

(*ii*) Plutonium (Z = 94)
Electronic configuration = $[R_n]5f^6 6d^0 7s^2$
Oxidation states = +3, +4, +5, +6, +7

(*iii*) Uranium (Z = 92)
Electronic configuration = $[R_n]5f^3 6d^1 7s^2$
Oxidation states = +3, +4, +5, +6

(*iv*) Neptunium (Z = 93)
Electronic configuration = $[R_n]\ 5f^4 6d^1 7s^2$
Oxidation states = +3, +4, +5, +6, +7

26. General electronic configuration of actionoids is $(n-2)f^{1-14}(n-1)d^{0-2}ns^2$. Which of the following actinoids have one electron in 6*d* orbital?

(*i*) U (Atomic no. 92)
(*ii*) Np (Atomic no.93)
(*iii*) Pu (Atomic no. 94)
(*iv*) Am (Atomic no. 95)

Ans. (*i*) and (*ii*)

Explanation: $U \rightarrow 5f^3 6d^1 7s^2$
$Np \rightarrow 5f^4 6d^1 7s^2$

27. Which of the following lanthanoids show +2 oxidation state besides the characteristic oxidation state +3 of lanthanoids?

(*i*) Ce
(*ii*) Eu
(*iii*) Yb
(*iv*) Ho

Ans. (*ii*) and (*iii*)

Explanation:

(*i*) Cerium (Z = 57)
E.C. = $[Xe]\ 4f^5 5d^0 6s^2$
Oxidation states of Ce = +3, +4

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(*ii*) Europium ($Z = 63$)
E.C. = [Xe] $4f^7 5d^0 6s^2$
Oxidation states of Eu = +2, +3

(*iii*) Ytterbium ($Z = 70$)
E.C. = [Xe] $4f^{14} 5d^0 6s^2$
Oxidation states of Yb = +2, +3

(*iv*) Holmium ($Z = 67$)
E.C. = [Xe] $4f^{11} 5d^0 6s^2$
Oxidation state of Ho = +3

28. Which of the following ions show higher spin only magnetic moment value?

(*i*) Ti^{3+}
(*ii*) Mn^{2+}
(*iii*) Fe^{2+}
(*iv*) Co^{3+}

Ans. (*ii*) and (*iii*)

Explanation: (*ii*) $Mn^{2+} = [Ar]3d^5 \,.\, \left[t_{2g}^3\ e_g^2\right)$

(*iii*) $Fe^{2+} = [Ar]3d^6 \left[t_{2g}^4\ e_{2g}^2\right)$

According CFT, electron pair up in t_{2g} and fe^{2+} and Mn^{2+} will show higher spin magnetic value.

29. Transition elements form binary compounds with halogens. Which of the following elements will form MF_3 type compounds?

(*i*) Cr
(*ii*) Co
(*iii*) Cu
(*iv*) Ni

Ans. (*i*) and (*ii*)

Explanation: Only Co and Cr can form halides like MF_3 beyond Mn no metal has a trihalide except FeX_3, and CoF_3.

30. Which of the following will not act as oxidising agents?

(*i*) CrO_3
(*ii*) MoO_3
(*iii*) WO_3
(*iv*) CrO_4^{2-}

Ans. (*ii*) and (*iii*)

Explanation: Higher oxidation states of W and Mo are more stable that is why they will not act as oxidizing agent.

31. Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because ____________.

(*i*) it has variable ionisation enthalpy
(*ii*) it has a tendency to attain noble gas configuration
(*iii*) it has a tendency to attain f^0 configuration
(*iv*) it resembles Pb^{4+}

Ans. (*ii*) and (*iii*)

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Explanation: This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or completely filled *f* subshell. Thus, the formation of Ce(IV) is favoured by its noble gas configuration.

III. SHORT ANSWER TYPE

32. Why does copper not replace hydrogen from acids?

Ans. The unique behaviour of Cu, having a positive $E^\ominus = +\,0.34V$ accounts for its inability to liberate H_2 from acids.

33. Why $E^\ominus$ values for Mn, Ni and Zn are more negative than expected?

Ans. The stability of the half-filled d sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their $E^\ominus$ values, whereas for Ni is related to the highest negative $\Delta_{hyd}H$.

34. Why first ionisation enthalpy of Cr is lower than that of Zn?

Ans. The value of first ionisation enthalpy of Cr is lower because of the absence of any change in the *d* configuration and the value for Zn is higher because it represents an ionisation from the 4*s* level.

35. Transition elements show high melting points. Why?

Ans. The high melting points of these metals are attributed to the involvement of greater number of electrons from $(n-1)d$ in addition to the *ns* electrons in the interatomic metallic bonding.

36. When Cu^{2+} ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of chemical equation.

Ans. $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$

When Cu^{2+} reacts with potassium iodide white precipitate of Cu_2I_2 is formed.

37. Out of Cu_2Cl_2 and $CuCl_2$, which is more stable and why?

Ans. $CuCl_2$ is more stable than Cu_2Cl_2. The stability of $Cu^{2+}(aq)$ rather than $Cu^{+}(aq)$ is due to the much more negative $\Delta_{hyd}H^\ominus$ of $Cu^{2+}(aq)$ than Cu^+, which is more than to compensate for the second ionisation enthalpy of Cu.

38. When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess, reacts with NH_3 to give an explosive compound (C). Identify compounds A, B and C.

Ans.

$$\underset{\substack{(A)\\(\text{Brown compound})}}{MnO_2} + 4HCl \rightarrow MnCl_2 + \underset{(B)}{Cl_2} + 2H_2O$$

$$NH_3 + \underset{(\text{Excess})}{Cl_2} \rightarrow \underset{(C)}{NCl_3} + 3HCl$$

MnO_2 is a brown compound of Mn which reacts with HCl to give Cl_2 gas. This gas forms explosive compound NCl_3.

39. Although fluorine is more electronegative than oxygen, but the ability of oxygen to stabilise higher oxidation states exceeds that of fluorine. Why?

Ans. The ability of oxygen to stabilise high oxidation states exceeds that of fluorine because oxygen has the ability to form multiple bond with the metal.

40. Although Cr^{3+} and Co^{2+} ions have same number of unpaired electrons but the magnetic moment of Cr^{3+} is 3.87 B.M. and that of Co^{2+} is 4.87 B.M. Why?

Ans. Magnetic moment is associated with its spin angular momentum and orbital angular momentum however due to symmetrical electronic configuration there is no orbital motion in Cr^{3+}. In Co^{2+} appreciable orbital contribution takes place.

41. Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why?

Ans. All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5*f* and 6*d* subshells. The fourteen electrons are formally added to 5*f*, though not in thorium ($Z = 90$) but from Pa onwards the 5*f* orbitals are complete at element 103. Although the 5*f* orbitals resemble the 4*f* orbitals(lanthanoids) in their angular part of the wave-function, they are not as buried as 4*f* orbitals and hence 5*f* electrons can participate in bonding to a far greater extent that is why ionization enthalpy of lanthanoids Ce, Pr and Nd are higher than Th, Pa and U.

42. Although Zr belongs to 4*d* and H*f* belongs to 5*d* transition series but it is quite difficult to separate them. Why?

Ans. The almost identical radii of Zr (160 pm) and H*f* (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

43. Although +3 oxidation states is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?

Ans. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or completely filled *f* subshell. Thus, the formation of Ce(IV) is favoured by its noble gas configuration.

44. Explain why does colour of $KMnO_4$ disappear when oxalic acid is added to its solution in acidic medium.

Ans. In acidic medium

$$\underset{\text{(Pink)}}{MnO_4^-} + 8H^+ + 5e^- \rightarrow \underset{\text{(Colourless)}}{Mn^{2+}} + 4H_2O$$

Oxalate ion is oxidized to CO_2 by acidified $KMnO_4$ and itself changes to Mn^{2+} ion which is colourless.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 2CO_2 + 8H_2O$$

45. When orange solution containing $Cr_2O_7^{2-}$ ion is treated with an alkali, a yellow solution is formed and when H^+ ions are added to yellow solution, an orange solution is obtained. Explain why does this happen?

Ans. Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.

Acidification of Na_2CrO_4:

$$\underset{\text{(Yellow)}}{2Na_2CrO_4} + H_2SO_4 \rightarrow \underset{\text{(Orange)}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

Or

$$\underset{\text{(yellow)}}{2\,CrO_4^{2-}} + 2H^+ \underset{\text{High pH}}{\overset{\text{Low pH}}{\rightleftharpoons}} \underset{\text{(orange)}}{Cr_2\,O_7^{2-}} + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

46. A solution of $KMnO_4$ on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?

Ans. Oxidising behaviour of $KMnO_4$ depends on pH of the solution.

In acidic medium (pH < 7)

$$MnO_4^- + 8H^+ + 5e^- \rightarrow \underset{\text{(Colourless)}}{Mn^{2+}} + 4H_2O$$

In alkaline medium (pH > 7)

$$MnO_4^- + e^- \rightarrow \underset{\text{(Green)}}{MnO_4^{2-}}$$

In neutral medium (pH = 7)

$$MnO_4^- + 2H_2O + 3e^- \rightarrow \underset{\text{(Brown precipiate)}}{MnO_2} + 4OH^-$$

47. The second and third rows of transition elements resemble each other much more than they resemble the first row. Explain why?

Ans. When atomic sizes of one series are compared with those of the corresponding elements in the other series. The curves show an increase from the first (3*d*) to the second (4*d*) series of the elements but the radii of the third (5*d*) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4*f* orbitals which must be filled before the 5*d* series of elements begin. The filling of 4*f* before 5*d* orbital results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number.

48. $E^\ominus$ of Cu is + 0.34V while that of Zn is – 0.76V. Explain.

Ans. The high energy to transform Cu(*s*) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy. $E^\ominus$ for Mn, Ni and Zn are more negative than expected from the trend. The completely filled d^{10} configuration in Zn^{2+} are related to their $E^\ominus$ values.

49. The halides of transition elements become more covalent with increasing oxidation state of the metal. Why?

Ans. Size of the transition elements decreases as the oxidation states of element increases. Small size favours more covalent character.

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50. While filling up of electrons in the atomic orbitals, the 4s orbital is filled before the 3*d* orbital but reverse happens during the ionisation of the atom. Explain why?

Ans. During filling of electrons ($n + 1$) rule is followed. Hence 4*s* has lower energy than 3*d* orbital. After the orbitals are filled 4*s* go beyond 3*d*. 4*s* is farther from nucleus than 3*d*. Thus the removal of electron from 4*s* is easier in comparison to 3*d*.

51. Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain.

Ans. From Sc to Cu ionization enthalpy increases that is why reactivity decreases regularly from Sc to Cu.

IV. MATCHING TYPE

Note: Match the items of Column I and Column II in the following questions.

52. Match the catalysts given in Column I with the processes given in Column II.

Column I (Catalyst)	Column II (Processes)
(*i*) Ni in the presence of hydrogen	(*a*) Zieglar Natta cataylst
(*ii*) Cu_2Cl_2	(*b*) Contact process
(*iii*) V_2O_5	(*c*) Vegetable oil to ghee
(*iv*) Finely divided iron	(*d*) Sandmeyer reaction
(*v*) $TiCl_4 + Al(CH_3)_3$	(*e*) Haber's Process
	(*f*) Decomposition of $KClO_3$

Ans. (*i*) → (*c*) (*ii*) → (*d*) (*iii*) → (*b*)
(*iv*) → (*e*) (*v*) → (*a*)

Explanation: Catalyst → Process

(*i*) Ni in presence of $H_2 \rightarrow$ Vegetable oil to ghee
(*ii*) $Cu_2Cl_2 \rightarrow$ Sandmayer reaction
(*iii*) $V_2O_5 \rightarrow$ Contact process
(*iv*) Finely divided iron → Haber's process
(*v*) $TiCl_4 + Al(CH_3)_3 \rightarrow$ Zieglar Natta catalyst

53. Match the compounds/elements given in Column I with uses given in Column II.

Column I (Compound/element)	Column II (Use)
(*i*) Lanthanoid oxide	(*a*) Production of iron alloy
(*ii*) Lanthanoid	(*b*) Television screen
(*iii*) Misch metal	(*c*) Petroleum cracking
(*iv*) Magnesium based alloy is constituent of	(*d*) Lanthanoid metal + iron

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(*v*) Mixed oxides of lanthanoids are employed	(*e*) Bullets
	(*f*) In X-ray screen

Ans. (*i*) → (*b*) (*ii*) → (*a*) (*iii*) → (*d*)
(*iv*) → (*e*) (*v*) → (*c*)

Explanation: Compound /element → use

(*i*) Lanthanoid oxide → television screen
(*ii*) Lanthanoid → production of iron alloy
(*iii*) Misch metal → lanthanoid metal + iron
(*iv*) Magnesium based alloy → bullets
(*v*) Mixed oxide of lanthanoids are employed → petroleum cracking

54. Match the properties given in Column I with the metals given in Column II.

Column I (Property)	Column II (Metal)
(*i*) An element which can show +8 oxidation state	(*a*) Mn
(*ii*) 3*d* block element that can show upto +7 oxidation state	(*b*) Cr
(*iii*) 3*d* block element with highest melting point	(*c*) Os
	(*d*) Fe

Ans. (*i*) → (*c*) (*ii*) → (*a*) (*iii*) → (*b*)

Explanation:

(*i*) An element can show +8 oxidation states → Os
(*ii*) 3*d* block element that can show upto +7 oxidation states → Mn
(*iii*) 3*d* block element with highest melting point → Cr

55. Match the statements given in Column I with the oxidation states given in Column II.

Column I	Column II
(*i*) Oxidation state of Mn in MnO_2 is	(*a*) +2
(*ii*) Most stable oxidation state of Mn is	(*b*) +3
(*iii*) Most stable oxidation state of Mn in oxides is	(*c*) +4
(*iv*) Characteristic oxidation state of lanthanoids is	(*d*) +5
	(*e*) +7

Ans. (*i*) → (*c*) (*ii*) → (*a*) (*iii*) → (*e*)
(*iv*) → (*b*)

Explanation:

(*i*) Oxidation state of Mn in MnO_2 → +4
(*ii*) Most stable oxidation state of Mn → +2
(*iii*) Most stable oxidation state of Mn in oxides is → +7
(*iv*) Characteristic oxidation state of lanthanoid → +3

56. Match the solutions given in Column I and the colours given in Column II.

Column I (Aqueous solution of salt)	Column II (Colour)
(*i*) $FeSO_4.7H_2O$	(*a*) Green
(*ii*) $NiCl_2.4H_2O$	(*b*) Light pink
(*iii*) $MnCl_2.4H_2O$	(*c*) Blue
(*iv*) $CoCl_2.6H_2O$	(*d*) Pale green
(*v*) Cu_2Cl_2	(*e*) Pink
	(*f*) Colourless

Ans. (*i*) → (*d*) (*ii*) → (*a*) (*iii*) → (*b*)
(*iv*) → (*e*) (*v*) → (*f*)

Explanation:

(*i*) $FeSO_4 . 7H_2O$ → Pale green
(*ii*) $NiCl_2 . 4H_2O$ → Green
(*iii*) $MnCl_2 . 4H_2O$ → Light pink
(*iv*) $CoCl_2 . 6H_2O$ → Pink
(*v*) Cu_2Cl_2 → Colourless

57. Match the property given in Column I with the element given in Column II.

Column I (Property)	Column II (Elements)
(*i*) Lanthanoid which shows +4 oxidation state	(*a*) Pm
(*ii*) Lanthanoid which can show +2 oxidation state	(*b*) Ce
(*iii*) Radioactive lanthanoid	(*c*) Lu
(*iv*) Lanthanoid which has $4f^7$ electronic configuration in +3 oxidation state	(*d*) Eu
(*v*) Lanthanoid which has $4f^{14}$ electronic configuration in +3 oxidation state	(*e*) Gd
	(*f*) Dy

Ans. (*i*) → (*b*) (*ii*) → (*d*) (*iii*) → (*a*)
(*iv*) → (*e*) (*v*) → (*c*)

Explanation:

(*i*) Lanthanoid shows +4 oxidation state → Cerium (Ce)
(*ii*) Lanthanoid shows +2 oxidation state → Europium (Eu)
(*iii*) Radioactive lanthanoid → Promethium (Pm)
(*iv*) Lanthanoid having $4f^7$configuration in +3 states → Gadolinium (Gd)
(*v*) Lanthanoid having $4f^{14}$ configuration in +3 states → Lutetium (Lu)

58. Match the properties given in Column I with the metals given in Column II.

Column I (Property)	Column II (Metal)
(*i*) Element with highest second ionisation enthalpy	(*a*) Co
(*ii*) Element with highest third ionisation enthalpy	(*b*) Cr
(*iii*) M in $M(CO)_6$ is	(*c*) Cu
(*iv*) Element with highest heat of atomisation	(*d*) Zn
	(*e*) Ni

Ans. (*i*) → (*c*) (*ii*) → (*d*) (*iii*) → (*b*)
(*iv*) → (*a*)

Explanation:

(*i*) Element with highest second ionization enthalpy → Cu
(*ii*) Element with highest third ionization enthalpy → Zn
(*iii*) Metal carbonyl with formula $M(CO)_6$ → Cr as it forms $Cr(CO)_6$
(*iv*) Highest heat of atomisation → Co

V. ASSERTION AND REASON TYPE

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Both assertion and reason are true, and reason is the correct explanation of the assertion.
(*ii*) Both assertion and reason are true but reason is not the correct explanation of assertion.
(*iii*) Assertion is not true but reason is true.
(*iv*) Both assertion and reason are false.

59. Assertion : Cu^{2+} iodide is not known.
Reason : Cu^{2+} oxidises I^- to iodine.

Ans. (*i*)

Explanation: All Cu(II) halides are known except the iodide. In this case, Cu^{2+} oxidises I^- to I_2:

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$$

60. Assertion : Separation of Zr and Hf is difficult.
Reason : Because Zr and Hf lie in the same group of the periodic table.

Ans. (*ii*)

Explanation: The almost identical radii of Zr (160 pm) and Hf (159pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

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61. Assertion : Actinoids form relatively less stable complexes as compared to lanthanoids.

Reason : Actinoids can utilise their 5*f* orbitals along with 6*d* orbitals in bonding but lanthanoids do not use their 4*f* orbital for bonding.

Ans. (*iii*)

Explanation: The actinoids are highly reactive metals this is because the 5*f* electrons, will therefore be more effectively shielded from the nuclear charge than the 4*f* electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

62. Assertion : Cu cannot liberate hydrogen from acids.

Reason : Because it has positive electrode potential.

Ans. (*i*)

Explanation: Cu having a positive $E^\ominus$ accounts for its inability to liberate H_2 from acids. Only oxidising acids (nitric and hot concentrated sulphuric acid) react with Cu, as the acids being reduced. The high energy to transform Cu(*s*) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy.

63. Assertion : The highest oxidation state of osmium is +8.

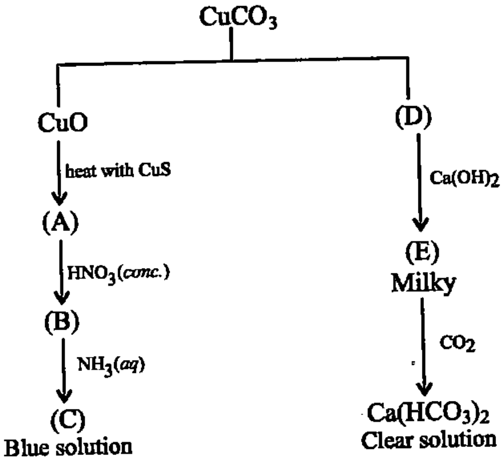
Reason : Osmium is a 5*d*-block element.

Ans. (*ii*)

Explanation: By using all the electrons from 6*s* and 5*d* with expanded octet osmium can show maximum +8 oxidation states.

VI. LONG ANSWER TYPE

64. Identify A to E and also explain the reactions involved.



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Ans.

$A = Cu$ $B = Cu(NO_3)_2$ $C = [Cu(NH_3)_4]$ $D = CO_2$

$E = CaCO_3$ $F = Cu_2[Fe(CN)_6]$ $G = Ca(HCO_3)_2$

$$CuCO_3 \rightarrow CuO + CO_2$$

$$\underset{(B)}{CuO} + CuS \rightarrow \underset{(A)}{Cu} + SO_2$$

$$Cu + 4HNO_3(conc.) \rightarrow \underset{(B)}{Cu(NO_3)_2} + 2NO + 2H_2O$$

$$\underset{(B)}{Cu^{2+}} + NH_3 \rightarrow \underset{(C)}{[Cu(NH_3)_4]}$$

$$Ca(OH)_2 + \underset{(D)}{CO_2} \rightarrow \underset{(E)}{CaCO_3} + H_2O$$

65. When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid, compound (C) can be crystallised from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and also explain the reactions.

Ans. $A = FeCr_2O_4$ $B = Na_2CrO_4$ $C = Na_2Cr_2O_7 . 2H_2O$ $D = K_2Cr_2O_7$

$$\underset{(A)}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \rightarrow \underset{(B)}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$$2NaCrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

$$\underset{(C)}{Na_2Cr_2O_7} + 2KCl \rightarrow \underset{(D)}{K_2Cr_2O_7} + 2NaCl$$

66. When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark green solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.

Ans. (A) MnO_2 (B) K_2MnO_4 (C) $KMnO_4$ (D) KIO_3

$$\underset{(A)}{2MnO_2} + 4KOH + O_2 \rightarrow \underset{(B)}{2K_2MnO_4} + 2H_2O$$

$$3\,MnO_4^{2-} + 4H^+ \rightarrow \underset{(C)}{2\,MnO_4^-} + MnO_2 + 2H_2O$$

$$3\,MnO_4^{2-} + H_2O + KI \rightarrow \underset{(A)}{2MnO_2} + 2OH^- + \underset{(D)}{KIO_3}$$

67. On the basis of Lanthanoid contraction, explain the following:

(*i*) Nature of bonding in La_2O_3 and Lu_2O_3.

(*ii*) Trends in the stability of oxo salts of lanthanoids from La to Lu.

(*iii*) Stability of the complexes of lanthanoids.
(*iv*) Radii of 4*d* and 5*d* block elements.
(*v*) Trends in acidic character of lanthanoid oxides.

Ans. Explanation:

(*i*) Because of lathanoid contraction La_2O_3 is more ionic and Lu_2O_3 is more covalent.

(*ii*) As the size decreases from lanthanum to lutetium the stability of oxosalts decreases.

(*iii*) With the decrease in size of Lanthanoids stability of the complex formed by lanthanoids decreases.

(*iv*) Radii of 4*d* and 5*d* elements will be almost same.

(*v*) Acidic character increases from lanthanum to lutetium.

68. (*a*) Answer the following questions:

(*i*) Which element of the first transition series has highest second ionisation enthalpy?

(*ii*) Which element of the first transition series has highest third ionisation enthalpy?

(*iii*) Which element of the first transition series has lowest enthalpy of atomisation?

(*b*) Identify the metal and justify your answer.

(*i*) Carbonyl $M(CO)_5$ (*ii*) MO_3F

Ans. (*a*) (*i*) Exchange the second ionisation enthalpy shows unusually high values for Cr and Cu first trasition series where the d^5 and d^{10} configurations of the M^+ ions are disrupted, with considerable loss of energy.

(*ii*) The trend in the third ionisation enthalpies is not complicated by the 4*s* orbital factor and shows the greater difficulty of removing an electron from the d^5 (Mn^{2+}) and d^{10} (Zn^{2+}) ions.

(*iii*) because of the completely filled 3*d* sub shell no unpaired electron is left for metallic bonding.

(*b*) (*i*) It is $Fe(CO)_5$ by EAN rule

EAN $= x + 2 \times 5 = 36$ (Kr is the nearest inert gas)

$x = 26$ (atomic no. of the metal) so the metal is iron

(*ii*) MO_3F is MnO_3F

In MO_3F let us assume $M = x$

$x + 3 \times (-2) + (-1) = 0$

$x = +7$

M is in +7 oxidation state so that the given compound is MnO_3F

69. Mention the type of compounds formed when small atoms like H, C and N get trapped inside the crystal lattice of transition metals. Also give physical and chemical characteristics of these compounds.

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Ans. Interstitial compounds are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent.

The principal physical and chemical characteristics of these compounds are as follows:

(*i*) They have high melting points, higher than those of pure metals.
(*ii*) They are very hard, some borides approach diamond in hardness.
(*iii*) They retain metallic conductivity.
(*iv*) They are chemically inert.

70. (*a*) Transition metals can act as catalysts because these can change their oxidation state. How does Fe(III) catalyse the reaction between iodide and persulphate ions?

(*b*) Mention any three processes where transition metals act as catalysts.

Ans. (*a*) The reaction between iodide and persulphate ions.

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

An explanation of this catalytic action can be given as:

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$
$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$$

(*b*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

In the above reaction Fe is used as catalyst.

$$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

$$2SO_2 + O_2 \xrightarrow{V_2O_3} 2SO_3$$

71. A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating compound (C) with conc. H_2SO_4 and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.

Ans. $A = KMnO_4 \quad B = K_2MnO_4 \quad C = MnO_2 \quad D = MnCl_2$

$$\underset{(A)}{KMnO_4} \xrightarrow{\Delta} \underset{(B)}{K_2MnO_4} + \underset{(C)}{MnO_2} + O_2$$

$$MnO_2 + KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_2 + 4NaCl + 4H_2SO_4 \rightarrow \underset{(D)}{MnCl_2} + 2NaHSO_4 + 2H_2O + Cl_2$$

Since, compound (C) on heating with conc. H_2SO_4 and NaCl gives Cl_2 gas. So it is manganese dioxide (MnO_2).

□□□

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9

Coordination Compounds

1. Which of the following complexes formed by Cu^{2+} ions is most stable?
   - (*i*) $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$, log K = 11.6
   - (*ii*) $Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN)_4]^{2-}$, log K = 27.3
   - (*iii*) $Cu^{2+} + 2en \rightleftharpoons [Cu(en)_2]^{2+}$, log K = 15.4
   - (*iv*) $Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}$, log K = 8.9

Ans. (*ii*)

Explanation: Greater the value of log K greater the stability of the complex compound.

2. The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$
   - (*i*) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$
   - (*ii*) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$
   - (*iii*) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$
   - (*iv*) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

Ans. (*iii*)

Explanation: In strong field ligand, there is more energy separation than weak field ligand it means that as the strength of ligand increases crystal field splitting energy increases.

$$\Delta E = hc/\lambda \text{ or } \Delta E \propto 1/\lambda$$

As ΔE increases, wavelength of light absorbed decreases.

3. When 0.1 mol $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to
   - (*i*) 1:3 electrolyte
   - (*ii*) 1:2 electrolyte
   - (*iii*) 1:1 electrolyte
   - (*iv*) 3:1 electrolyte

Ans. (*ii*)

4. When 1 mol $CrCl_3 \cdot 6H_2O$ is treated with excess of $AgNO_3$, 3 mol of AgCl are obtained. The formula of the complex is:
   - (*i*) $[CrCl_3(H_2O)_3] \cdot 3H_2O$
   - (*ii*) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$
   - (*iii*) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$
   - (*iv*) $[Cr(H_2O)_6]Cl_3$

Ans. (*iv*)

Explanation: 1 mol of AgCl is precipitated by one Cl^- ion.
3 mol of AgCl is precipitated by $3Cl^-$ ions. So the formula of the complex is Cr $[(H_2O)_6]Cl_3$

5. The correct IUPAC name of $[Pt(NH_3)_2Cl_2]$ is
   - (*i*) Diamminedichloridoplatinum (II)

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(*ii*) Diamminedichloridoplatinum (IV)
(*iii*) Diamminedichloridoplatinum (0)
(*iv*) Dichloridodiammineplatinum (IV)

Ans. (*i*)

Explanation: The complex compound is $[Pt(NH_3)_2Cl_2]$.
NH_3 is a neutral ligand and named as amine.
Cl is anion ligand and named as chloride. Di or tri is prefixed to represent the number.
So the name of the compound is – Diamminedichloridoplatinum (II).
(II) represent the oxidation state of platinum.

6. The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?

(*i*) $[Fe(CO)_5]$	(*ii*) $[Fe(CN)_6]^{3-}$
(*iii*) $[Fe(C_2O_4)_3]^{3-}$	(*iv*) $[Fe(H_2O)_6]^{3+}$

Ans. (*iii*)

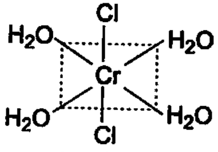
Explanation: When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelate ligand. The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands.

7. Indicate the complex ion which shows geometrical isomerism.

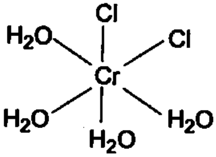
(*i*) $[Cr(H_2O)_4Cl_2]^+$	(*ii*) $[Pt(NH_3)_3Cl]$
(*iii*) $[Co(NH_3)_6]^{3+}$	(*iv*) $[Co(CN)_5(NC)]^{3-}$

Ans. (*i*)

Explanation: Because it is a MA_4B_2 type co-ordination compound. Possible geometrical isomers are



trans-isomer



cis-isomer

8. The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be

(*i*) 18,000 cm^{-1}	(*ii*) 16,000 cm^{-1}
(*iii*) 8,000 cm^{-1}	(*iv*) 20,000 cm^{-1}

Ans. (*iii*)

Explanation: CFSE for octahedral and tetrahedral complex is related as

$$\Delta' = \frac{4}{9}\Delta_o$$

where Δ_o = CFSE for octahedral complex
Δ_t = CFSE for tetrahedral complex

$$\Delta_o = 18000\ \text{cm}^{-1}$$
$$\Delta_t = \frac{4}{9} \times 18000 = 8{,}000\ \text{cm}^{-1}$$

9. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are

(*i*) linkage isomers (*ii*) coordination isomers
(*iii*) ionisation isomers (*iv*) geometrical isomers

Ans. (*i*)

Explanations: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS—, which may bind through the nitrogen to give M—NCS or through sulphur to give M—SCN.

10. The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$ represent

(*i*) linkage isomerism (*ii*) ionisation isomerism
(*iii*) coordination isomerism (*iv*) no isomerism

Ans. (*iv*)

Explanation: Isomers means having same molecular formula but different structural formula but in the above question the molecular formula is different. Hence they are not isomers.

11. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is **not** a chelating agent?

(*i*) thiosulphato (*ii*) oxalato
(*iii*) glycinato (*iv*) ethane-1,2-diamine

Ans. (*i*)

Explanation: Geometry of thiosulphato is not favourable to chelate a metal ion.

12. Which of the following species is **not** expected to be a ligand?

(*i*) NO (*ii*) NH_4^+
(*iii*) $NH_2CH_2CH_2NH_2$ (*iv*) CO

Ans. (*ii*)

Explanation: Ligand must have a lone pair electron to form M-L (metal-ligand bond)

13. What kind of isomerism exists between $[Cr(H_2O)_6]Cl_3$ (violet) and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (greyish-green)?

(*i*) linkage isomerism (*ii*) solvate isomerism
(*iii*) ionisation isomerism (*iv*) coordination isomerism

Ans. (*ii*)

Explanation: This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.

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14. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is :
    (*i*) Platinum diaminechloronitrite
    (*ii*) Chloronitrito-N-ammineplatinum (II)
    (*iii*) Diamminechloridonitrito-N-platinum (II)
    (*iv*) Diamminechloronitrito-N-platinate (II)

Ans. (*iii*)

Explanation: The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula). Names of the anionic ligands end in –o. State of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

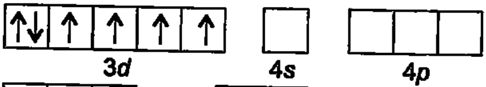
Note : In the following questions two or more options may be correct.

15. Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic?
    (*i*) $[Co(NH_3)_6]^{3+}$ (*ii*) $[Mn(CN)_6]^{3-}$
    (*iii*) $[Fe(CN)_6]^{4-}$ (*iv*) $[Fe(CN)_6]^{3-}$

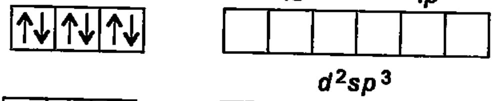
Ans. (*i*) and (*iii*)

Explanation:

(*i*) Orbitals of Co^{3+} ion



d^2sp^3 hybridised orbitals of Co^{3+}



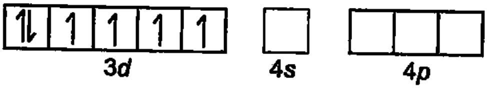
$[Co(NH_3)_6]^{3+}$ (inner orbital or low spin complex)

Six pairs of electrons from six NH_3 molecules

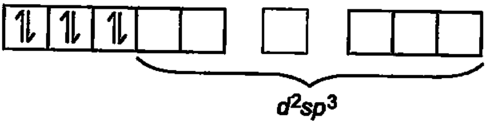
No. of unpaired electron= 0

Magnetic property = diamagnetic

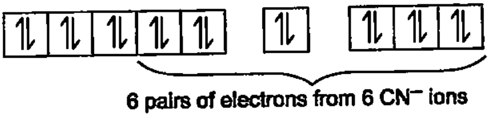
(*ii*) Electronic configuration is $3d^6$ orbitals of Fe^{2+} ion:



As CN^- is a strong field ligand, it causes the pairing of the unpaired 3*d* electrons. Since there are six ligands around the central metal ion, the most feasible hybridization d^2sp^3. d^2sp^3 hybridized oribtals of Fe^{2+} are:



6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3 orbitals. Then,



Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

16. Atomic number of Mn, Fe, Co and Ni are 25, 26, 27 and 28 respectively. Which of the following outer orbital octahedral complexes have same number of unpaired electrons?

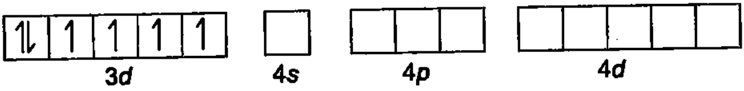
(*i*) $[MnCl_6]^{3-}$ (*ii*) $[FeF_6]^{3-}$

(*iii*) $[CoF_6]^{3-}$ (*iv*) $[Ni(NH_3)_6]^{2+}$

Ans. (*i*) and (*iii*)

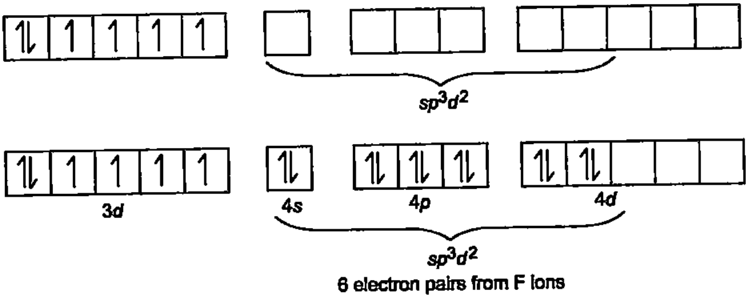
Explanation: Outer orbital complex or high spin complex

Orbitals of Co^{3+} ion:



Again, fluoride ion is a weak field ligand. It cannot cause the pairing of the 3*d* electrons. As a result, the Co^{3+} ion will undergo sp^3d^2 hybridization sp^3d^2.

Hybridized orbitals of Co^{3+} ion are:



Similarly $[MnCl_6]^{3-}$ is also outer orbital complex or high spin complex. Magnetic property-paramagnetic no. of unpaired electron = 4

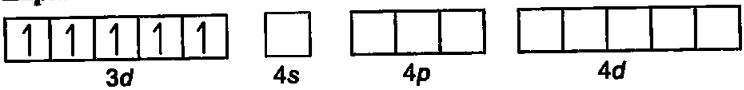
17. Which of the following options are correct for $[Fe(CN)_6]^{3-}$ complex?

(*i*) d^2sp^3 hybridisation (*ii*) sp^3d^2 hybridisation

(*iii*) paramagnetic (*iv*) diamagnetic

Ans. (*i*) and (*iii*)

Explanation:



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6 electron pairs from CN ions occupy the six hybrid d^2sp^3 orbitals.
No. of unpaired electron = 1
Magnetic property = paramagnetic

18. An aqueous pink solution of cobalt(II) chloride changes to deep blue on addition of excess of HCl. This is because____________.

(*i*) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_6]^{4-}$
(*ii*) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_4]^{2-}$
(*iii*) tetrahedral complexes have smaller crystal field splitting than octahedral complexes.
(*iv*) tetrahedral complexes have larger crystal field splitting than octahedral complex.

Ans. (*ii*) and (*iii*)

Explanation: Aqueous pink solution of cobalt (II) chloride is due to electric transition of electron from t_{2g} to e_g energy level of $[Co(H_2O_6)]^{2+}$ complex. When excess of HCl is added to this solution.

19. Which of the following complexes are homoleptic?

(*i*) $[Co(NH_3)_6]^{3+}$ (*ii*) $[Co(NH_3)_4Cl_2]^+$
(*iii*) $[Ni(CN)_4]^{2-}$ (*iv*) $[Ni(NH_3)_4Cl_2]$

Ans. (*i*) and (*iii*)

Explanation: Complexes in which a metal is bound to only one kind of donor groups, e.g., $[Co(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups. e.g., $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

20. Which of the following complexes are heteroleptic?

(*i*) $[Cr(NH_3)_6]^{3+}$ (*ii*) $[Fe(NH_3)_4Cl_2]^+$
(*iii*) $[Mn(CN)_6]^{4-}$ (*iv*) $[Co(NH_3)_4Cl_2]$

Ans. (*ii*) and (*iv*)

Explanation: Already explained in answer no.19.

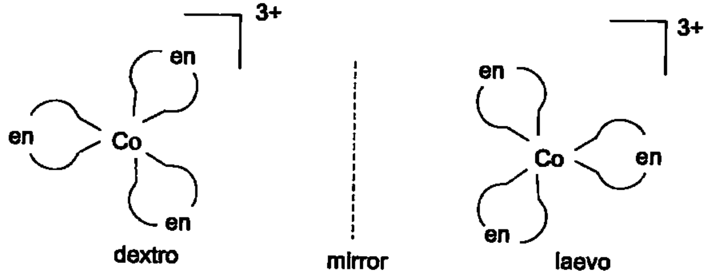
21. Identify the optically active compounds from the following :

(*i*) $[Co(en)_3]^{3+}$ (*ii*) trans– $[Co(en)_2Cl_2]^+$
(*iii*) cis–$[Co(en)_2Cl_2]^+$ (*iv*) $[Cr(NH_3)_5Cl]$

Ans. (*i*) and (*iii*)

Explanation: Optical Isomerism

(*i*)



Optical isomers (d and 1) of $[Co(en)_3]^{3+}$

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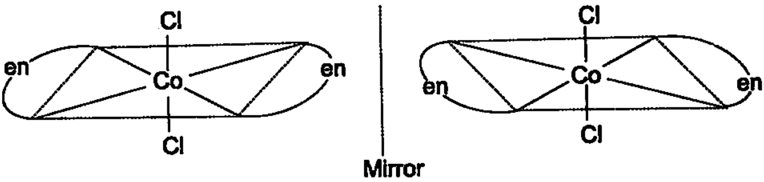
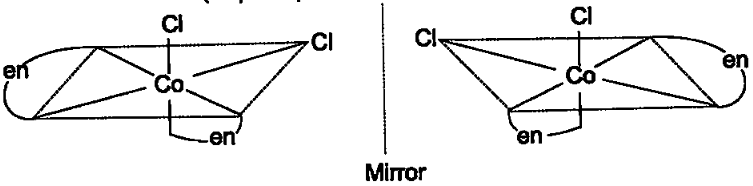


Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Superimposable mirror images)



Cis $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Non-superimposable mirror images)

Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called *chiral*. The two forms are called dextro (*d*) and laevo (*l*).

22. Identify the correct statements for the behaviour of ethane-1, 2-diamine as a ligand.

(*i*) It is a neutral ligand. (*ii*) It is a didentate ligand.
(*iii*) It is a chelating ligand. (*iv*) It is a unidentate ligand.

Ans. (*i*), (*ii*) and (*iii*)

Explanation: When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1, 2-diamine) or C_2O_4 2-(oxalate), the ligand is said to be didentate and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelate ligand. Ethane-1, 2-diamine is a neutral ligand.

23. Which of the following complexes show linkage isomerism?

(*i*) $[Co(NH_3)_5(NO_2)]^{2+}$ (*ii*) $[Co(H_2O)_5CO]^{3+}$
(*iii*) $[Cr(NH_3)_5 SCN]^{2+}$ (*iv*) $[Fe(en)_2Cl_2]^+$

Ans. (*i*) and (*iii*)

Explanation: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand. NCS^-, which may bind through the nitrogen to give M-NCS or through sulphur to give M-SCN. Jorgensen discovered such behaviour in the complex $[Co(NH_3)_5NO_2Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound

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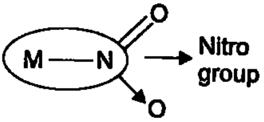
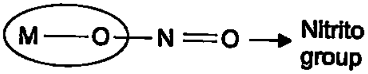
through oxygen (—ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen (—NO_2).

(*a*) 

(The donor atom is N)



(The donor atom is oxygen)

III. SHORT ANSWER TYPE

24. Arrange the following complexes in the increasing order of conductivity of their solution: $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_6]Cl_3$, $[Cr(NH_3)_5Cl]Cl_2$.

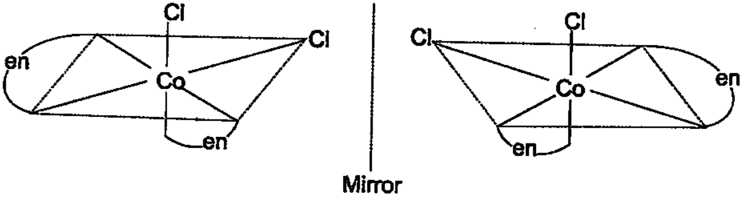
Ans. Complex which give more ions on dissolution is more conducting.
$[Co(NH_3)_6]Cl_3 > [Cr(NH_3)_5Cl]Cl_2 > [Co(NH_3)_4Cl_2]Cl > [Co(NH_3)_3Cl_3]$

25. A coordination compound $CrCl_3 \cdot 4H_2O$ precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of two ions. Write structural formula of the compound and name it.

Ans. Since only two ions are present in the solution only one Cl^- is present outside the sphere.

The formula of the complex is $[Co(H_2O)_4Cl_2]Cl$ and its IUPAC name is Tetraaquadichloridocobalt (III) chloride.

26. A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of the complex? Give one example of such complex.

Ans. 

Cis $[CoCl)_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)

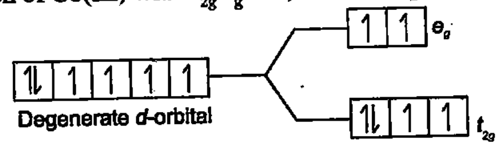
An optically active complex of the type$[M(AA)_2X_2]^{n+}$

27. Magnetic moment of $[MnCl_4]^{2-}$ is 5.92 BM. Explain giving reason.

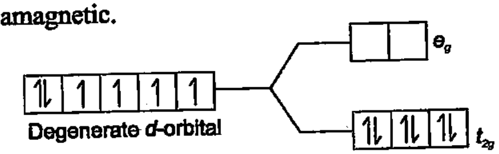
Ans. Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the *d* orbital.

28. On the basis of crystal field theory explain why Co(III) forms paramagnetic octahedral complex with weak field ligands whereas it forms diamagnetic octahedral complex with strong field ligands.

Ans. With weak field ligands $\Delta_0 < P$ (pairing energy) so, the electronic configuration of Co(III) with $t_{2g}^4 e_g^2$ i.e., it has 4 unpaired electrons



In strong field ligands $\Delta_o > P$ (pairing energy). So pairing occurs, thus, the electronic configuratioin will be $t_{2g}^6 e_g^0$. It has no unpaired electron and is diamagnetic.



29. Why are low spin tetrahedral complexes not formed?

Ans. In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\,\Delta_0$.

30. Give the electronic configuration of the following complexes on the basis of Crystal Field Splitting theory.

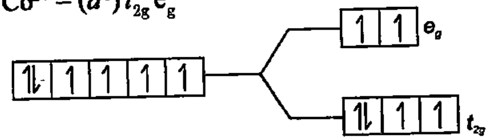
$[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$.

Ans. According to spectrochemical series ligands can be arranged in a series in the order of increasing field strength

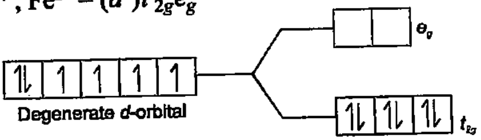
$$CN^- > NH_3 > F^-$$

Thus CN^- and NH_3 are strong field ligand pair up the t_{2g} electrons before filling e_g set.

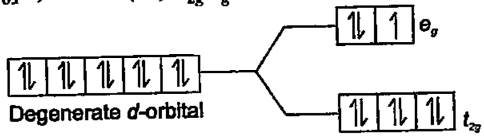
$[CoF_6]^{3-}$, $Co^{3+} = (d^6)\, t_{2g}^4 e_g^2$



$[Fe(CN)_6]^{4-}$, $Fe^{2+} = (d^6) t_{2g}^6 e_g^0$



$[Cu(NH_3)_6]^{2+}$, $Cu^{2+} = (d^9)\ t_{2g}^6 e_g^3$



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31. Explain why $[Fe(H_2O)_6]^{3+}$ has magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM.

Ans. Magnetic moment

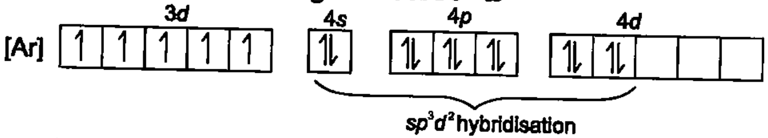
$$\mu = \sqrt{n(n+2)}$$

(*i*) $[Fe(H_2O)_6]^{3+}$ has magnetic moment value = 5.92 BM

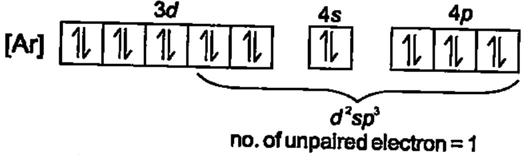
It means no. of unpaired electron = 5

For $[Fe(H_2O)_6]^{3+}$

The electronic configuration of Fe^{3+} is



(*ii*) This is an outer orbital complex CN^- is strong ligand $\Delta_o > P$ for CN^- Electronic configuration of Fe^{3+}



$\therefore \quad \mu = 1.74$ BM

32. Arrange following complex ions in increasing order of crystal field splitting energy (Δ_o) :

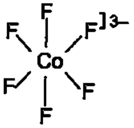
$$[Cr(Cl)_6]^{3-}, [Cr(CN)_6]^{3-}, [Cr(NH_3)_6]^{3+}.$$

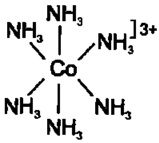
Ans. Crystal field splitting energy increases in the order $[Cr(Cl)_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}$

Because according to spectrochemical series the order of field strength $Cl^- < NH_3 < CN^-$

33. Why do compounds having similar geometry have different magnetic moment?

Ans. It is due to the presence of weak and strong field ligands in complexes. If CFSE is high, the complex will show low value of magnetic moment and vice-versa, e.g., $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, the former is paramagnetic, and the latter is diamagnetic because f^- is a strong field ligand while both have similar geometry.





34 $CuSO_4 \cdot 5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why?

Ans. In $CuSO_4.5H_2O$, water acts as ligand as a result it causes crystal field splitting. Hence d—d transition is possible in $CuSO_4 . 5H_2O$ and shows colour. In the anhydrous $CuSO_4$ due to the absence of water (ligand), crystal field splitting is not possible and hence no colour.

35. Name the type of isomerism when ambidentate ligands are attached to central metal ion. Give two examples of ambidentate ligands.

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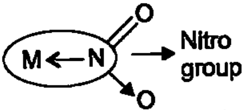
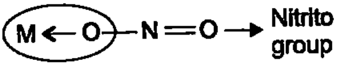
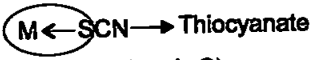
Ans. Ambidentate ligands are ligands that can attach themselves to the central metal atom through two different atoms. For example



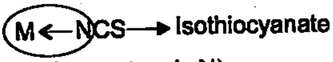
(The donor atom is N)



(The donor atom is oxygen)



(The donor atom is S)



(The donor atom is N)

IV. MATCHING TYPE

Note: In the following questions match the items given in Columns I and Column II.

36. Match the complex ions given in Column I with the colours given in Column II and assign the correct code :

Column I (Complex ion)	Column II (Colour)
A. $[Co(NH_3)_6]^{3+}$	1. Violet
B. $[Ti(H_2O)_6]^{3+}$	2. Green
C. $[Ni(H_2O)_6]^{2+}$	3. Pale blue
D. $[Ni(H_2O)_4(en)]^{2+}$ (*aq*)	4. Yellowish orange
	5. Blue

Code :

(*i*)	A (1)	B (2)	C (4)	D (5)
(*ii*)	A (4)	B (3)	C (2)	D (1)
(*iii*)	A (3)	B (2)	C (4)	D (1)
(*iv*)	A (4)	B (1)	C (2)	D (3)

Ans. (*ii*)

Explanation:

Complex ion	Colour
A. $[Co(NH_3)_6]^{3+}$	Yellowish orange
B. $[Ti(H_2O)_6]^{3+}$	Pale blue
C. $[Ni(H_2O)_6]^{2+}$	Green
D. $[Ni(H_2O)_4(en)]^{2+}$ (*aq*)	Violet

37. Match the coordination compounds given in Column I with the central metal atoms given in Column II and assign the correct code:

Column I (Coordination Compound)	Column II (Central metal atom)
A. Chlorophyll	1. rhodium
B. Blood pigment	2. cobalt
C. Wilkinson catalyst	3. calcium
D. Vitamin B_{12}	4. iron
	5. magnesium

Code :

(*i*) A (5)	B (4)	C (1)	D (2)
(*ii*) A (3)	B (4)	C (5)	D (1)
(*iii*) A (4)	B (3)	C (2)	D (1)
(*iv*) A (3)	B (4)	C (1)	D (2)

Ans. (*i*)

Column I	Column II
A. Chlorophyll	Magnesium
B. Blood pigment	Iron
C. Wilkinson catalyst	Rhodium
D. Vitamin B_{12}	Cobalt

38. Match the complex ions given in Column I with the hybridisation and number of unpaired electrons given in Column II and assign the correct code:

Column I (Complex ion)	Column II (Hybridisation, number of unpaired electrons)
A. $[Cr(H_2O)_6]^{3+}$	1. dsp^2, 1
B. $[Co(CN)_4]^{2-}$	2. sp^3d^2, 5
C. $[Ni(NH_3)_6]^{2+}$	3. d^2sp^3, 3
D. $[MnF_6]^{4-}$	4. sp^3, 4
	5. sp^3d^2, 2

Code :

(*i*) A (3)	B (1)	C (5)	D (2)
(*ii*) A (4)	B (3)	C (2)	D (1)
(*iii*) A (3)	B (2)	C (4)	D (1)
(*iv*) A (4)	B (1)	C (2)	D (3)

Ans. (*ii*)

Column I	Column II
A. $[Cr(H_2O)_6]^{3+}$	sp^3, 4
B. $[Co(CN)_4]^{2-}$	d^2sp^3, 3
C. $[Ni(NH_3)_6]^{2+}$	sp^3d^2, 5
D. $[MnF_6]^{4-}$	dsp^2, 1

39. Match the complex species given in Column I with the possible isomerism given in Column II and assign the correct code :

Column I (Complex species)	Column II (Isomerism)
A. $[Co(NH_3)_4Cl_2]^+$	1. optical
B. cis-$[Co(en)_2Cl_2]^+$	2. ionisation
C. $[Co(NH_3)_5(NO_2)]Cl_2$	3. coordination
D. $[Co(NH_3)_6][Cr(CN)_6]$	4. geometrical
	5. linkage

Code :

(*i*)	A (1)	B (2)	C (4)	D (5)
(*ii*)	A (4)	B (3)	C (2)	D (1)
(*iii*)	A (4)	B (1)	C (5)	D (3)
(*iv*)	A (4)	B (1)	C (2)	D (3)

Ans. (*iv*)

Column I	Column II
A. $[Co(NH_3)_4Cl_2]^+$	geometrical
B. cis-$[Co(en)_2Cl_2]^+$	optical
C. $[Co(NH_3)_5(NO_2)]Cl_2$	ionisation
D. $[Co(NH_3)_6][Cr(CN)_6]$	coordination

40. Match the compounds given in Column I with the oxidation state of cobalt present in it (given in Column II) and assign the correct code.

Column I (Compound)	Column II (Oxidation state of Co)
A. $[Co(NCS)(NH_3)_5](SO_3)$	1. + 4
B. $[Co(NH_3)_4Cl_2]SO_4$	2. 0
C. $Na_4[Co(S_2O_3)_3]$	3. + 1
D. $[Co_2(CO)_8]$	4. + 2
	5. + 3

Code :

(*i*)	A (1)	B (2)	C (4)	D (5)
(*ii*)	A (4)	B (3)	C (2)	D (1)
(*iii*)	A (5)	B (1)	C (4)	D (2)
(*iv*)	A (4)	B (1)	C (2)	D (3)

Ans. (*i*)

Column I	Column II
A. $[Co(NCS)(NH_3)_5](SO_3)$	+ 4
B. $[Co(NH_3)_4Cl_2]SO_4$	0
C. $Na_4[Co(S_2O_3)_3]$	+2
D. $[Co_2(CO)_8]$	+3

V. ASSERTION AND REASON TYPE

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are true, reason is the correct explanation of assertion.

(*ii*) Assertion and reason both are true but reason is not the correct explanation of assertion.

(*iii*) Assertion is true but reason is false.

(*iv*) Assertion is false, reason is true.

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41. **Assertion** : Toxic metal ions are removed by the chelating ligands.
Reason : Chelate complexes tend to be more stable.

Ans. (*i*)

Explanation: Toxic metal ions are removed by the chelating ligands. Metal ligand form stable complex compound with the toxic metal ions and remove them from the solution.

42. **Assertion** : $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature.
Reason : Unpaired electrons are present in their *d*-orbitals.

Ans. (*ii*)

Explanation: $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature. They form more stable complex after gaining electrons.

43. **Assertion** : Linkage isomerism arises in coordination compounds containing ambidentate ligand.
Reason : Ambidentate ligand has two different donor atoms.

Ans. (*i*)

Explanation: Linkage isomerism arises in coordination compounds containing ambidentate ligand because ambidentate ligand has two different donor atoms.

44. **Assertion** : Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.
Reason : Geometrical isomerism is not shown by complexes of coordination number 6.

Ans. (*ii*)

Explanation: Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism due to plane of symmetry shown by them.

45. **Assertion** : $([Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
Reason : Because it has d^2sp^3 type hybridisation.

Ans. (*iv*)

Explanation: $([Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to not two for one $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation.

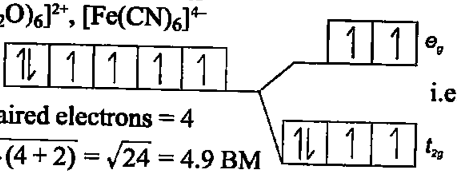
VI. LONG ANSWER TYPE

46. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following :

(*i*) $[CoF_6]^{3-}$, $[Co(H_2O)_6]^{2+}$, $[Co(CN)_6]^{3-}$
(*ii*) $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{4-}$

Ans. (*i*) $[CoF_6]^{3-}$

$Co^{3+} = 3d^6$



i.e. $t_{2g}^4 e_g^2$

Number of unpaired electrons = 4

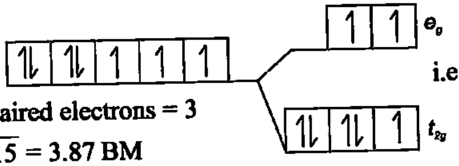
$\sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.9$ BM

$[Co(H_2O)_6]^{2+}$

$Co^{2+} = 3d^7$

Number of unpaired electrons = 3

$\sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM

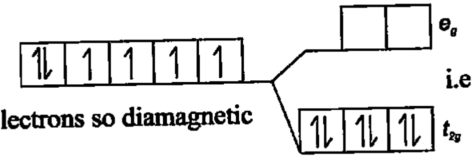


i.e. $t_{2g}^5 e_g^2$

$[Co(CN)_6]^{3-}$

$Co^{3+} = 3d^6$

No unpaired electrons so diamagnetic



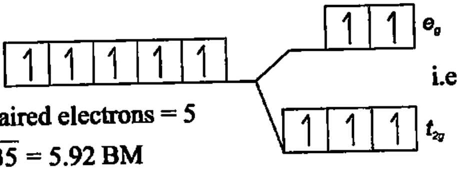
i.e. $t_{2g}^6 e_g^2$

(*ii*) $[FeF_6]^{3-}$

$Fe^{3+} = 3d^5$

Number of unpaired electrons = 5

$\sqrt{5(5+2)} = \sqrt{35} = 5.92$ BM



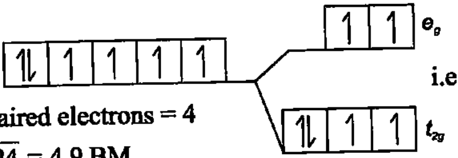
i.e. $t_{2g}^3 e_g^2$

$[Fe(H_2O)_6]^{2+}$

$Fe^{2+} = 3d^6$

Number of unpaired electrons = 4

$\sqrt{4(4+2)} = \sqrt{24} = 4.9$ BM



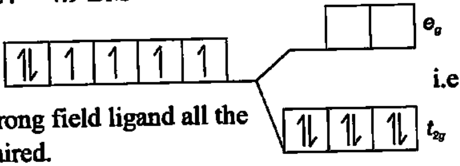
i.e. $t_{2g}^4 e_g^2$

$[Fe(CN)_6]^{4-}$

$Fe^{2+} = 3d^6$

Since CN^- is strong field ligand all the electrons get paired.

No unpaired electrons so diamagnetic



i.e. $t_{2g}^6 e_g^2$

47. Using valence bond theory, explain the following in relation to the complexes given below:

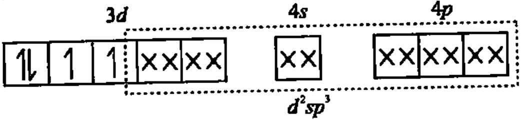
$[Mn(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$, $[FeCl_6]^{4-}$

(*i*) Type of hybridisation. (*ii*) Inner or orbital complex.

(*iii*) Magnetic behaviour. (*iv*) Spin only magnetic moment value.

Ans. $[Mn(CN)_6]^{3-}$

$Mn^{3+} = 3d^4$



(*i*) d^2sp^3

(*ii*) Inner orbital complex

(*iii*) Paramagnetic

(*iv*) $\sqrt{2(2+2)} = \sqrt{8} = 2.87$ BM

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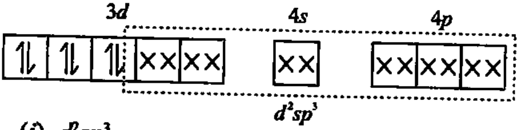
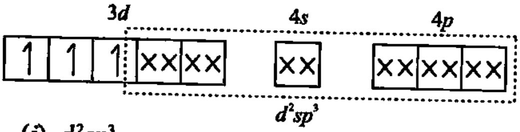
$[Co(NH_3)_6]^{3+}$
$Co^{3+} = 3d^6$



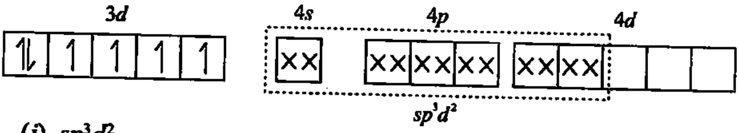
(*i*) d^2sp^3
(*ii*) Inner orbital complex
(*iii*) Diamagnetic
(*iv*) Zero

$[Cr(H_2O)_6]^{3+}$



(*i*) d^2sp^3
(*ii*) Inner orbital complex
(*iii*) Paramagnetic
(*iv*) 3.87 BM

$[FeCl_6]^{4-}$
$Fe^{2+} = 3d^6$



(*i*) sp^3d^2
(*ii*) Outer orbital complex
(*iii*) Paramagnetic
(*iv*) 4.9 BM

48. $CoSO_4Cl \cdot 5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$. Answer the following questions.

(*i*) Identify 'A' and 'B' and write their structural formulas.
(*ii*) Name the type of isomerism involved.
(*iii*) Give the IUPAC name of 'A' and 'B'.

Ans. (*i*) A – $[Co(NH_3)_5SO_4]Cl$
B – $[Co(NH_3)_5Cl]SO_4$
(*ii*) Ionisation isomerism.
(*iii*) A. Pentaamminesulphatocobalt(III) chloride.
B. Pentaamminechlorocobalt(III) sulphate.

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49. What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex?

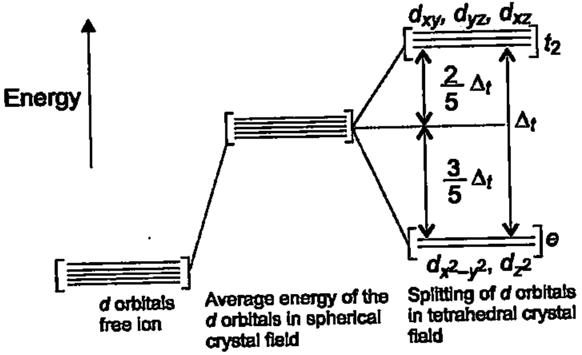
Ans. White light as it passes through the sample, so the light that emerges is no longer white. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red.

Coordination entity	Wavelength of light absorbed (*nm*)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow ░	Violet ▓
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green ▒	Red ■
$[Co(NH_3)_6]^{3+}$	475	Blue ■	Yellow Orange ▒
$[Co(CN_6]^{3-}$	310	Ultraviolet Not in visible region	Pale Yellow ░
$[Cu(H_2O)_4]^{2+}$	600	Red ■	Blue ■
$[Ti(H_2O)_6]^{3+}$	498	Blue Green ▒	Violet ▓

Above table gives the relationship of the different wavelength absorbed and the colour observed.

50. Why are different colours observed in octahedral and tetrahedral complexes for the same metal and same ligands?

Ans. In tetrahedral coordination entity formation, the *d* orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\,\Delta_0$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.



d orbital splitting in a tetrahedral crystal field.

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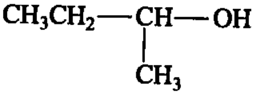
10

Haloalkanes and Haloarenes

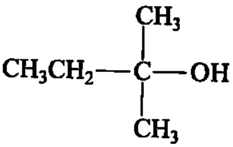
I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. The order of reactivity of following alcohols with halogen acids is ________.

(A) $CH_3CH_2-CH_2-OH$

(B) 

$CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-OH$

(C) 

$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

(i) (A) > (B) > (C) (ii) (C) > (B) > (A)

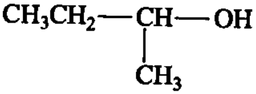
(iii) (B) > (A) > (C) (iv) (A) > (C) > (B)

Ans. (ii)

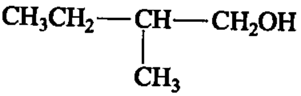
Explanation: Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides, 3^0 alkyl halides undergo S_N1 reaction very fast because of the high stability of 3^0 carbocations.

2. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

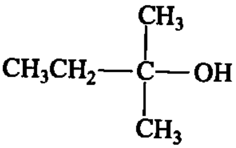
(i) $CH_3CH_2-CH_2-OH$

(ii) 

$CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-OH$

(iii) 

$CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

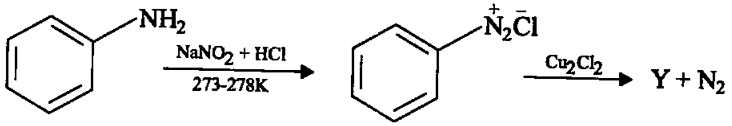
(iv) 

$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

Ans. (iv)

Explanation: The reactions of primary and secondary alcohols with HCl require the presence of a catalyst, $ZnCl_2$. With tertiary alcohols, the reaction is conducted by simply shaking with concentrated HCl at room temperature. The order of reactivity of alcohols with a given haloacid is 3° > 2° > 1°.

3. Identify the compound Y in the following reaction.



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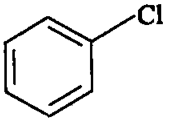
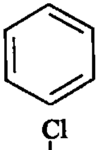
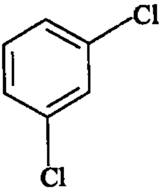
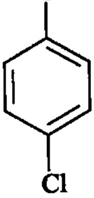
(i) 

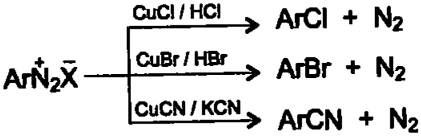
(ii) 

(iii) 

(iv) 

Ans. (i)

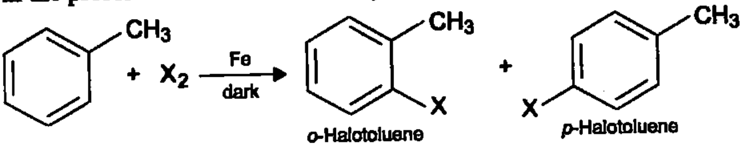
Explanation: The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.

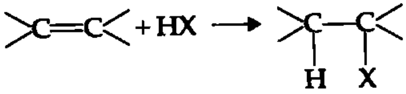


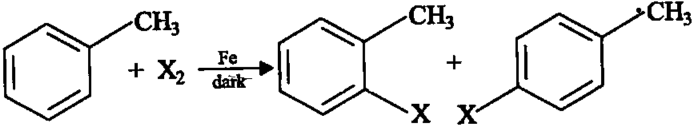
4. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is
   - (i) Electrophilic elimination reaction
   - (ii) Electrophilic substitution reaction
   - (iii) Free radical addition reaction
   - (iv) Nucleophilic substitution reaction

Ans. (ii)

Explanation: Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.



5. Which of the following is halogen exchange reaction?
   - (i) $RX + NaI \longrightarrow RI + NaX$
   - (ii) 

   - (iii) $R—OH + HX \xrightarrow{ZnCl_2} R—X + H_2O$
   - (iv) 

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Ans. (*i*)

Explanation: Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.

NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

6. Which reagent will you use for the following reaction?

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

(*i*) Cl_2/UV light (*ii*) $NaCl + H_2SO_4$

(*iii*) Cl_2 gas in dark

(*iv*) Cl_2 gas in the presence of iron in dark

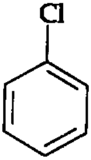
Ans. (*i*)

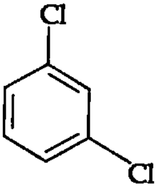
Explanation: Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono- and polyhaloalkanes, which is difficult to separate as pure compounds. Consequently, the yield of any one free radical chlorination or bromination of alkanes gives a complex

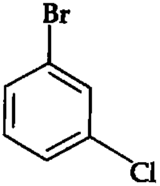
$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

7. Arrange the following compounds in the increasing order of their densities.

(*a*) 

(*b*) 

(*c*) 

(*d*) 

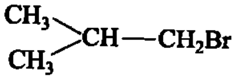
(*i*) (*a*) < (*b*) < (*c*) < (*d*) (*ii*) (*a*) < (*c*) < (*d*) < (*b*)

(*iii*) (*d*) < (*c*) < (*b*) < (*a*) (*iv*) (*b*) < (*d*) < (*c*) < (*a*)

Ans. (*i*)

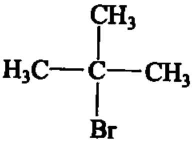
Explanation: Density is related to molecular mass. Higher the mass, higher will be the density of the molecule.

8. Arrange the following compounds in increasing order of their boiling points.

(a) 

$$(CH_3)_2CH{-}CH_2Br$$

(b) $CH_3CH_2CH_2CH_2Br$

(c) 

$$H_3C{-}\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}{-}CH_3$$

(*i*) (*b*) < (*a*) < (*c*) (*ii*) (*a*) < (*b*) < (*c*)

(*iii*) (*c*) < (*a*) < (*b*) (*iv*) (*c*) < (*b*) < (*a*)

Ans. (*iii*)

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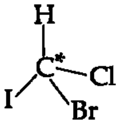
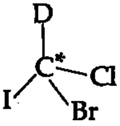
Explanation: As the branching increases, surface area of the molecule decreases. Because of these the vander Waals force of attraction between the molecule decreases and cosequently boiling point decreases.

9. In which of the following molecules carbon atom marked with asterisk (*) is asymmetric?

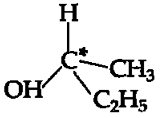
(*a*)



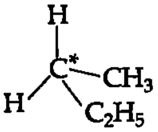
(*b*)



(*c*)



(*d*)

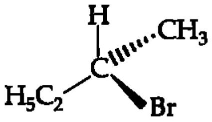


(*i*) (a), (b), (c), (d) (*ii*) (a), (b), (c)
(*iii*) (b), (c), (d) (*iv*) (a), (c), (d)

Ans. (*ii*)

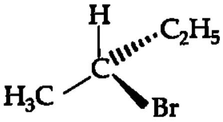
Explanation: Carbon atom attached with four different groups is known as assymetric carbon.

10. Which of the following structures is enantiomeric with the molecule (A) given below:

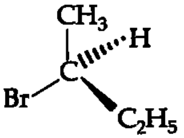


(A)

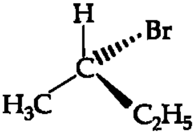
(*i*)



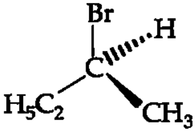
(*ii*)



(*iii*)



(*iv*)



Ans. (*i*)

Explanation: The sterioisomers related to each other as non-super impossable mirror images are called enantiomers. Enantiomers possess identical physical properties

11. Which of the following is an example of *vic*-dihalide?

(*i*) Dichloromethane (*ii*) 1,2-dichloroethane
(*iii*) Ethylidene chloride (*iv*) Allyl chloride

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Ans. (*ii*)

Explanation: In 1, 2 dichloroethane, the two chlorine atoms are attached to two adjacent carbon atoms.

12. The position of –Br in the compound in $CH_3CH{=}CHC(Br)(CH_3)_2$ can be classified as ____________.

(*i*) Allyl (*ii*) Aryl

(*iii*) Vinyl (*iv*) Secondary

Ans. (*i*)

Explanation: These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom next to carbon-carbon double bond (C=C) *i.e.*, to an allylic carbon.

13. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction?

(*i*) Cl^- (*ii*) Cl^+

(*iii*) $AlCl_3$ (*iv*) $[AlCl_4]^-$

Ans. (*ii*)

14. Ethylidene chloride is a/an ____________.

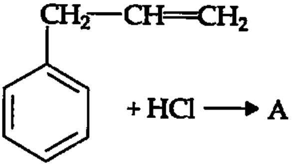
(*i*) *vic*-dihalide (*ii*) *gem*-dihalide

(*iii*) allylic halide (*iv*) vinylic halide

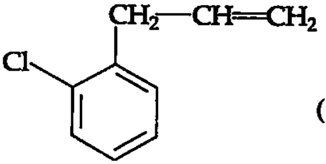
Ans. (*ii*)

Explanation: In *gem*-dihalides, halogen atoms are present on the same carbon atom. They are known as alkylidene halides $CH_3—CHCl_2$. Both halogen atoms are present on same carbon atom so, it is *gem*-dihalide.

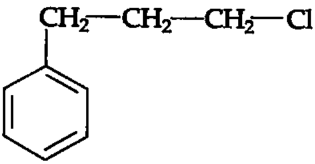
15. What is 'A' in the following reaction?



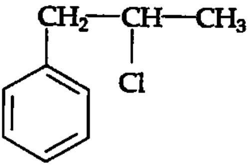
(*i*)



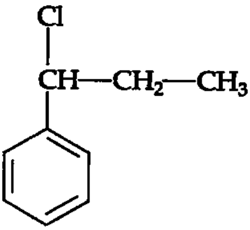
(*ii*)



(*iii*)



(*iv*)



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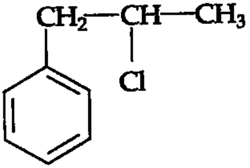
Ans. (*iii*)



Explanation: In this reaction addition of HCl takes place on doubly bonded carbon atom in accordance with Markovnikov's rule i.e., addition of negative addenum will take place on the carbon which has lesser number of hydrogen.

16. A primary alkyl halide would prefer to undergo ______________.

(*i*) S_N1 reaction (*ii*) S_N2 reaction

(*iii*) α-Elimination (*iv*) Racemisation

Ans. (*ii*)

Explanation: S_N2 type (bimolecular nucleophilic substitution). These reactions proceed in one step and the rate of reaction depends on concentration of alkyl halide as well as nucleophile *i.e.* $r = k[RX][Nu]$. It is a second order reaction. During S_N2 reaction inversion in configuration occurs *i.e.*, starting with dextrorotatory halide a laevo product is obtained and vice-versa.

17. Which of the following alkyl halides will undergo S_N1 reaction most readily?

(*i*) $(CH_3)_3C—F$ (*ii*) $(CH_3)_3C—Cl$

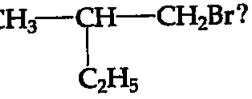
(*iii*) $(CH_3)_3C—Br$ (*iv*) $(CH_3)_3C—I$

Ans. (*iv*)

Explanation: **S_N1 type** (unimolecular nucleophilic substitution). These reactions proceed in two steps. The rate of reaction is dependent on step 1 *i.e.*, only on the concentration of alkyl halide $r = k\,[RX]$. It is a first order reaction.

R----------X bond length in case of iodine is highest and that is why lowest bond dissociation enthalpy. Therefore, I^- is known as best leaving group.

18. Which is the correct IUPAC name for



$CH_3—\underset{\displaystyle C_2H_5}{\underset{|}{C}H}—CH_2Br$?

(*i*) 1-Bromo-2-ethylpropane

(*ii*) 1-Bromo-2-ethyl-2-methylethane

(*iii*) 1-Bromo-2-methylbutane

(*iv*) 2-Methyl-1-bromobutane

Ans. (*iii*)

Explanation: Numbering will start from the carbon attached with halogen group and the longest chain will be selected.

19. What should be the correct IUPAC name for diethylbromomethane?

(*i*) 1-Bromo-1,1-diethylmethane

(*ii*) 3-Bromopentane

(*iii*) 1-Bromo-1-ethylpropane

(*iv*) 1-Bromopentane

Ans. (*i*)

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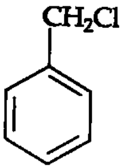
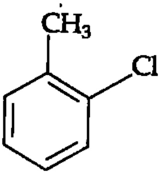
20. The reaction of toluene with chlorine in the presence of iron and in the absence of light yields ____________.

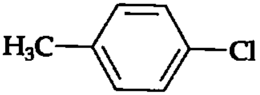
(*i*)



(*ii*)



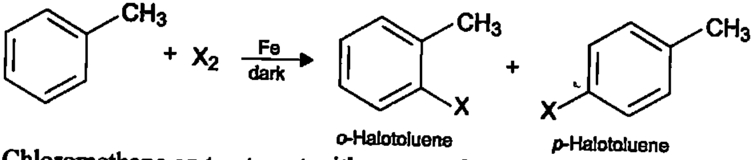
(*iii*)



(*iv*) Mixture of (*ii*) and (*iii*)

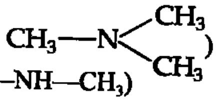
Ans. (*iv*)

Explanation:



21. Chloromethane on treatment with excess of ammonia yields mainly

(*i*) N, N-Dimethylmethanamine (



$CH_3{-}N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$)

(*ii*) N–methylmethanamine ($CH_3{-}NH{-}CH_3$)

(*iii*) Methanamine (CH_3NH_2)

(*iv*) Mixture containing all these in equal proportion

Ans. (*iii*)

Explanation: Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt.

$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

22. Molecules whose mirror image is non superimposable over them are known as chiral. Which of the following molecules is chiral in nature?

(*i*) 2-Bromobutane
(*ii*) 1-Bromobutane
(*iii*) 2-Bromopropane
(*iv*) 2-Bromopropan-2-ol

Ans. (*i*)

Explanation: The objects which are nonsuperimposable on their mirror images are called enantiomers. It occurs on that molecule which contains asymmetric carbon or chiral carbon *i.e.*, a carbon atom attached with four different group.

23. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows ______.

(*i*) S_N1 mechanism
(*ii*) S_N2 mechanism
(*iii*) Any of the above two depending upon the temperature of reaction
(*iv*) Saytzeff rule

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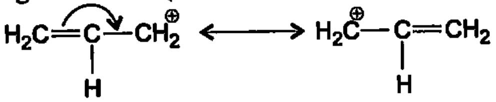
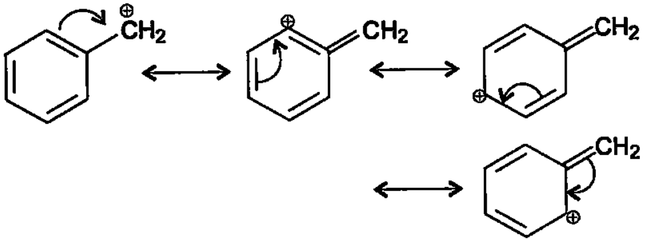
Ans. (*i*)

Explanation: Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides, 3^0 alkyl halides undergo S_N1 reaction very fast because of the high stability of 3^0 carbocations.

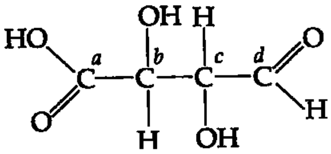
For the same reasons, allylic and benzylic halides show high reactivity towards the S_N1 reaction. The carbocation thus formed gets stabilised through resonance (Unit 12. Class XI) as shown below:



$$H_2C=\underset{H}{\underset{|}{C}}-\overset{\oplus}{C}H_2 \longleftrightarrow H_2\overset{\oplus}{C}-\underset{H}{\underset{|}{C}}=CH_2$$



24. Which of the carbon atoms present in the molecule given below are a symmetric?



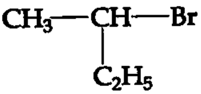
(*i*) *a*, *b*, *c*, *d*
(*ii*) *b*, *c*
(*iii*) *a*, *d*
(*iv*) *a*, *b*, *c*

Ans. (*ii*)

Explanation: If all the substituents attached to that carbon are different, such a carbon is called asymmetric carbon or stereocentre. The resulting molecule would lack symmetry and is referred to as asymmetric molecule. The asymmetry of the molecule is responsible for the optical activity in such organic compounds.

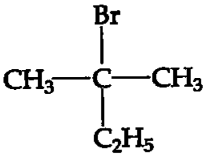
25. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion?

(*a*)



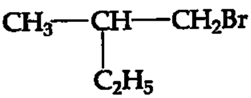
$CH_3-\underset{C_2H_5}{\underset{|}{CH}}-Br$

(*b*)



$CH_3-\overset{Br}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}-CH_3$

(*c*)



$CH_3-\underset{C_2H_5}{\underset{|}{CH}}-CH_2Br$

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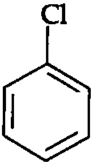
(*i*) (*a*)   (*ii*) (*a*), (*b*), (*c*)
(*iii*) (*b*), (*c*)   (*iv*) (*a*), (*c*)

Ans. (*i*)

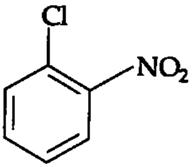
Explanation: A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as racemic mixture or racemic modification. A racemic mixture is represented by prefixing *dl* or case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation.

Note : In the questions 26 to 29 arrange the compounds in increasing order of rate of reaction towards nucleophilic substitution.

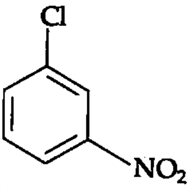
26. (*a*)



(*b*)



(c)



(*i*) (*a*) < (*b*) < (*c*)   (*ii*) (*c*) < (*b*) < (*a*)
(*iii*) (*a*) < (*c*) < (*b*)   (*iv*) (*c*) < (*a*) < (*b*)

Ans. (*iii*)

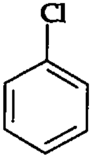
Explanation: Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(*i*) *Resonance effect :* In haloarenes, the electron pairs on halogen atom are in conjugation with electrons of the ring. C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

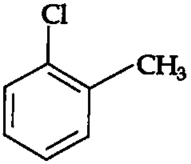
(*ii*) *Difference in hybridisation of carbon atom in C—X bond:* In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2-hybridised. The sp^2 hybridised carbon with a greater *s*-character is more electronegative and can hold the electron pair of C—X bond more tightly than *sp3*-hybridised carbon in haloalkane with less *s*-chararcter.

(*iii*) *Instability of phenyl cation:* In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out. The presence of an electron withdrawing group ($—NO_2$) at *ortho-* and *para-* positions increases the reactivity of haloarenes.

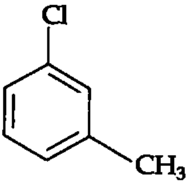
27. (*a*)



(*b*)



(*c*)



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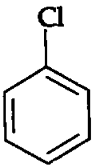
(*i*) (*a*) < (*b*) < (*c*)
(*ii*) (*a*) < (*c*) < (*b*)
(*iii*) (*c*) < (*b*) < (*a*)
(*iv*) (*b*) < (*c*) < (*a*)

Ans. (*iv*)

Explanation: The presence of electron releasing group at ortho-and para-positions decreases the reactivity of haloarenes. Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

28. (*a*)



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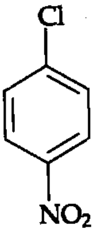
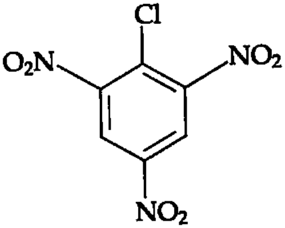


(*c*)

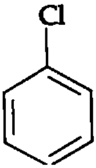


(*i*) (*c*) < (*b*) < (*a*)
(*ii*) (*b*) < (*c*) < (*a*)
(*iii*) (*a*) < (*c*) < (*b*)
(*iv*) (*a*) < (*b*) < (*c*)

Ans. (*iv*)

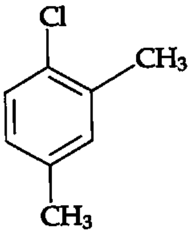
Explanation: The presence of an electron withdrawing group ($—NO_2$) at *ortho-* and *para*-positions increases the reactivity of haloarenes. The presence of nitro group at *ortho-* and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho-* and *para-* positions with respect to the halogen substituent is stabilised by $—NO_2$ group.

29. (*a*)



(*b*)

(*c*)



(*i*) (*a*) < (*b*) < (*c*)
(*ii*) (*b*) < (*a*) < (*c*)
(*iii*) (*c*) < (*b*) < (*a*)
(*iv*) (*a*) < (*c*) < (*b*)

Ans. (*iii*)

Explanation: The presence of electron releasing group at ortho-and para- positions decreases the reactivity of haloarenes. Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes. More the electron releasing group is attached lesser, will be the rate of reaction.

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30. Which is the correct increasing order of boiling points of the following compounds?

1-Iodobutane, 1-Bromobutane, 1-Chlorobutane, Butane

(*i*) Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane
(*ii*) 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane < Butane
(*iii*) Butane < 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane
(*iv*) Butane < 1-Chlorobutane < 1-Iodobutane < 1-Bromobutane

Ans. (*i*)

Explanation: For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI > RBr > RCl > RF. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

31. Which is the correct increasing order of boiling points of the following compounds?

1-Bromoethane, 1-Bromopropane, 1-Bromobutane, Bromobenzene

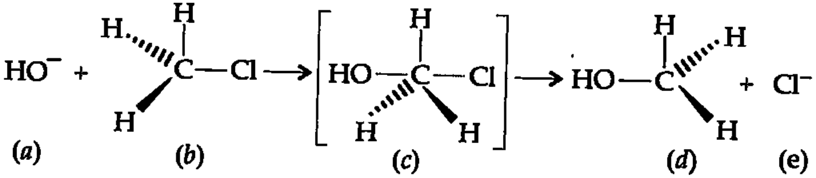
(*i*) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane
(*ii*) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane
(*iii*) 1-Bromopropane < 1-Bromobutane < 1-Bromoethane < Bromobenzene
(*iv*) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

Ans. (*iv*)

Explanation: The attractions get stronger as the molecules get bigger in size and have more electrons.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note: In the following questions two or more options may be correct.
Consider the following reaction and answer the questions no. 32–34.



32. Which of the statements are correct about above reaction?

(*i*) (*a*) and (*e*) both are nucleophiles.
(*ii*) In (*c*) carbon atom is sp^3 hybridised.
(*iii*) In (*c*) carbon atom is sp^2 hybridised.
(*iv*) (*a*) and (*e*) both are electrophiles.

Ans. (*i*) and (*iii*)

Explanation: It depicts a bimolecular nucleophilic displacement (S_N2) reaction; the incoming nucleophile interacts with alkyl halide causing the carbon halide bond to break while forming a new carbon-OH bond. These two processes take place simultaneously in a single step and no intermediate is formed. As the reaction progresses and the bond between

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the nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens. In part (c) it is the transition state where carbon atom of the substrate molecule is sp^2 hybridised.

33. Which of the following statements are correct about this reaction?

(*i*) The given reaction follows S_N2 mechanism.
(*ii*) (*b*) and (*d*) have opposite configuration.
(*iii*) (*b*) and (*d*) have same configuration.
(*iv*) The given reaction follows S_N1 mechanism.

Ans. (*i*) and (*ii*)

Explanation: As the S_N2 reaction progresses and the bond between the nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens. As this happens, the configuration of carbon atom under attack inverts in much the same way as an umbrella is turned inside out when caught in a strong wind, while the leaving group is pushed away. This process is called as inversion of configuration.

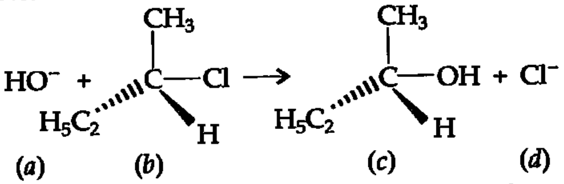
34. Which of the following statements are correct about the reaction intermediate?

(*i*) Intermediate (c) is unstable because in this carbon is attached to 5 atoms.
(*ii*) Intermediate (c) is unstable because carbon atom is sp^2 hybridised.
(*iii*) Intermediate (c) is stable because carbon atom is sp^2 hybridised.
(*iv*) Intermediate (c) is less stable than the reactant (b).

Ans. (*i*) and (*iv*)

Explanation: In the transition state, the carbon atom is simultaneously bonded to incoming nucleophile and the outgoing leaving group and such structures are unstable and cannot be isolated. This is because the carbon atom in the transition state is simultaneously bonded to five atoms and therefore is unstable.

Answer Q. No. 35 and 36 on the basis of the following reaction.



35. Which of the following statements are correct about the mechanism of this reaction?

(*i*) A carbocation will be formed as an intermediate in the reaction.
(*ii*) OH^- will attach the substrate (b) from one side and Cl^- will leave it simultaneously from other side.
(*iii*) An unstable intermediate will be formed in which OH^- and Cl^- will be attached by weak bonds.
(*iv*) Reaction proceeds through S_N1 mechanism.

Ans. (*i*) and (*iv*)

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Explanation: It occurs in two steps. In step I, the polarised C—Cl bond undergoes slow cleavage to produce a carbocation and a chloride ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction. It must be noted that the 2° halides may proceed either through S_N1 or S_N2 type. The preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction depict that the reaction is followed by S_N1 mechanism.

36. Which of the following statements are correct about the kinetics of this reaction?
    (*i*) The rate of reaction depends on the concentration of only (b).
    (*ii*) The rate of reaction depends on concentration of both (a) and (b).
    (*iii*) Molecularity of reaction is one.
    (*iv*) Molecularity of reaction is two.

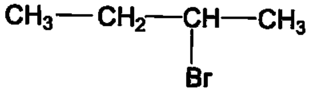
Ans. (*i*) and (*iii*)

Explanation: S_N1 occurs in two steps. In step I, the polarised C—Cl bond undergoes slow cleavage to produce a carbocation and a chloride ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction. Step I is the slowest and reversible. It involves the C–Cl bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent. Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion.

37. Haloalkanes contain halogen atom (s) attached to the sp^3 hybridised carbon atom of an alkyl group. Identify haloalkane from the following compounds.
    (*i*) 2-Bromopentane
    (*ii*) Vinyl chloride (chloroethene)
    (*iii*) 2-chloroacetophenone
    (*iv*) Trichloromethane

Ans. (*i*) and (*iv*)

Explanation:



$$CH_3—CH_2—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$$

Here the –bromo group is attached to a carbon which is sp^3 hybridised. Similarly, in trichloromethane also the carbon atom is sp^3 hybridised which is directly attached to the chloro group. In vinyl chloride and 2-chloroacetophenone, halo group is attached to sp^2 carbon.

38. Ethylene chloride and ethylidene chloride are isomers. Identify the correct statements.
    (*i*) Both the compounds form same product on treatment with alcoholic KOH.
    (*ii*) Both the compounds form same product on treatment with aq.NaOH.

(*iii*) Both the compounds form same product on reduction.

(*iv*) Both the compounds are optically active.

Ans. (*i*) and (*iii*)

Explanation: Both will give ethyne on treatment with alc. KOH and both will give ethane on reduction.

39. Which of the following compounds are *gem*-dihalides?

(*i*) Ethylidene chloride (*ii*) Ethylene dichloride

(*iii*) Methylene chloride (*iv*) Benzyl chloride

Ans. (*i*) and (*iii*) $\underset{\substack{\text{Ethylidene chloride} \\ (gem\text{-dihalide})}}{H_3C{-}CHCl_2}$ and methylene chloride CH_2Cl_2.

40. Which of the following are secondary bromides?

(*i*) $(CH_3)_2CHBr$ (*ii*) $(CH_3)_3C\ CH_2Br$

(*iii*) $CH_3CH(Br)CH_2CH_3$ (*iv*) $(CH_3)_2CBrCH_2CH_3$

Ans. (*i*) and (*iii*)

Explanation: $(CH_3)_2CHBr$ - Bromide group is attached to sec –carbon or 2°C. $CH_3CH(Br)CH_2CH_3$ - here also, the Bromide group is attached to sec- carbon or 2°C.

41. Which of the following compounds can be classified as aryl halides?

(*i*) *p*-$ClC_6H_4CH_2CH(CH_3)_2$

(*ii*) *p*-$CH_3CHCl(C_6H_4)CH_2CH_3$

(*iii*) *o*-BrH_2C-$C_6H_4CH(CH_3)CH_2CH_3$

(*iv*) C_6H_5-Cl

Ans. (*i*) and (*iv*)

Explanation: *Aryl halides*: These are the compounds in which the halogen atom is bonded to the sp^2-hybridised carbon atom of an aromatic ring.

42. Alkyl halides are prepared from alcohols by treating with

(*i*) HCl + $ZnCl_2$ (*ii*) Red P + Br_2

(*iii*) H_2SO_4 + KI (*iv*) All the above

Ans. (*i*) and (*ii*)

Explanation:

$$R{-}OH + HX \xrightarrow{ZnCl_2} R{-}X + H_2O$$

$$R{-}OH \xrightarrow[X_2 = Br_2,\, I_2]{\text{red } P/X_2} R{-}X$$

43. Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of ____________ or ____________.

(*i*) Ca F_2 (*ii*) CoF_2

(*iii*) Hg_2F_2 (*iv*) NaF

Ans. (*ii*) and (*iii*)

Explanation: The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3. The reaction is termed as Swarts reaction.

$$CH_3Br + AgF \rightarrow CH_3F^- + Ag^-Br$$

III. SHORT ANSWER TYPE

44. Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does preparation of aryl iodides requires presence of an oxidising agent?

Ans. Preparation of aryl iodides requires presence of an oxidising agent because, the HI formed during the reaction is a strong reducing agent, which make the reaction reversible.

That is why iodination is carried out in presence of strong oxidizing agent which covert HI into iodine.

45. Out of o-and p-dibromobenzene which one has higher melting point and why?

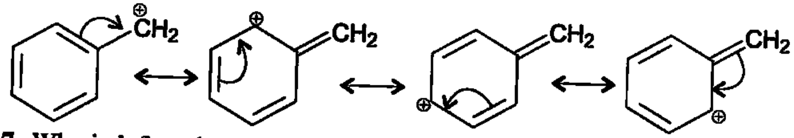
Ans. The *para*-isomers are high melting as compared to their *ortho* and *meta*-isomers. It is due to symmetry of *para*-isomers that fits in crystal lattice better as compared to *ortho*- and *meta*-isomers.

46. Which of the compounds will react faster in S_N1 reaction with the ^-OH ion?

$$CH_3—CH_2—Cl \text{ or } C_6H_5—CH_2—Cl$$

Ans. S_N1 reaction depends on the stability of the carbocation since the benzylic cation is more stable than alkyl carbocation.

Benzylic carbocation can be stabilized by resonance. Thus, the rate will be faster in $C_6H_5CH_2Cl$.



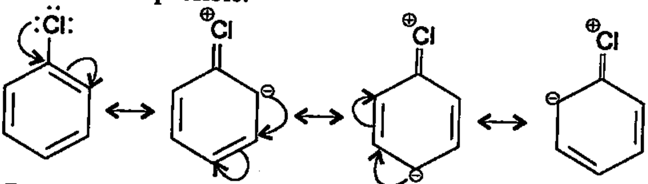
47. Why iodoform has appreciable antiseptic property?

Ans. It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodinens:

48. Haloarenes are less reactive than haloalkanes and haloalkenes. Explain.

Ans. Haloarenes are less reactive than haloalkanes and haloalkenes due to following reasons:

(*i*) *Resonance effect:* In haloarenes, the electron pairs on halogen atom are in conjugation with electrons of the ring and the following resonating structures are possible.



C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than

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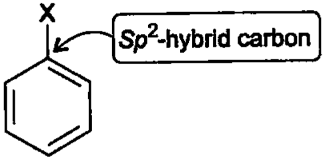
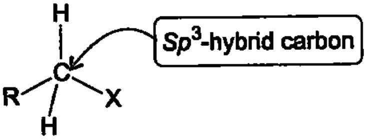
haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(*ii*) *Difference in hybridisation of carbon atom in C—X bond:* In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2 hybridised.





The sp^2 hybridised carbon with a greater *s*-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3 hybridised carbon in haloalkane with less *s* chararcter. Thus, C—Cl bond-length in haloalkane is 177 pm while in haloarene is 169 pm. Since, it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(*iii*) *Instability of phenyl cation:* Because of the possible repulsion, it is less likely for the electron-rich nucleophile to approach electron-rich arenes.

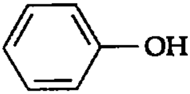
49. Discuss the role of Lewis acids in the preparation of aryl bromides and chlorides in the dark.

Ans. Role of Lewis acid in this reaction is to generate electrophile. Arenes are characterised by electrophilic substitution reactions proceeded via the following three steps:

(*a*) Generation of the eletrophile
(*b*) Formation of carbocation intermediate
(*c*) Removal of proton from the carbocation intermediate.

50. Which of the following compounds (*a*) and (*b*) will not react with a mixture of NaBr and H_2SO_4. Explain why?

(*a*) $CH_3CH_2CH_2OH$ (*b*)



Ans. Phenol will not react with NaBr + H_2SO_4

C—O bond in phenols has partial double bond character due to this it is difficult to cleave.

51. Which of the products will be major product in the reaction given below? Explain.

$$\underset{}{CH_3CH{=}CH_2} + HI \longrightarrow \underset{(A)}{CH_3CH_2CH_2I} + \underset{(B)}{CH_3CHICH_3}$$

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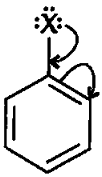
Ans. 'B' will be the major product as the reaction is followed by the formation of carbocation; and secondary carbocation is more stable.

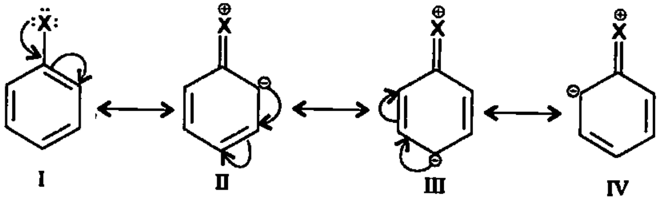
52. Why is the solubility of haloalkanes in water very low?

Ans. The haloalkanes are only very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low.

53. Draw other resonance structures related to the following structure and find out whether the functional group present in the molecule is ortho, para directing or meta directing.



Ans. Ortho-para directing due to increase in the electron density at ortho and para positions.



54. Classify the following compounds as primary, secondary and tertiary halides.

(*i*) 1-Bromobut-2-ene (*ii*) 4-Bromopent-2-ene

(*iii*) 2-Bromo-2-methylpropane

Ans. $CH_3—CH{=}CH—CH_2—Br$ (primary halide)

$CH_3—CH{=}CH—CHBr—CH_3$ (secondary halide)

$(CH_3)_3CBr$ (tertiary halide)

55. Compound 'A' with molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.

(*i*) Write down the structural formula of both compounds 'A' and 'B'.

(*ii*) Out of these two compounds, which one will be converted to the product with inverted configuration.

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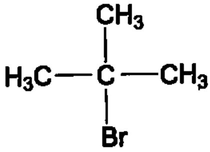
Ans. A is *tert*-butyl Bromide



$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3$$

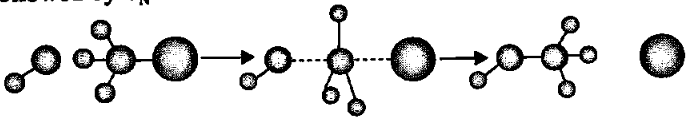
Since the rate of reaction depends on the concentration of A only, it is followed by S_N1 mechanism.

'B' is *sec*-butyl bromide -

$$CH_3CH_2\underset{\underset{\displaystyle Br}{|}}{C}HCH_3$$

As the compound B is optically active, it must be 2-bromobutane.

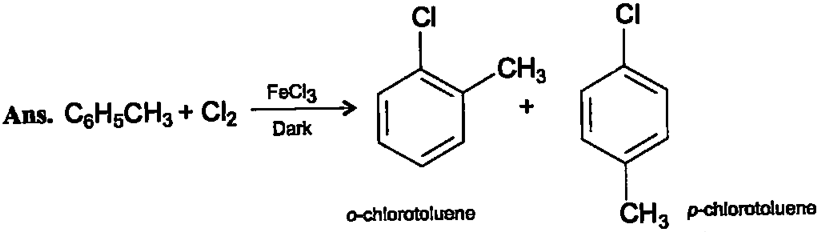
As the rate of reaction depends on the concentration of both it means it is followed by S_N2 mechanism.



S_N2 results in inversion of configuration.

56. Write the structures and names of the compounds formed when compound 'A' with molecular formula, C_7H_8 is treated with Cl_2 in the presence of $FeCl_3$.

Ans.



57. Identify the products A and B formed in the following reaction :

(*a*) $CH_3-CH_2-CH=CH-CH_3 + HCl \longrightarrow A + B$

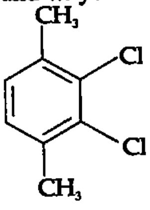
Ans. $CH_3CH_2-CH=CH-CH_3 + HCl \longrightarrow$

$CH_3CH_2-CHCl-CH_2-CH_3 + CH_3CH_2-CH_2-CHCl-CH_3$

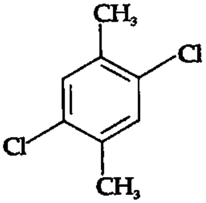
2- chloropentane (Minor) 3-chloropentane (Major)

Sec carbocation is more stable than primary. The major product is 3-chloropentane.

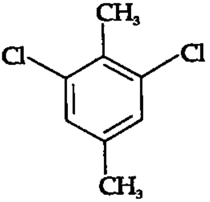
58. Which of the following compounds will have the highest melting point and why?



(I)



(II)



(III)

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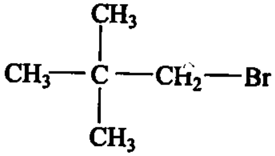
Ans. Compound II will have higher melting point since both CH_3 and Cl are at para position. The *para*-isomers are high melting as compared to their *ortho* and *meta*-isomers. It is due to symmetry of *para*-isomers that fits in crystal lattice better as compared to *ortho*- and *meta*-isomers.

59. Write down the structure and IUPAC name for neo-pentylbromide.

Ans. IUPAC Name: 1-Bromo-2,2 dimethylpropane

Structure:



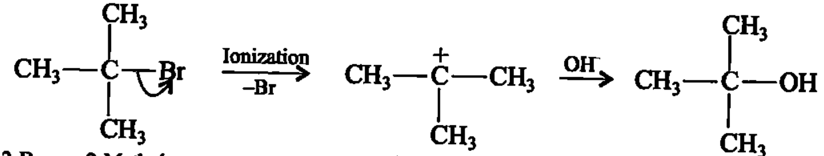
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-Br$$

60. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photo chlorination. Give the structure of the hydrocarbon.

Ans. As hydrocarbon is alkane whose general formula is Co H_{2n+2}. Hence it is C5H12 as molar mass is 72. As such alkane on monochlorination forms single product hence it must have only one type of hydrogen. Due to this reason, such alkane can only be 2, 2-dimethylpropane (neo-pentane).

61. Name the alkene which will yield 1-chloro-1-methylcyclohexane by its reaction with HCl. Write the reactions involved.

Ans. It can be any one in between; 2-bromo-2-methylpropane (Hi) is a 3° alkyi bromide. It readily undergoes ionization for a stable 3° carbocation. Therefore, it reacts with aq. KOH most readily.



2-Bromo-2-Methylpropane

3$^+$ carbocation (stable)

2-methyl-2-proponal

62. Which of the following haloalkanes reacts with aqueous KOH most easily? Explain giving reason.

(*i*) 1-Bromobutane (*ii*) 2-Bromobutane

(*iii*) 2-Bromo-2-methylpropane (iv) 2-Chlorobutane

Ans. (*iii*) **Reason:** The tertiary carbocation formed in the reaction is stable.

63. Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of $ZnCl_2$?

Ans. Method is not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond.

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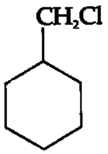
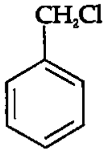
64. Which of the following compounds would undergo S_N1 reaction faster and why?



(A)



(B)

Ans. 'B'compound will undergo S_N1 reaction faster because the carbocation formed gets stabilised through resonance.

Resonating structure of Benzyl is shown in ans: no. 46.

65. Allyl chloride is hydrolysed more readily than n-propyl chloride. Why?

Ans. Allyl chloride will be hydrolyzed more readily because the reaction proceeds through S_N1 mechanism and carbocation formed in case of allylic chloride is stabilized by resonance whereas; carbocation formed by propyl chloride is not stabilized by resonance.

66. Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?

Ans. Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols and amines are sufficiently acidic to convert them to corresponding hydrocarbons.

It is therefore necessary to avoid even traces of moisture from a Grignard reagent.

67. How do polar solvents help in the first step in S_N1 mechanism?

Ans. S_N1 occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction. Step I is the slowest and reversible. It involves the C—Br bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent.

68. Write a test to detect the presence of double bond in a molecule.

Ans. Presence of multiple bond in a molecule can be tested by following methods: The alkaline potassium permanganate solution is known as Baeyer's reagent. It has bright pink colour. It oxidizes alkenes to glycols which is colourless. This reaction is used as a test for the presence of double bond in a molecule. This is also known as Baeyer's test.

$$CH_3—CH{=}CH_2 \xrightarrow[(ii)\,H^+\,\Delta]{(i)\,Alk.KMnO_4} CH_3COOH + CO_2 + H$$

Bromine water test can also be done to detect the presence of double bond.

69. Diphenyls are potential threat to the environment. How are these produced from arylhalides?

Ans. Diphenyl can be prepared by treating two molecules of aryl halide with two molecules of sodium in presence of dry ether. The reaction is called Wurtz -fittig reaction.

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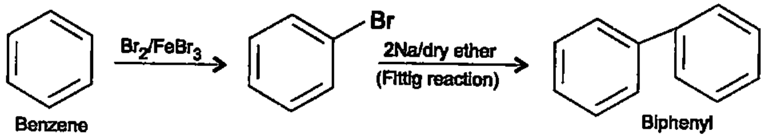
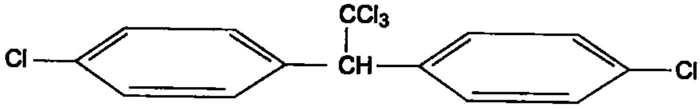


70. What are the IUPAC names of the insecticide DDT and benzenehexachloride? Why is their use banned in India and other countries?

Ans. IUPAC name of DDT is 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane



DDT

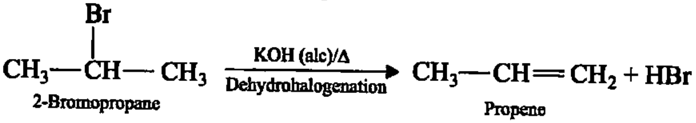
IUPAC name of benzenehexachloride is 1,2,3,4,5,6-hexachlorocyclohexane.

DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time. Thus the use of DDT was banned.

71. Elimination reactions (especially β-elimination) are as common as the nucleophilic substitution reaction in case of alkyl halides. Specify the reagents used in both cases.

Ans. When a haloalhydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from beta-carbon and a halogen atom from the α-carbon atom. As a result, an alkene is formed as a product.

Since beta-hydrogenation is involved in elimination, it is often called beta-elimination. An alkyl halide with α-hydrogen atoms when reacted with a base or a nucleophile has two competing routes: substitution (S_N1 and S_N2) and elimination. Which route will be taken up, depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions. For example:

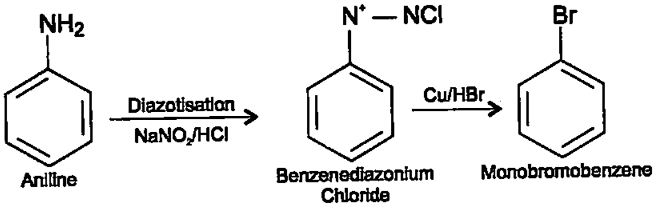


$$\underset{\text{2-Bromopropane}}{CH_3-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3} \xrightarrow[\text{Dehydrohalogenation}]{\text{KOH (alc)}/\Delta} \underset{\text{Propene}}{CH_3-CH=CH_2} + HBr$$

When same alkyl halide treated with aq KOH at low temperature, the product will be 2-propanol.

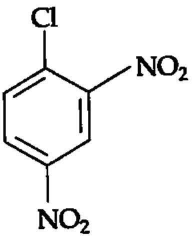
72. How will you obtain monobromobenzene from aniline?

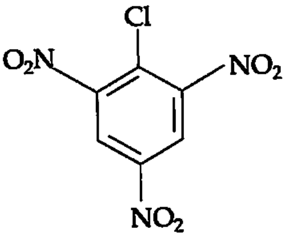
Ans. **Sandmeyer's reaction:** When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by —Cl or —Br.



73. Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution:


(I)


(II)


(III)

Ans. The order of reactivity will be I < II < III

The presence of nitro group at *ortho-* and *para* -positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho-* and *para-* positions with respect to the halogen substituent is stabilised by $-NO_2$ group.

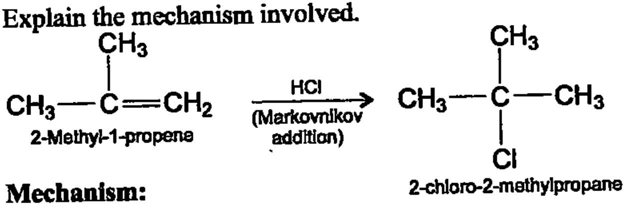
74. tert-Butylbromide reacts with aq. NaOH by S_N1 mechanism while n-butylbromide reacts by S_N2 mechanism. Why?

Ans. *n*-butyl bromide reacts by S_N2 mechanism because there is less steric hinderance. Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles. Thus, the order of reactivity followed is:

Primary halide > Secondary halide > Tertiary halide. Further, in S_N1 greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides, 3^0 alkyl halides undergo S_N1 reaction very fast because of the high stability of 3^0 carbocations.

75. Predict the major product formed when HCl is added to isobutylene. Explain the mechanism involved.

Ans.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow[\text{(Markovnikov addition)}]{HCl} CH_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

2-Methyl-1-propene

2-chloro-2-methylpropane

Mechanism:

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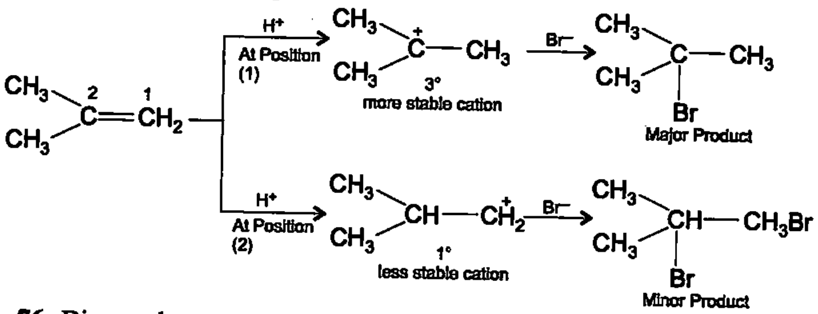
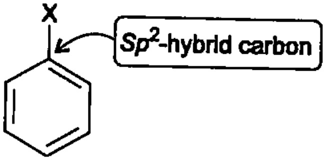
Markovnikov rule: Negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms, e.g.

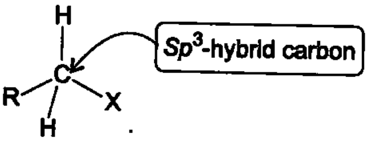


76. Discuss the nature of C—X bond in the haloarenes.

Ans. In haloarenes, C—X bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2-hybridised.





The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3 hybridised carbon in haloalkane with less s-chararcter. Thus, C—Cl bond-length in haloalkane is 177pm while in haloarene is 169 pm.

77. How can you obtain iodoethane from ethanol when no other iodine containing reagent except NaI is available in the laboratory?

Ans. $C_2H_5OH \xrightarrow{ZnCl_2/conc\ HCl} C_2H_5Cl + NaI \xrightarrow{dry\ acetone} C_2H_5I + NaCl$

78. Cyanide ion acts as an ambident nucleophile. From which end it acts as a stronger nucleophile in aqueous medium? Give reason for your answer.

Ans. Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. Actually cyanide group is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways $:C\equiv N:^-$], i.e., linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides. It acts

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as a stronger nucleophile from the carbon end because it will lead to the formation of C—C bond which is more stable than the C—N bond.

$$\underset{\text{Ethylchloride}}{CH_3—CH_2—Cl} \xrightarrow[\text{(nucleophilic substitution)}]{\text{KCN, aq. ethanol}} \underset{\text{Propanenitrile}}{CH_3—CH_2—CN}$$

IV. MATCHING TYPE

Note : Match the items given in Column I and Column II in the following questions:

79. Match the compounds given in Column I with the effects given in Column II.

Column I	Column II
(*i*) Chloramphenicol	(*a*) Malaria
(*ii*) Thyroxine	(*b*) Anaesthetic
(*iii*) Chloroquine	(*c*) Typhoid fever
(*iv*) Chloroform	(*d*) Goiter
	(*e*) Blood substituent

Ans. (*i*) → (*c*) (*ii*) → (*d*) (*iii*) → (*a*) (*iv*) → (*b*)

Explanation:

Column I	Column II
(*i*) Chloramphenicol	(*c*) Typhoid fever (chloramphenicol is a broad-spectrum antibiotic used in the treatment of typhoid fever)
(*ii*) Thyroxine	(*d*) Goiter (Thyroxine is a hormone secreted by thyroid gland. Patient with hyperthyroidism have an enlarged thyroid gland *i.e.*, goiter)
(*iii*) Chloroquine	(*a*) Malaria (Chloroquine prevents the development of malaria in blood)
(*iv*) Chloroform	(*b*) Anaesthetic (Chloroform is a colourless volatile liquid. Its vapours decreases the activity of central nervous system and is used as an anaesthetic.)

80. Match the items of Column I and Column II.

Column I	Column II
(*i*) S_N1 reaction	(*a*) *vic*-dibromides
(*ii*) Chemicals in fire extinguisher	(*b*) *gem*-dihalides
(*iii*) Bromination of alkenes	(*c*) Racemisation
(*iv*) Alkylidene halides	(*d*) Saytzeff rule
(*v*) Elimination of HX from alkyl halide	(*e*) Chlorobromocarbons

Ans. (*i*) → (*c*) (*ii*) → (*e*) (*iii*) → (*a*) (*iv*) → (*b*) (*v*) → (*d*)

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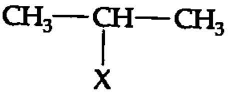
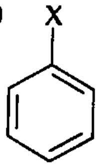
Explanation:

Column I	Column II
(*i*) S_N1 reaction	(*c*) Racemisation (S_N1 reactions results in the formation of racemic mixture. A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as racemic mixture or racemic modification)
(*ii*) Chemicals in the fire extinguisher	(*e*) Chlorobromocarbons (used as fire extinguisher)
(*iii*) Bromination of alkenes	(*a*) *vic*- dibromides (These are the compounds in which the halogen atom is bonded to an sp^2 hybridised carbon atom of a carbon-carbon double bond)
(*iv*) Alkylidene halides	(*b*) *gem*-dihalides ((halogen atoms are present on the same carbon atom)
(*v*) Elimination of HX from alkyl halide	(*d*) Saytzeff rule (in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.)

81. Match the structures of compounds given in Column I with the classes of compounds given in Column II.

Column I	Column II
(*i*)  $CH_3-\underset{\underset{X}{\vert}}{CH}-CH_3$	(*a*) Aryl halide
(*ii*) $CH_2=CH-CH_2-X$	(*b*) Alkyl halide
(*iii*) 	(*c*) Vinyl halide
(*iv*) $CH_2=CH-X$	(*d*) Allyl halide

Ans. (*i*) → (*b*) (*ii*) → (*d*) (*iii*) → (*a*) (*iv*) → (*c*)

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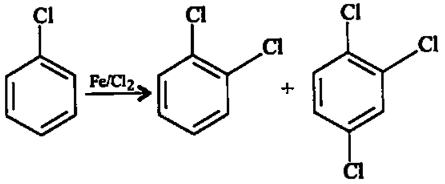
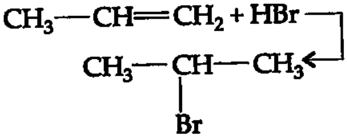
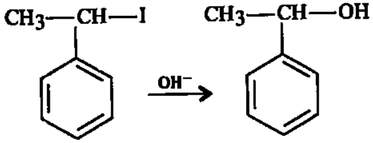
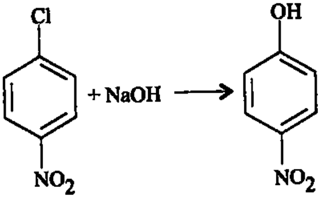
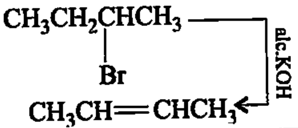
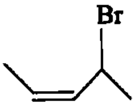
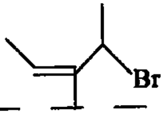
82. Match the reactions given in Column I with the types of reactions given in Column II.

Column I	Column II
(*i*) 	(*a*) Nucleophilic aromatic substitution
(*ii*)  $CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{Br}{\underset{\mid}{CH}}-CH_3$	(*b*) Electrophilic aromatic substitution
(*iii*) 	(*c*) Saytzeff elimination
(*iv*) 	(*d*) Electrophilic addition
(*v*)  $CH_3CH_2\underset{Br}{\underset{\mid}{C}}HCH_3 \xrightarrow{alc.KOH} CH_3CH=CHCH_3$	(*e*) Nucleophilic substitution (S_N1)

Ans. (*i*) → (*b*) (*ii*) → (*d*) (*iii*) → (*e*) (*iv*) → (*a*) (*v*) → (*c*)

83. Match the structures given in Column I with the names in Column II.

Column I	Column II
(*i*) 	(*a*) 4-Bromopent-2-ene
(*ii*) 	(*b*) 4-Bromo-3-methylpent-2-ene

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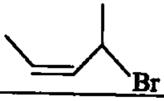
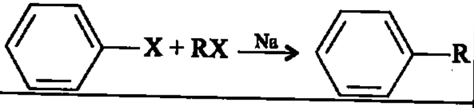
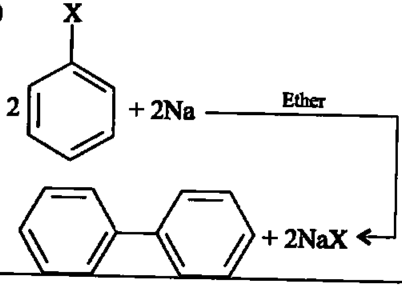
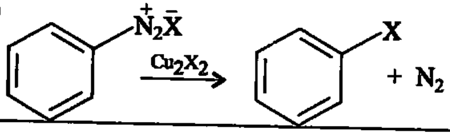
(*iii*) 	(*c*) 1-Bromo-2-methylbut-2-ene
(*iv*) 	(*d*) 1-Bromo-2-methylpent-2-ene

Ans. (*i*) → (*a*) (*ii*) → (*c*) (*iii*) → (*b*) (*iv*) → (*d*)

84. Match the reactions given in Column I with the names given in Column II.

Column I	Column II
(*i*) 	(*a*) Fittig reaction
(*ii*) 	(*b*) Wurtz-Fittig reaction
(*iii*) 	(*c*) Finkelstein reaction
(*iv*) $C_2H_5Cl + NaI \xrightarrow{\text{dry acetone}} C_2H_5I + NaCl$	(*d*) Sandmeyer reaction

Ans. (*i*) → (*b*) (*ii*) → (*a*) (*iii*) → (*d*) (*iv*) → (*c*)

V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are correct and reason is correct explanation of assertion.

(*ii*) Assertion and reason both are wrong statements.

(*iii*) Assertion is correct but reason is wrong statement.

(*iv*) Assertion is wrong but reason is correct statement.

(*v*) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

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85. **Assertion** : Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.

Reason : Phosphorus chlorides give pure alkyl halides.

Ans. (*ii*)

Explanation: Thionyl chloride is preferred because the other two products are escapable gases. Hence, the reaction gives pure alkyl halides.

86. **Assertion** : The boiling points of alkyl halides decrease in the order : RI > RBr > RCl > RF

Reason : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

Ans. (*v*)

Explanation: For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI > RBr > RCl > RF. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

87. **Assertion** : KCN reacts with methyl chloride to give methyl isocyanide

Reason : CN^- is an ambident nucleophile.

Ans. (*iv*)

Explanation: KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond.

88. **Assertion** : tert-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

Reason : In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

Ans. (*i*)

Explanation: Wurtz reaction: A reaction in which alkyl halides react with sodium in dry ether to give a hydrocarbon containing double the number of carbon atoms present in the halide.

89. **Assertion** : Presence of a nitro group at *ortho* or *para* position increases the reactivity of haloarenes towards nucleophilic substitution.

Reason : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

Ans. (*i*)

Explanation: The presence of nitro group at *ortho*- and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho-* and *para-* positions with respect to the halogen substituent is stabilised by —NO_2 group.

90. Assertion : In monohaloarenes, further electrophilic substitution occurs at *ortho* and *para* positions.

Reason : Halogen atom is a ring deactivator.

Ans. (*v*)

Explanation: Halogen atom besides being slightly deactivating is *o, p*-directing; therefore, further substitution occurs at *ortho-* and *para-* positions with respect to the halogen atom. The *o, p*-directing influence of halogen atom can be easily understood if we consider the resonating structures.

91. Assertion : Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.

Reason : Oxidising agent oxidises I_2 into HI.

Ans. (*iii*)

Explanation: Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO_3, HIO_4) to oxidise the HI formed during iodination.

92. Assertion : It is difficult to replace chlorine by –OH in chlorobenzene in comparison to that in chloroethane.

Reason : Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance.

Ans. (*i*)

Explanation: It is difficult to replace chlorine by —OH in chlorobenzene in comparison to that in chloroethane.

93. Assertion : Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.

Reason : This reaction proceeds through the formation of a carbocation.

Ans. (*iii*)

Explanation: Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration because the reaction proceeds through S_N2 mechanism.

94. Assertion : Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene

Reason : —NO_2 group is a *m*-directing group.

Ans. (*iv*)

Explanation: Halogen atom besides being slightly deactivating is o, *p*-directing; therefore, further substitution occurs at *ortho-* and *para-* positions with respect to the halogen atom.

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VI. LONG ANSWER TYPE

95. Some alkyl halides undergo substitution whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.

Ans. An alkyl halide with hydrogen atoms, when reacted with a base or a nucleophile, has two competing routes: substitution (S_N1 and S_N2) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions. Thus, a bulkier nucleophile will prefer to act as a base and abstracts a proton rather than approach a tetravalent carbon atom (steric reasons) and vice-versa.

Similarly, a primary alkyl halide will prefer a S_N2 reaction, a secondary halide-S_N2 or elimination depending upon the strength of base/ nucleophile and a tertiary halide- S_N1 or elimination depending upon the stability of carbocation or the more substituted alkene.

$$(ii)\ \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc)/}\Delta} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

If the same reaction is carried out in presence of aq KOH, 1-propanol will be the product.

96. Some halogen containing compounds are useful in daily life. Some compounds of this class are responsible for exposure of flora and fauna to more and more of UV light which causes destruction to a great extent. Name the class of these halocompounds. In your opinion, what should be done to minimise harmful effects of these compounds.

Ans. **Dichloromethane (Methylene Chloride):** Dichloromethane is widely used as a solvent, as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent.

Trichloromethane (Chloroform): Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22.

Triiodomethane (Iodoform): It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself.

Tetrachloromethane (Carbon tetrachloride): It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.

Freons: The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use.

Green chemistry is a production process that aims at using the existing knowledge and principles of chemistry for developing and implementing chemical products and processes to reduce the use and generation of substances hazardous to the environment. The release of different harmful chemicals (particulates, gases, organic and inorganic wastes) causes environmental pollution. In green chemistry, the reactants to be used in chemical reactions are chosen in such a way that the yield of the end products is up to 100%. This prevents or limits chemical pollutants from being introduced.

97. Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides? How can we enhance the reactivity of aryl halides?

Ans. Aryl halides are extremely less reactive towards nucleophilic substitution due to following reasons:

(*i*) **Resonance effect:** In haloarenes, the electron pairs on halogen atom are in conjugation with the ring. C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(*ii*) **Difference in hybridisation of carbon atom in C—X bond:** In haloalkane, the carbon atom attached to halogen is sp^3-hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2-hybridised.

(*iii*) **Instability of phenyl cation:** In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out. Because of the possible repulsion, it is less likely for the electron-rich nucleophile to approach electron-rich arenes.

❑❑❑

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11 Alcohols, Phenols and Ethers

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields

(*i*) *o*-Cresol
(*ii*) *m*-Cresol
(*iii*) 2, 4-Dihydroxytoluene
(*iv*) Benzyl alcohol

Ans. (*iv*)

Explanation: Monochlorination of toluene in sunlight gives benzyl chloride. On hydrolysis with aq. NaOH, benzyl chloride, shows nucleophilic substitution reaction to give benzyl alcohol.

2. How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?

(*i*) 1
(*ii*) 2
(*iii*) 3
(*iv*) 4

Ans. (*i*)

Explanation: If all four groups or atoms attached to the carbon atom are different, such a carbon is called asymmetric carbon or chiral carbon.

3. What is the correct order of reactivity of alcohols in the following reaction?

$$R—OH + HCl \xrightarrow{ZnCl_2} R—Cl + H_2O$$

(*i*) $1° > 2° > 3°$
(*ii*) $1° < 2° > 3°$
(*iii*) $3° > 2° > 1°$
(*iv*) $3° > 1° > 2°$

Ans. (*iii*)

Explanation: This reaction is a type of nucleophilic substitution reaction in which — OH group is replaced by — Cl. The intermediate formed by tertiary alcohol is more stable as 3° carbocation is more stable than primary and secondary carbocation. Thus, the order of reactivity of alcohol will be $3° > 2° > 1°$.

4. CH_3CH_2OH can be converted into CH_3CHO by ____________.

(*i*) catalytic hydrogenation
(*ii*) treatment with $LiAlH_4$
(*iii*) treatment with pyridinium chlorochromate
(*iv*) treatment with $KMnO_4$

Ans. (*iii*)

Explanation: A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

5. The process of converting alkyl halides into alcohols involves____________.

(*i*) addition reaction
(*ii*) substitution reaction
(*iii*) dehydrohalogenation reaction
(*iv*) rearrangement reaction

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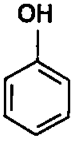
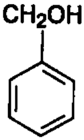
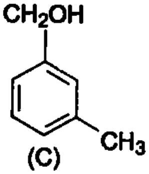
Ans. (*ii*)

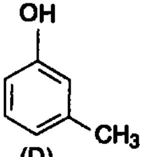
Explanation: The reaction is a type of nucleophilic substitution reaction in which —Cl group is replaced by —OH .

6. Which of the following compounds is aromatic alcohol?


(A)


(B)


(C)

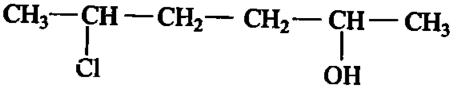

(D)

(*i*) A, B, C, D
(*ii*) A, D
(*iii*) B, C
(*iv*) A

Ans. (*iii*)

Explanation: Phenol is also known as, carbolic acid and it cannot be considered as aromatic alcohol. On the other hand in compound (B) and (C)—OH group is bonded to sp^3 hybridized carbon which is bonded to benzene ring.

7. Give IUPAC name of the compound given below.



$$\underset{\displaystyle Cl}{CH_3—\underset{|}{C}H—CH_2—CH_2—\underset{|}{C}H—CH_3}$$

$$CH_3—\underset{\underset{\displaystyle Cl}{|}}{CH}—CH_2—CH_2—\underset{\underset{\displaystyle OH}{|}}{CH}—CH_3$$

(*i*) 2-Chloro-5-hydroxyhexane
(*ii*) 2-Hydroxy-5-chlorohexane
(*iii*) 5-Chlorohexan-2-ol
(*iv*) 2-Chlorohexan-5-ol

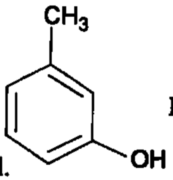
Ans. (*iii*)

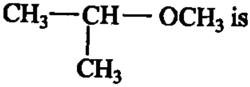
Explanation: —OH group will be given priority.

8. IUPAC name of *m*-cresol is ___________.

(*i*) 3-methylphenol
(*ii*) 3-chlorophenol
(*iii*) 3-methoxyphenol
(*iv*) benzene-1,3-diol

Ans. (*i*)

Explanation:  IUPAC name of the compound is 3-methylphenol.



9. IUPAC name of the compound $CH_3—\underset{\underset{\displaystyle CH_3}{|}}{CH}—OCH_3$ is ___________.

(*i*) 1-methoxy-1-methylethane
(*ii*) 2-methoxy-2-methylethane
(*iii*) 2-methoxypropane
(iv) isopropylmethyl ether

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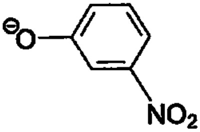
Ans. (*iii*)

Explanation: IUPAC name of the compound is 2-methoxypropane.

10. Which of the following species can act as the strongest base?

(*i*) $^{\ominus}OH$ (*ii*) $^{\ominus}OR$

(*iii*) $^{\ominus}O\,C_6H_5$ (*iv*)



Ans. (*ii*)

Explanation: Weakest acid has the strongest conjugate base. Among all the four options ROH is the weakest acid.

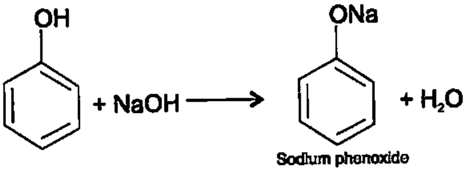
11. Which of the following compounds will react with sodium hydroxide solution in water?

(*i*) C_6H_5OH (*ii*) $C_6H_5CH_2OH$

(*iii*) $(CH_3)_3COH$ (*iv*) C_2H_5OH

Ans. (*i*)

Explanation:



12. Phenol is less acidic than _____________.

(*i*) ethanol (*ii*) *o*-nitrophenol

(*iii*) *o*-methylphenol (*iv*) *o*-methoxyphenol

Ans. (*ii*)

Explanation: In substituted phenols, the presence of electron withdrawing groups such as nitro groups, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

13. Which of the following is most acidic?

(*i*) Benzyl alcohol (*ii*) Cyclohexanol

(*iii*) Phenol (*iv*) *m*-Chlorophenol

Ans. (*iv*)

Explanation: *m*-chlorophenol is most acidic. Alpha carbon of benzyl alcohol and cyclohexanol is sp^3 hybridized. In *m*-chlorophenol, it is sp^2 hybridized. In *m*-chlorophenol, electron withdrawing group —Cl is present at *meta* position.

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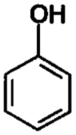
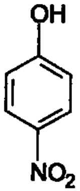
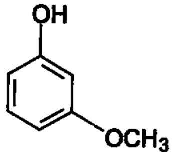
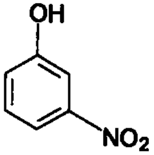
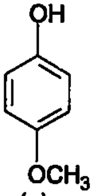
14. Mark the correct order of decreasing acid strength of the following compounds.


(*a*)


(*b*)


(*c*)


(*d*)

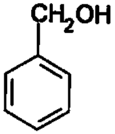

(*e*)

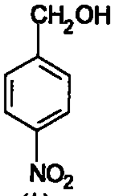
(*i*) (*e*) > (*d*) > (*b*) > (*a*) > (*c*) (*ii*) (*b*) > (*d*) > (*a*) > (*c*) > (*e*)
(*iii*) (*d*) > (*e*) > (*c*) > (*b*) > (*a*) (*iv*) (*e*) > (*d*) > (*c*) > (*b*) > (*a*)

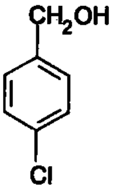
Ans. (*ii*)

Explanation: same as answer no. 12.

15. Mark the correct increasing order of reactivity of the following compounds with HBr/HCl.


(*a*)


(*b*)


(*c*)

(*i*) (*a*) < (*b*) < (*c*) (*ii*) (*b*) < (*a*) < (*c*)
(*iii*) (*b*) < (*c*) < (*a*) (*iv*) (*c*) < (*b*) < (*a*)

Ans. (*iii*)

Explanation: It is type of nucleophilic substitution reaction followed by S_N1 mechanism. S_N1 mechanism depends on the stability of carbocation. Presence of electron withdrawing group will decrease the stability of carbocation.

16. Arrange the following compounds in increasing order of boiling point.
Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

(*i*) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
(*ii*) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
(*iii*) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol
(*iv*) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

Ans. (*i*)

Explanation: The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area.)

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II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note : In the following questions two or more options may be correct.

17. Which of the following are used to convert RCHO into RCH_2OH?

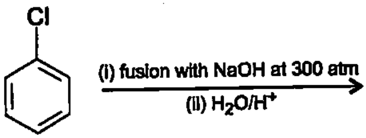
(*i*) H_2/Pd (*ii*) $LiAlH_4$
(*iii*) $NaBH_4$ (*iv*) Reaction with RMgX followed by hydrolysis

Ans. (*i*), (*ii*), (*iii*)

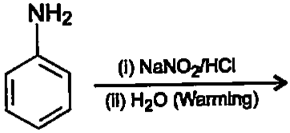
Explanation: Aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation. It is also prepared by treating aldehydes and ketones with sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$).

18. Which of the following reactions will yield phenol?

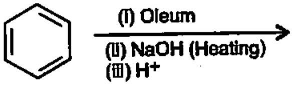
(*i*)



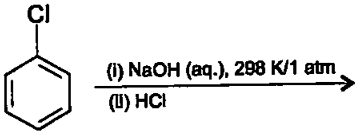
(*ii*)



(*iii*)

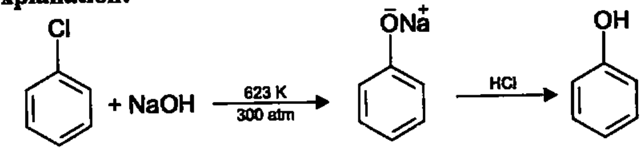


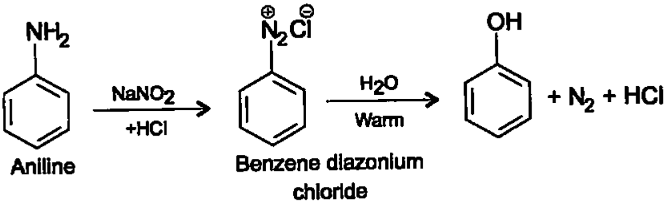
(*iv*)

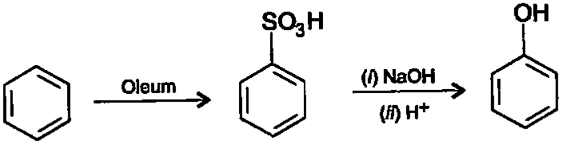


Ans. (*i*), (*ii*) and (*iii*)

Explanation:







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19. Which of the following reagents can be used to oxidise primary alcohols to aldehydes?

(*i*) CrO_3 in anhydrous medium. (*ii*) $KMnO_4$ in acidic medium.

(*iii*) Pyridinium chlorochromate.

(*iv*) Heat in the presence of Cu at 573K.

Ans. (*i*), (*iii*) and (*iv*)

Explanation: Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

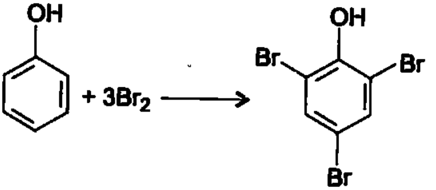
20. Phenol can be distinguished from ethanol by the reactions with ________.

(*i*) Br_2/water (*ii*) Na

(*iii*) Neutral $FeCl_3$ (*iv*) All the above

Ans. (*i*) and (*iii*)

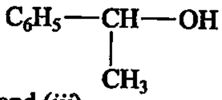
Explanation: Ethanol does not give any reaction with neutral $FeCl_3$ solution while phenol gives violet color with neutral $FeCl_3$. When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate. Ethanol does not react with bromine water

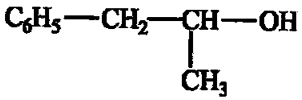


2,4,6-Tribromophenol

21. Which of the following are benzylic alcohols?

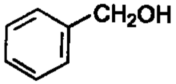
(*i*) $C_6H_5—CH_2—CH_2OH$ (*ii*) $C_6H_5—CH_2OH$

(*iii*)

$C_6H_5—\underset{\displaystyle CH_3}{\underset{|}{CH}}—OH$

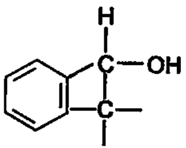
(*iv*)

$C_6H_5—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—OH$

Ans. (*ii*) and (*iii*)

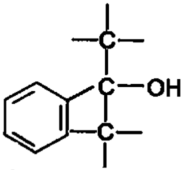
Explanation: Benzylic alcohols: In these alcohols, the —OH group is attached to a sp^3– hybridised carbon atom next to an aromatic ring. For example,



Primary



Secondary

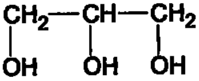


Tertiary

Allylic and benezylic alcohols may be primary, secondary or tertiary.

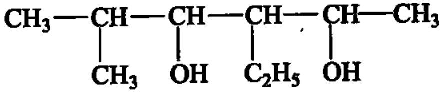
III. SHORT ANSWER TYPE

22. What is the structure and IUPAC name of glycerol?

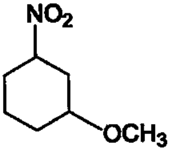
Ans. 

$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$ IUPAC name is propane-1,2,3-triol.

23. Write the IUPAC name of the following compounds.

(A) 

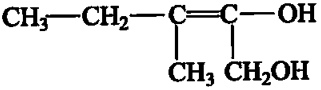
$CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-\underset{C_2H_5}{CH}-\underset{OH}{CH}-CH_3$

(B) 

Ans. (A) 3-Ethyl-5-methylhexane-2,4-diol,

(B) 1-Methoxy-3-nitrocyclohexane

24. Write the IUPAC name of the compound given below:

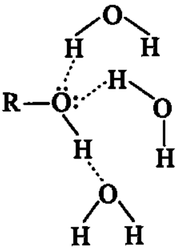


$CH_3-CH_2-\underset{CH_3}{C}=\underset{CH_2OH}{C}-OH$

Ans. 3-Methylpent-2-ene-1,2-diol

25. Name the factors responsible for the solubility of alcohols in water.

Ans. Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules as shown. The solubility decreases with increase in size of alkyl/aryl (hydrophobic groups).



26. What is denatured alcohol?

Ans. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

27. Suggest a reagent for the following conversion.

Ans. Pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl

$CH_3-CH=CH-CH_2OH$ PCC $CH_3-CH=CH-CHO$

28. Out of 2-chloroethanol and ethanol which is more acidic and why?

Ans. The acidic character of alcohols is due to the polar nature of O–H bond. 2-Chloroethanol, is more acidic due to –I effect of chlorine atom. It increases the polarity of O—H bond and increases the acidic strength.

29. Suggest a reagent for conversion of ethanol to ethanal.

Ans. A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

30. Suggest a reagent for conversion of ethanol to ethanoic acid.

Ans. Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly.

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31. Out of *o*-nitrophenol and *p*-nitrophenol, which is more volatile? Explain.

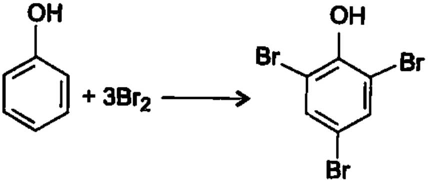
Ans. *o*-nitrophenol, due to intramolecular hydrogen bonding, is more volatile in nature. In *para*-nitrophenol, there is intermolecular hydrogen bonding.

32. Out of *o*-nitrophenol and *o*-cresol which is more acidic?

Ans. In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic.

33. When phenol is treated with bromine water, white precipitate is obtained. Give the structure and the name of the compound formed.

Ans. When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



2,4,6-Tribromophenol

34. Arrange the following compounds in increasing order of acidity and give a suitable explanation. Phenol, *o*-nitrophenol, *o*-cresol

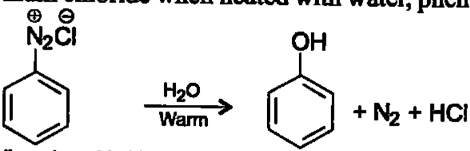
Ans. Increasing order of acidity will be *o*-cresol < phenol < *o*-nitrophenol. Explanation is same as answer no. 32.

35. Alcohols react with active metals e.g. Na, K etc. to give corresponding alkoxides. Write down the decreasing order of reactivity of sodium metal towards primary, secondary and tertiary alcohols.

Ans. Decreasing order of reactivity of sodium metal is:
$1° > 2° > 3°$

36. What happens when benzene diazonium chloride is heated with water?

Ans. Benzene diazonium chloride when heated with water, phenol is formed.



Benzene diazonium chloride

37. Arrange the following compounds in decreasing order of acidity.
H_2O, ROH, $HC\equiv CH$

Ans. $H_2O > ROH > HC\equiv CH$

38. Name the enzymes and write the reactions involved in the preparation of ethanol from sucrose by fermentation.

Ans. Ethanol, C_2H_5OH, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such

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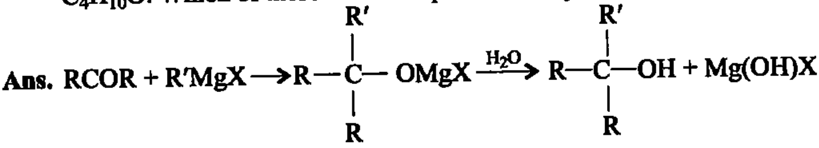
as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase.

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

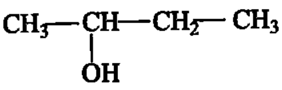
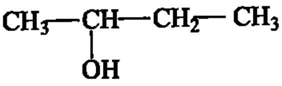
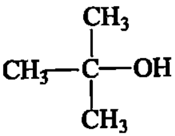
39. How can propan-2-one be converted into tert- butyl alcohol?

Ans. Using Grignard reagent.

40. Write the structures of the isomers of alcohols with molecular formula $C_4H_{10}O$. Which of these exhibits optical activity?

Ans. 

$$RCOR + R'MgX \longrightarrow R-\overset{R'}{\underset{R}{C}}-OMgX \xrightarrow{H_2O} R-\overset{R'}{\underset{R}{C}}-OH + Mg(OH)X$$

$CH_3-CH_2-CH_2-CH_2-OH$	*n*-Butyl alcohol	Butan-1-ol
 $CH_3-\underset{OH}{CH}-CH_2-CH_3$	sec-Butyl alcohol	Butan-2-ol
 $CH_3-\underset{OH}{CH}-CH_2-CH_3$	Isobutyl alcohol	2-Methylpropan-1-ol
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol

The asymmetry of the molecule is responsible for the optical activity in a molecule.

In the above structures, it is only butan-2-ol which is asymmetric because of the chiral carbon *i.e.* the carbon atom attached to four different substituents. Hence, it is optically active.

41. Explain why is OH group in phenols more strongly held as compared to OH group in alcohols.

Ans. In phenols, the —OH group is attached to sp^2 hybridised carbon of an aromatic ring. The carbon– oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring whereas in alcohols, the oxygen of the —OH group is attached to carbon by a sigma bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen. That is why —OH group in phenol is more strongly held as compared to alcohol.

42. Explain why nucleophilic substitution reactions are not very common in phenols.

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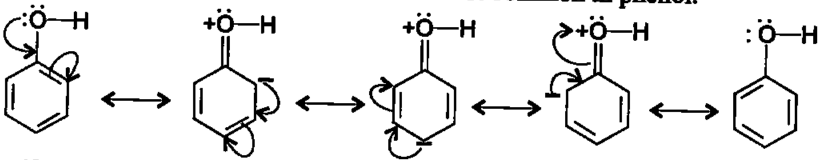
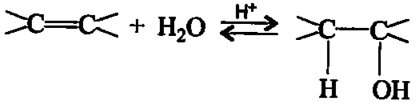
Ans. The —OH group attached to the benzene ring activates it towards electrophilic substitution reaction. Also, it directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to the resonance effect caused by —OH group. That is why nucleophilic substitution reaction is not common in phenol.

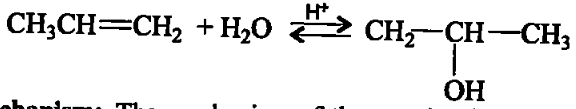


43. Preparation of alcohols from alkenes involves the electrophilic attack on alkene carbon atom. Explain its mechanism.

Ans.



$$>C=C< + H_2O \overset{H^+}{\rightleftharpoons} >\underset{H}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}<$$

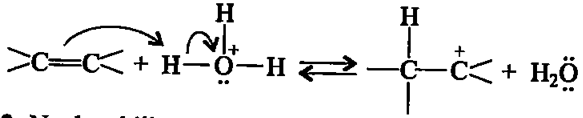


$$CH_3CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

Mechanism: The mechanism of the reaction involves the following three steps:

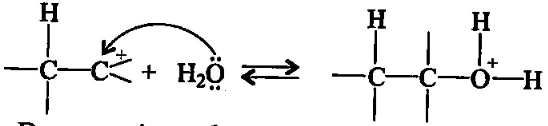
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

$H_2O + H^+ \longrightarrow H_3O^+$



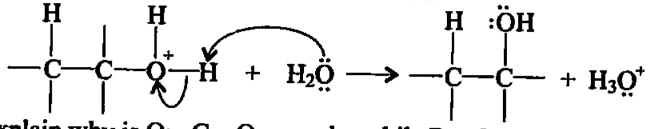
$$>C=C< + H-\underset{..}{\overset{\overset{H}{|}}{\overset{+}{O}}}-H \rightleftharpoons -\underset{|}{\overset{\overset{H}{|}}{C}}-\overset{+}{C}< + H_2\ddot{O}$$

Step 2: Nucleophilic attack of water on carbocation.



$$-\underset{|}{\overset{\overset{H}{|}}{C}}-\overset{+}{C}< + H_2\ddot{O} \rightleftharpoons -\underset{|}{\overset{\overset{H}{|}}{C}}-\underset{|}{\overset{|}{C}}-\overset{\overset{H}{|}}{\overset{+}{O}}-H$$

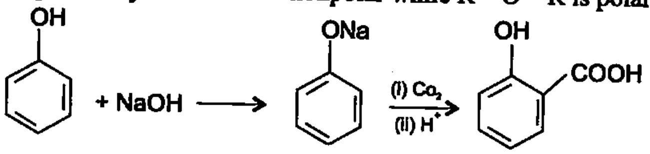
Step 3: Deprotonation to form an alcohol.



$$-\underset{|}{\overset{\overset{H}{|}}{C}}-\underset{|}{\overset{\overset{H}{|}}{C}}-\overset{\overset{H}{|}}{\overset{+}{O}}-H + H_2\ddot{O} \longrightarrow -\underset{|}{\overset{\overset{H}{|}}{C}}-\underset{|}{\overset{\overset{:\ddot{O}H}{|}}{C}}- + H_3O^+$$

44. Explain why is O=C=O nonpolar while R—O—R is polar.

Ans.



2-Hydroxybenzoic acid
(Salicyclic acid)

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45. Why is the reactivity of all the three classes of alcohols with conc. HCl and $ZnCl_2$ (Lucas reagent) different?

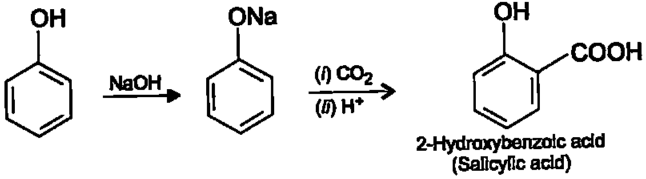
Ans. **Reaction with hydrogen halides:** Alcohols react with hydrogen halides to form alkyl halides

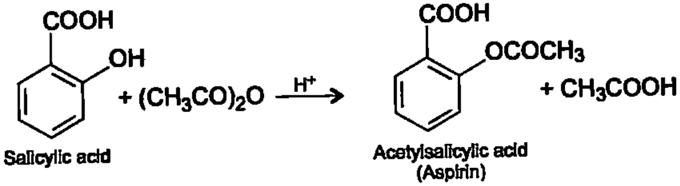
$$ROH + HX \longrightarrow R—X + H_2O$$

The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (Lucas test). Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature. The reaction is followed by the formation of carbocation since tertiary carbocation is most stable. Thus, the order of reactivity will be 3° > 2° > 1°.

46. Write steps to carry out the conversion of phenol to aspirin.

Ans.





Acetylation of salicylic acid produces aspirin.

47. Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?

Ans. Phenol will be easily nitrated since the —OH group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to *ortho* and *para* positions in the ring as these positions become electron rich due to the resonance effect caused by —OH group.

48. In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?

Ans. Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.

49. Dipole moment of phenol is smaller than that of methanol. Why?

Ans. Due to electron withdrawing effect of phenyl group, the C—O bond in phenol is less polar, whereas in case of methanol the methyl group

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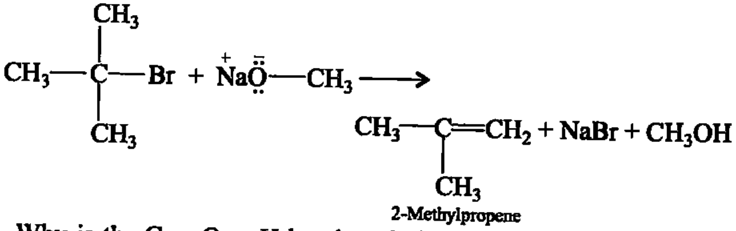
has electron releasing effect and hence C—O bond in it is more polar. Dipole moment depends upon the polarity of bonds.

50. Ethers can be prepared by Williamson synthesis in which an alkyl halide is reacted with sodium alkoxide. Di-*tert*-butyl ether can't be prepared by this method. Explain.

Ans. In Williamson synthesis an alkyl halide is allowed to react with sodium alkoxide

$$R—X + R'—\ddot{\underset{\cdot\cdot}{O}}\,Na \longrightarrow R—\ddot{\underset{\cdot\cdot}{O}}—R' + Na\,X$$

In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.



$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—Br + \overset{+}{Na}\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}—CH_3 \longrightarrow \underset{\text{2-Methylpropene}}{CH_3—\underset{CH_3}{C}=CH_2} + NaBr + CH_3OH$$

51. Why is the C—O—H bond angle in alcohols slightly less than the tetrahedral angle whereas the C—O—C bond angle in ether is slightly greater?

Ans. The bond angle in alcohols is slightly less than the tetrahedral angle (109°–28'). It is due to the repulsion between the unshared electron pairs of oxygen.

In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (—R) groups.

52. Explain why low molecular mass alcohols are soluble in water.

Ans. The low molecular mass alcohols are solube in water due to the presence of intermolecular hydrogen bonding between their molecules. Polar O-H group favours dissolution process whereas non polar alkyl group does not. As the size of the alkyl group-increases, it overcomes the effect of the polar nature $^{-}$OH group and the solubility decreases.

53. Explain why p-nitrophenol is more acidic than phenol.

Ans. In substituted phenols, the presence of electron withdrawing groups such as nitro groups, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion.

54. Explain why alcohols and ethers of comparable molecular mass have different boiling points?

Ans. The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers.

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55. The carbon-oxygen bond in phenol is slightly stronger than that in methanol. Why?

Ans. C—O bond in phenols has partial double bond character due to resonance and hence is difficult to cleave.

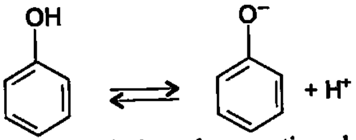
56. Arrange water, ethanol and phenol in increasing order of acidity and give reason for your answer.

Ans. phenol > water > ethanol

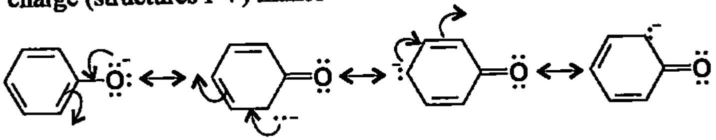
$$\underset{\text{Base}}{R—\ddot{\underset{\cdot\cdot}{O}}{:}^{-}} + \underset{\text{Acid}}{H—\ddot{O}—H} \longrightarrow \underset{\text{Conjugate acid}}{R—O—H} + \underset{\text{Conjugate base}}{:\ddot{\underset{\cdot\cdot}{O}}H^{-}}$$

an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide). The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. The ionisation of an alcohol and a phenol takes place as follows:

$$R—\ddot{\underset{\cdot\cdot}{O}}—H \rightleftharpoons R—\ddot{\underset{\cdot\cdot}{O}}{:}^{-} + H^{+}$$



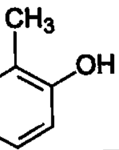
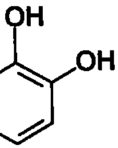
In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes



IV. MATCHING TYPE

Note : Match the items of Column I and Column II in the following questions.

57. Match the structures of the compounds given in Column I with the name of the compounds given in Column II.

Column I	Column II
(*i*) 	(*a*) Hydroquinone
(*ii*) 	(*b*) Phenetole

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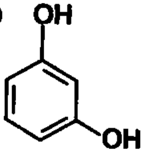
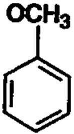
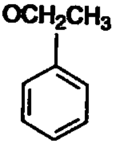
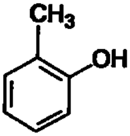
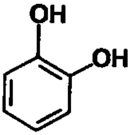
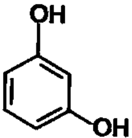
(*iii*) 	(*c*) Catechol
(*iv*) 	(*d*) *o*-Cresol
(*v*) 	(*e*) Quinone
(*vi*) 	(*f*) Resorcinol (g) Anisole

Ans. (*i*) → (*d*) (*ii*) → (*c*) (*iii*) → (*f*) (*iv*) → (*a*) (*v*) → (*g*) (*vi*) → (*b*)

Explanation:

Column I	Column II
(*i*)  o-Cresol 2-Methylphenol	(*d*) *o*-cresol
(*ii*)  Catechol Benzene 1,2-diol	(*c*) Catechol
(*iii*)  Resorcinol Benzene 1,3 diol	(*f*) Resorcinol

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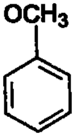
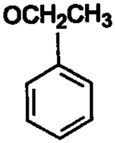
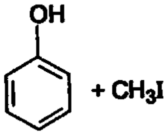
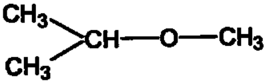
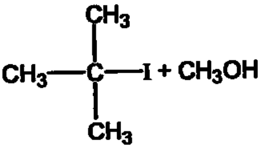
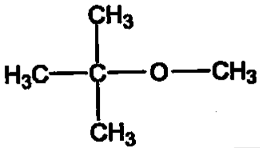
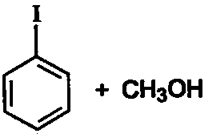
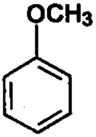
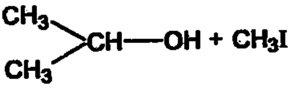
(iv)  Hydroquinone or quinol Benzene 1,4 diol	(*a*) Hydroquinone
(*v*)  Methoxybenzene	(*g*) Anisole
(*vi*)  Ethoxybenzene	(*b*) Phenetole

58. Match the starting materials given in Column I with the products formed by these (Column II) in the reaction with HI.

Column I	Column II
(*i*) $CH_3—O—CH_3$	(*a*) 
(*ii*) 	(*b*) 
(*iii*) 	(*c*) 
(*iv*) 	(*d*) $CH_3—OH + CH_3—I$ (*e*) 

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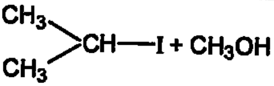
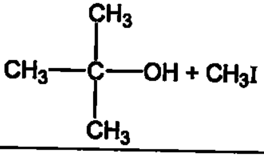
	(*f*) 
	(*g*)  $CH_3-C(CH_3)_2-OH + CH_3I$

Ans. (*i*) → (*d*) (*ii*) → (*e*) (*iii*) → (*b*) (*iv*) → (*a*)

59. Match the items of column I with items of column II.

Column I	Column II
(*i*) Antifreeze used in car engine	(*a*) Neutral ferric chloride
(*ii*) Solvent used in perfumes	(*b*) Glycerol
(*iii*) Starting material for picric acid	(*c*) Methanol
(*iv*) Wood spirit	(*d*) Phenol
(*v*) Reagent used for detection of phenolic group	(*e*) Ethleneglycol
(*v*) By product of soap industry used in cosmetics	(*f*) Ethanol

Ans. (*i*) → (*e*) (*ii*) → (*f*) (*iii*) → (*d*) (*iv*) → (*c*) (*v*) → (*a*) (*vi*) → (*b*)

Explanation:

(*i*) Ethleneglycol (IUPAC name of ethylene glycol is ethane-1,2 - diol a small percentage of it is used in antifreeze formulation)

(*ii*) Ethanol (it is less irritating to skin so it is used in perfumes)

(*iii*) Phenol (by the reaction of phenol with conc. HNO_3 phenol can be converted into picric acid)

(*iv*) Methanol (methanol is known as wood spirit as it was obtained by destructive distillation of wood)

(*v*) Neutral ferric chloride (Neutral ferric chloride gives violet colour when treated with phenol)

(*vi*) Glycerol (It is the by product in soap industry and is used in cosmetics)

60. Match the items of column I with items of column II.

Column I	Column II
(*i*) Methanol	(*a*) Conversion of phenol to *o*-hydroxysalicylic acid
(*ii*) Kolbe's reaction	(*b*) Ethyl alcohol
(*iii*) Williamson's synthesis	(*c*) Conversion of phenol to salicylaldehyde
(*iv*) Conversion of 2° alcohol to ketone	(*d*) Wood spirit
(*v*) Reimer-Tiemann reaction	(*e*) Heated copper at 573K
(*vi*) Fermentation	(*f*) Reaction of alkyl halide with sodium alkoxide

Ans. (*i*) → (*d*) (*ii*) → (*a*) (*iii*) → (*f*) (*iv*) → (*e*) (*v*) → (*c*) (*vi*) → (*b*)

Explanation:

(*i*) Methanol Wood spirit (methanol is known as wood spirit as it was obtained by destructive distillation of wood).

(*ii*) Kolbe's reaction Conversion of phenol to ortho-hydroxyl salicylic acid (reaction of phenol with CO_2 gas gives ortho-hydroxysalicylic acid)

(*iii*) Williamson's synthesis ⟶ Reaction of alkyl halide with sodium alkoxide (Reaction of alkyl halide with sodium alkoxide gives ether. It is a very important method for the preparation of ether)

(*iv*) Conversion of 2° alcohol to ketone ⟶ Heated copper at 573 K (by dehydrogenation of secondary alcohol it is converted into ketone).

(*v*) Reimer-Tiemann reaction ⟶ Conversion of phenol to salicylaldehyde (phenol is treated with chloroform in presence of NaOH and salicyldehyde is formed as the product)

(*vi*) Fermentation ⟶ Ethylalcohol (ethanol is prepared by the fermentation of sugar).

V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are correct and reason is correct explanation of assertion.

(*ii*) Assertion and reason both are wrong statements.

(*iii*) Assertion is correct statement but reason is wrong statement.

(*iv*) Assertion is wrong statement but reason is correct statement.

(*v*) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

61. **Assertion** : Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol.

Reason : Addition of water in acidic medium proceeds through the formation of primary carbocation.

Ans. (*ii*)

Correct assertion: Addition reaction of water to but-1-ene in acidic medium yields butan-2-ol.

Correct reason: Addition of water in acidic medium proceeds through the formation of secondary carbocation.

62. **Assertion** : *p*-nitrophenol is more acidic than phenol.

Reason : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

Ans. (*i*)

Explanation: *P*-nitro phenol is more acidic as nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance.

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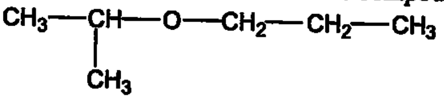
63. **Assertion** : IUPAC name of the compound



$CH_3-\underset{\underset{CH_3}{|}}{CH}-O-CH_2-CH_2-CH_3$ is 2-Ethoxy-2-methylethane.

Reason : In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by —OR or —OAr group [where R = alkyl group and Ar = aryl group]

Ans. (*iv*)

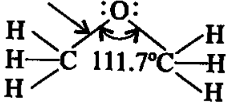
Explanation: Correct assertion is the IUPAC name of the compound is 1-(2-propoxy) propane.

64. **Assertion** : Bond angle in ethers is slightly less than the tetrahedral angle.

Reason : There is a repulsion between the two bulky (—R) groups.

Ans. (*iv*)

Explanation: 141 pm



Methoxymethane

65. **Assertion** : Boiling points of alcohols and ethers are high.

Reason : They can form intermolecular hydrogen-bonding.

Ans. (*ii*)

Explanation: Correct assertion: Boiling points of alcohols are higher than that of ethers of comparable molecular mass.

Correct reason: Alcohols can form intermolecular hydrogen bonding while ethers cannot.

66. **Assertion** : Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

Reason : Lewis acid polarises the bromine molecule.

Ans. (*iv*)

Explanation: Bromination of phenol cannot be carried out in presence of Lewis acid.

67. **Assertion** : *o*-Nitrophenol is less soluble in water than the *m*- and *p*-isomers.

Reason : *m*- and *p*- Nitrophenols exist as associated molecules.

Ans. (*v*)

Explanation: Due to intramolecular hydrogen bonding *o*-Nitrophenol does not form hydrogen bond with water.

68. **Assertion** : Ethanol is a weaker acid than phenol.

Reason : Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

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Ans. (*iii*)

Explanation: Phenoxide ion is stabilized by resonance which is not possible in alkoxide ion.

69. Assertion : Phenol forms 2, 4, 6 – tribromophenol on treatment with Br_2 in carbon disulphide at 273K.

Reason : Bromine polarises in carbon disulphide.

Ans. (*ii*)

Explanation: Correct assertion: Phenol on treatment with bromine water can form 2,4,6-tribromophenol

Correct reason: In water, phenol gives phenoxide ions which activate the ring towards electrophilic substitution reaction.

70. Assertion : Phenols give *o*-and *p*-nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.

Reason : —OH group in phenol is o-, p- directing.

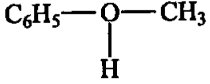
Ans. (*iv*)

Explanation: Phenol on treatment with dil. HNO_3 forms o-nitrophenol and p-nitrophenol.

VI. LONG ANSWER TYPE

71. Write the mechanism of the reaction of HI with methoxybenzene.

Ans. In case of anisole, methylphenyl oxonium ion, is



$C_6H_5—\underset{\displaystyle H}{\overset{+}{O}}—CH_3$

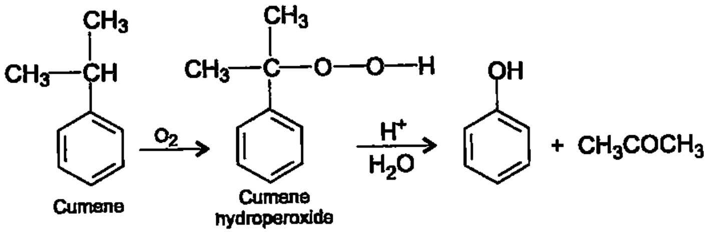
formed by protonation of ether. The bond between O—CH_3 is weaker than the bond between O—C_6H_5 because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Therefore, the attack by I^- ion breaks O—CH_3 bond to form CH_3I. Phenols do not react further to give halides because the sp^2 hybridised carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

72. (*a*) Name the starting material used in the industrial preparation of phenol.

(*b*) Write complete reaction for the bromination of phenol in aqueous and non aqueous medium.

(*c*) Explain why Lewis acid is not required in bromination of phenol?

Ans. (*a*) The starting material used in the industrial preparation of phenol is cumene.



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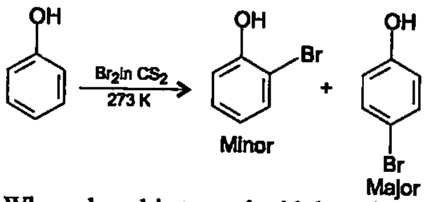
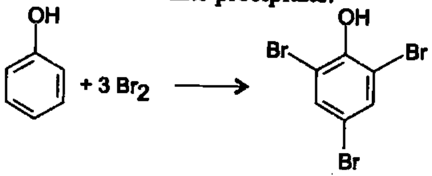
(*b*)



When phenol is treated with bromine water. 2,4,6-tribromophenol is formed as white precipitate.

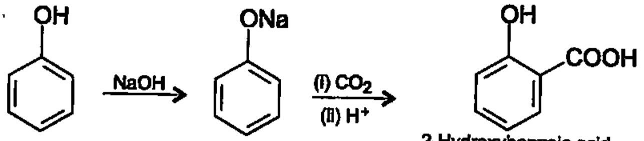


2,4,6-Tribromophenol

(*c*) The usual halogenation of benzene takes place in the presence of a Lewis acid, such as $FeBr_3$, which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of —OH group attached to the benzene ring.

73. How can phenol be converted to aspirin?

Ans.



2-Hydroxybenzoic acid
(Salicylic acid)

2-hydroxybenzoic acid on treatment with acetic anhydride will give aspirin.

74. Explain a process in which a biocatalyst is used in industrial preparation of a compound known to you.

Ans. Ethanol, C_2H_5OH, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions *i.e.* in absence of air. Carbon dioxide is released during fermentation.

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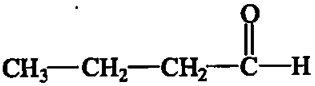
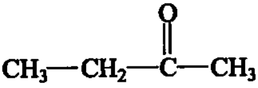
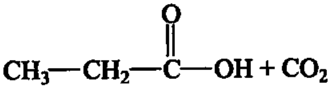
12 Aldehydes, Ketones and Carboxylic Acids

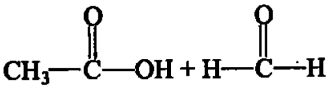
I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions?

(*i*) 
$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$

(*ii*) 
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

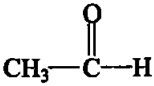
(*iii*) 
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH + CO_2$

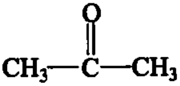
(*iv*) 
$CH_3-\overset{\overset{O}{\|}}{C}-OH + H-\overset{\overset{O}{\|}}{C}-H$

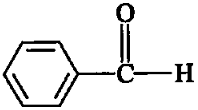
Ans. (*ii*)

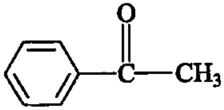
Explanation: Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde. Addition takes place by Markovnikoff's rule.

2. Which of the following compounds is most reactive towards nucleophilic addition reactions?

(*i*) 
$CH_3-\overset{\overset{O}{\|}}{C}-H$

(*ii*) 
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(*iii*) 

(*iv*) 

Ans. (*i*)

Explanation: Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl more effectively than in former. In benzaldehyde also, it is difficult for the nucleophile to attack on the substrate molecule.

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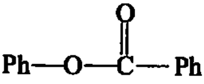
3. The correct order of increasing acidic strength is ____________.
   (*i*) Phenol < Ethanol < Chloroacetic acid < Acetic acid
   (*ii*) Ethanol < Phenol < Chloroacetic acid < Acetic acid
   (*iii*) Ethanol < Phenol < Acetic acid < Chloroacetic acid
   (*iv*) Chloroacetic acid < Acetic acid < Phenol < Ethanol

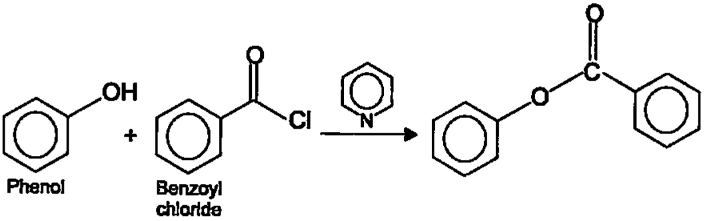
Ans. (*iii*)

Explanation: Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion. That is why carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Thus, the order of increasing acidic strength is — Ethanol < Phenol < Acetic acid < Chloroacetic acid.

4. Compound  $Ph—O—\overset{\overset{O}{\|}}{C}—Ph$ can be prepared by the reaction of ____________.
   (*i*) Phenol and benzoic acid in the presence of NaOH
   (*ii*) Phenol and benzoyl chloride in the presence of pyridine
   (*iii*) Phenol and benzoyl chloride in the presence of $ZnCl_2$
   (*iv*) Phenol and benzaldehyde in the presence of palladium

Ans. (*ii*)

Explanation: Compound Ph—COO—Ph can be prepared by the reaction of



This is an example of Schotten-Baumann reaction.

5. The reagent which does not react with both, acetone and benzaldehyde.
   (*i*) Sodium hydrogensulphite (*ii*) Phenyl hydrazine
   (*iii*) Fehling's solution (*iv*) Grignard reagent

Ans. (*iii*)

Explanation: Fehling's test: Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are

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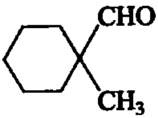
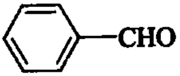
oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.

6. Cannizzaro's reaction is not given by ____________.

(i) 

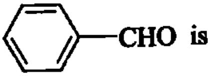
(ii) 

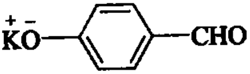
(iii) H CHO

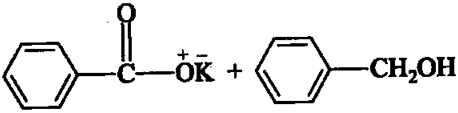
(iv) CH_3CHO

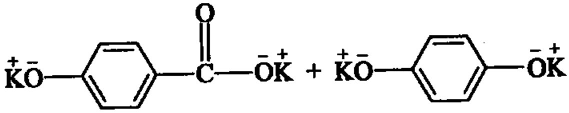
Ans. (iv)

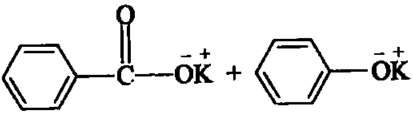
Explanation: Cannizzaro reaction: Aldehydes which do not have an alpha hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt. CH_3CHO has one α hydrogen that is why it will not give Fehling's test.

7. Which product is formed when the compound  is treated with concentrated aqueous KOH solution?

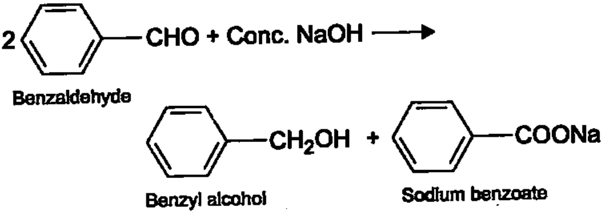
(i) 

(ii) 

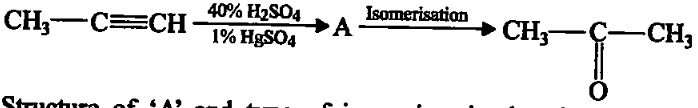
(iii) 

(iv) 

Ans. (ii)

Explanation: 

Similar reaction will occur with KOH.

8. 

$$CH_3—C{\equiv}CH \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} A \xrightarrow{\text{Isomerisation}} CH_3—\underset{\underset{O}{\parallel}}{C}—CH_3$$

Structure of 'A' and type of isomerism in the above reaction are respectively.

(*i*) Prop–1–en–2–ol, metamerism

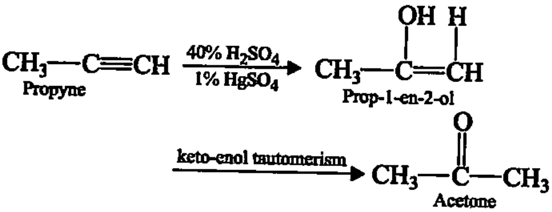
(*ii*) Prop-1-en-1-ol, tautomerism

(*iii*) Prop-2-en-2-ol, geometrical isomerism

(*iv*) Prop-1-en-2-ol, tautomerism

Ans. (*iv*)

Explanation: Chemical reaction can be shown as



$$\underset{\text{Propyne}}{CH_3—C{\equiv}CH} \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} \underset{\text{Prop-1-en-2-ol}}{CH_3—\overset{\overset{OH}{|}}{C}{=}\overset{\overset{H}{|}}{C}H}$$

$$\xrightarrow{\text{keto-enol tautomerism}} \underset{\text{Acetone}}{CH_3—\overset{\overset{O}{\parallel}}{C}—CH_3}$$

A is prop-1-en-2-ol, which undergo tautomerism to form acetone.

9. Compounds A and C in the following reaction are __________.

$$CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} (A) \xrightarrow{H_2SO_4, \Delta} (B) \xrightarrow[\text{oxidation}]{\text{Hydroboration}} (C)$$

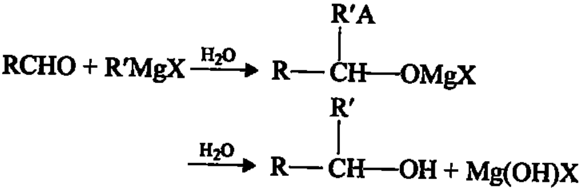
(*i*) identical

(*ii*) positional isomers

(*iii*) functional isomers

(*iv*) optical isomers

Ans. (*ii*)

Explanation: 

$$RCHO + R'MgX \xrightarrow{H_2O} R—\overset{\overset{R'A}{|}}{C}H—OMgX$$

$$\xrightarrow{H_2O} R—\overset{\overset{R'}{|}}{C}H—OH + Mg(OH)X$$

From the above reaction, it is clear that acetaldehyde on treatment with Grignard reagent followed by hydrolysis will give propane-2-ol as the product.

Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid *e.g.*, concentrated H_2SO_4 or H_3PO_4 now the product B will be propene which on hydroboration oxidation will give propane-1-ol.

Thus, propane-2-ol and propane -1-ol are position isomers.

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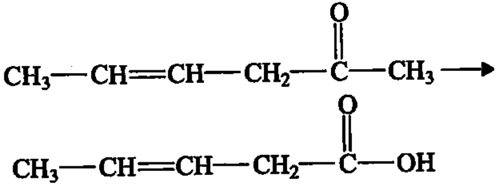
10. Which is the most suitable reagent for the following conversion?



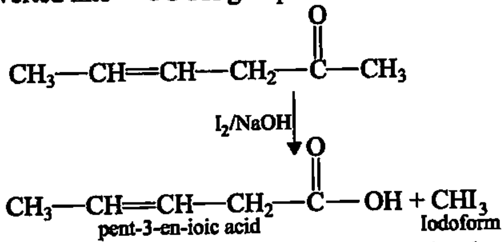
$$CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(*i*) Tollens' reagent (*ii*) Benzoyl peroxide

(*iii*) I_2 and NaOH solution (*iv*) Sn and NaOH solution

Ans. (*iii*)

Explanation: Iodoform test is used for $—COCH_3$ group which is converted into —COOH group.



$$CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{I_2/NaOH} \underset{\text{pent-3-en-ioic acid}}{CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Iodoform}}{CHI_3}$$

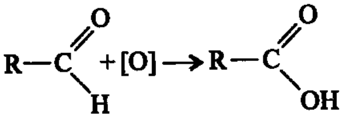
11. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?

(*i*) Butan-1-ol (*ii*) Butan-2-ol

(*iii*) Both of these (*iv*) None of these

Ans. (*ii*)

Explanation: Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc.

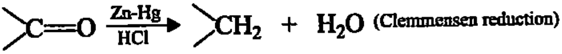


12. In Clemmensen Reduction carbonyl compound is treated with ________.

(*i*) Zinc amalgam + HCl (*ii*) Sodium amalgam + HCl

(*iii*) Zinc amalgam + nitric acid (*iv*) Sodium amalgam + HNO_3

Ans. (*i*)

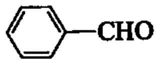
Explanation: 

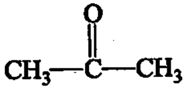
II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note : In the following questions two or more options may be correct.

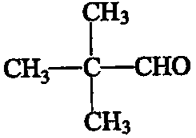
13. Which of the following compounds do not undergo aldol condensation?

(*i*) $CH_3—CHO$

(*ii*) 

(*iii*) 

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

(*iv*) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CHO$$

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Ans. (*ii*) and (*iv*)

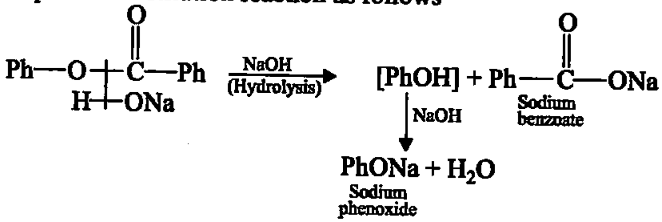
Explanation: *Aldol condensation:* Aldehydes and ketones having at least one alpha-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form beta-hydroxy aldehydes (aldol) or beta-hydroxy ketones (ketol), respectively. This is known as Aldol reaction. In (*ii*) and (*iv*) alpha hydrogen is absent.

14. Treatment of compound $Ph-O-\overset{\overset{O}{\|}}{C}-Ph$ with NaOH solution yields

(*i*) Phenol
(*ii*) Sodium phenoxide
(*iii*) Sodium benzoate
(*iv*) Benzophenone

Ans. (*ii*) and (*iii*)

Explanation: Treatment of compound $Ph-O-\overset{\overset{O}{\|}}{C}-Ph$ with NaOH yields sodium phenoxide and sodium benzoate by means of nucleophillic substitution reaction as follows



$$Ph-O+\overset{\overset{O}{\|}}{C}-Ph \;\; (H+ONa) \xrightarrow[\text{(Hydrolysis)}]{NaOH} [PhOH] + \underset{\text{Sodium benzoate}}{Ph-\overset{\overset{O}{\|}}{C}-ONa}$$

$$[PhOH] \xrightarrow{NaOH} \underset{\text{Sodium phenoxide}}{PhONa} + H_2O$$

15. Which of the following conversions can be carried out by Clemmensen Reduction?

(*i*) Benzaldehyde into benzyl alcohol
(*ii*) Cyclohexanone into cyclohexane
(*iii*) Benzoyl chloride into benzaldehyde
(*iv*) Benzophenone into diphenyl methane

Ans. (*ii*) and (*iv*)

Explanation: The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid [Clemmensen reduction)

$$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2 + H_2O \text{ (Clemmensen reduction)}$$

In (*ii*) and (*iv*) only the carbonyl compound is converted into hydrocarbon.

16. Through which of the following reactions number of carbon atoms can be increased in the chain?

(*i*) Grignard reaction
(*ii*) Cannizzaro's reaction
(*iii*) Aldol condensation
(*iv*) HVZ reaction

Ans. (*i*) and (*iii*)

Explanation: Grignard reaction and aldol condensation is used to increase the number of carbon atom in the chain as follows:

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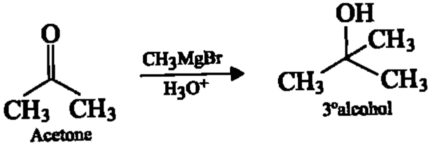
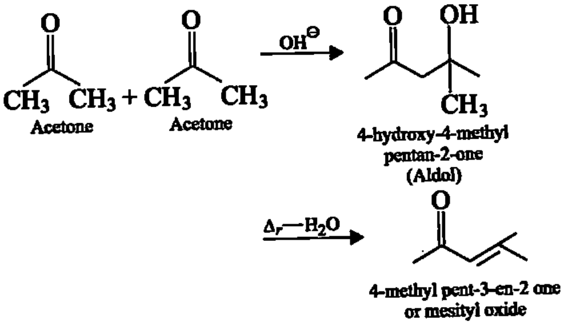
Grignard reaction



Aldol condensation



While other two reactions, cannizzaro reaction and HVZ reaction don't lead to increase in number of carbon atoms.

17. Benzophenone can be obtained by ____________.

(*i*) Benzoyl chloride + Benzene + $AlCl_3$

(*ii*) Benzoyl chloride + Diphenyl cadmium

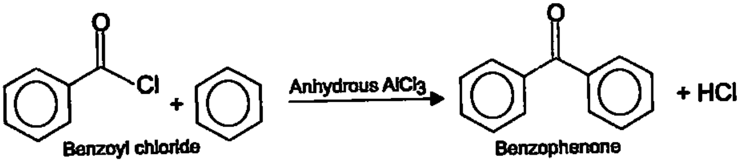
(*iii*) Benzoyl chloride + Phenyl magnesium chloride

(*iv*) Benzene + Carbon monoxide + $ZnCl_2$

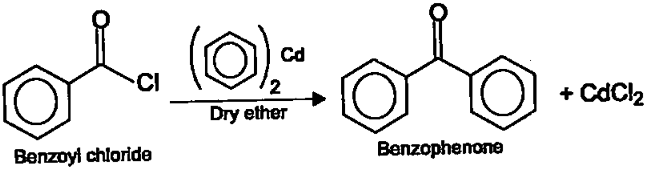
Ans. (*i*) and (*ii*)

Explanation:

(*a*) Benzophenone can be obtained by Friedel-Craft acylation reaction. The reaction is shown as



(*b*) Benzophenone can also be obtained by the reaction between benzoyl chloride and diphenyl cadmium.



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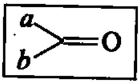
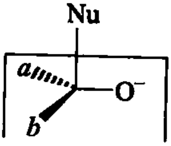
18. Which of the following is the correct representation for intermediate of nucleophilic addition reaction to the given carbonyl compound (A) :

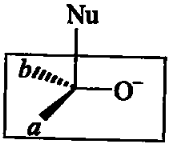


(A)

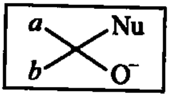
(*i*)



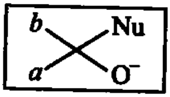
(*ii*)



(*iii*)

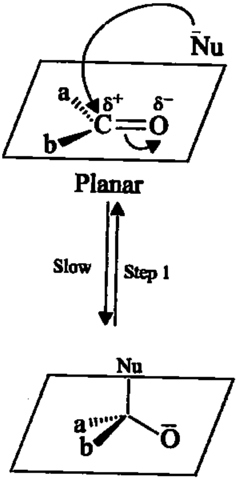


(*iv*)



Ans. (*i*) and (*ii*)

Explanation:



III. SHORT ANSWER TYPE

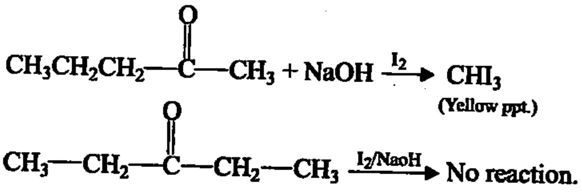
19. Why is there a large difference in the boiling points of butanal and butan-1-ol?

Ans. Boiling points of aldehydes are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

20. Write a test to differentiate between pentan-2-one and pentan-3-one.

Ans. 2-pentanone has a CH_3CO-group, hence gives positive iodoform test. 3-pentanone does not have a CH_3CO-group, hence does not give positive iodoform test.

Iodoform Test:

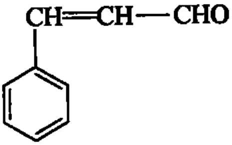


$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + NaOH \xrightarrow{I_2} \underset{\text{(Yellow ppt.)}}{CHI_3}$$

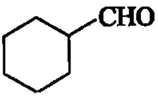
$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3 \xrightarrow{I_2/NaoH} \text{No reaction.}$$

21. Give the IUPAC names of the following compounds.

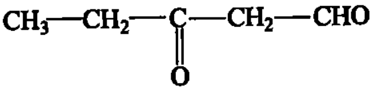
(*i*)



(*ii*)



(*iii*)



$CH_3—CH_2—\underset{\underset{O}{\|}}{C}—CH_2—CHO$

(*iv*) $CH_3—CH=CH—CHO$

Ans. (*i*) 3-Phenylprop-2-enal (*ii*) Cyclohexanecarbaldehyde

(*iii*) 3-oxopentanal (*iv*) But-2-enal

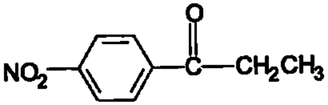
22. Give the structure of the following compounds.

(*i*) 4-Nitropropiophenone

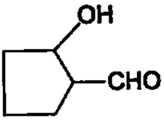
(*ii*) 2-Hydroxycyclopentanecarbaldehyde

(*iii*) Phenyl acetaldehyde

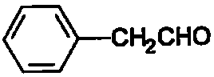
Ans. (*i*)



(*ii*)



(*iii*)

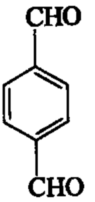


23. Write IUPAC names of the following structures.

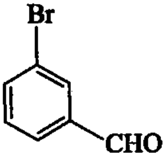
(*i*)

$\underset{CHO}{\overset{CHO}{|}}$

(*ii*)



(*iii*)

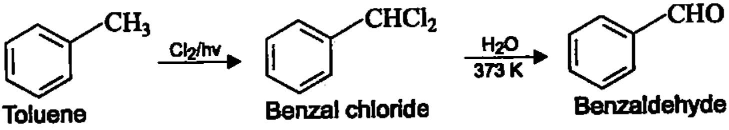


Ans. (*i*) Ethane-1, 2-dial (*ii*) Benzene-1, 4-dicarbaldehyde

(*iii*) 3-Bromobenzaldehyde

24. Benzaldehyde can be obtained from benzal chloride. Write reactions for obtaining benzalchloride and then benzaldehyde from it.

Ans.



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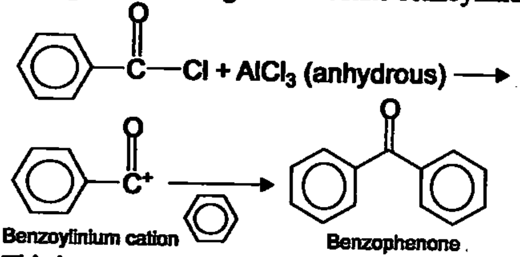
25. Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous $AlCl_3$. Name the reaction also.

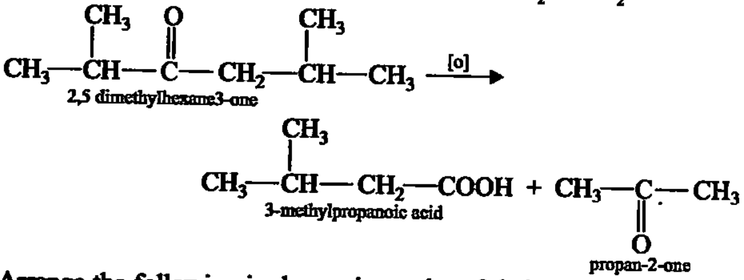
Ans. Benzene, on reaction with benzoyl chloride undergo formation of benzophenone through intermediate benzoylinium cation.



This is an example of Friedel-Craft acylation reaction.

26. Oxidation of ketones involves carbon-carbon bond cleavage. Name the products formed on oxidation of 2, 5-dimethylhexan-3-one.

Ans. Being an unsymmetrical ketone, oxidation occurs on either side of the C = O group giving a mixture of 2-methyl propanoic acid, 3-methylbutanoic acid and prepan 2-one. Propan-2-one on further oxidation gives a mixture of ethanoic acid and methanoic acid. Subsequent oxidation of methanoic acid gives CO_2 and H_2O.



$$\underset{\text{2,5 dimethylhexane3-one}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3} \xrightarrow{[o]}$$

$$\underset{\text{3-methylpropanoic acid}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-COOH} + \underset{\text{propan-2-one}}{CH_3-\underset{O}{\underset{\|}{C}}-CH_3}$$

27. Arrange the following in decreasing order of their acidic strength and give reason for your answer.

CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$

Ans. $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$

Explanation: Effect of substituents on the acidity of carboxylic acids: Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.

28. What product will be formed on reaction of propanal with 2-methylpropanal in the presence of NaOH? What products will be formed? Write the name of the reaction also.

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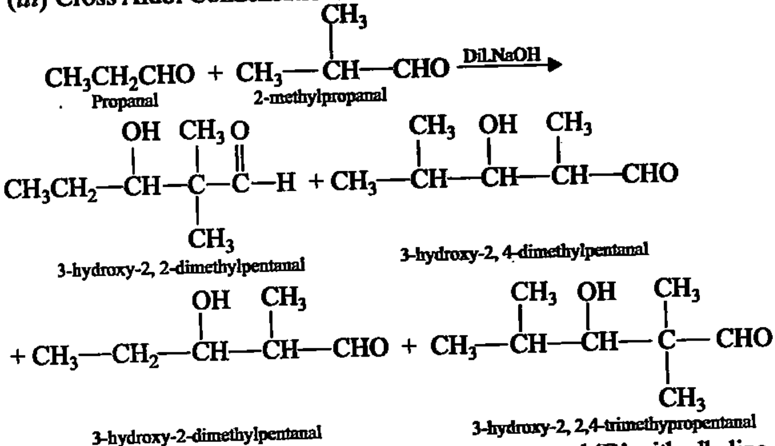
Ans. (*i*) A mixture of two aldehydes or ketones, atleast one of these must contains α-hydrogen undergo cross-aldol condensation.

(*ii*) A mixture of four product is formed.

(*iii*) Cross Aldol Condensation.



$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{2-methylpropanal}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-CHO} \xrightarrow{\text{Dil.NaOH}}$$

$$\underset{\text{3-hydroxy-2, 2-dimethylpentanal}}{CH_3CH_2-\overset{OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-H} + \underset{\text{3-hydroxy-2, 4-dimethylpentanal}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CHO}$$

$$+ \underset{\text{3-hydroxy-2-dimethylpentanal}}{CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CHO} + \underset{\text{3-hydroxy-2, 2,4-trimethypropentanal}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CHO}$$

29. Compound 'A' was prepared by oxidation of compound 'B' with alkaline $KMnO_4$. Compound 'A' on reduction with lithium aluminium hydride gets converted back to compound 'B'. When compound 'A' is heated with compound B in the presence of H_2SO_4 it produces fruity smell of compound C to which family the compounds 'A', 'B' and 'C' belong to?

Ans. Since, B and A on heating together in the presence of acid produces ester (a fruity smell).

$$\underset{\text{Alcohol}}{[B]} \xrightarrow[\text{[O]}]{\text{Alk.}KMnO_4} \underset{\text{Carboxylic acid}}{[A]}$$

$$\underset{\text{Acid}}{[A]} + \underset{\text{Alcohol}}{[B]} \overset{H_2SO_4}{\rightleftharpoons} \underset{\substack{\text{Ester}\\ \text{(fruity smell)}}}{[C]} + H_2O$$

30. Arrange the following in decreasing order of their acidic strength. Give explanation for the arrangement.

C_6H_5COOH, FCH_2COOH, NO_2CH_2COOH

Ans. $NO_2CH_2COOH > FCH_2COOH > C_6H_5COOH$

Explanation: Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects.

31. Alkenes ($>C=C<$) and carbonyl compounds ($>C=O$), both contain a π bond but alkenes show electrophilic addition reactions whereas carbonyl compounds show nucleophilic addition reactions. Explain.

Ans. Nature of chemical reaction occurring on $>C=C<$ bond or $>C=O$ bond can be explained on the basis of nature of bond between $>C=C<$ and $>C=O$.

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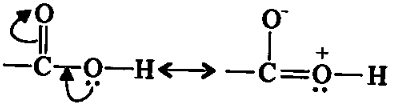
$>C{=}C<$
Non-polar covalent compound

$>C{=}O$
Polar covalent compound
* Due to electronegativity difference between carbon and oxygen

Thus, in $>C{=}O$ carbon acquires partially positive charge and O acquires partially negative charge and show nucleophilic addition reaction due to the electrophilic carbonyl carbon. On the other hand, $>C{=}C<$ undergo electrophilic addition reaction due to nucleophilic nature of $>C{=}C<$ which contains π bond.

32. Carboxylic acids contain carbonyl group but do not show the nucleophilic addition reaction like aldehydes or ketones. Why?

Ans. Due to resonance as shown below the partial positive charge on carbonyl carbon atom is reduced.



33. Identify the compounds A, B and C in the following reaction.

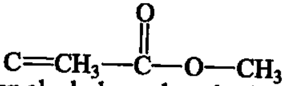
$$CH_3{-}Br \xrightarrow{Mg/ether} (A) \xrightarrow[\text{(ii) Water}]{\text{(i) } CO_2} (B) \xrightarrow[\Delta]{CH_3OH/H^+} (C)$$

Ans. Complete chemical conversion can be done as

$$\underset{\text{Bromomethane}}{CH_3{-}Br} \xrightarrow{Mg/ether} \underset{\substack{[A]\\ \text{Methyl magnesium}\\ \text{bromide}}}{CH_3MgBr} \xrightarrow[\text{(ii) Water}]{\text{(i) } CO_2} \underset{\substack{[B]\\ \text{Ethanoic acid}}}{CH_3COOH}$$

$$\xrightarrow{CH_3OH/H^+} \underset{\substack{[C]\\ \text{Methyl ethanoate}}}{CH_3COOCH_3}$$

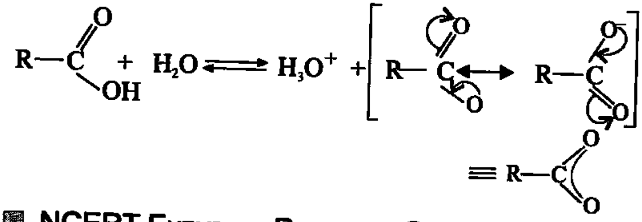
Hence, A = CH_3MgBr, B = CH_3COOH, C=



$CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3$

34. Why are carboxylic acids more acidic than alcohols or phenols although all of them have hydrogen atom attached to a oxygen atom (—O—H)?

Ans. The higher acidity of carboxylic acids as compared to phenols can be understood similarly. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion.



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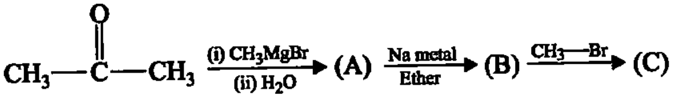
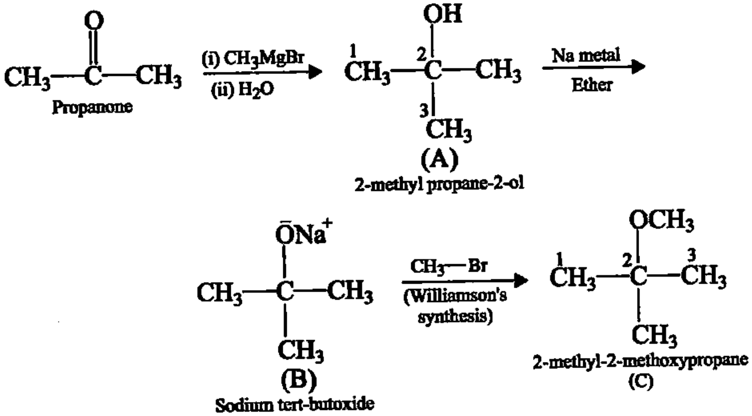
35. Complete the following reaction sequence.

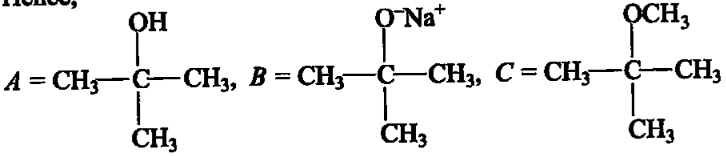


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} (A) \xrightarrow[\text{Ether}]{\text{Na metal}} (B) \xrightarrow{CH_3-Br} (C)$$

Ans.



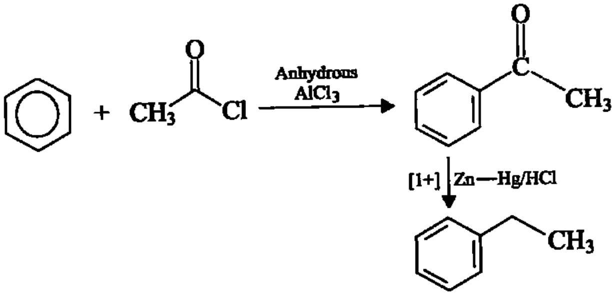
Hence,



$$A = CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3,\ B = CH_3-\overset{O^-Na^+}{\underset{CH_3}{C}}-CH_3,\ C = CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_3$$

36. Ethylbenzene is generally prepared by acetylation of benzene followed by reduction and not by direct alkylation. Think of a possible reason.

Ans. Preparation of ethylbenzene from acylation of benzene and reduction can be shown as



Ethylbenzene

37. Can Gattermann-Koch reaction be considered similar to Friedel Craft's acylation?

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Ans. Yes. The reason being that in F.C. acylation reactions, benzene (or any other arene) is treated with an acid chloride in presence of anyhd. $AlCl_3$. Since HCOCl (Formyl Chloride) is not stable. Therefore, in Gattermann-Koch reaction, it is prepared in situ by reacting CO with HCl gas in presence of anhydrous $AlCl_3$. Thus, Gattermann-Koch "action is similar to F.C. acylation reaction".

IV. MATCHING TYPE

Note : Match the items of Column I and Column II in the following questions.

38. Match the common names given in Column I with the IUPAC names given in Column II.

Column I (Common names)	Column II (IUPAC names)
(*i*) Cinnamaldehyde	(*a*) Pentanal
(*ii*) Acetophenone	(*b*) Prop-2-enal
(*iii*) Valeraldehyde	(*c*) 4-Methylpent-3-en-2-one
(*iv*) Acrolein	(*d*) 3-Phenylprop-2-enal
(*v*) Mesityl oxide	(*e*) 1-Phenylethanone

Ans. (*i*) → (*d*) (*ii*) → (*e*) (*iii*) → (*a*) (*iv*) → (*b*) (*v*) → (*c*)

39. Match the acids given in Column I with their correct IUPAC names given in Column II.

Column I (Acids)	Column II (IUPAC names)
(*i*) Phthalic acid	(*a*) Hexane-1,6-dioic acid
(*ii*) Oxalic acid	(*b*) Benzene-1,2-dicarboxylic acid
(*iii*) Succinic acid	(*c*) Pentane-1,5-dioic acid
(*iv*) Adipic acid	(*d*) Butane-1,4-dioic acid
(*v*) Glutaric acid	(*d*) Ethane-1,2-dioic acid

Ans. (*i*) → (*b*) (*ii*) → (*e*) (*iii*) → (*d*) (*iv*) → (*a*) (*v*) → (*c*)

40. Match the reactions given in Column I with the suitable reagents given in Column II.

Column I (Reactions)	Column II (Reagents)
(*i*) Benzophenone → Diphenylmethane	(*a*) $LiAlH_4$
(*ii*) Benzaldehyde → 1-Phenylethanol	(*b*) DIBAL—H
(*iii*) Cyclohexanone → Cyclohexanol	(*c*) Zn(Hg)/Conc. HCl
(*iv*) Phenyl benzoate → Benzaldehyde	(*d*) CH_3MgBr

Ans. (*i*) → (*a*) (*ii*) → (*b*) (*iii*) → (*c*) (*iv*) → (*d*)

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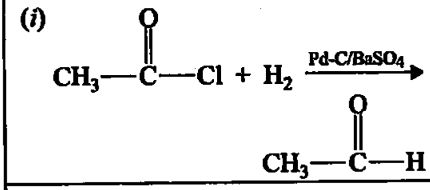
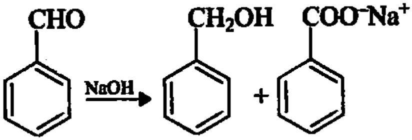
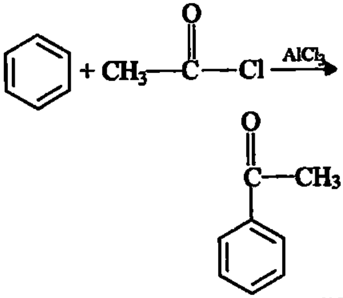
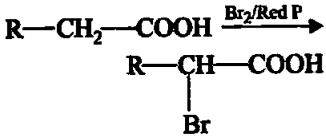
41. Match the example given in Column I with the name of the reaction in Column II.

Column I (Example)	Column II (Reaction)
(*i*)  $CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd-C/BaSO_4} CH_3-\overset{O}{\overset{\|}{C}}-H$	(*a*) Friedel-Crafts acylation
(*ii*) 	(*b*) HVZ reaction
(*iii*) 	(*c*) Aldol condensation
(*iv*)  $R-CH_2-COOH \xrightarrow{Br_2/Red\ P} R-\underset{Br}{\underset{\|}{CH}}-COOH$	(*d*) Cannizzaro's reaction
(*v*) $CH_3-CN \xrightarrow[(ii)\ H_2O/H^+]{(i)\ SnCl_2/HCl} CH_3CHO$	(*e*) Rosenmund's reduction
(*vi*) $2CH_3CHO \xrightarrow{NaOH} CH_3-CH{=}CHCHO$	(*f*) Stephen's reaction

Ans. (*i*) → (*e*) (*ii*) → (*d*) (*iii*) → (*a*) (*iv*) → (*b*) (*v*) → (*f*) (*vi*) → (*c*)

V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are correct and reason is correct explanation of assertion.

(*ii*) Assertion and reason both are wrong statements.

(*iii*) Assertion is correct statement but reason is wrong statement.

(*iv*) Assertion is wrong statement but reason is correct statement.

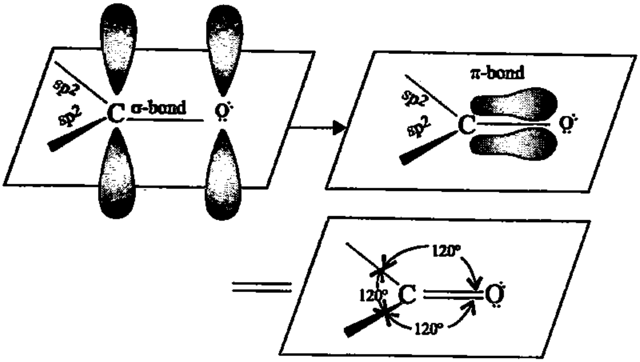
(*v*) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

42. Assertion : Formaldehyde is a planar molecule.

Reason : It contains sp^2 hybridised carbon atom.

Ans. (*i*)

Explanation:



Orbital diagram for the formation of carbonyl group.

43. Assertion : Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.

Reason : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

Ans. (*v*)

Explanation: Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehling's reagent also oxidise aldehydes.

$$R—CHO \xrightarrow{[O]} R—COOH$$

44. Assertion : The α-hydrogen atom in carbonyl compounds is less acidic.

Reason : The anion formed after the loss of α-hydrogen atom is resonance stabilised.

Ans. (*iv*)

Explanation: Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.

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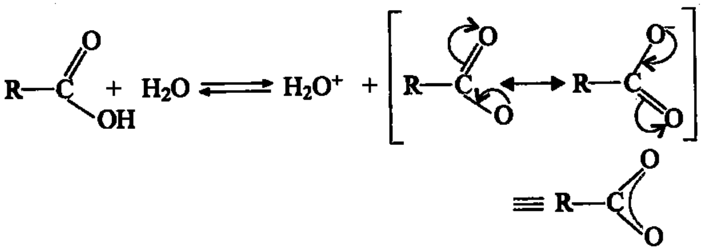


45. Assertion : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

Ans. (*iii*)

Explanation: Aldehydes which do not have an alpha α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

46. Assertion : Aldehydes and ketones, both react with Tollens' reagent to form silver mirror.

Reason : Both, aldehydes and ketones contain a carbonyl group.

Ans. (*iv*)

Explanation: Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage. The mild oxidising agents given below are used to distinguish aldehydes from ketones:

(*i*) **Tollens' test:** On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3\bar{O}H \longrightarrow RCO\bar{O} + 2Ag + 2H_2O + 4NH_3$$

VI. LONG ANSWER TYPE

47. An alkene 'A' (Mol. formula C_5H_{10}) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound 'C' does not give Fehling's test but forms iodoform. Identify the compounds A, B and C. Write the reaction for ozonolysis and formation of iodoform from B and C.

Ans. Molecular formula = C_5H_{10}

$$\text{Degree of unsaturation} = (C_n + 1) - \frac{H_n}{2}$$

where, C_n = number of carbon atoms

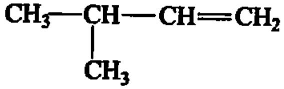
$$H_n = \text{number of hydrogen atoms} = (5+1) - \frac{10}{2} = 1$$

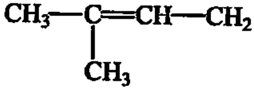
Compound A will be either alkene or cyclic hydrocarbon. Since, *A* is undergoing ozonolysis hence *A* must be an alkene.

Possible structures of alkene are

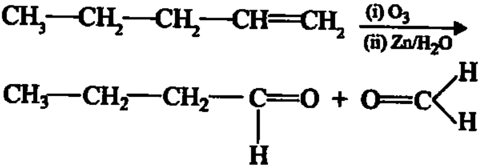
I. $CH_3—CH_2—CH_2—CH{=}CH_2$

II. $CH_3—CH_2—CH{=}CH—CH_3$

III. 
$CH_3—\underset{\underset{CH_3}{|}}{CH}—CH{=}CH_2$

IV. 
$CH_3—\underset{\underset{CH_3}{|}}{C}{=}CH—CH_2$

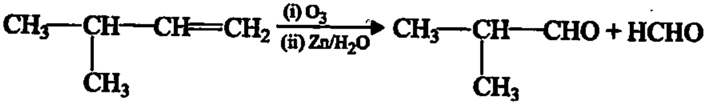
Ozonolysis of structure I produces aldehyde only


$$CH_3—CH_2—CH_2—CH{=}CH_2 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} CH_3—CH_2—CH_2—\underset{\underset{H}{|}}{C}{=}O + O{=}C\begin{matrix}H\\H\end{matrix}$$

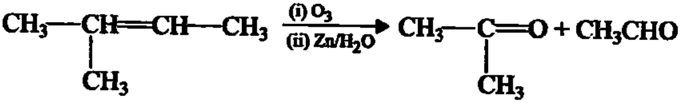
Ozonolysis of structure II produces aldehyde only

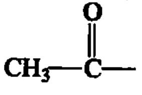
$$CH_3—CH_2—CH{=}CH—CH_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} CH_3—CH_2—CHO + CH_3CHO$$

Ozonolysis of structure III produces aldehyde only


$$CH_3—\underset{\underset{CH_3}{|}}{CH}—CH{=}CH_2 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} CH_3—\underset{\underset{CH_3}{|}}{CH}—CHO + HCHO$$

Ozonolysis of structure IV produces both aldehyde and ketone


$$CH_3—\underset{\underset{CH_3}{|}}{CH}{=}CH—CH_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} CH_3—\underset{\underset{CH_3}{|}}{C}{=}O + CH_3CHO$$

After ozonolysis of each of structures I, II and III produces only aldehydes as both components. But as given in the question one compound doesn't give Fehling's test but must give iodoform test. Hence, compound must be a ketone with  $CH_3—\overset{\overset{O}{\|}}{C}—$ group. Hence, correct structure is IV.

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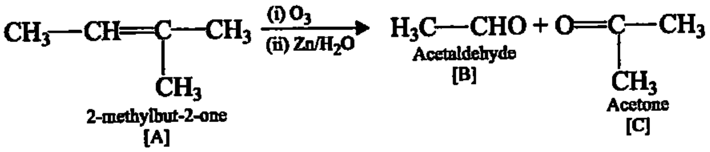


$$\underset{\underset{[A]}{\text{2-methylbut-2-one}}}{CH_3{-}CH{=}\underset{\underset{CH_3}{|}}{C}{-}CH_3} \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} \underset{\underset{[B]}{\text{Acetaldehyde}}}{H_3C{-}CHO} + \underset{\underset{[C]}{\text{Acetone}}}{O{=}\underset{\underset{CH_3}{|}}{C}{-}CH_3}$$

Formation of iodoform from '*B*' and '*C*' may be explained as follows:

$$\underset{\underset{[B]}{\text{Acetaldehyde}}}{CH_3CHO} + 3I_2 + 4NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium formate}}{HCOONa} + 3NaI + 3H_2O$$

$$\underset{\underset{[C]}{\text{Acetone}}}{CH_3COCH_3} + 3I_2 + 4NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium acetate}}{CH_3COONa} + 3NaI + 3H_2O$$

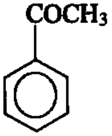
48. An aromatic compound 'A' (Molecular formula C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollens' or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' (Molecular formula $C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.

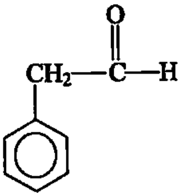
Ans. Molecular formula = C_8H_8O

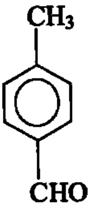
Degree of unsaturation = $(C_n + 1) - \frac{H_n}{2} = (8+1) - \frac{8}{2} = 9 - 4 = 5$

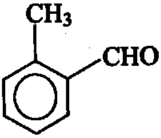
Degree of unsaturation > 5 *i.e.*, it may contain benzene ring having degree of unsaturation equal to 4 and one degree of unsaturation must be carbonyl group.

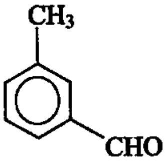
Thus, possible structures are

(*i*)


(*ii*)


(*iii*)


(*iv*)


(*v*)


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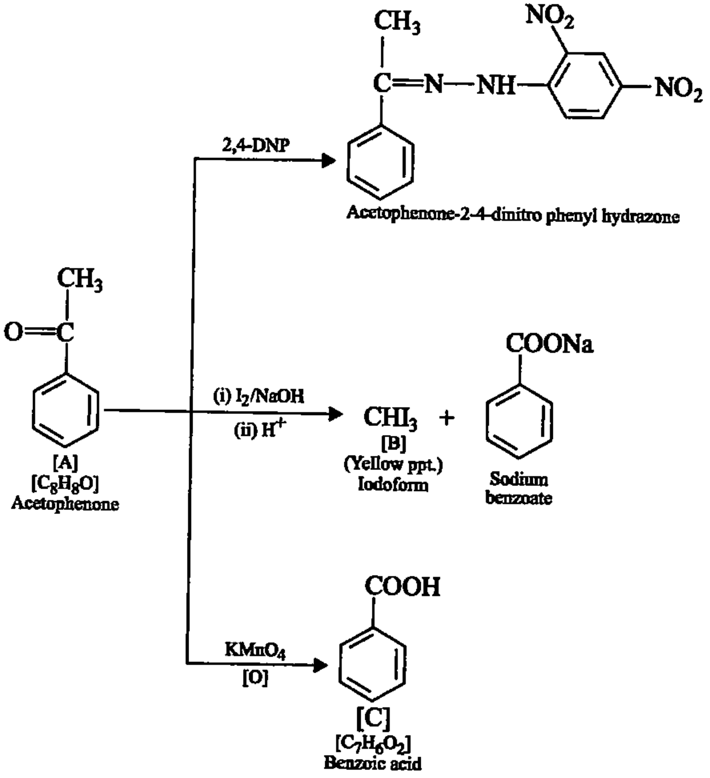
According to question, compound '*A*' does not respond to Tollens' or Fehling's test, so, it is a ketone, not aldehyde. Therefore, structure I is correct. Complete reaction sequence is as follows:



49. Write down functional isomers of a carbonyl compound with molecular formula C_3H_6O. Which isomer will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reaction conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why?

Ans. Functional isomers of C_3H_6O containing carbonyl group are

$$\underset{\text{Propanal}}{CH_3CH_2CHO} \quad \text{and} \quad \underset{\text{Propanone}}{CH_3COCH_3}$$

(*a*) Propanal, CH_3CH_2CHO will react faster with HCN because there is less steric hindrance and electronic factors, which increases its electrophilicity.

(*b*) The reaction mechanism is as follows:

$$HCN + OH^- \rightleftharpoons :\bar{C}N + H_2O$$

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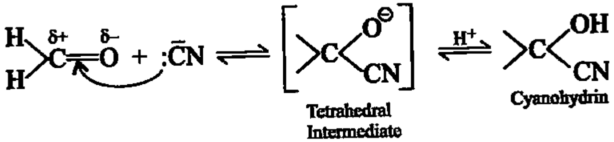

The reaction does not lead to completion because it is a reversible reaction. Equilibrium is established.

(*c*) If a strong acid is added to the reaction mixture, the reaction is inhibited because production of $\bar{C}N$ ions prevented.

50. When liquid 'A' is treated with a freshly prepared ammoniacal silver nitrate solution, it gives bright silver mirror. The liquid forms a white crystalline solid on treatment with sodium hydrogensulphite. Liquid 'B' also forms a white crystalline solid with sodium hydrogensulphite but it does not give test with ammoniacal silver nitrate. Which of the two liquids is aldehyde? Write the chemical equations of these reactions also.

Ans. Since the liquid *A* reduces ammoniacal silver nitrate, (Tollen's reagent), 'A' is aldehyde.

1. $$\underset{\text{Aldehyde}}{RCHO} + 2[Ag(NH_3)_2]NO_3 + 2NH_4OH \longrightarrow RCOOH + \underset{\text{Silver mirror}}{2Ag\downarrow} + H_2O + 4NH_3 + 2NH_4NO_3$$

Note: Aldehyde and ketone both gives white crystalline solid with sodium hydrogensulphite but this is only aldehyde which gives Tollens' test and Fehling's test.

□□□

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13 Amines

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

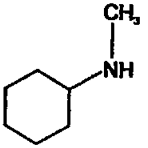
1. Which of the following is a 3° amine?

(*i*) 1-methylcyclohexylamine (*ii*) Triethylamine
(*iii*) tert-butylamine (*iv*) N-methylaniline

Ans. (*ii*)

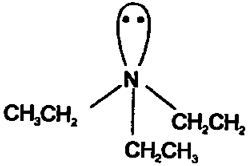
Explanation: The structure of given amines are as follows:

(*a*)



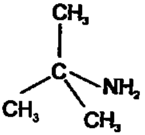
1-methylcyclohexylamine
(2° amine)

(*b*)



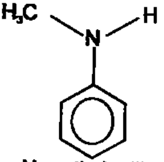
Triethylamine
(3° amine)

(*c*)



tert-butylamine
(1° amine)

(*d*)



N-methylaniline

Hence, triethylamine is tertiary amine. The correct choice is (*ii*).

2. The correct IUPAC name for $CH_2{=}CHCH_2NHCH_3$ is

(*i*) Allylmethylamine (*ii*) 2-amino-4-pentene
(*iii*) 4-aminopent-1-ene (*iv*) N-methylprop-2-en-1-amine

Ans. (*iv*)

Explanation: IUPAC name of the compound is N-methylprop-2-en-1-amine.

3. Amongst the following, the strongest base in aqueous medium is __________.

(*i*) CH_3NH_2 (*ii*) $NCCH_2NH_2$
(*iii*) $(CH_3)_2NH$ (*iv*) $C_6H_5NHCH_3$

Ans. (*iii*)

Explanation: Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.

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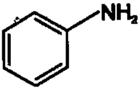
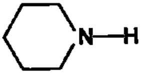
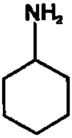
Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups.

4. Which of the following is the weakest Brönsted base?

(*i*)


(*ii*)


(*iii*)


(*iv*) CH_3NH_2

Ans. (*i*)

Explanation: In aniline or other arylamines, the —NH_2 group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation.

5. Benzylamine may be alkylated as shown in the following equation:

$$C_6H_5CH_2NH_2 + R{-}X \longrightarrow C_6H_5CH_2NHR$$

Which of the following alkylhalides is best suited for this reaction through S_N1 mechanism?

(*i*) CH_3Br (*ii*) C_6H_5Br
(*iii*) $C_6H_5CH_2Br$ (*iv*) C_2H_5Br

Ans. (*iii*)

Explanation: S_1N reaction proceeds through the formation of carbocation since in $C_6H_5CH_2Br$ benzyl carbocation is formed which is stabilized by resonance.

6. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

(*i*) H_2 (excess)/Pt (*ii*) $LiAlH_4$ in ether
(*iii*) Fe and HCl (*iv*) Sn and HCl

Ans. (*ii*)

Explanation: Nitroalkanes can be easily reduced to the corresponding primary amines with $LiAlH_4$.

$$CH_3CH_2{-}NO_2 \xrightarrow[\text{Dry ether}]{\text{LiAlH4}} \underset{\text{Ethylamine}}{CH_3CH_2{-}NH_2}$$

In contrast, aromatic nitro compounds on reduction with $LiAlH_4$ give $a = 0$ compounds and not primary amines.

$$2C_6H_5{-}NO_2 \xrightarrow[\text{Dry ether}]{\text{LiAlH4}} \underset{\text{Azobenzene}}{C_6H_5{-}N{=}N{-}C_6H_5}$$

7. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is ___________.

(*i*) Sodium amide, $NaNH_2$
(*ii*) Sodium azide, NaN_3

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(*iii*) Potassium cyanide, KCN

(*iv*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

Ans. (*iii*)

8. The source of nitrogen in Gabriel synthesis of amines is ____________.

(*i*) Sodium azide, NaN_3

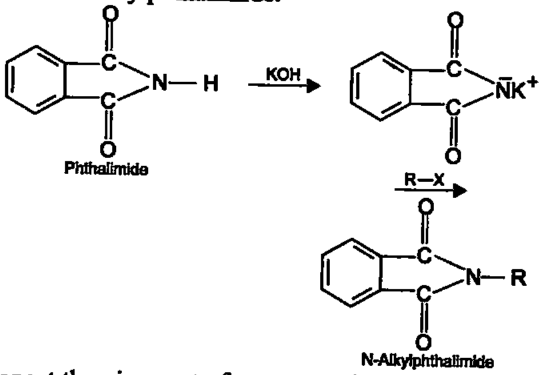
(*ii*) Sodium nitrite, $NaNO_2$

(*iii*) Potassium cyanide, KCN

(*iv*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

Ans. (*iv*)

Explanation: Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



9. Amongst the given set of reactants, the most appropriate for preparing 2° amine is _____.

(*i*) 2° R—Br + NH_3

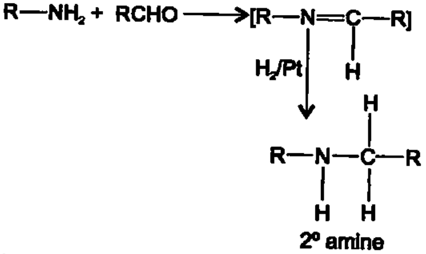
(*ii*) 2° R—Br + NaCN followed by H_2/Pt

(*iii*) 1° R—NH_2 + RCHO followed by H_2/Pt

(*iv*) 1° R—Br (2 mol) + potassium phthalimide followed by H_3O^+/heat

Ans. (*iii*)

Explanation: Chemical transformation can be shown as



$$R{-}NH_2 + RCHO \longrightarrow [R{-}N{=}\underset{\displaystyle H}{\underset{|}{C}}{-}R] \xrightarrow{H_2/Pt} R{-}\underset{\displaystyle H}{\underset{|}{N}}{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}{-}R$$

2° amine

While other given set of reactants give primary amine only.

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10. The best reagent for converting 2–phenylpropanamide into 2-phenylpropanamine is ______.

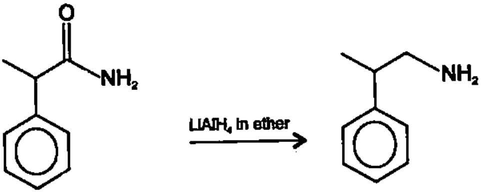
(*i*) excess H_2 (*ii*) Br_2 in aqueous NaOH

(*iii*) iodine in the presence of red phosphorus

(*iv*) $LiAlH_4$ in ether

Ans. (*iv*)

Explanation: The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is $LiAlH_4$ in ether. Reaction is as given below:



2-phenylpropanamide 2-phenylpropanamine

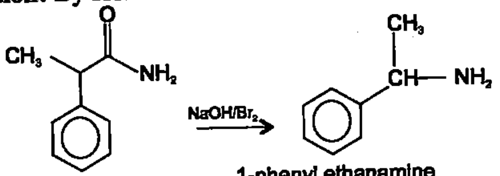
11. The best reagent for converting, 2-phenylpropanamide into 1-phenylethanamine is ____________.

(*i*) excess H_2/Pt (*ii*) NaOH/Br_2

(*iii*) $NaBH_4$/methanol (*iv*) $LiAlH_4$/ether

Ans. (*ii*)

Explanation: By Hoffmann bromamide reaction with NaOH/Br_2



1-phenyl ethanamine

12. Hoffmann Bromamide Degradation reaction is shown by __________.

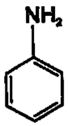
(*i*) $ArNH_2$ (*ii*) $ArCONH_2$

(*iii*) $ArNO_2$ (*iv*) $ArCH_2NH_2$

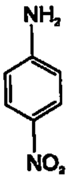
Ans. (*ii*)

Explanation: Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom.

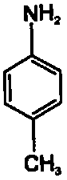
13. The correct increasing order of basic strength for the following compounds is _________.



(I)



(II)



(III)

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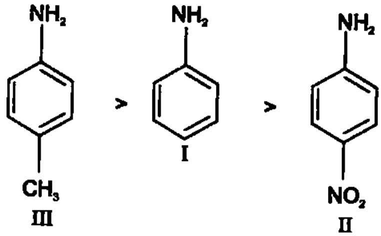
(*i*) II < III < I (*ii*) III < I < II

(*iii*) III < II < I (*iv*) II < I < III

Ans. (*iv*)

Explanation: The correct increasing order of basic strength is as follows:



Greater the electron density towards ring, greater will be its basic strength. Electron withdrawing group decreases basic strength while electron donating group increases basic strength.

14. Methylamine reacts with HNO_2 to form _________.

(*i*) $CH_3—O—N=O$ (*ii*) $CH_3—O—CH_3$

(*iii*) CH_3OH (*iv*) CH_3CHO

Ans. (*iii*)

Explanation:

$$R—NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R—\overset{+}{N}_2\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

15. The gas evolved when methylamine reacts with nitrous acid is _________.

(*i*) NH_3 (*ii*) N_2

(*iii*) H_2 (*iv*) C_2H_6

Ans. (*ii*)

Explanation: Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohol.

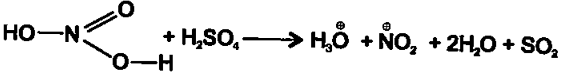
16. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiates the reaction is _________.

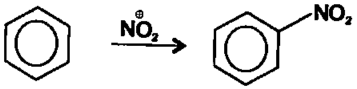
(*i*) NO_2 (*ii*) NO^+

(*iii*) NO_2^+ (*iv*) NO_2^-

Ans. (*iii*)

Explanation: Nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3 proceeds as





This reaction is known as electrophilic substitution reaction.

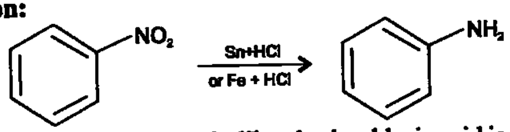
17. Reduction of aromatic nitro compounds using Fe and HCl gives __________.

(*i*) aromatic oxime (*ii*) aromatic hydrocarbon

(*iii*) aromatic primary amine (*iv*) aromatic amide

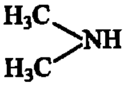
Ans. (*iii*)

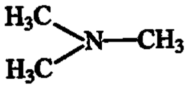
Explanation:

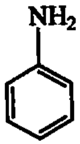


18. The most reactive amine towards dilute hydrochloric acid is __________.

(*i*) $CH_3—NH_2$

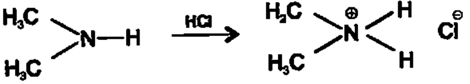
(*ii*)

$(H_3C)_2NH$

(*iii*)

$(H_3C)_2N—CH_3$

(*iv*)


Ans. (*ii*)

Explanation: Greater will be the strength of base, greater will be its reactivity towards dilute HCl. Hence, $(CH_3)_2NH$ has highest basic strength as it has highest reactivity.



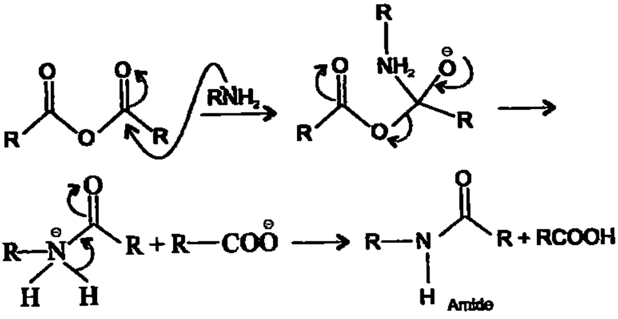
19. Acid anhydrides on reaction with primary amines give __________.

(*i*) amide (*ii*) imide

(*iii*) secondary amine (*iv*) imine

Ans. (*i*)

Explanation: Acid anhydride on reaction with primary amine produces amide as



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20. The reaction $Ar\overset{+}{N_2}Cl^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuCl$ is named as ________.

(*i*) Sandmeyer reaction
(*ii*) Gatterman reaction
(*iii*) Claisen reaction
(*iv*) Carbylamine reaction

Ans. (*i*)

Explanation:

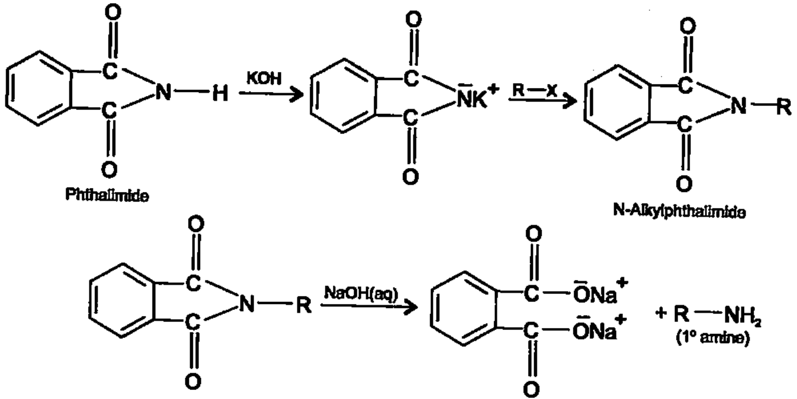
$$Ar\overset{+}{N_2}\overset{-}{X} \begin{cases} \xrightarrow{CuCl/HCl} ArCl + N_2 \\ \xrightarrow{CuBr/HBr} ArBr + N_2 \\ \xrightarrow{CuCN/KCN} ArCN + N_2 \end{cases}$$

21. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is

(*i*) Hoffmann Bromamide reaction
(*ii*) Gabriel phthalimide synthesis
(*iii*) Sandmeyer reaction
(*iv*) Reaction with NH_3

Ans. (*ii*)

Explanation:



22. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride.

(*i*) Aniline
(*ii*) Phenol
(*iii*) Anisole
(*iv*) Nitrobenzene

Ans. (*iv*)

Explanation: Nitrobenzene will not undergo azo coupling reaction with benzene diazonium chloride while other three undergo diazo coupling reaction very easily. Diazonium cation is a weak E^+ and hence reacts with electron rich compounds containing electron donating group, *i.e.* $—OH_1—NH_2$ and $—OCH_3$ groups and not with compounds containing electron withdrawing group, *i.e.*, NO_2 etc.

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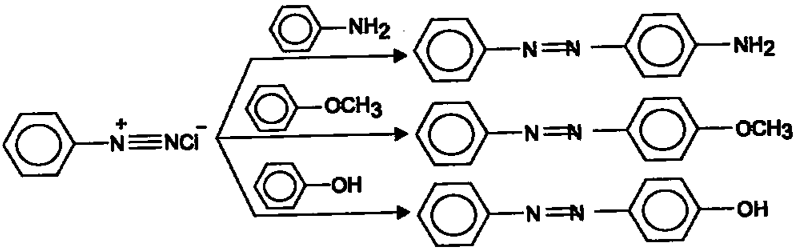
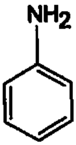
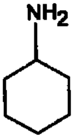
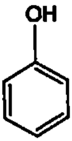
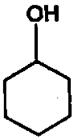


23. Which of the following compounds is the weakest Brönsted base?

(*i*)


(*ii*)


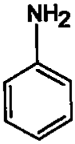
(*iii*)


(*iv*)


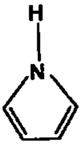
Ans. (*iii*)

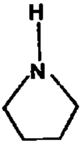
Explanation: Phenol is the weakest Brönsted base as it is the strongest acid among the four choices given above. Stronger the acid weaker is its conjugate base.

24. Among the following amines, the strongest Brönsted base is ________.

(*i*)


(*ii*) NH_3

(*iii*)


(*iv*)


Ans. (*iv*)

Explanation: Pyrrolidine is strongest of two base as lone pair of nitrogen does not involved in resonance and also due to presence of two alkyl basic strength becomes high among given four compounds.

25. The correct decreasing order of basic strength of the following species is ________.

H_2O, NH_3, OH^-, NH_2^-

(*i*) $NH_2^- > OH^- > NH_3 > H_2O$
(*ii*) $OH^- > NH_2^- > H_2O > NH_3$
(*iii*) $NH_3 > H_2O > NH_2^- > OH^-$
(*iv*) $H_2O > NH_3 > OH^- > NH_2^-$

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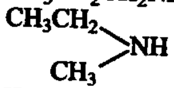
Ans. (*i*)

Explanation: Basic strength depends upon the electron donating capacity of the central atom, here amide is most basic due to presence of negative charge and two lone pair of electrons on nitrogen atom.

26. Which of the following should be most volatile?

(I) $CH_3CH_2CH_2NH_2$ (II) $(CH_3)_3N$

(III)



(IV) $CH_3CH_2CH_3$

(*i*) II (*ii*) IV (*iii*) I (*iv*) III

Ans. (*ii*)

Explanation: Hydrocarbon is most volatile because of the absence of hydrogen bonding. 1°, 2°, 3° amines are less volatile because of high boiling point due to hydrogen bonding.

27. Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant?

(*i*) Reaction of nitrite with $LiAlH_4$.

(*ii*) Reaction of amide with $LiAlH_4$ followed by treatment with water.

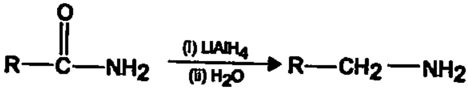
(*iii*) Heating alkylhalide with potassium salt of phthalimide followed by hydrolysis.

(*iv*) Treatment of amide with bromine in aqueous solution of sodium hydroxide.

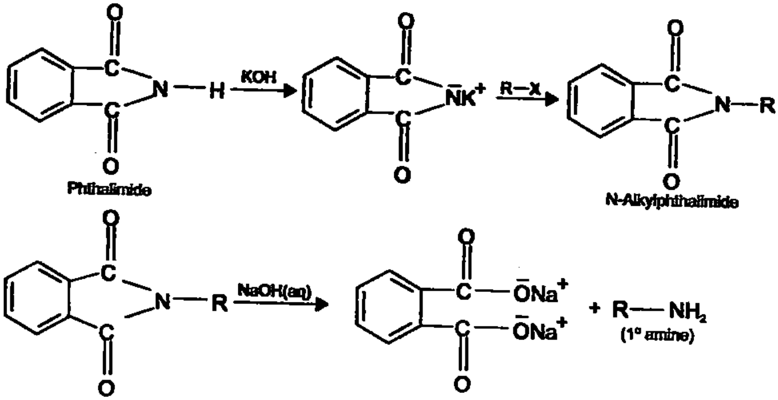
Ans. (*iv*)

Explanation: Only treatment of amide with Br_2 is aqueous solution of NaOH will give an amine with lesser number of carbon atoms than in the reactant while $RCONH_2$ Br_2/NaOH RNH_2 all the reamaining reactions given an amine with the same number of carbon atoms as in the reactant.

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$



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II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

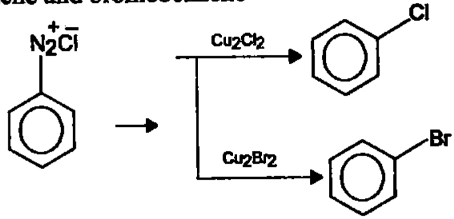
Note : In the following questions two or more options may be correct.

28. Which of the following cannot be prepared by Sandmeyer's reaction?

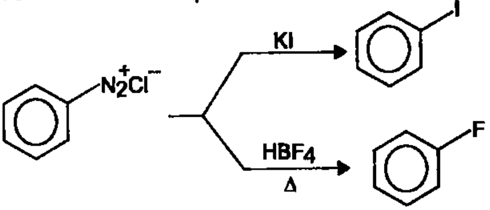
(*i*) Chlorobenzene	(*ii*) Bromobenzene
(*iii*) Iodobenzene	(*iv*) Fluorobenzene

Ans. (*iii*) and (*iv*)

Explanation: Sandmeyer's reaction is used for preparation of chlorobenzene and bromobenzene



Iodobenzene and fluorobenzene can be prepared by direct reaction of diazonium salt KI and HBF_4/Δ.

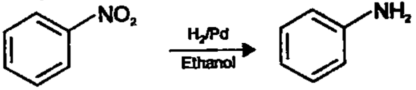


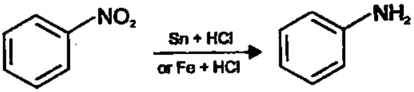
29. Reduction of nitrobenzene by which of the following reagent gives aniline?

(*i*) Sn/HCl	(*ii*) Fe/HCl
(*iii*) H_2-Pd	(*iv*) Sn/NH_4OH

Ans. (*i*), (*ii*) and (*iii*)

Explanation: Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium.





30. Which of the following species are involved in the carbylamine test?

(*i*) R—NC	(*ii*) $CHCl_3$
(*iii*) $COCl_2$	(*iv*) $NaNO_2$ + HCl

Ans. (*i*) and (*ii*)

Explanation: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or

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carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction.

$$R—NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R—NC + 3KCl + 3H_2O$$

31. The reagents that can be used to convert benzenediazonium chloride to benzene are ________.

(*i*) $SnCl_2/HCl$ (*ii*) CH_3CH_2OH

(*iii*) H_3PO_2 (*iv*) $LiAlH_4$

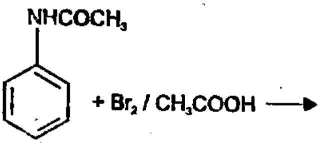
Ans. (*ii*) and (*iii*)

Explanation: Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanal, respectively.

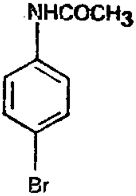
$$Ar\overset{+}{N}_2\overset{-}{Cl} + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$Ar\overset{+}{N}_2\overset{-}{Cl} + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl$$

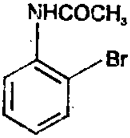
32. The product of the following reaction is ________.



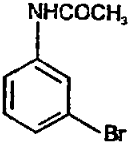
(*i*)



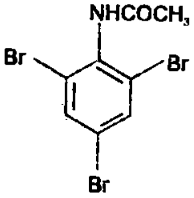
(*ii*)



(*iii*)

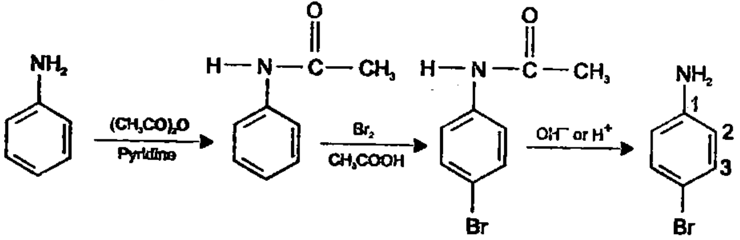


(*iv*)



Ans. (*i*) and (*ii*)

Explanation: Activating effect of —$NHCOCH_3$ group is less than that of amino group.



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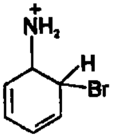
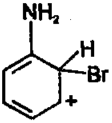
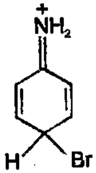
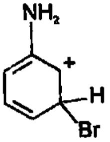
33. Arenium ion involved in the bromination of aniline is __________.

(i) 

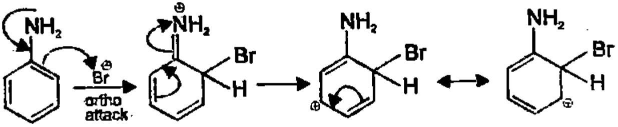
(ii) 

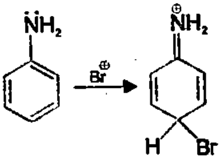
(iii) 

(iv) 

Ans. (i), (ii) and (iii)

Explanation: Arenium ion involved in the bromination of aniline are as follows:

(i) 

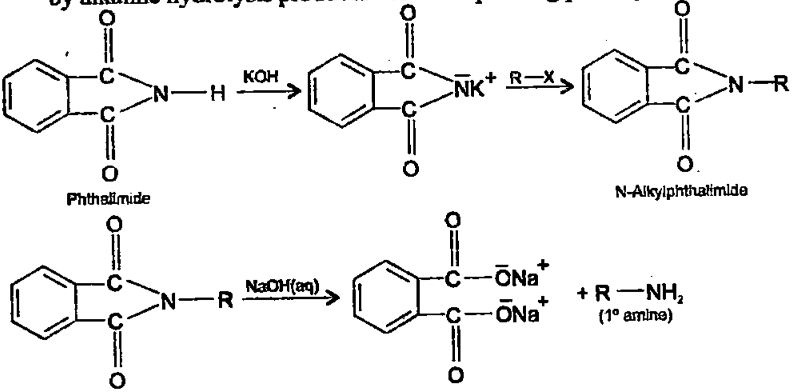
(ii) 

34. Which of the following amines can be prepared by Gabriel synthesis?

(i) Isobutyl amine
(ii) 2-Phenylethylamine
(iii) N-methylbenzylamine
(iv) Aniline

Ans. (i) and (ii)

Explanation: Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



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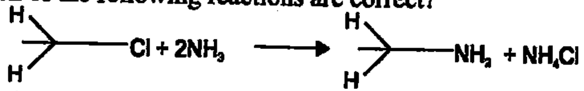
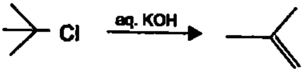
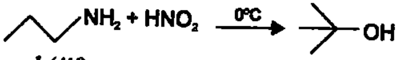
35. Which of the following reactions are correct?

(*i*) 

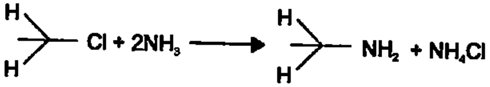
(*ii*) 

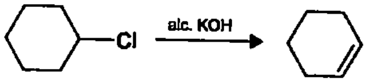
(*iii*) 

(*iv*) 

Ans. (*i*) and (*iii*)

Explanation:

(*i*) 

(*iii*) 

(*i*) is a nucleophilic substitution reaction.

(*iii*) is an elimination reaction.

36. Under which of the following reaction conditions, aniline gives *p*-nitro derivative as the major product?

(*i*) Acetyl chloride/pyridine followed by reaction with conc. H_2SO_4 + conc. HNO_3.

(*ii*) Acetic anyhdride/pyridine followed by conc. H_2SO_4 + conc. HNO_3.

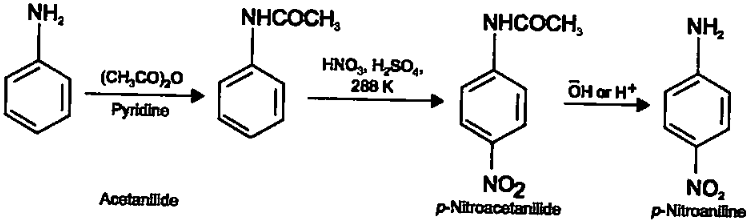
(*iii*) Dil. HCl followed by reaction with conc. H_2SO_4 + conc. HNO_3.

(*iv*) Reaction with conc. HNO_3 + conc. H_2SO_4.

Ans. (*i*) and (*ii*)

Explanation: Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is formed.

However, by protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.



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37. Which of the following reactions belong to electrophilic aromatic substitution?

(*i*) Bromination of acetanilide

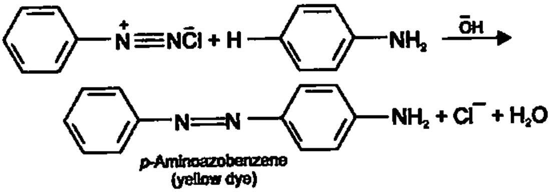
(*ii*) Coupling reaction of aryldiazonium salts

(*iii*) Diazotisation of aniline

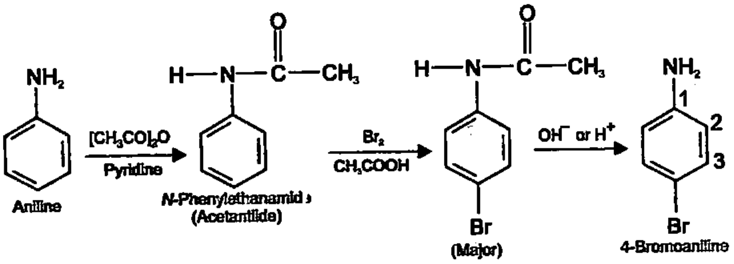
(*iv*) Acylation of aniline

Ans. (*i*) and (*ii*)

Explanation: Benzene diazonium chloride reacts with phenol in which the phenol molecule at *its para* position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. This is an example of electrophilic substitution reaction.The reaction can be shown as:



Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline. By protecting the —NH_2 group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.



III. SHORT ANSWER TYPE

38. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?

Ans. In the case of nitration, the electrophile, nitronium ion, $\overset{+}{NO_2}$ dis produced by transfer of a proton (from sulphuric acid) to nitric acid in the following manner:

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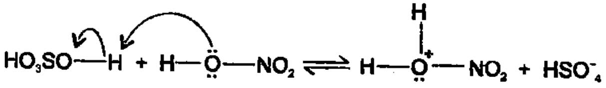
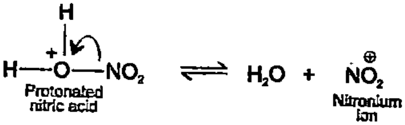
Step I

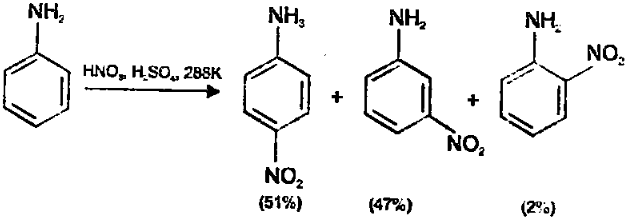


Step II

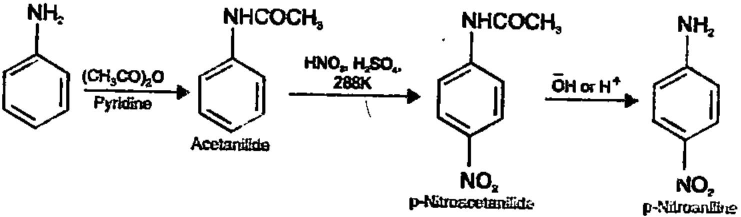


39. Why is NH_2 group of aniline acetylated before carrying out nitration?

Ans. Direct nitration of aniline yields carry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.



However by protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.



40. What is the product when $C_6H_5CH_2NH_2$ reacts with HNO_2?

Ans. $C_6H_5CH_2OH$

41. What is the best reagent to convert nitrile to primary amine?

Ans. Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation, produce primary amines.

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

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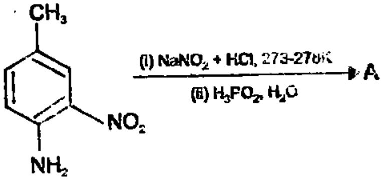
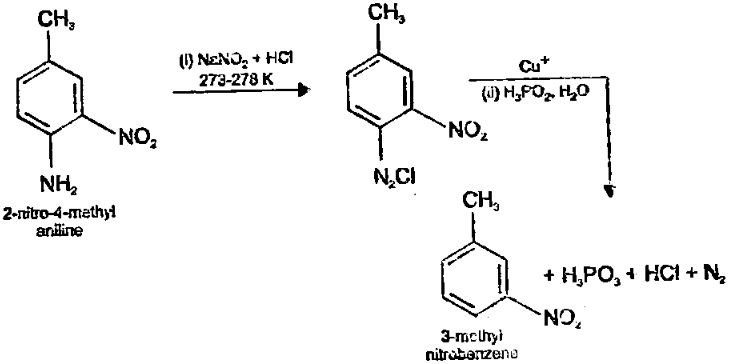
42. Give the structure of 'A' in the following reaction.

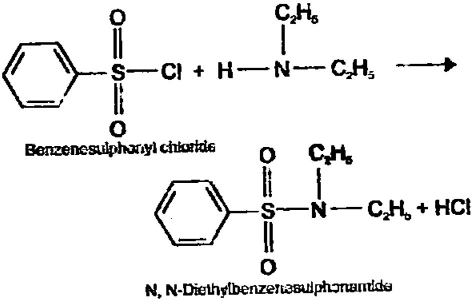


Ans. Complete conversion can be shown as



43. What is Hinsberg reagent?

Ans. Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), is also known as Hinsberg's reagent. It reacts with primary and secondary amines to form sulphonamides. Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$). Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N−diethylamine reacts with Hinsberg's reagent to form N, N−diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.



44. Why is benzenediazonium chloride not stored and is used immediately after its preparation?

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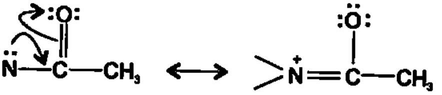
Ans. Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273–278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into diazonium salts is known as diazotisation. Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

Benzenediazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state.

45. Why does acetylation of —NH_2 group of aniline reduce its activating effect?

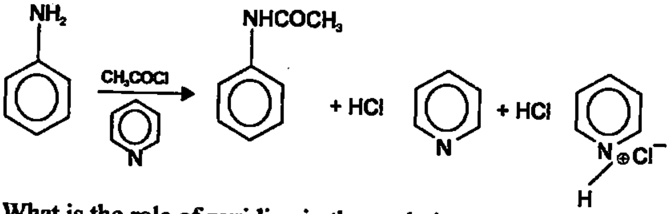
Ans. The activating effect of —NH_2 group can be controlled by protecting the —NH_2 group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

The lone part of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:



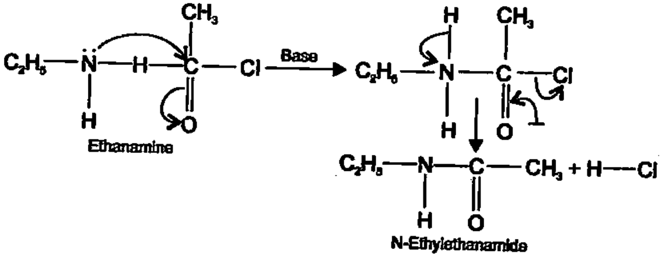
46. Explain why $MeNH_2$ is stronger base than MeOH?

Ans. Pyridine being a base, is used to remove the side product i.e., HCl from reaction mixture.



47. What is the role of pyridine in the acylation reaction of amines?

Ans. The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.



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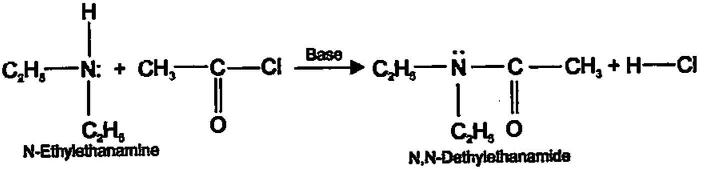
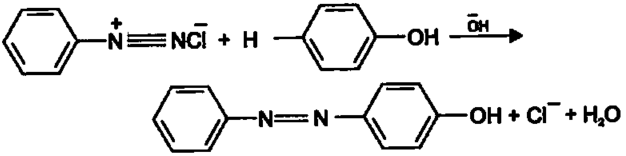
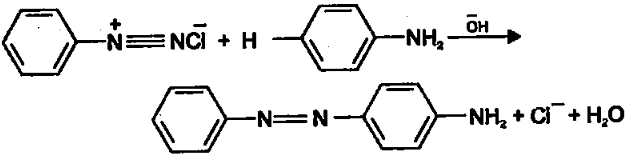


48. Under what reaction conditions (acidic/basic), the coupling reaction of aryldiazonium chloride with aniline is carried out?

Ans. The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its *para* position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction.



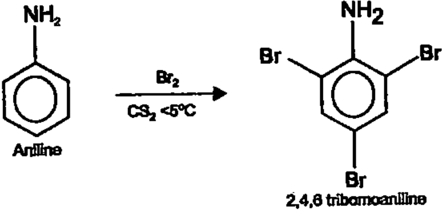
p-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene (yellow dye)

49. Predict the product of reaction of aniline with bromine in non-polar solvent such as CS_2.

Ans. Aniline on reaction with Br_2 in non-polar solvent CS_2 produces 2, 4, 6-tribromoaniline.



Aniline has high reactivity towards bromine as it gives the triply substituted product.

50. Arrange the following compounds in increasing order of dipole moment.

$$CH_3CH_2CH_3,\ CH_3CH_2NH_2,\ CH_3CH_2OH$$

Ans. Dipole moment of amine, alcohol and hydrocarbon can be explained on the basis of bond polarity of C—H, N—H and O—H bond.

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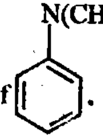
As the bond polarity increases, dipole moment increases
$CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$.

51. What is the structure and IUPAC name of the compound, allyl amine?

Ans. Structural formula of allyl amine is as follows:

$$CH_2{=}CH{-}CH_2{-}NH_2$$

prop-2-ene-1-amine

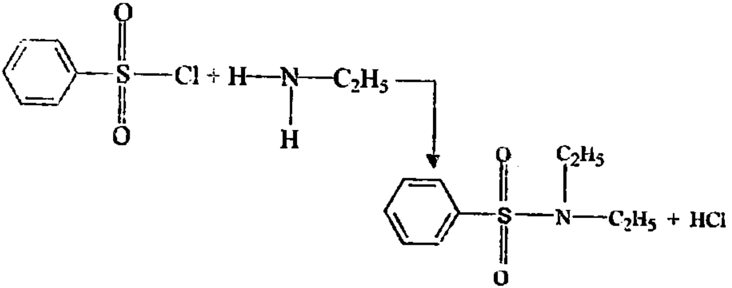
52. Write down the IUPAC name of .

Ans. N,N-Dimethylaminobenzene.

53. A compound Z with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid, insoluble in alkali. Identify Z.

Ans. Z is an aliphatic amine which gives a solid insoluble in base.

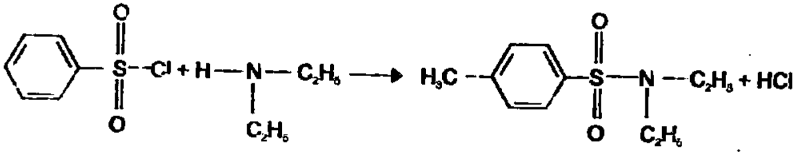
The reaction of benzenesulphonyl chloride with primary amine yields N-alkylbenzenesulphonamide.



N-Ethylbenzenesulphonamide (soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

In the reaction with secondary amine, N,N-dialkyllbenzenesulphonamide is formed.



N,N-Diethylbenzenesulphonamide

Since N, N-diethylbenzenesulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

54. A primary amine, RNH_2 can be reacted with $CH_3{-}X$ to get secondary amine, $R{-}NHCH_3$ but the only disadvantage is that 3° amine and quaternary ammonium salts are also obtained as side products. Can you suggest a method where RNH_2 forms only 2° amine?

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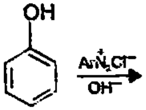
Ans. Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines.

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

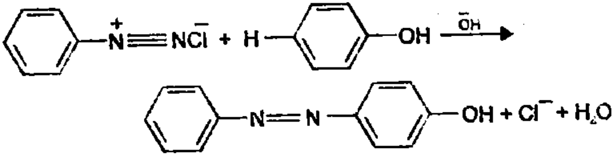
On catalytic reduction the isocyanide will give a secondary amine with one methyl group.

$$RNC \xrightarrow{H_2/Pd} RNHCH_3.$$

55. Complete the following reaction.



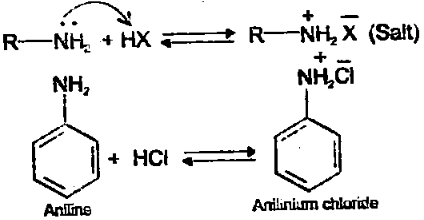
Ans. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.



p-Hydroxyazobenzene (orange dye)

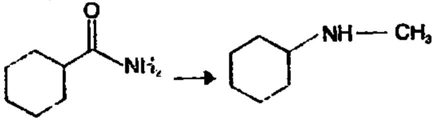
56. Why is aniline soluble in aqueous HCl?

Ans. Amines, being basic in nature, react with acids to form salts.

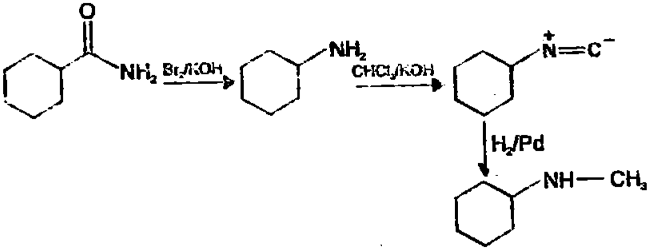


Amine salts are soluble in water.

57. Suggest a route by which the following conversion can be accomplished.



Ans.



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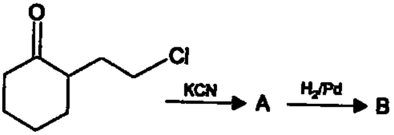
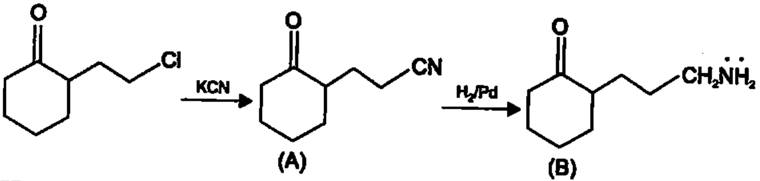
58. Identify A and B in the following reaction.



Ans.

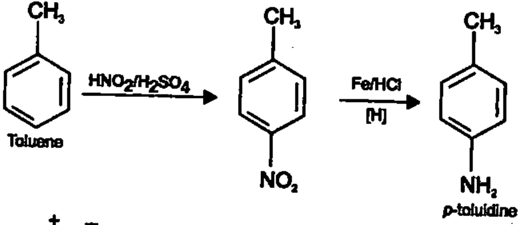


59. How will you carry out the following conversions?

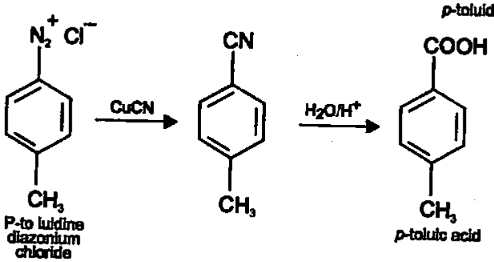
(*i*) toluene → p-toluidine

(*ii*) p-toluidine diazonium chloride → *p*-toluic acid

Ans. (*i*)



(*ii*)

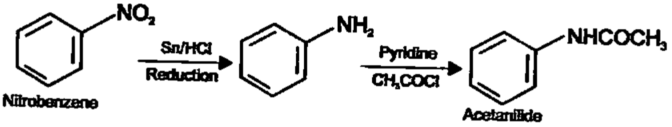


60. Write following conversions:

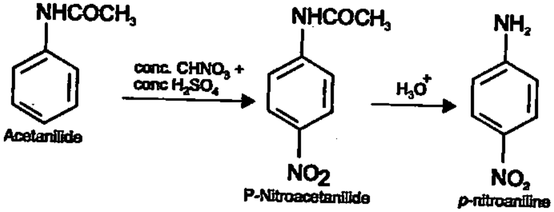
(i) nitrobenzene → acetanilide

(ii) acetanilide → *p*-nitroaniline

Ans. (*i*)



(*ii*)



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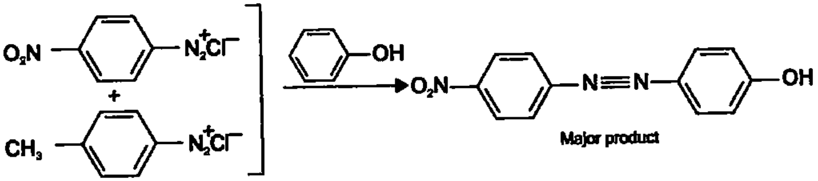
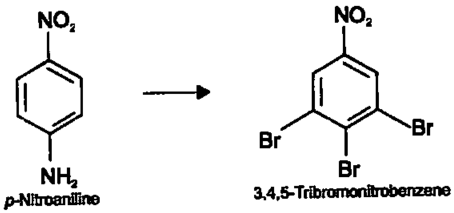
61. A solution contains 1 g mol. each of *p*-toluene diazonium chloride and *p*-nitrophenyl diazonium chloride. To this 1 g mol. of alkaline solution of phenol is added. Predict the major product. Explain your answer.

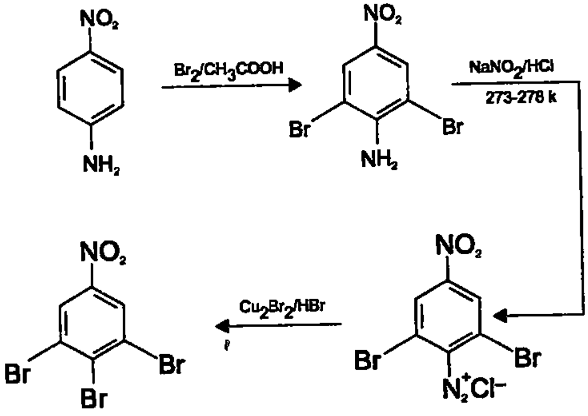
Ans. So, nitrophenyl diazonium chloride couples preferentially with phenol.



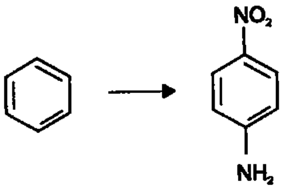
62. How will you bring out the following conversion?



Ans. Complete conversion of above reaction can be shown as



63. How will you carry out the following conversion?



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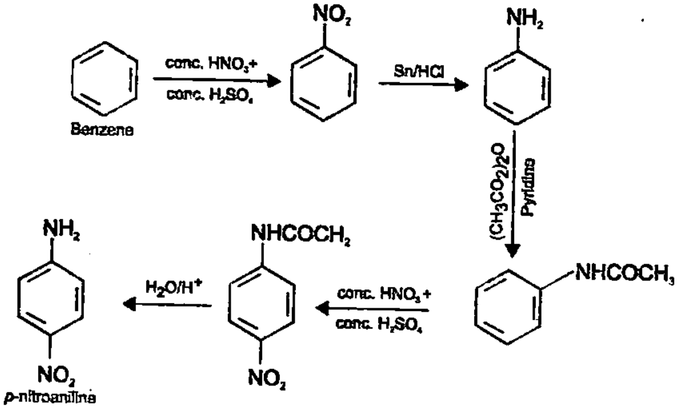
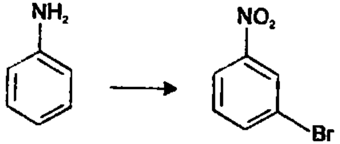
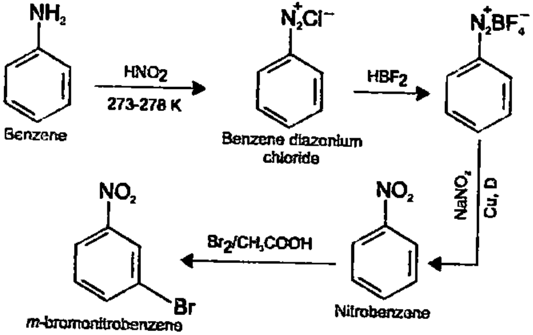
Ans. Conversion of benzene to p-nitroaniline can be done as



64. How will you carry out the following conversion?

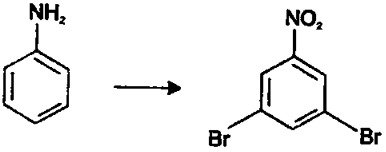


Ans. Conversion of aniline to *m*-bromo nitrobenzene can be completed as

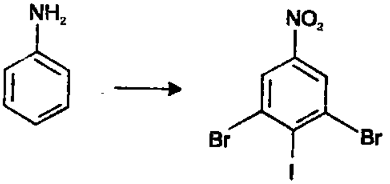


65. How will you carry out the following conversions?

(*i*)



(*ii*)



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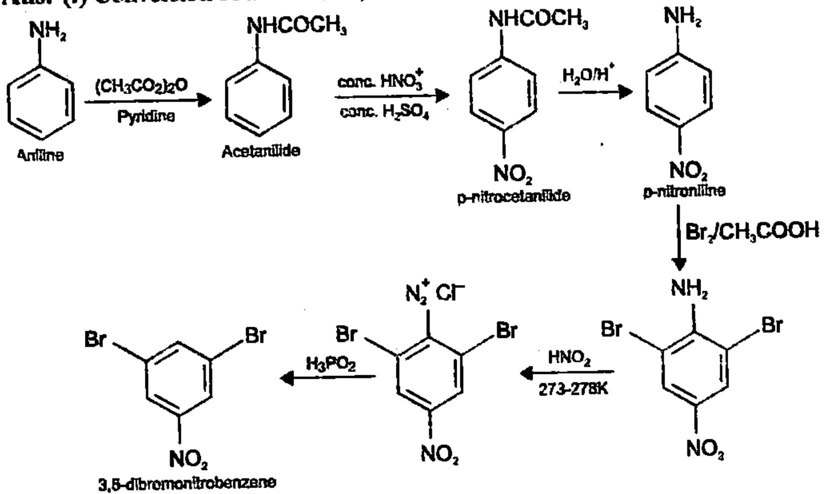
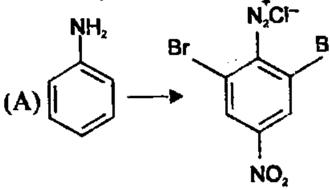
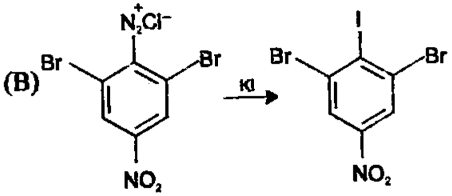
Ans. (*i*) Conversion of aniline to 3,5-dibromonitrobenzene can be completed as



(*ii*) Conversion (A) given below is same as in part (i) given above after that reaction (B) can be carried out.





IV. MATCHING TYPE

Note : Match the items of Column I and Column II in the following questions.

66. Match the reactions given in Column I with the statements given in Column II.

Column I	Column II
(*i*) Ammonolysis	(*a*) Amine with lesser number of carbon atoms
(*ii*) Gabriel phthalimide synthesis	(*b*) Detection test for primary amines.

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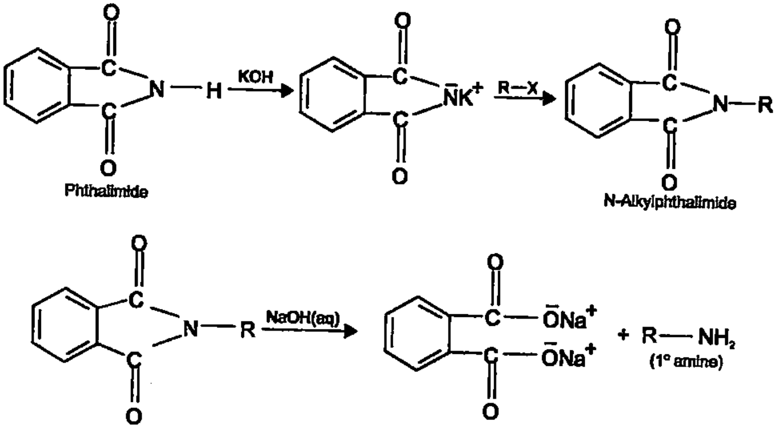
(*iii*) Hoffmann Bromamide reaction	(*c*) Reaction of phthalimide with KOH and R—X
(*iv*) Carbylamine reaction	(*d*) Reaction of alkylhalides with NH_3

Ans. (*i*) → (*d*) (*ii*) → (*c*) (*iii*) → (*a*) (*iv*) → (*b*)

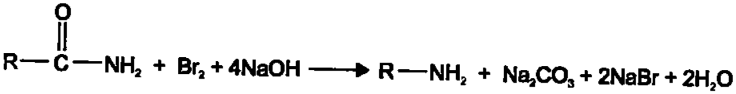
Explanation:

(*i*) This process of cleavage of the C—X bond by ammonia molecule is known as ammonolysis.

(*ii*) Reaction of phthalimide with KOH and R—X.



(*iii*) Amine with lesser number of carbon atoms



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(*iv*) Detection test for primary amines

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R-NC + 3KCl + 3H_2O$$

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

Column I	Column II
(*i*) Benzenesulphonyl chloride	(*a*) Zwitter ion
(*ii*) Sulphanilic acid	(*b*) Hinsberg reagent
(*iii*) Alkyl diazonium salts	(*c*) Dyes
(*iv*) Aryl diazonium salts	(*d*) Conversion to alcohols

Ans. (*i*) → (*b*) (*ii*) → (*a*) (*iii*) → (*d*) (*iv*) → (*c*)

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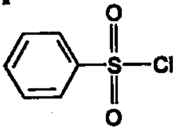
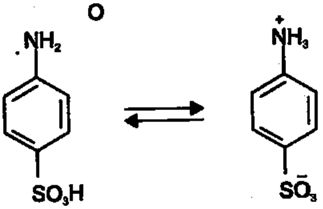
Explanation:

(*i*)

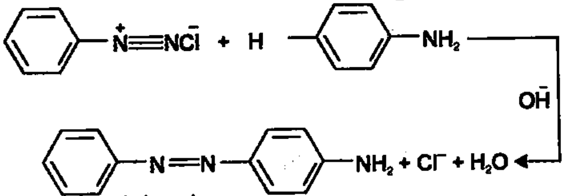


(*ii*)



(*iii*) $R—NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R—\overset{+}{N}_2Cl^-] \xrightarrow{H_2O} ROH + Na_2 + HCl$

(*iv*)



p-Aminoazobenzene
(yellow dye)

V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Both assertion and reason are wrong.

(*ii*) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(*iii*) Assertion is correct statement but reason is wrong statement.

(*iv*) Both assertion and reason are correct statements and reason is correct explanation of assertion.

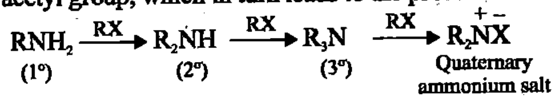
(*v*) Assertion is wrong statement but reason is correct statement.

68. Assertion : Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.

Reason : Acyl group sterically hinders the approach of further acyl groups.

Ans. (*iii*)

Explanation: Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule. Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-NH_2$ or $>NH$ group by the acetyl group, which in turn leads to the production of amides.



$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

69. **Assertion** : Hoffmann's bromamide reaction is given by primary amines.
Reason : Primary amines are more basic than secondary amines.

Ans. (*iii*)

Explanation: Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.

70. **Assertion** : N-Ethylbenzene sulphonamide is soluble in alkali.
Reason : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

Ans. (*iv*)

Explanation: The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

71. **Assertion** : N, N-Diethylbenzenesulphonamide is insoluble in alkali.
Reason : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

Ans. (*ii*)

Explanation: Since N, N-diethylbenzenesulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

72. **Assertion** : Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.
Reason : $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

Ans. (*iv*)

Explanation: Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

73. **Assertion** : Aromatic 1° amines can be prepared by Gabriel Phthalimide Synthesis.
Reason : Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.

Ans. (*i*)

Explanation: Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

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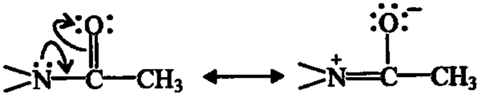
74. **Assertion** : Acetanilide is less basic than aniline.
Reason : Acetylation of aniline results in decrease of electron density on nitrogen.

Ans. (*iv*)

Explanation: The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:



Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of $-NHCOCH_3$ group is less than that of amino group.

VI. LONG ANSWER TYPE

75. A hydrocarbon 'A', (C_4H_8) on reaction with HCl gives a compound 'B', (C_4H_9Cl), which on reaction with 1 mol of NH_3 gives compound 'C', ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 mols of acetaldehyde. Identify compounds 'A' to 'D'. Explain the reactions involved.

Ans. (*i*) Addition of HCl to compound 'A' shows that compound 'A' is alkene. Compound 'B' is C_4H_9Cl.

(*ii*) Compound 'B' reacts with NH_3, it forms amine 'C'.

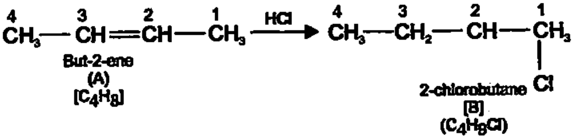
$$\underset{(A)}{C_4H_8} \xrightarrow{HCl} \underset{(B)}{C_4H_9Cl} \xrightarrow{NH_3} \underset{(C)}{C_4H_{11}N} \text{ or } C_4H_9NH_2$$

(*iii*) 'C' gives diazonium salt with $NaNO_2/HCl$, which yields an optically active alcohol. So, 'C' is alphatic amine.

(*iv*) 'A' on ozonolysis produces 2 moles of CH_3CHO. So, 'A' is $CH_3—CH=CH—CH_3$ (But-2-ene).

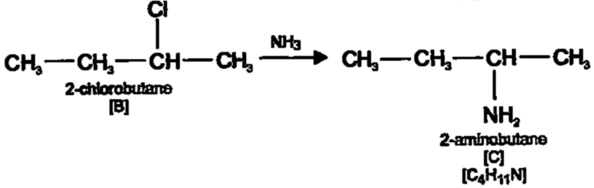
Reactions:

(*i*)



$$\underset{\substack{\text{But-2-ene}\\(A)\\[C_4H_8]}}{\overset{4}{CH_3}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_3}} \xrightarrow{HCl} \underset{\substack{\text{2-chlorobutane}\\[B]\\(C_4H_9Cl)}}{\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}-\underset{\substack{|\\Cl}}{\overset{1}{CH_3}}}$$

(*ii*)



$$\underset{\substack{\text{2-chlorobutane}\\[B]}}{CH_3-CH_2-\overset{\substack{Cl\\|}}{CH}-CH_3} \xrightarrow{NH_3} CH_3-CH_2-\underset{\substack{|\\NH_2\\\text{2-aminobutane}\\[C]\\[C_4H_{11}N]}}{CH}-CH_3$$

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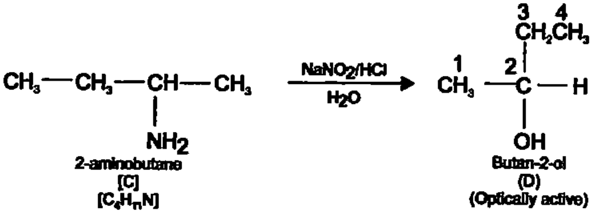
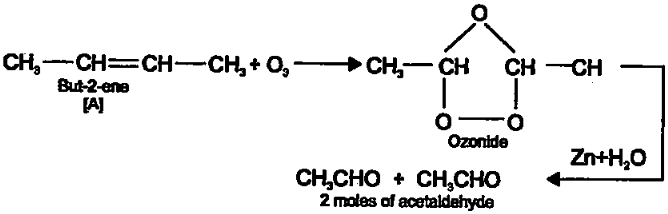
(*iii*)

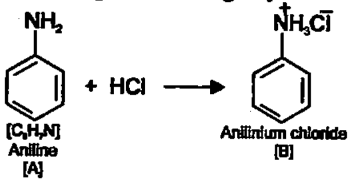


(*iv*)

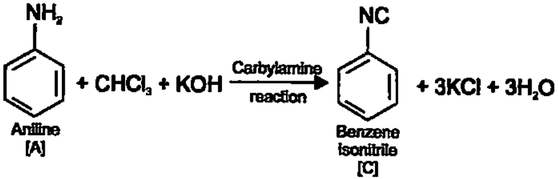


76. A colourless substance 'A' (C_6H_7N) is sparingly soluble in water and gives a water soluble compound 'B' on treating with mineral acid. On reacting with $CHCl_3$ and alcoholic potash 'A' produces an obnoxious smell due to the formation of compound 'C'. Reaction of 'A' with benzenesulphonyl chloride gives compound 'D' which is soluble in alkali. With $NaNO_2$ and HCl, 'A' forms compound 'E' which reacts with phenol in alkaline medium to give an orange dye 'F'. Identify compounds 'A' to 'F'.

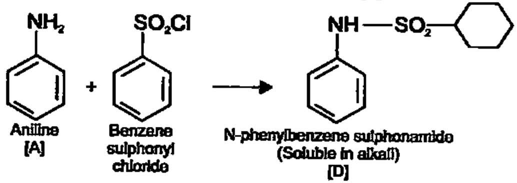
Ans. (*i*)



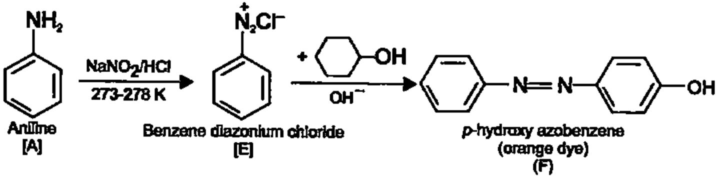
(*ii*)



(*iii*)



(*iv*)



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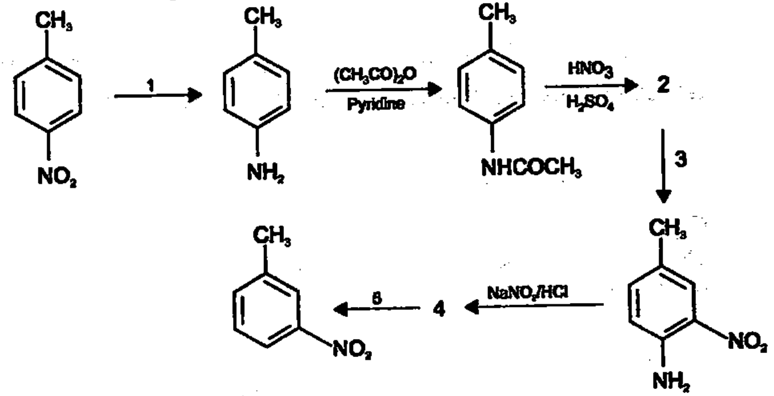
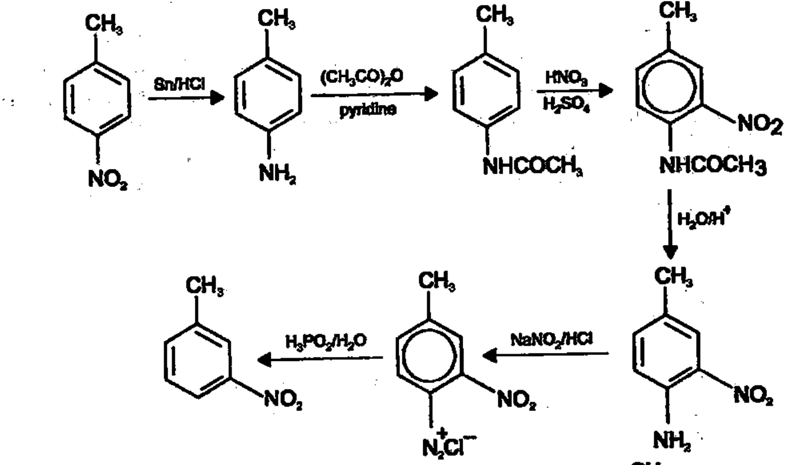
77. Predict the reagent or the product in the following reaction sequence.

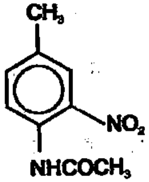


Ans. The correct sequence can be represented as follows including all reagents.



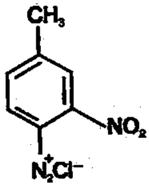
Hence; (*i*) 1 = Sn/HCl

(*ii*) 2 =



(*iii*) 3 = H_2O H^+

(*iv*) 4 =



(*v*) 5 = H_3PO_2/H_2O

□□□

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14 ■■■ Biomolecules

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Glycogen is a branched chain polymer of α-D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by the formation of C1–C6 glycosidic linkage. Structure of glycogen is similar to __________.

(*i*) Amylose
(*ii*) Amylopectin
(*iii*) Cellulose
(*iv*) Glucose

Ans. (*ii*)

Explanation: Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages. These are the most commonly encountered carbohydrates in nature. Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of alpha-D-glucose units in which chain is formed by C_1–C_4 glycosidic linkage whereas branching occurs by C_1–C_6 glycosidic linkage.

2. Which of the following polymer is stored in the liver of animals?

(*i*) Amylose
(*ii*) Cellulose
(*iii*) Amylopectin
(*iv*) Glycogen

Ans. (*iv*)

Explanation: The carbohydrates are stored in animal body as glycogen. It is also known as *animal starch* because its structure is similar to amylopectin and is rather more highly branched. It is present in liver, muscles and brain.

3. Sucrose (cane sugar) is a disaccharide. One molecule of sucrose on hydrolysis gives __________.

(*i*) 2 molecules of glucose
(*ii*) 2 molecules of glucose + 1 molecule of fructose
(*iii*) 1 molecule of glucose + 1 molecule of fructose
(*iv*) 2 molecules of fructose

Ans. (*iii*)

Explanation: Sucrose: One of the common disaccharides is sucrose which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(–) fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-Fructose}}{C_6H_{12}O_6}$$

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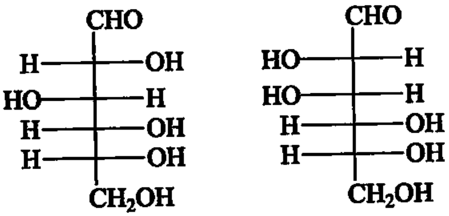
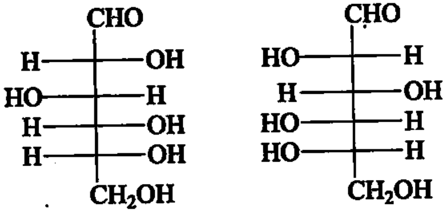
4. Which of the following pairs represents anomers?

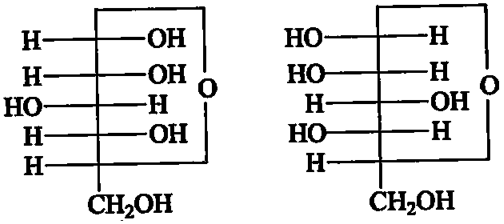
(*i*)



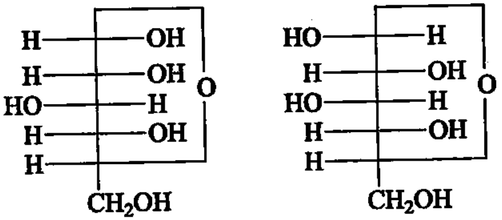
(*ii*)



(*iii*)



(*iv*)



Ans. (*iii*)

Explanation: The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called anomeric carbon (the aldehyde carbon before cyclisation). Such isomers, *i.e.*, alpha-form and beta-form, are called anomers.

5. Proteins are found to have two different types of secondary structures viz. α-helix and β-pleated sheet structure. α-helix structure of protein is stabilised by :

(*i*) Peptide bonds	(*ii*) van der Waals forces
(*iii*) Hydrogen bonds	(*iv*) Dipole-dipole interactions

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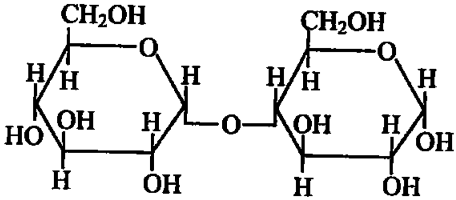
Ans. (*iii*)

Explanation: α-helix and β-pleated sheet structure: These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between >C=O and —NH— groups of the peptide bond.

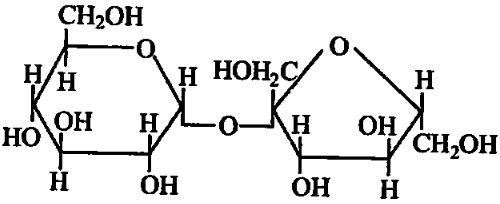
α-Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the —NH group of each amino acid **residue hydrogen bonded** to the >C=O of an adjacent turn of the helix.

6. In disaccharides, if the reducing groups of monosaccharides *i.e.,* aldehydic or ketonic groups are bonded, these are non-reducing sugars. Which of the following disaccharide is a non-reducing sugar?

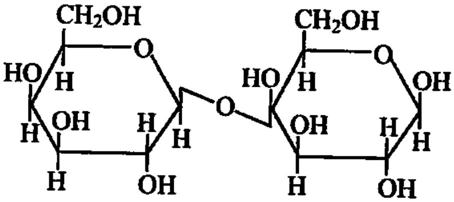
(*i*)



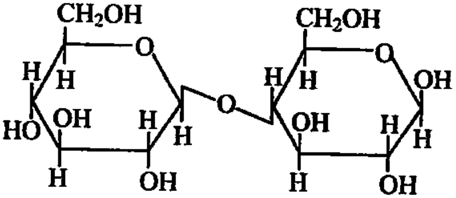
(*ii*)



(*iii*)



(*iv*)



Ans. (*ii*)

Explanation: Sucrose: One of the common disaccharides is sucrose which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(–) fructose. These two monosaccharides are held together by a glycosidic linkage between C1 of α-glucose and C2 of beta-fructose.

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Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.

7. Which of the following acids is a vitamin?

(*i*) Aspartic acid | (*ii*) Ascorbic acid
(*iii*) Adipic acid | (*iv*) Saccharic acid

Ans. (*ii*)

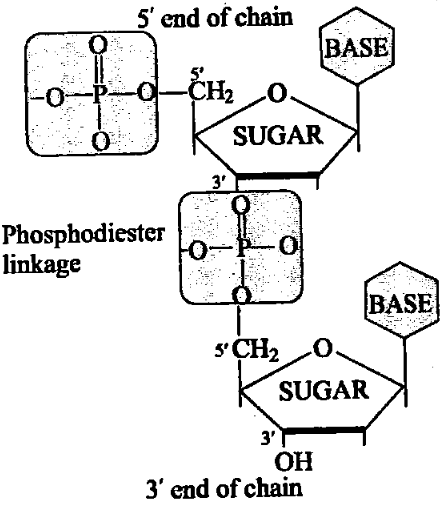
Explanation: Vitamin C is also known as Ascorbic acid.

8. Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present?

(*i*) 5′ and 3′ | (*ii*) 1′ and 5′
(*iii*) 5′ and 5′ | (*iv*) 3′ and 3′

Ans. (*i*)

Explanation: Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar.



9. Nucleic acids are the polymers of ______________.

(*i*) Nucleosides | (*ii*) Nucleotides
(*iii*) Bases | (*iv*) Sugars

Ans. (*ii*)

Explanation: Nucleic acids are long chain polymers of nucleotides, so they are also called polynucleotides

10. Which of the following statements is not true about glucose?

(*i*) It is an aldohexose.
(*ii*) On heating with HI it forms n-hexane.
(*iii*) It is present in furanose form.
(*iv*) It does not give 2, 4-DNP test.

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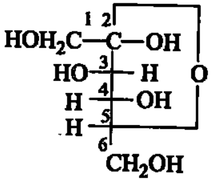
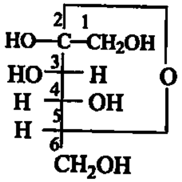
Ans. (*iii*)

Explanation: Fructose is present in furanose form.



α-D-(–) - Fructofuranose



β-D-(–) - Fructofuranose

11. Each polypeptide in a protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is said to be __________.
    (*i*) primary structure of proteins.
    (*ii*) secondary structure of proteins.
    (*iii*) tertiary structure of proteins.
    (*iv*) quaternary structure of proteins.

Ans. (*i*)

Explanation: Sequence of amino acids is said to be primary structure of proteins.

12. DNA and RNA contain four bases each. Which of the following bases is not present in RNA?
    (*i*) Adenine
    (*ii*) Uracil
    (*iii*) Thymine
    (*iv*) Cytosine

Ans. (*iii*)

Explanation: DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).

13. Which of the following B group vitamins can be stored in our body?
    (*i*) Vitamin B_1
    (*ii*) Vitamin B_2
    (*iii*) Vitamin B_6
    (*iv*) Vitamin B_{12}

Ans. (*iv*)

Explanation: Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

14. Which of the following bases is not present in DNA?
    (*i*) Adenine
    (*ii*) Thymine
    (*iii*) Cytosine
    (*iv*) Uracil

Ans. (*iv*)

Explanation: Uracil is present in RNA but not in DNA.

15. Three cyclic structures of monosaccharides are given below which of these are anomers?

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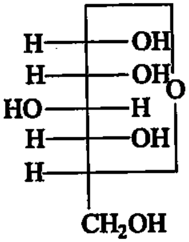
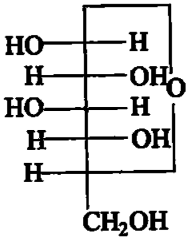
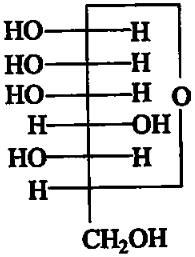


(I)



(II)

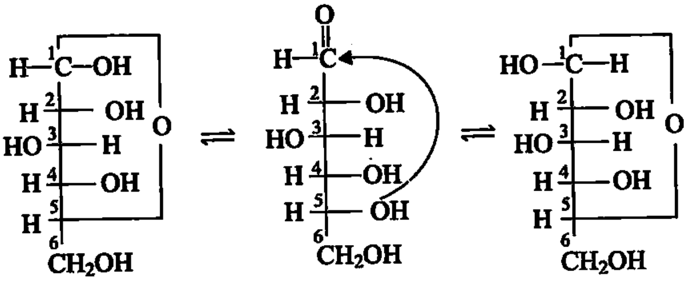


(III)

(*i*) I and II
(*ii*) II and III
(*iii*) I and III
(*iv*) III is anomer of I and II

Ans. (*i*)

Explanation: This behaviour could not be explained by the open chain structure (I) for glucose. It was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure. It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation. This explains the absence of —CHO group and also existence of glucose in two forms as shown below.



α-D-(+)-Glucose

β-D-(+)-Glucose

16. Which of the following reactions of glucose can be explained only by its cyclic structure?
(*i*) Glucose forms pentaacetate.
(*ii*) Glucose reacts with hydroxylamine to form an oxime.
(*iii*) Pentaacetate of glucose does not react with hydroxylamine.
(*iv*) Glucose is oxidised by nitric acid to gluconic acid.

Ans. (*iii*)

Explanation: The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.

17. Optical rotations of some compounds along with their structures are given below. Which of them have D configuration?

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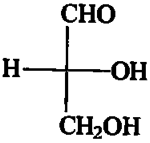
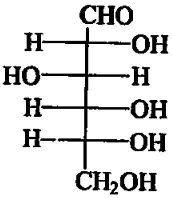
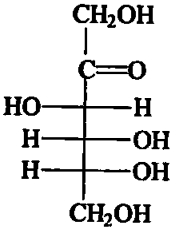

(+) rotation

(I)


(+) rotation

(II)

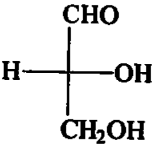

(–) rotation

(III)

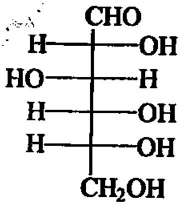
(*i*) I, II, III
(*ii*) II, III
(*iii*) I, II
(*iv*) III

Ans. (*i*)

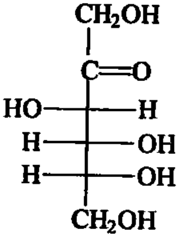
Explanation: All those compounds which can be chemically correlated to (+) isomer of glyceraldehyde are said to have D-configuration whereas those which can be correlated to (–) isomer of glyceraldehyde are said to have L-configuration.


(+) rotation

(I)

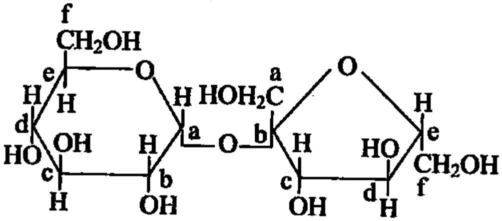

(+) rotation

(II)


(–) rotation

(III)

18. Structure of a disaccharide formed by glucose and fructose is given below. Identify anomeric carbon atoms in monosaccharide units.



(*i*) 'a' carbon of glucose and 'a' carbon of fructose.
(*ii*) 'a' carbon of glucose and 'e' carbon of fructose.
(*iii*) 'a' carbon of glucose and 'b' carbon of fructose.
(*iv*) 'f' carbon of glucose and 'f' carbon of fructose.

Ans. (*iii*)

Explanation: Two monosaccharides are held together by a glycosidic linkage between C1 of α-glucose and C2 of β-fructose.

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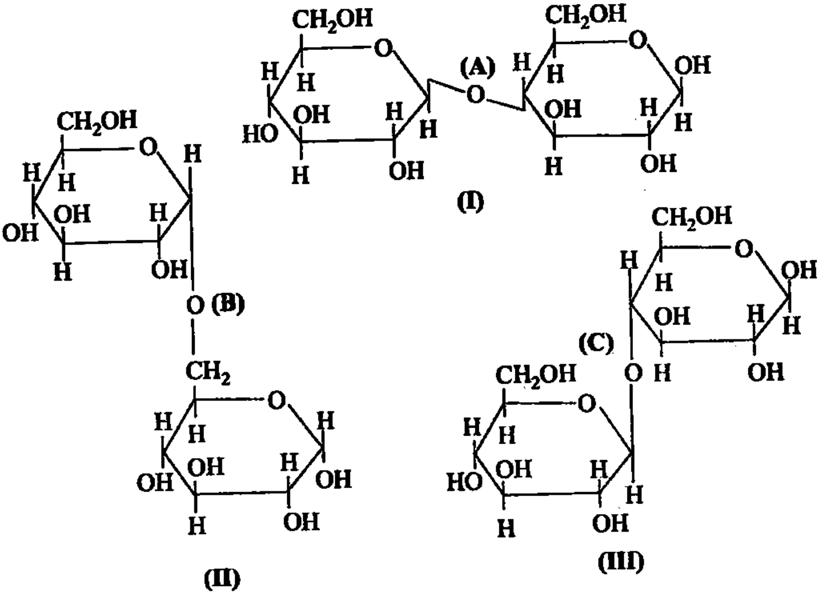
19. Three structures are given below in which two glucose units are linked. Which of these linkages between glucose units are between C1 and C4 and which linkages are between C1 and C6?



(*i*) (A) is between C1 and C4, (B) and (C) are between C1 and C6

(*ii*) (A) and (B) are between C1 and C4, (C) is between C1 and C6

(*iii*) (A) and (C) are between C1 and C4, (B) is between C1 and C6

(*iv*) (A) and (C) are between C1 and C6, (B) is between C1 and C4

Ans. (*iii*)

II. MULTIPLE CHOICE QUESTIONS (TYPE II)

Note : In the following questions two or more options may be correct.

20. Carbohydrates are classified on the basis of their behaviour on hydrolysis and also as reducing or non-reducing sugar. Sucrose is a __________.

(*i*) monosaccharide

(*ii*) disaccharide

(*iii*) reducing sugar

(*iv*) non-reducing sugar

Ans. (*ii*), (*iv*)

Explanation: One of the common disaccharides is sucrose which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(–) fructose. These two monosaccharides are held together by a glycosidic linkage between C1 of α-glucose and C2 of β-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.

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21. Proteins can be classified into two types on the basis of their molecular shape i.e., fibrous proteins and globular proteins. Examples of globular proteins are :

(*i*) Insulin
(*ii*) Keratin
(*iii*) Albumin
(*iv*) Myosin

Ans. (*i*), (*iii*)

Explanation: Globular proteins: This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

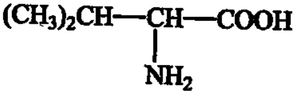
22. Which of the following carbohydrates are branched polymer of glucose?

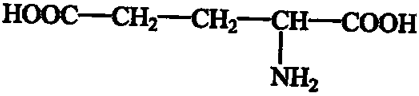
(*i*) Amylose
(*ii*) Amylopectin
(*iii*) Cellulose
(*iv*) Glycogen

Ans. (*ii*), (*iv*)

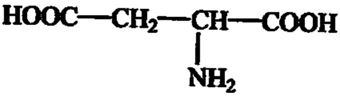
Explanation: Amylopectin is insoluble in water and constitutes about 80–85% of starch. It is a branched chain polymer of-D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage. **Glycogen:** The carbohydrates are stored in animal body as glycogen. It is also known as *animal starch* because its structure is similar to amylopectin and is rather more highly branched.

23. Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Which of the following are acidic?

(*i*)

$(CH_3)_2CH-\underset{NH_2}{\underset{|}{CH}}-COOH$

(*ii*)

$HOOC-CH_2-CH_2-\underset{NH_2}{\underset{|}{CH}}-COOH$

(*iii*) $H_2N-CH_2-CH_2-CH_2-COOH$

(*iv*)

$HOOC-CH_2-\underset{NH_2}{\underset{|}{CH}}-COOH$

Ans. (*ii*), (*iv*)

Explanation: Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Equal number of amino and carboxyl groups makes it neutral; more number of amino than carboxyl groups makes it basic and more carboxyl groups as compared to amino groups makes it acidic.

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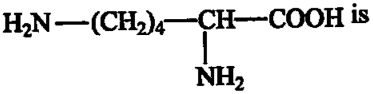
24. Lysine, 

$H_2N-(CH_2)_4-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$ is ________.

(*i*) α-Amino acid (*ii*) Basic amino acid
(*iii*) Amino acid synthesised in body (*iv*) β-Amino acid

Ans. (*i*), (*ii*)

25. Which of the following monosaccharides are present as five membered cyclic structure (furanose structure)?

(*i*) Ribose (*ii*) Glucose
(*iii*) Fructose (*iv*) Galactose

Ans. (*i*), (*iii*)

Explanation: Fructose: It also exists in two cyclic forms which are obtained by the addition of —OH at C5 to the group. The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms.

26. In fibrous proteins, polypeptide chains are held together by ________.

(*i*) van der Waals forces (*ii*) disulphide linkage
(*iii*) electrostatic forces of attraction (*iv*) hydrogen bonds

Ans. (*i*), (*ii*)

Explanation: In fibrous proteins, main forces which stabilize structures of proteins are disulphide linkages and van der Waals.

27. Which of the following are purine bases?

(*i*) Guanine (*ii*) Adenine
(*iii*) Thymine (*iv*) Uracil

Ans. (*i*), (*ii*)

28. Which of the following terms are correct about enzyme?

(*i*) Proteins (*ii*) Dinucleotides
(*iii*) Nucleic acids (*iv*) Biocatalysts

Ans. (*i*), (*iv*)

Explanation: Life is possible due to the coordination of various chemical reactions in living organisms. This occurs with the help of certain biocatalysts called enzymes. Almost all the enzymes are globular Protein.

III. SHORT ANSWER TYPE

29. Name the sugar present in milk. How many monosaccharide units are present in it? What are such oligosaccharides called?

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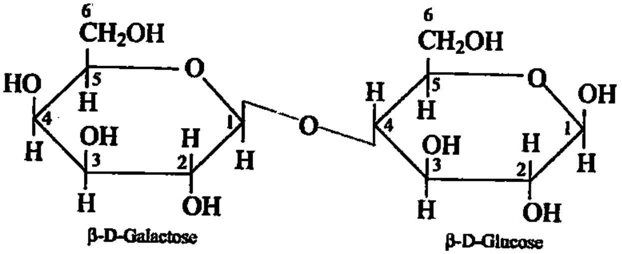
Ans. Lactose is commonly known as milk sugar since this disaccharide is found in milk. It is composed of β -D-galactose and β-D-glucose. The linkage is between C1 of galactose and C4 of glucose.



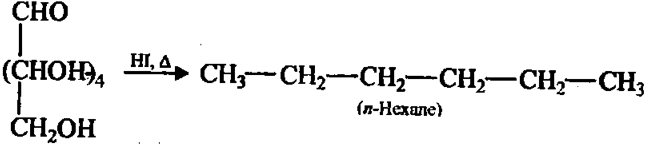
Lactose

30. How do you explain the presence of all the six carbon atoms in glucose in a straight chain?

Ans. Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose. It is probably the most abundant organic compound on earth. It was assigned the structure given below on the basis of the following evidences:

(*i*) Its molecular formula was found to be $C_6H_{12}O_6$.

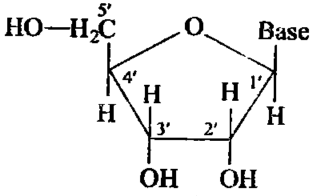
(*ii*) On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.



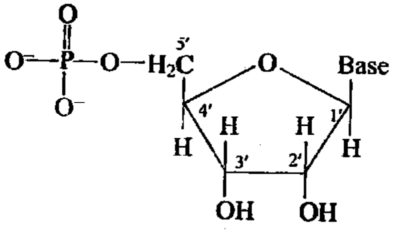
$$\begin{matrix}\text{CHO}\\ |\\ (\text{CHOH})_4\\ |\\ \text{CH}_2\text{OH}\end{matrix} \xrightarrow{\text{HI, }\Delta} \underset{(n\text{-Hexane})}{CH_3—CH_2—CH_2—CH_2—CH_2—CH_3}$$

31. In nucleoside a base is attached at 1′ position of sugar moiety. Nucleotide is formed by linking of phosphoric acid unit to the sugar unit of nucleoside. At which position of sugar unit is the phosphoric acid linked in a nucleoside to give a nucleotide?

Ans. In nucleosides, the sugar carbons are numbered as 1′, 2′, 3′ etc. in order to distinguish these from the bases [Fig. (a)]. When nucleoside is linked to phosphoric acid at 5′-position of sugar moiety, we get a nucleotide [Fig. (b)].



(a)



(b)

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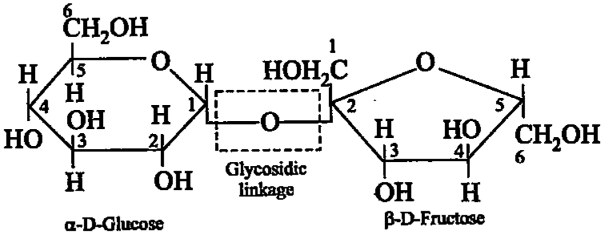
32. Name the linkage connecting monosaccharide units in polysaccharides.

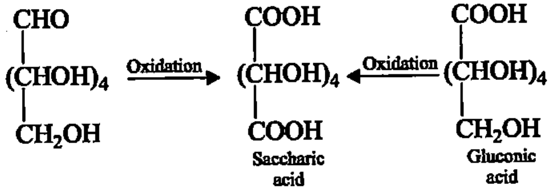
Ans. The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called *glycosidic linkage.*



Sucrose

33. Under what conditions glucose is converted to gluconic and saccharic acid?

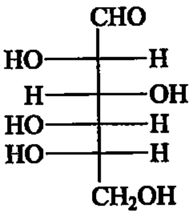
Ans. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (—OH) group in glucose.



34. Monosaccharides contain carbonyl group hence are classified, as aldose or ketose. The number of carbon atoms present in the monosaccharide molecule are also considered for classification. In which class of monosaccharide will you place fructose?

Ans. Fructose is an important ketohexose. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose. Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose.

35. The letters 'D' or 'L' before the name of a stereoisomer of a compound indicate the correlation of configuration of that particular stereoisomer. This refers to their relation with one of the isomers of glyceraldehyde. Predict whether the following compound has 'D' or 'L' configuration.



Ans. The letters 'D' or 'L' before the name of any compound indicate the relative configuration of a particular stereoisomer. This refers to their relation with a particular isomer of glyceraldehyde.

D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule. It may be remembered that 'D' and 'L' have no relation with the optical activity of the compound. For assigning the configuration of monosaccharides, it is the lowest asymmetric carbon atom which is compared. The given compound has L-configuration.

36. Aldopentoses named as ribose and 2-deoxyribose are found in nucleic acids. What is their relative configuration?

Ans. Configuration assigned is O. Thus, robose is β-D-ribose Deoxyribose is β-D-2-deoxyribose.

37. Which sugar is called invert sugar? Why is it called so?

Ans. Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar.

38. Amino acids can be classified as α-, β-, γ-, δ- and so on depending upon the relative position of amino group with respect to carboxyl group. Which type of amino acids form polypetide chain in proteins?

Ans. α-amino acids form polypetide chain in proteins.

39. α-Helix is a secondary structure of proteins formed by twisting of polypeptide chain into right handed screw like structures. Which type of interactions are responsible for making the α-helix structure stable?

Ans. In α-helix, a polypeptide chain is stabilised by the formation of hydrogen bonds between —NH— group of amino acids in one turn with the >C ═O groups of amino acids belonging to adjacent turn.

40. Some enzymes are named after the reaction, where they are used. What name is given to the class of enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate.

Ans. Oxidoreductase is class of enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate.

41. During curdling of milk, what happens to sugar present in it?

Ans. When milk is curdeled, its sugar get oxidize to form lactic acid.

42. How do you explain the presence of five —OH groups in glucose molecule?

Ans. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five —OH groups. Since it exists as a stable compound, five —OH groups should be attached to different carbon atoms.

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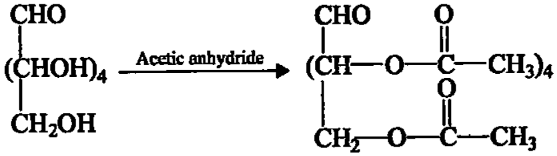
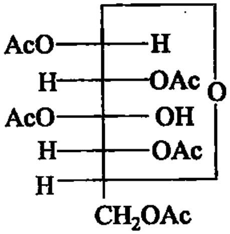
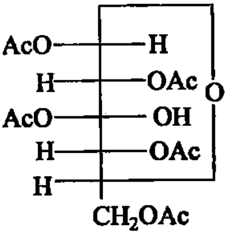


43. Why does compound (A) given below not form an oxime?



(A)

Ans. Glucose pentaacetate (structure A) doesn't have a free —OH group at C1 and so can't be converted to the open chain form to give —CHO group and hence doesn't form the oxime.



(Structure A)

44. Why must vitamin C be supplied regularly in diet?

Ans. Vitamin C are soluble in water. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored in our body.

45. Sucrose is dextrorotatory but the mixture obtained after hydrolysis is laevorotatory. Explain.

Ans. Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory.

46. Amino acids behave like salts rather than simple amines or carboxylic acids. Explain.

Ans. Amino acids behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule. In aqueous

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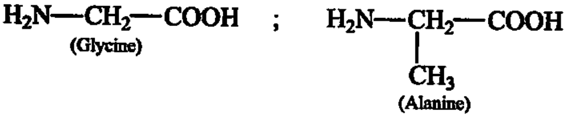
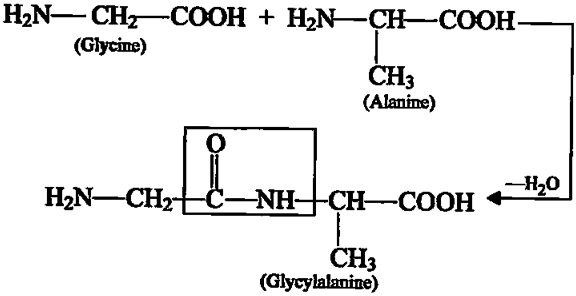
solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as *zwitter ion.*

47. Structures of glycine and alanine are given below. Show the peptide linkage in glycylalanine.



$$\underset{\text{(Glycine)}}{H_2N-CH_2-COOH} \quad ; \quad \underset{\text{(Alanine)}}{H_2N-\underset{\displaystyle CH_3}{\underset{|}{CH_2}}-COOH}$$

Ans. Glycylalanin, carboxyl group of glycine combines with the amino group of alanine.



$$\underset{\text{(Glycine)}}{H_2N-CH_2-COOH} + \underset{\text{(Alanine)}}{H_2N-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH} \xrightarrow{-H_2O} \underset{\text{(Glycylalanine)}}{H_2N-CH_2-\boxed{\overset{\displaystyle O}{\overset{\|}{C}}-NH}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH}$$

48. Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to a physical change like change in temperature or a chemical change like, change in pH, denaturation of protein takes place. Explain the cause.

Ans. Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

49. Activation energy for the acid catalysed hydrolysis of sucrose is 6.22 kJ mol^{-1}, while the activation energy is only 2.15 kJ mol^{-1} when hydrolysis is catalysed by the enzyme sucrase. Explain.

Ans. Enzymes are needed only in small quantities for the progress of a reaction. Similar to the action of chemical catalysts, enzymes are said to reduce the magnitude of activation energy. For example, activation energy for acid hydrolysis of sucrose is 6.22 kJ mol^{-1}, while the activation energy is only 2.15 kJ mol^{-1} when hydrolysed by the enzyme, sucrase.

50. How do you explain the presence of an aldehydic group in a glucose molecule?

Ans. Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.

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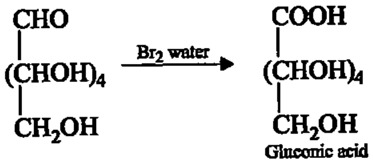
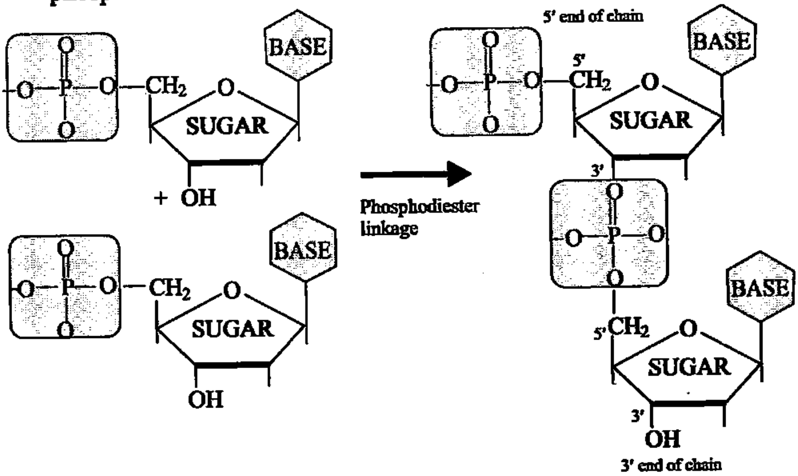


$$\underset{\substack{|\\ (CHOH)_4\\ |\\ CH_2OH}}{CHO} \xrightarrow{Br_2\ water} \underset{\substack{|\\ (CHOH)_4\\ |\\ CH_2OH}}{COOH}$$

51. Which moieties of nucleosides are involved in the formation of phosphodiester linkages present in dinucleotides? What does the word diester in the name of linkage indicate? Which acid is involved in the formation of this linkage?

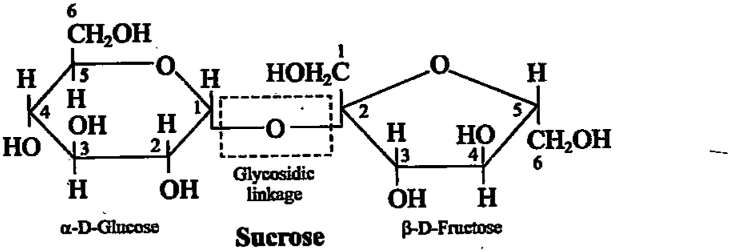
Ans. When nucleoside is linked to phosphoric acid at 5-position of sugar moiety, it forms a nucleotide. Nucleotides are joined together by phosphodiester link between 5′ and 3′ carbon atoms of the pentose sugar.



Phospheric acid is involved in the formation of this linkage.

52. What are glycosidic linkages? In which type of biomolecules are they present?

Ans. The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharides are held together by a glycosidic linkage between C1 of α-glucose and C2 of β-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, between two monosaccharide units through oxygen atom is called glycosidic linkage.



Sucrose

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53. Which monosaccharide units are present in starch, cellulose and glucose and which linkages link these units?

Ans. In starch and glycogen, glycosidic α-linkage is present. Cellulose is a straight chain polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

54. How do enzymes help a substrate to be attacked by the reagent effectively?

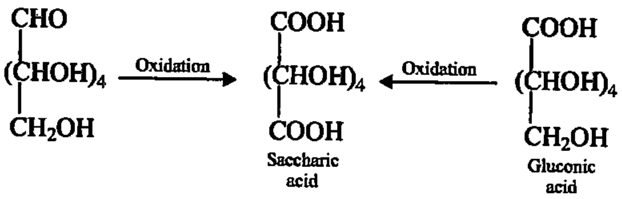
Ans. Enzymes are highly specific. They react with substrate molecule and form intermediate complex. They reduce the magnitude of activation energy.

55. Describe the term D- and L- configuration used for amino acids with examples.

Ans. Amino acid exist both in 'D' and 'L' forms. Most naturally occurring amino acids have L-configuration. L-Amino acids are represented by writing the —NH_2 group on left hand side and D-amino acids are represented by writing the —NH_2 group on right hand side.

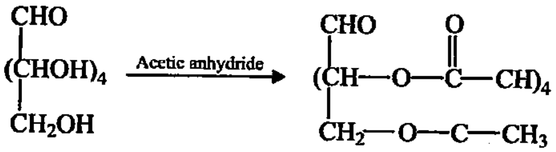
56. How will you distinguish 1° and 2° hydroxyl groups present in glucose? Explain with reactions.

Ans. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (—OH) group in glucose.



$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow{\text{Oxidation}} \begin{array}{c}COOH\\ |\\ (CHOH)_4\\ |\\ COOH\\ \text{Saccharic}\\ \text{acid}\end{array} \xleftarrow{\text{Oxidation}} \begin{array}{c}COOH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\\ \text{Gluconic}\\ \text{acid}\end{array}$$

Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five —OH groups. Since it exists as a stable compound, five —OH groups should be attached to different carbon atoms.



$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow{\text{Acetic anhydride}} \begin{array}{l}CHO\\ |\\ (CH—O—\overset{\overset{\displaystyle O}{\|}}{C}—CH)_4\\ |\\ CH_2—O—C—CH_3\end{array}$$

57. Coagulation of egg white on boiling is an example of denaturation of protein. Explain it in terms of structural changes.

Ans. During denaturation 2 and 3 structures are destroyed but 1° structure remains intact. The coagulation of egg white on boiling is a common example of denaturation.

IV. MATCHING TYPE

Note : Match the items of Column I and Column II in the following questions. More than one option in Column II may match with the items given in Column I.

58. Match the vitamins given in Column I with the deficiency disease they cause given in Column II.

Column I (Vitamins)	**Column II (Diseases)**
(*i*) Vitamin A	(*a*) Pernicious anaemia
(*ii*) Vitamin B_1	(*b*) Increased blood clotting time
(*iii*) Vitamin B_{12}	(*c*) Xerophthalmia
(*iv*) Vitamin C	(*d*) Rickets
(*v*) Vitamin D	(*e*) Muscular weakness
(*vi*) Vitamin E	(*f*) Night blindness
(*vii*) Vitamin K	(*g*) Beri Beri (*h*) Bleeding gums (*i*) Osteomalacia

Ans. (*i*) → (*c*) (*ii*) → (*g*) (*iii*) → (*a*) (*iv*) → (*h*) (*v*) → (*d*) (*vi*) → (*e*) (*vii*) → (*b*)

Explanation:

(*i*)	Xerophthalmia (hardening of cornea of eye) night blindness.
(*ii*)	Beri beri (loss of appetite, retarded growth).
(*iii*)	Pernicious anaemia (RBC deficient in haemoglobin).
(*iv*)	Scurvy (bleeding gums).
(*v*)	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults).
(*vi*)	Increased fragility of RBCs and muscular weakness.
(*vii*)	Increased blood clotting time.

59. Match the following enzymes given in Column I with the reactions they catalyse given in Column II.

Column I (Enzymes)	**Column II (Reactions)**
(*i*) Invertase	(*a*) Decomposition of urea into NH_3 and CO_2
(*ii*) Maltase	(*b*) Conversion of glucose into ethyl alcohol
(*iii*) Pepsin	(*c*) Hydrolysis of maltose into glucose
(*iv*) Urease	(*d*) Hydrolysis of cane sugar
(*v*) Zymase	(*e*) Hydrolysis of proteins into peptides

Ans. (*i*) → (*d*) (*ii*) → (*c*) (*iii*) → (*e*) (*iv*) → (*a*) (*v*) → (*b*)

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V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are correct statements and reason explains the assertion.

(*ii*) Both assertion and reason are wrong statements.

(*iii*) Assertion is correct statement and reason is wrong statement.

(*iv*) Assertion is wrong statement and reason is correct statement.

(*v*) Assertion and reason both are correct statements but reason does not explain assertion.

60. Assertion : D (+)-Glucose is dextrorotatory in nature.

Reason : 'D' represents its dextrorotatory nature.

Ans. (*iii*)

Explanation: Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule. The letters 'D' or 'L' before the name of any compound indicate the relative configuration of a particular stereoisomer.

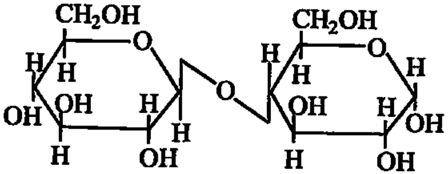
61. Assertion : Vitamin D can be stored in our body.

Reason : Vitamin D is fat soluble vitamin.

Ans. (*i*)

Explanation: *Fat soluble vitamins* are soluble in fat and oils but insoluble in water. They can be stored in liver and adipose (fat storing) tissues.

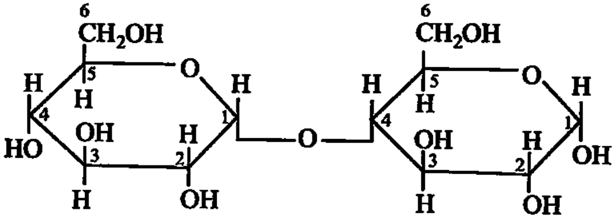
62. Assertion : β-glycosidic linkage is present in maltose,



Reason : Maltose is composed of two glucose units in which C–1 of one glucose unit is linked to C–4 of another glucose unit.

Ans. (*iv*)

Explanation:



(I) α-D-Glucose

(II) α-D-Glucose

Maltose

maltose is composed of two α-D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II).

63. **Assertion :** All naturally occurring α-amino acids except glycine are optically active.

Reason : Most naturally occurring amino acids have L-configuration.

Ans. (*v*)

Explanation: Except glycine, all other naturally occurring α-amino acids are optically active, since the α-carbon atom is asymmetric. These exist both in 'D' and 'L' forms. Most naturally occurring amino acids have L-configuration. L-Amino acids are represented by writing the —NH_2 group on left hand side.

64. **Assertion :** Deoxyribose, $C_5H_{10}O_4$ is not a carbohydrate.

Reason : Carbohydrates are hydrates of carbon so compounds which follow $C_x(H_2O)_y$ formula are carbohydrates.

Ans. (*ii*)

Explanation: Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing hetero-cyclic compounds (called bases). In DNA molecules, the sugar moiety is β-D-2-deoxyribose.

65. **Assertion :** Glycine must be taken through diet.

Reason : It is an essential amino acid.

Ans. (*ii*)

Explanation: The amino acids, which can be synthesised in the body, are known as non essential amino acids. Glycine is an example of non essential amino acid.

66. **Assertion :** In presence of enzyme, substrate molecule can be attacked by the reagent effectively.

Reason : Active sites of enzymes hold the substrate molecule in a suitable position.

Ans. (*i*)

Explanation: In presence of enzyme, substrate molecule can be attacked by the reagent effectively because active sites of enzymes hold the substrate molecule in a suitable position.

VI. LONG ANSWER TYPE

67. Write the reactions of D-glucose which can't be explained by its open-chain structure. How can cyclic structure of glucose explain these reactions?

Ans. Following reactions and facts could not be explained by open chain structure of glucose.

- Despite having the aldehyde group, glucose does not give 2,4-DNP test, Schiff's test and it does not form the hydrogensulphite addition product with $NaHSO_3$.
- The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.

It was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure. It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation.

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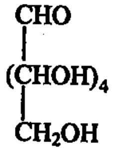
68. On the basis of which evidences D-glucose was assigned the following structure?



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Ans. Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose. It is probably the most abundant organic compound on earth. It was assigned the structure given below on the basis of the following evidences:

(*i*) Its molecular formula was found to be $C_6H_{12}O_6$.

(*ii*) On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain. Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group ($>C=0$) in glucose. Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.

69. Carbohydrates are essential for life in both plants and animals. Name the carbohydrates that are used as storage molecules in plants and animals, also name the carbohydrate which is present in wood or in the fibre of cotton cloth.

Ans. Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals. Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. Cell wall of bacteria and plants is made up of cellulose. We build furniture, etc. from cellulose in the form of wood and clothe ourselves with cellulose in the form of cotton fibre.

70. Explain the terms primary and secondary structure of proteins. What is the difference between α-helix and β-pleated sheet structure of proteins?

Ans. **Primary structure of proteins:** Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.

Secondary Structure of Proteins: The secondary structure of protein refers to the shape in which a long polypeptide chain. The secondary can exist. They are found to exist in two different types of structures viz. α-helix and β-pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between carbonyl group and —NH— groups of the peptide bond. α-Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw

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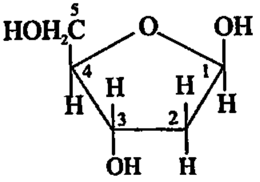
(helix) with the carbonyl and —NH group of each amino acid residue hydrogen bonded to the (>C=0) of an adjacent turn of the helix.

In β-structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds.

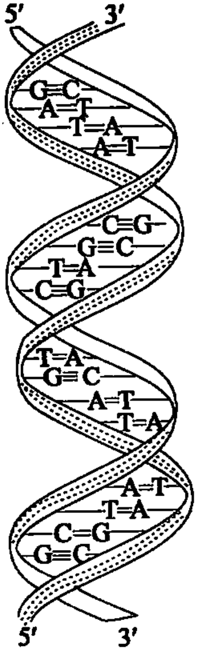
71. Write the structures of fragments produced on complete hydrolysis of DNA. How are they linked in DNA molecule? Draw a diagram to show pairing of nucleotide bases in double helix of DNA.

Ans. Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is β-D-2-deoxyribose.

Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases.



β-D-2-deoxyribose



Double strand helix structure for DNA

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15 Polymers

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Which of the following polymers of glucose is stored by animals?

(*i*) Cellulose	(*ii*) Amylose
(*iii*) Amylopectin	(*iv*) Glycogen

Ans. (*iv*) Glycogen

Explanation: Glycogen is a polymer of glucose found in lever, brain and muscles of animals.

2. Which of the following is not a semisynthetic polymer?

(*i*) *cis*-polyisoprene	(*ii*) Cellulose nitrate
(*iii*) Cellulose acetate	(*iv*) Vulcanised rubber

Ans. (*i*) *cis*-polyisoprene

Explanation: *cis*-polyisoprene is not a semisynthetic polymer whereas others are semisynthetic polymers.

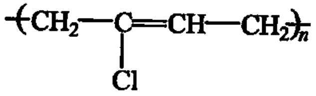
3. The commercial name of polyacrylonitrile is ____________.

(*i*) Dacron	(*ii*) Orlon (acrilan)
(*iii*) PVC	(*iv*) Bakelite

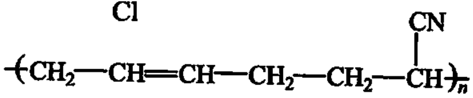
Ans. (*ii*) Orlon (acrilan)

Explanation: Polyacrylonitrile is used as a substitute for wool in making commercial fibres as orlon or acrilan.

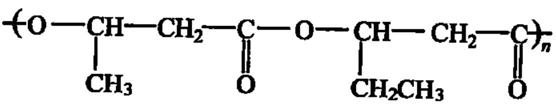
4. Which of the following polymer is biodegradable?

(*i*) 

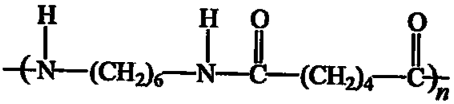
$\left(CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2 \right)_n$

(*ii*) 

$\left(CH_2-CH=CH-CH_2-CH_2-\overset{\overset{CN}{|}}{CH} \right)_n$

(*iii*) 

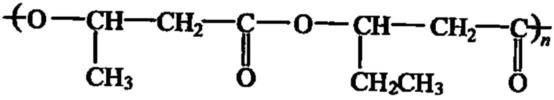
$\left(O-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-\underset{\underset{O}{\|}}{C} \right)_n$

(*iv*) 

$\left(\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C} \right)_n$

Ans. (*iii*)

Explanation: *Poly* β-hydroxybutyrate – co-β-hydroxy valerate (PHBV):



$\left(O-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-\underset{\underset{O}{\|}}{C} \right)_n$

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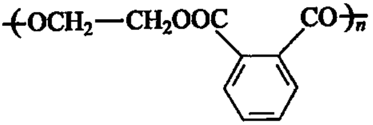
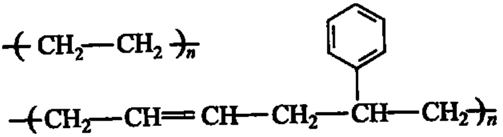
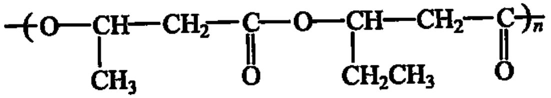
It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. PHBV is used in speciality packaging orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

5. In which of the following polymers ethylene glycol is one of the monomer units?

(i) 

(ii) $\left(CH_2—CH_2 \right)_n$

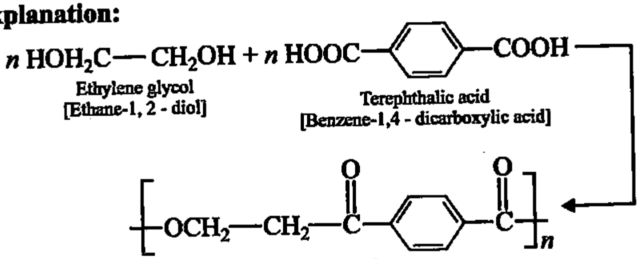
(iii) 

(iv) 

$\left(O—\underset{\underset{CH_3}{|}}{CH}—CH_2—\underset{\underset{O}{\|}}{C}—O—\underset{\underset{CH_2CH_3}{|}}{CH}—CH_2—\underset{\underset{O}{\|}}{C} \right)_n$

Ans. (i)

Explanation:



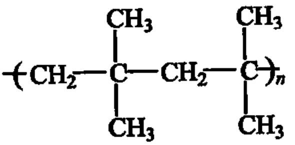
Terylene or dacron

6. Which of the following statements is **not** true about low density polythene?

(i) Tough
(ii) Hard
(iii) Poor conductor of electricity
(iv) Highly branched structure

Ans. (ii)

Explanation: Low density polythene: It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmosphere at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst). They are flexible in nature.

7.  $\left(CH_2—\overset{CH_3}{\underset{CH_3}{C}}—CH_2—\overset{CH_3}{\underset{CH_3}{C}} \right)_n$ is a polymer having monomer units ________________.

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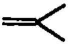
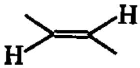
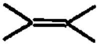
(*i*) 

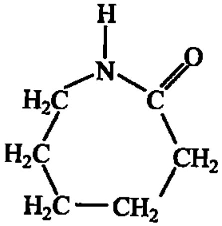
(*ii*) 

(*iii*) 

(*iv*) 

Ans. (*i*)

8. Which of the following polymer can be formed by using the following monomer unit?



(*i*) Nylon 6, 6
(*ii*) Nylon 2–nylon 6
(*iii*) Melamine polymer
(*iv*) Nylon-6

Ans. (*iv*)

Explanation: Nylon-6: It is obtained by heating caprolactum with water at a high temperature

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note : In the following questions two or more options may be correct.

9. Which of the following polymers, need atleast one diene monomer for their preparation?

(*i*) Dacron
(*ii*) Buna-S
(*iii*) Neoprene
(*iv*) Novolac

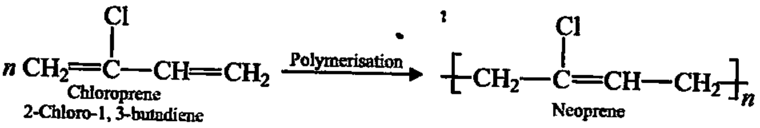
Ans. (*ii*) and (*iii*)

Explanation:

$$\underset{\text{1, 3-Butadiene}}{n\,CH_2{=}CH{-}CH{=}CH_2} + n\,\underset{\text{Styrene}}{C_6H_5{-}CH{=}CH_2}$$

$$\longrightarrow \underset{\substack{\text{Butadiene-styrene copolymer}\\ \text{(Buna - S)}}}{\left(CH_2{-}CH{=}CH{-}CH_2{-}CH{-}CH_2\right)_n}$$

Neoprene or polychloroprene is formed by the free radical polymerisation of chloroprene.



$$\underset{\substack{\text{Chloroprene}\\ \text{2-Chloro-1, 3-butadiene}}}{n\,CH_2{=}\overset{\overset{\displaystyle Cl}{|}}{C}{-}CH{=}CH_2} \xrightarrow{\text{Polymerisation}} \underset{\text{Neoprene}}{\left[CH_2{-}\overset{\overset{\displaystyle Cl}{|}}{C}{=}CH{-}CH_2\right]_n}$$

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10. Which of the folloiwng are characteristics of thermosetting polymers?

(*i*) Heavily branched cross linked polymers.
(*ii*) Linear slightly branched long chain molecules.
(*iii*) Become infusible on moulding so cannot be reused.
(*iv*) Soften on heating and harden on cooling, can be reused.

Ans. (*i*) and (*iii*)

Explanation: Thermosetting polymers: These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused.

11. Which of the following polymers are thermoplastic?

(*i*) Teflon (*ii*) Natural rubber
(*iii*) Neoprene (*iv*) Polystyrene

Ans. (*i*) and (*iv*)

Explanation: Thermoplastic polymers: These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

12. Which of the following polymers are used as fibre?

(*i*) Polytetrafluoroethane (*ii*) Polychloroprene
(*iii*) Nylon (*iv*) Terylene

Ans. (*iii*) and (*iv*)

Explanation: Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

13. Which of the following are addition polymers?

(*i*) Nylon (*ii*) Melamine formaldehyde resin
(*iii*) Orlon (*iv*) Polystyrene

Ans. (*i*) and (*iv*)

Explanation: The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, e.g., the formation of polythene from ethene and polypropene from propene. However, the addition polymers formed by the polymerisation of a single monomeric species are known as homopolymers.

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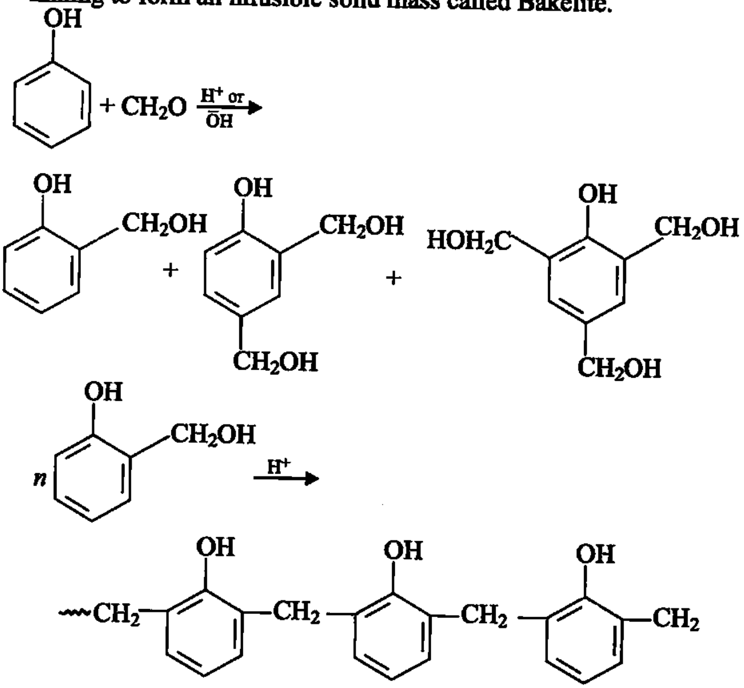
14. Which of the following polymers are condensation polymers?

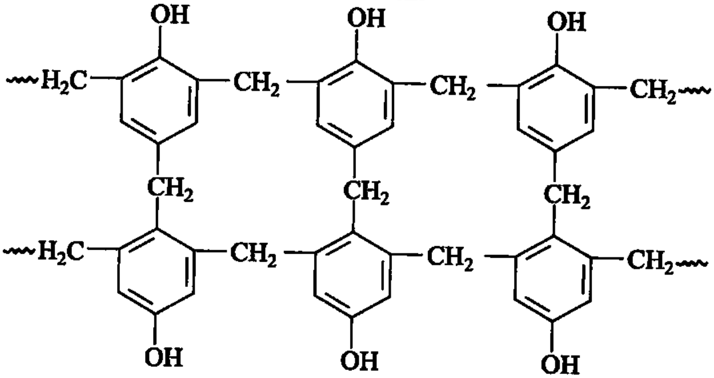
(*i*) Bakelite
(*ii*) Teflon
(*iii*) Butyl rubber
(*iv*) Melamine formaldehyde resin

Ans. (*i*) and (*iv*)

Explanation: Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called Bakelite.



Novolac



Bakelite

Melamine formaldehyde polymer is formed by the condensation polymerisation of melamine and formaldehyde.

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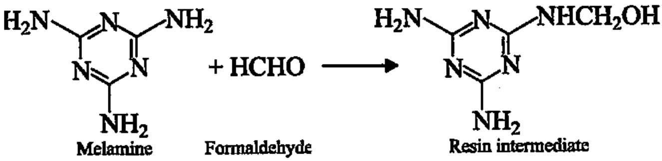

15. Which of the following monomers form biodegradable polymers?

(*i*) 3-hydroxybutanoic acid + 3-hydroxypentanoic acid

(*ii*) Glycine + amino caproic acid

(*iii*) Ethylene glycol + phthalic acid

(*iv*) Caprolactum

Ans. (*i*) and (*ii*)

Explanation: *Poly-β-hydroxybutyrate co-β-hydroxy valerate (PHBV)* It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. PHBV is used in speciality packaging orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

Nylon 2–nylon 6: It is an alternating polyamide copolymer of glycine ($H_2N—CH_2—COOH$) and amino caproic acid [$H_2N(CH_2)_5COOH$] and is biodegradable.

16. Which of the following are example of synthetic rubber?

(*i*) Polychloroprene

(*ii*) Polyacrylonitrile

(*iii*) Buna-N

(*iv*) *cis*-polyisoprene

Ans. (*i*) and (*iii*)

Explanation: Synthetic rubbers are either homopolymers of 1, 3 - butadiene derivatives or copolymers of 1, 3 - butadiene or its derivatives with another unsaturated monomer.

17. Which of the following polymers can have strong intermolecular forces?

(*i*) Nylon

(*ii*) Polystyrene

(*iii*) Rubber

(*iv*) Polyesters

Ans. (*i*) and (*iv*)

Explanation: *Polyamides:* These polymers possessing amide linkages are important examples of synthetic fibres and are termed as nylons.

Polyesters: These are the polycondensation products of dicarboxylic acids and diols. Dacron or terylene is the best known example of polyesters.

18. Which of the following polymers have vinylic monomer units?

(*i*) Acrilan

(*ii*) Polystyrene

(*iii*) Nylon

(*iv*) Teflon

Ans. (*i*), (*ii*) and (*iv*)

Explanation: *Polyacrylonitrile:* The addition polymerisation of acrylonitrile in presence of a peroxide catalyst leads to the formation

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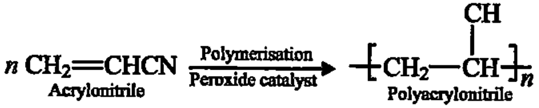
of polyacrylonitrile. Polyacrylonitrile is used as a substitute for wool in making commercial fibres as orlon or acrilan.



$$\underset{\text{Acrylonitrile}}{n\,CH_2{=}CHCN} \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \underset{\text{Polyacrylonitrile}}{-\!\!\left[CH_2-\overset{\overset{\displaystyle CH}{|}}{CH}\right]\!\!-_{n}}$$

Polystyrene has the monomer unit styrene. Teflon is manufactured by heating tetrafluoroethene with a free radical or persulphate catalyst at high pressures.

19. Vulcanisation makes rubber ______________.

(*i*) more elastic
(*ii*) soluble in inorganic solvent
(*iii*) crystalline
(*iv*) more stiff

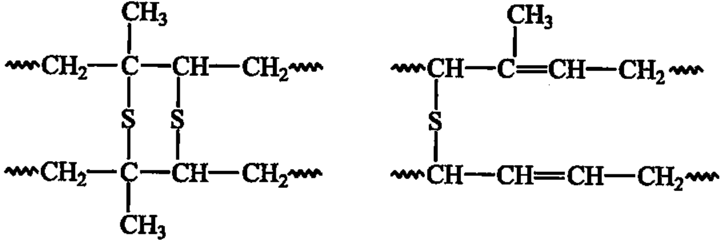
Ans. (*i*) and (*iv*)

Explanation: To improve upon physical properties of natural rubber a process of vulcanisation is carried out. This process consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K to 415 K. On vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.

III. SHORT ANSWER TYPE

20. A natural linear polymer of 2-methyl-1, 3-butadiene becomes hard on treatment with sulphur between 373 to 415 K and —S—S— bonds are formed between chains. Write the structure of the product of this treatment?

Ans. In the manufacture of tyre rubber, 5% of sulphur is used as a crosslinking agent. The probable structures of vulcanised rubber molecules are depicted below:



21. Identify the type of polymer.

—A—A—A—A—A—A—

Ans. The addition polymers formed by the polymerisation of a single monomeric species are known as homopolymers,

22. Identify the type of polymer.

—A—B—B—A—A—A—B—A—

Ans. The polymers made by addition polymerisation from two different monomers are termed as copolymers, e.g., Buna-S, Buna-N, etc.

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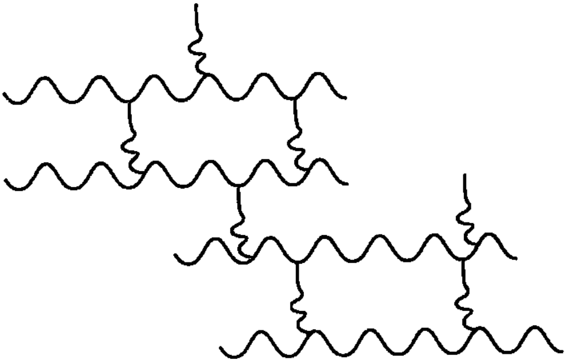
23. Out of chain growth polymerisation and step growth polymerisation, in which type will you place the following.

$$-(A)_m- + -(A)_n- \longrightarrow -(A)_m-(A)_n- \text{ or } -(A-A)_{m+n}-$$

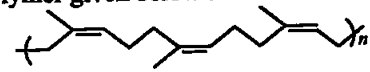
Ans. This is a type of chain growth polymerisation.

24. Identify the type of polymer given in the following figure.

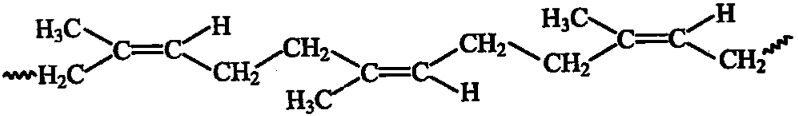


Ans. *Cross linked or Network polymers:* These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, *e.g.* bakelite, melamine, etc.

25. Identify the polymer given below :



Ans. The *cis*-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.



Natural rubber

26. Why are rubbers called elastomers?

Ans. Rubber is a natural polymer and possesses elastic properties. It is also termed as elastomer and has a variety of uses. It is manufactured from rubber latex which is a colloidal dispersion of rubber in water.

27. Can enzyme be called a polymer?

Ans. Enzymes are biocatalysts. They are basically proteins thus they are also considered as polymer.

28. Can nucleic acids, proteins and starch be considered as step growth polymers?

Ans. Yes, this type of polymerisation generally involves a repetitive condensation reaction between two bi-functional monomers. These

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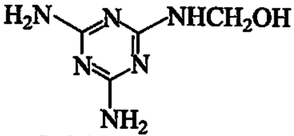
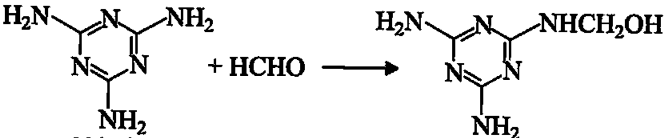
polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers.

29. How is the following resin intermediate prepared and which polymer is formed by this monomer unit?



Resin intermediate

Ans. Melamine formaldehyde polymer is formed by the condensation polymerisation of melamine and formaldehyde.



Melamine Formaldehyde Resin intermediate

30. To have practical applications why are cross links required in rubber?

Ans. To improve upon physical properties of natural rubber, a process of vulcanisation is carried out. This process consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K to 415 K. On vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.

31. Why does *cis*-polyisoprene possess elastic property?

Ans. The *cis*-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

32. What is the structural difference between HDP and LDP? How does the structure account for different behaviour and nature, hence the use of a polymer?

Ans. ***Low density polythene:*** It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst). The low density polythene (LDP) obtained through the free radical addition and H-atom abstraction has highly branched structure.

High density polythene: It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres. High density polythene (HDP) thus produced, consists of linear molecules and has a high density due to close packing.

It is also chemically inert and more tougher and harder. It is used for manufacturing buckets, dustbins, bottles, pipes.

33. What is the role of benzoyl peroxide in addition polymerisation of alkenes? Explain its mode of action with the help of an example.

Ans. Role of benzoyl peroxide is to generate free radicals. A variety of alkenes or dienes and their derivatives are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, *tert*-butyl peroxide, etc. For example, the polymerisation of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator. The process starts with the addition of phenyl free radical formed by the peroxide to the ethene double bond thus generating a new and larger free radical. This step is called chain initiating step.

34. Which factor imparts crystalline nature to a polymer like nylon?

Ans. Polymers possessing amide linkages are important examples of synthetic fibres and are termed as nylons strong intermolecular forces like hydrogen bonding, lead to close packing of chains that imparts crystalline character.

35. Name the polymers used in laminated sheets and give the name of monomeric units involved in its formation.

Ans. Urea formaldehyde resins. Monomer units are:

Urea + formaldehyde

36. Which type of biomolecules have some structural similarity with synthetic polyamides? What is this similarity?

Ans. Proteins are also like polyamides. Proteins and polyamide both contains amide linkages.

37. Why should the monomers used in addition polymerisation through free radical pathway be very pure?

Ans. Pure monomers are required because even the traces of impurities may act like inhibitors which leads to the formation of polymers with shorter chain length.

IV. MATCHING TYPE

Note : Match the items of Column I with the items in Column II.

38. Match the polymer of column I with correct monomer of column II.

Column I	Column II
(*i*) High density polythene	(*a*) Isoprene
(*ii*) Neoprene	(*b*) Tetrafluoroethene
(*iii*) Natural rubber	(*c*) Chloroprene
(*iv*) Teflon	(*d*) Acrylonitrile
(*v*) Acrilan	(*e*) Ethene

Ans. (*i*) → (*e*) (*ii*) → (*c*) (*iii*) → (*a*)
(*iv*) → (*b*) (*v*) → (*d*)

Explanation:

Column I	Column II
(*i*) High density polythene	It is formed when addition poly-merisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst
(*ii*) Neoprene	Neoprene or polychloroprene is formed by the free radical polymerisation of chloroprene
(*iii*) Natural rubber	Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene)
(*iv*) Teflon	Teflon is manufactured by heating tetrafluoroethene with a free radical or persulphate catalyst at high pressures
(*v*) Acrilan	The addition polymerisation of acrylonitrile in presence of a peroxide catalyst leads to the formation of polyacrylonitrile

39. Match the polymers given in Column I with their chemical names given in Column II.

Column I	Column II
(*i*) Nylon 6	(*a*) Polyvinyl chloride
(*ii*) PVC	(*b*) Polyacrylonitrile
(*iii*) Acrilan	(*c*) Polycaprolactum
(*iv*) Natural rubber	(*d*) Low density polythene
(*v*) LDP	(*e*) *cis*-polyisoprene

Ans. (*i*) → (*c*) (*ii*) → (*a*) (*iii*) → (*b*)
(*iv*) → (*e*) (*v*) → (*d*)

Explanation:

Column I	Column II
(*i*) Nylon 6	It is obtained by heating caprolactum with water at a high temperature.
(*ii*) PVC	Polymer of vinyl chloride
(*iii*) Acrilan	The addition polymerisation of acrylonitrile in presence of a peroxide catalyst leads to the formation of polyacrylonitrile
(*iv*) Natural rubber	Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis- 1, 4 polyisoprene.
(*v*) LDP	The low density polythene (LDP) obtained through the free radical addition and H-atom abstraction has highly branched structure

40. Match the polymers given in Column I with their commercial names given in Column II.

Column I	Column II
(*i*) Polyester of glycol and phthalic acid	(*a*) Novolac
(*ii*) Copolymer of 1, 3-butadiene and styrene	(*b*) Glyptal
(*iii*) Phenol and formaldehyde resin	(*c*) Buna-S
(*iv*) Polyester of glycol and terephthalic acid	(*d*) Buna-N
(*v*) Copolymer of 1, 3-butadiene and acrylonitrile	(*e*) Dacron

Ans. (*i*) → (*b*) (*ii*) → (*c*) (*iii*) → (*a*)
(*iv*) → (*e*) (*v*) → (*d*)

41. Match the polymers given in Column I with their main applications given in Column II.

Column I	Column II
(*i*) Bakelite	(*a*) Unbreakable crockery
(*ii*) Low density polythene	(*b*) Non-stick cookwares
(*iii*) Melamine-formaldehyde resin	(*c*) Packaging material for shock absorbance
(*iv*) Nylon 6	(*d*) Electrical switches
(*v*) Polytetrafluoroethane	(*e*) Squeeze bottles
(*vi*) Polystyrene	(*f*) Tyre, cords

Ans. (*i*) → (*d*) (*ii*) → (*e*) (*iii*) → (*a*)
(*iv*) → (*f*) (*v*) → (*b*) (*vi*) → (*c*)

42. Match the polymers given in Column I with the preferred mode of polymerisation followed by their monomers.

Column I	Column II
(*i*) Nylon-6,6	(*a*) Free radical polymerisation
(*ii*) PVC	(*b*) Ziegler-Natta polymerisation or coordination polymerisation
(*iii*) HDP	(*c*) Anionic polymerisation
	(*d*) Condensation polymerisation

Ans. (*i*) → (*d*) (*ii*) → (*a*) (*iii*) → (*b*)

43. Match the polymers given in Column I with the type of linkage present in them given in Column II.

Column I	Column II
(*i*) Terylene	(*a*) Glycosidic linkage
(*ii*) Nylon	(*b*) Ester linkage
(*iii*) Cellulose	(*c*) Phosphodiester linkage
(*iv*) Protein	(*d*) Amide linkage
(*v*) RNA	

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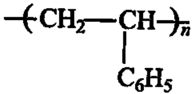
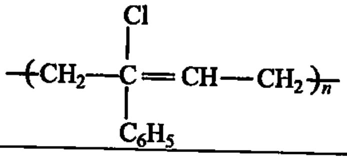
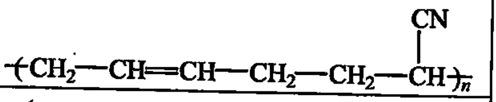
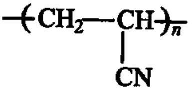
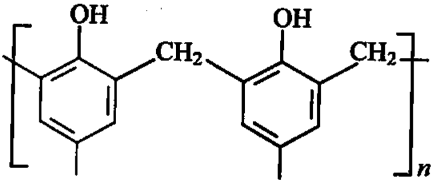
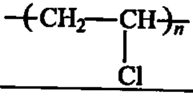
Ans. (*i*) → (*b*) (*ii*) → (*d*) (*iii*) → (*a*)
(*iv*) → (*d*) (*v*) → (*c*)

44. Match materials given in Column I with the polymers given in Column II.

Column I	Column II
(*i*) Natural rubber latex	(*a*) Nylon
(*ii*) Wood laminates	(*b*) Neoprene
(*iii*) Ropes and fibres	(*c*) Dacron
(*iv*) Polyester fabric	(*d*) Melamine formaldehyde resins
(*v*) Synthetic rubber	(*e*) Urea-formaldehyde resins
(*vi*) Unbreakable crockery	(*f*) *cis*-polyisoprene

Ans. (*i*) → (*f*) (*ii*) → (*e*) (*iii*) → (*a*)
(*iv*) → (*c*) (*v*) → (*b*) (*vi*) → (*d*)

45. Match the polymers given in Column I with their repeating units given in Column II.

Column I	Column II
(*i*) Acrilan	(*a*)  $\left(CH_2-\underset{\displaystyle C_6H_5}{\underset{\vert}{CH}}\right)_n$
(*ii*) Polystyrene	(*b*)  $\left(CH_2-\overset{\displaystyle Cl}{\overset{\vert}{\underset{\displaystyle C_6H_5}{\underset{\vert}{C}}}}=CH-CH_2\right)_n$
(*iii*) Neoprene	(*c*)  $\left(CH_2-CH=CH-CH_2-CH_2-\overset{\displaystyle CN}{\overset{\vert}{CH}}\right)_n$
(*iv*) Novolac	(*d*)  $\left(CH_2-\underset{\displaystyle CN}{\underset{\vert}{CH}}\right)_n$
(*v*) Buna—N	(*e*) 
	(*f*)  $\left(CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}\right)_n$

Ans. (*i*) → (*d*) (*ii*) → (*a*) (*iii*) → (*b*)
(*iv*) → (*e*) (*v*) → (*c*)

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V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are correct statements but reason does not explain assertion.

(*ii*) Assertion and reason both are correct statements and reason explains the assertion.

(*iii*) Both assertion and reason are wrong statements.

(*iv*) Assertion is correct statement and reason is wrong statement.

(*v*) Assertion is wrong statement and reason is correct statement.

46. Assertion : Rayon is a semi synthetic polymer and is taken as a better choice than cotton fabric.

Reason : Mechanical and aesthetic properties of cellulose can be improved by acetylation.

Ans. (*ii*)

47. Assertion : Most of the synthetic polymers are not biodegradable.

Reason : Polymerisation process induces toxic character in organic molecules.

Ans. (*iv*)

Explanation: Most of the synthetic polymers are not biodegradable. Because a large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric solid waste materials.

48. Assertion : Olefinic monomers undergo addition polymerisation.

Reason : Polymerisation of vinylchloride is initiated by peroxides/ persulphates.

Ans. (*i*)

Explanation: In addition polymerisation, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, *e.g.*, alkenes, alkadienes and their derivatives. This mode of polymerisation leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species.

49. Assertion : Polyamides are best used as fibres because of high tensile strength.

Reason : Strong intermolecular forces (like hydrogen bonding within polyamides) lead to close packing of chains and increase the crystalline character, hence, provide high tensile strength to polymers.

Ans. (*ii*)

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50. **Assertion** : For making rubber synthetically, isoprene molecules are polymerised.

Reason : Neoprene (a polymer of chloroprene) is a synthetic rubber.

Ans. (*v*)

Explanation: Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as *cis* - 1, 4 -polyisoprene.

51. **Assertion** : Network polymers are thermosetting.

Reason : Network polymers have high molecular mass.

Ans. (*i*)

Explanation: Thermosetting polymers: These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible.

52. **Assertion** : Polytetrafluoroethene is used in making non-stick cookwares.

Reason : Fluorine has highest electronegativity.

Ans. (*i*)

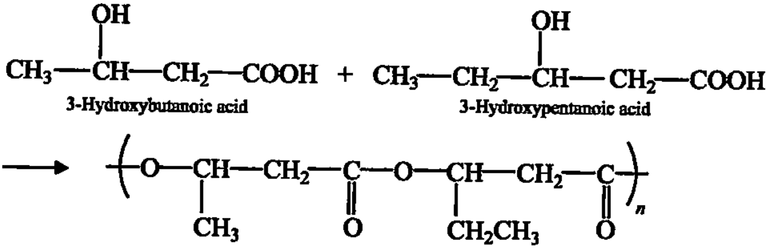
Explanation: Teflon is manufactured by heating tetrafluoroethene with a free radical or persulphate catalyst at high pressures. It is chemically inert and resistant to attack by corrosive reagents. It is used in making oil seals and gaskets and also used for non-stick surface coated utensils.

VI. LONG ANSWER TYPE

53. Synthetic polymers do not degrade in the environment for a long time. How can biodegradable synthetic polymers be made. Differentiate between biopolymers and biodegradable polymers and give examples of each type.

Ans. 1. *Poly-β-hydroxybutyrate – co-β-hydroxy valerate (PHBV)*

It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.



$$\mathrm{CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-COOH + CH_3-CH_2-\overset{\overset{OH}{|}}{C}H-CH_2-COOH \longrightarrow \left(O-\underset{\underset{CH_3}{|}}{C}H-CH_2-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{CH_2CH_3}{|}}{C}H-CH_2-\underset{\underset{O}{\|}}{C} \right)_n}$$

PHBV

2. Nylon 2–nylon 6: It is an alternating polyamide copolymer of glycine (H_2N-CH_2-COOH) and amino caproic acid [$H_2N(CH_2)_5COOH$] and is biodegradable.

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Biopolymers are the natural polymers found in plants and animals like protein, fat, cellulose etc. Biodegradable polymers are polymers that contain functional groups similar to the functional groups present in biopolymers. They are not resistant to the environmental degradation processes .

54. Differentiate between rubbers and plastics on the basis of intermolecular forces.

Ans. **Rubbers:** In rubber, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber.

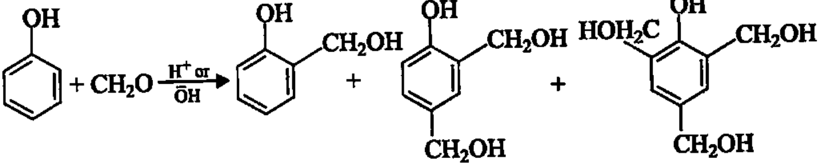
Plastics: These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres.

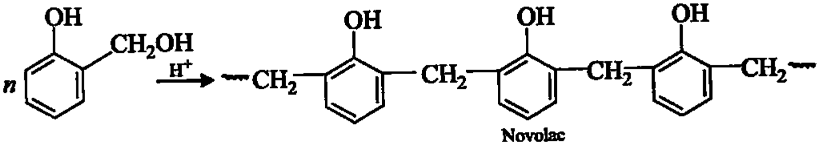
55. Phenol and formaldehyde undergo condensation to give a polymer (A) which on heating with formaldehyde gives a thermosetting polymer (B). Name the polymers. Write the reactions involved in the formation of (A). What is the structural difference between two polymers?

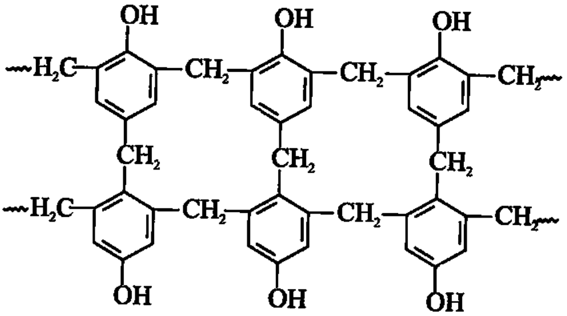
Ans. Phenol - formaldehyde polymers are the oldest synthetic polymers. These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst. The reaction starts with the initial formation of *o*-and/or *p*-hydroxymethylphenol derivatives, which further react with phenol to form compounds having rings joined to each other through $-CH_2$ groups. The initial product could be a linear product – Novolac.

Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called bakelite. It is used for making combs, phonograph records, electrical switches and handles of various utensils.

'A' is Novolac and 'B' is Bakelite.







Bakelite

56. Low density polythene and high density polythene, both are polymers of ethene but there is marked difference in their properties. Explain.

Ans.

LDP	HDP
1. It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst).	1. It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres.
2. (LDP) obtained through the free radical addition and H-atom abstraction has highly branched structure.	2. (HDP) consists of linear molecules and has a high density due to close packing.
3. Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity.	3. It is also chemically inert and more tough and hard.

57. Which of the following polymers soften on heating and harden on cooling? What are the polymers with this property collectively called? What are the structural similarities between such polymers? Bakelite, urea-formaldehyde resin, polythene, polyvinyls, polystyrene.

Ans. **Thermoplastic polymers** are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

Thermosetting polymers: These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.

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16 Chemistry In Everyday Life

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Which of the following statements is **not** correct?
   - (*i*) Some antiseptics can be added to soaps.
   - (*ii*) Dilute solutions of some disinfectants can be used as antiseptic.
   - (*iii*) Disinfectants are antimicrobial drugs.
   - (*iv*) Antiseptic medicines can be ingested.

Ans. (*iv*)

Explanation : Antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces. It either kill or prevent the growth of microorganisms. It should not be ingested.

2. Which is the correct statement about birth control pills?
   - (*i*) Contain estrogen only.
   - (*ii*) Contain progesterone only.
   - (*iii*) Contain a mixture of estrogen and progesterone derivatives.
   - (*iv*) Progesterone enhances ovulation.

Ans. (*iii*)

Explanation: Birth control pills essentially contain a mixture of synthetic estrogen and progesterone derivatives. Both of these compounds are hormones. Progesterone suppresses ovulation.

3. Which statement about aspirin is **not** true?
   - (*i*) Aspirin belongs to narcotic analgesics.
   - (*ii*) It is effective in relieving pain.
   - (*iii*) It has antiblood clotting action.
   - (*iv*) It is a neurologically active drug.

Ans. (*i*)

Explanation: Aspirin belongs to the class of non-narcotic analgesics.

4. The most useful classification of drugs for medicinal chemists is _____.
   - (*i*) on the basis of chemical structure.
   - (*ii*) on the basis of drug action.
   - (*iii*) on the basis of molecular targets.
   - (*iv*) on the basis of pharmacological effect.

Ans. (*iii*)

Explanation: Drugs usually interact with biomolecules such as carbohydrates, lipids, proteins and nucleic acids. These are called target molecules or drug targets. Drugs possessing some common structural features may have the same mechanism of action on targets. The classification based on molecular targets is the most useful classification for medicinal chemists.

5. Which of the following statements is correct?
   (*i*) Some tranquilisers function by inhibiting the enzymes which catalyse the degradation of noradrenaline.
   (*ii*) Tranquilisers are narcotic drugs.
   (*iii*) Transquilisers are chemical compounds that do not affect the message transfer from nerve to receptor.
   (*iv*) Tranquilisers are chemical compounds that can relieve pain and fever.

Ans. (*i*)

Explanation: Tranquilisers inhibit the enzymes which catalyse the degradation of noradrenaline. If the enzyme is inhibited, this important neurotransmitter is slowly metabolised and can activate its receptor for longer periods of time, thus counteracting the effect of depression. Iproniazid and phenelzine are two such drugs.

6. Salvarsan is arsenic containing drug which was first used for the treatment of ___________.
   (*i*) syphilis
   (*ii*) typhoid
   (*iii*) meningitis
   (*iv*) dysentry

Ans. (*i*)

Explanation: Paul Ehrlich, a German bacteriologist, conceived this idea. He investigated arsenic based structures in order to produce less toxic substances for the treatment of syphilis. He developed the medicine, arsphenamine, known as salvarsan.

7. A narrow spectrum antibiotic is active against ______________.
   (*i*) gram positive or gram negative bacteria.
   (*ii*) gram negative bacteria only.
   (*iii*) single organism or one disease.
   (*iv*) both gram positive and gram negative bacteria.

Ans. (*i*)

Explanation: Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be broad-spectrum antibiotics. But antibiotics that are effective against either Gram-positive or Gram-negative bacteria are narrow spectrum antibiotics.

8. The compound that causes general antidepressant action on the central nervous system belongs to the class of ____________.
   (*i*) analgesics
   (*ii*) tranquilizers
   (*iii*) narcotic analgesics
   (*iv*) antihistamines

Ans. (*ii*)

Explanation: Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases. If the level of noradrenaline is low for some reason, then the signal-sending activity becomes low, and the person suffers from depression. In such situations, antidepressant drugs are required.

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9. Compound which is added to soap to impart antiseptic properties is ________.
   (*i*) sodium laurylsulphate
   (*ii*) sodium dodecylbenzenesulphonate
   (*iii*) rosin (*iv*) bithional

Ans. (*iv*)

Explanation: Sodium laurylsulphate and sodium dodecylbenzenesulphonate are anionic detergent. Whereas, bithional is added to soaps to impart antiseptic properties of soap.

10. Equanil is ________.
   (*i*) artificial sweetener (*ii*) tranquilizer
   (*iii*) antihistamine (*iv*) antifertility drug

Ans. (*ii*)

Explanation: Equanil is a tranquilizer that help in controlling depression and hypertension.

11. Which of the following enhances leathering property of soap?
   (*i*) Sodium carbonate (*ii*) Sodium rosinate
   (*iii*) Sodium stearate (*iv*) Trisodium phosphate

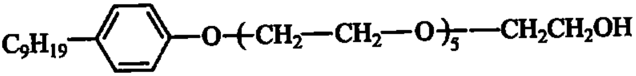
Ans. (*ii*)

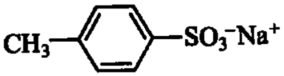
Explanation: A gum called, rosin is added while making them. It forms sodium rosinate which lathers well.

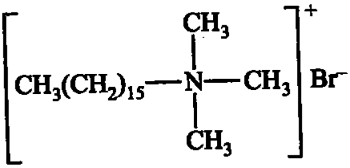
12. Glycerol is added to soap. It functions ________.
   (*i*) as a filler. (*ii*) to increase leathering.
   (*iii*) to prevent rapid drying. (*iv*) to make soap granules.

Ans. (*iii*)

13. Which of the following is an example of liquid dishwashing detergent?
   (*i*) $CH_3(CH_2)_{10}—CH_2OSO_3^- Na^+$

   (*ii*) 

   (*iii*) 

   (*iv*) 

   $$\left[CH_3(CH_2)_{15}—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}—CH_3\right]^+ Br^-$$

Ans. (*ii*)

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Explanation: Liquid dishwashing detergents are non-ionic type. Mechanism of cleansing action of this type of detergents is the same as that of soaps. These also remove grease and oil by micelle formation.

14. Polyethyleneglycols are used in the preparation of which type of detergents?

(*i*) Cationic detergents
(*ii*) Anionic detergents
(*iii*) Non-ionic detergents
(*iv*) Soaps

Ans. (*iii*)

Explanation: Non-ionic detergents do not contain any ion in their constitution. One such detergent is formed when stearic acid reacts with polyethyleneglycol.

$$\underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH} + \underset{\text{Polyethyleneglycol}}{HO(CH_2CH_2O)_nCH_2CH_2OH} \xrightarrow{-H_2O} CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$$

15. Which of the following is **not** a target molecule for drug function in body?

(*i*) Carbohydrates
(*ii*) Lipids
(*iii*) Vitamins
(*iv*) Proteins

Ans. (*iii*)

Explanation: Drugs usually intereact with biomolecules such as carbohydrates, lipids, proteins and nucleic acids. These are called drug targets. Vitamins are not a target molecule for drug function in body.

16. Which of the following statements is **not** true about enzyme inhibitors?

(*i*) Inhibit the catalytic activity of the enzyme.
(*ii*) Prevent the binding of substrate.
(*iii*) Generally a strong covalent bond is formed between an inhibitor and an enzyme.
(*iv*) Inhibitors can be competitive or non-competitive.

Ans. (*iii*)

Explanation: If the bond formed between an enzyme and an inhibitor is a strong covalent bond and cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesises then new enzyme.

17. Which of the following chemicals can be added for sweetening of food items at cooking temperature and does not provide calories?

(*i*) Sucrose
(*ii*) Glucose
(*iii*) Aspartame
(*iv*) Sucrolose

Ans. (*iv*)

Explanation: Sucrolose is trichloro derivative of sucrose. Its appearance and taste are like sugar. It is stable at cooking temperature. It does not provide calories.

18. Which of the following will **not** enhance nutritional value of food?

(*i*) Minerals	(*ii*) Artificial sweeteners
(*iii*) Vitamins	(*iv*) Aminoacids

Ans. (*ii*)

Explanation: Artificial sweetners are non caloric substitutes for sugar. They are often more sweeter than sugar but do not enhance nutritional value of food.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note: In the following questions two or more options may be correct?

19. Which of the following statements are **incorrect** about receptor proteins?

(*i*) Majority of receptor proteins are embedded in the cell membranes.

(*ii*) The active site of receptor proteins opens on the inside region of the cell.

(*iii*) Chemical messengers are received at the binding sites of receptor proteins.

(*iv*) Shape of receptor doesn't change during attachment of messenger.

Ans. (*ii*), (*iv*)

Explanation: (*ii*) Receptor proteins are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.

(*iv*) To accommodate a messenger, shape of the receptor site changes. This brings about the transfer of message into the cell.

20. Which of the following are **not** used as food preservatives?

(*i*) Table salt	(*ii*) Sodium hydrogencarbonate
(*iii*) Cane sugar	(*iv*) Benzoic acid

Ans. (*ii*), (*iii*)

Explanation: Food preservatives prevent spoilage of food due to microbial growth. The most commonly used preservatives include table salt, sugar, vegetable oils and sodium benzoate, C_6H_5COONa. Cane sugar and sodium hydrogencarbonate are not used as food preservatives.

21. Compounds with antiseptic properties are __________.

(*i*) $CHCl_3$	(*ii*) CHI_3

(*iii*) Boric acid

(*iv*) 0.3 ppm aqueous solution of Cl_2

Ans. (*ii*), (*iii*)

Explanation: Antiseptics are the chemicals which either kill or prevent the growth of microorganisms.

(*ii*) Iodoform is also used as an antiseptic for wounds.

(*iii*) Boric acid in dilute aqueous solution is weak antiseptic for eyes.

22. Which of the following statements are correct about barbiturates?

(*i*) Hypnotics or sleep producing agents.

(*ii*) These are tranquilizers.
(*iii*) Non-narcotic analgesics.
(*iv*) Pain reducing without disturbing the nervous system.

Ans. (*i*), (*ii*)

Explanation: Derivatives of barbituric acid viz., veronal, amytal, nembutal, luminal and seconal constitute an important class of tranquilizers. These derivatives are called barbiturates. Barbiturates are hypnotic, i.e. sleep producing agents.

23. Which of the following are sulpha drugs?

(*i*) Sulphapyridine
(*ii*) Prontosil
(*iii*) Salvarsan
(*iv*) Nardil

Ans. (*i*), (*ii*)

Explanation: These drugs inhibit the enzymes which catalyse the degradation of noradrenaline. Sulphapyridine and prontosil contain sulphur and hence are sulpha drugs.

24. Which of the following are antidepressants?

(*i*) Iproniazid
(*ii*) Phenelzine
(*iii*) Equanil
(*iv*) Salvarsan

Ans. (*i*), (*ii*), (*iii*)

Explanation: If the enzyme is inhibited, this important neurotransmitter is slowly metabolised and can activate its receptor for longer periods of time, thus counteracting the effect of depression. Iproniazid, phenelzine and equanil are such drugs.

25. Which of the following statements are **incorrect** about penicillin?

(*i*) An antibacterial fungus.
(*ii*) Ampicillin is its synthetic modification.
(*iii*) It has bacteriostatic effect.
(*iv*) It is a board spectrum antibiotic.

Ans. (*iii*), (*iv*)

Explanation: Penicillin is a narrow spectrum antibiotic. Ampicillin and Amoxycillin are synthetic modifications of penicillins. These have broad spectrum. Pencillin kill microbes and hence it has bacteriocidal effect.

26. Which of the following compounds are administered as antacids?

(*i*) Sodium carbonate
(*ii*) Sodium hydrogencarbonate
(*iii*) Aluminium carbonate
(*iv*) Magnesium hydroxide

Ans. (*ii*), (*iv*)

Explanation: Treatment for acidity was administration of antacids, such as sodium hydrogencarbonate or a mixture of aluminium and magnesium hydroxide.

27. Amongst the following antihistamines, which are antacids?

(*i*) Ranitidine
(*ii*) Brompheniramine

(*iii*) Terfenadine (*iv*) Cimetidine

Ans. (*i*), (*iv*)

Explanation: The drug cimetidine and ranitidine was designed to prevent the interaction of histamine with the receptors present in the stomach wall.

28. Veronal and luminal are derivatives of barbituric acid which are______.

(*i*) Tranquilizers (*ii*) Non-narcotic analgesic

(*iii*) Anti-allergic drugs (*iv*) Neurologically active drugs

Ans. (*i*), (*iv*)

Explanation: Derivatives of barbituric acid viz., veronal, amytal, nembutal, luminal and seconal constitute an important class of tranquilizers. These derivatives are called barbiturates.

29. Which of the following are anionic detergents?

(*i*) Sodium salts of sulphonated long chain alcohol.

(*ii*) Ester of stearic acid and polyethylene glycol.

(*iii*) Quarternary ammonium salt of amine with acetate ion.

(*iv*) Sodium salts of sulphonated long chain hydrocarbons.

Ans. (*i*), (*iv*)

Explanation: Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons.

30. Which of the following statements are correct?

(*i*) Cationic detergents have germicidal properties

(*ii*) Bacteria can degrade the detergents containing highly branched chains.

(*iii*) Some synthetic detergents can give foam even in ice cold water.

(*iv*) Synthetic detergents are not soaps.

Ans. (*i*), (*iii*), (*iv*)

Explanation: Cationic detergents have germicidal properties and are expensive, therefore, these are of limited use. Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap. These can be used both in soft and hard water as they give foam even in hard water.

III. SHORT ANSWER TYPE

31. What is the average molecular mass of drugs?

Ans. Drugs are chemicals of low molecular masses (~100 – 500u). These interact with macromolecular targets and produce a biological response.

32. Write the uses of medicines.

Ans. Medicines are used in diagnosis, prevention and treatment of diseases. If taken in doses higher than those recommended, most of the drugs used as medicines are potential poisons.

33. What are antiseptics?

Ans. Antiseptics are the chemicals which either kill or prevent the growth of microorganisms. Antiseptics are applied to the living tissues such as

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wounds, cuts, ulcers and diseased skin surfaces.

34. Which type of drugs come under antimicrobial drugs?

Ans. An antimicrobial tends to destroy or prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal agents), virus (antiviral agents), or other parasites (antiparasitic drugs) selectively. Antibiotics, antiseptics and disinfectants are antimicrobial drugs.

35. Where are receptors located?

Ans. Receptor proteins are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.

36. What is the harmful effect of hyperacidity?

Ans. Over production of acid in the stomach causes irritation and pain. In severe cases, ulcers are developed in the stomach.

37. Which site of an enzyme is called allosteric site?

Ans. Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site.

38. What type of forces are involved in binding of substrate to the active site of enzyme?

Ans. Substrates bind to the active site of the enzyme through a variety of interactions such as ionic bonding, hydrogen bonding, van der Waals interaction or dipole-dipole Interaction.

39. What is the commonality between the antibiotic arsphenamine and azodye?

Ans. Similarity in structures of salvarsan and azodyes. The –As = As– linkage present in arsphenamine resembles the –N = N – linkage present in azodyes in the sense that arsenic atom is present in place of nitrogen. He also noted tissues getting coloured by dyes selectively.

40. Which class of drugs is used in sleeping pills?

Ans. Tranquilizer drugs are used in sleeping pills. Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases. These relieve anxiety, stress, irritability or excitement by inducing a sense of well-being.

41. Aspirin is pain relieving antipyretic drug but can be used to prevent heart attack. Explain.

Ans. Aspirin inhibits the synthesis of chemicals known as prostaglandins which stimulate inflammation in the tissue and cause pain. These drugs are effective in relieving skeletal pain such as that due to arthritis. Aspirin prevents platelet coagulation and thus has anti blood clotting action, therefore can prevent blood clogging in heart.

42. Both antacids and antiallergic drugs are anthistamines but they cannot replace each other. Explain why?

Ans. Antiallergic and antacid drugs work on different receptors. Therefore,

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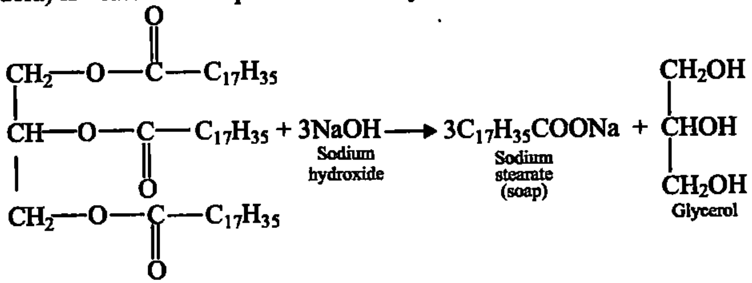
anithistamines remove allergy while antacid remove acidity.

43. What is a soft soap?

Ans. Only sodium and potassium soaps are soluble in water and are used for cleaning purposes. Generally potassium soaps are soft to the skin than sodium soaps. Hence known as soft soaps.

44. If soap has high alkali content it irritates skin.How can the amount of excess alkali be determined? What can be the source of excess alkali?

Ans. A solution of soap is titrated with standard hydrochloric acid. It is an acid-base titration. In this titration, phenolphthalein is used as an indicator. During the preparation of soap, fat (i.e. glyceryl ester of fatty acid) is heated with aqueous sodium hydroxide



$$\begin{array}{l} CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_{17}H_{35} \\ | \\ CH-O-\underset{\underset{\displaystyle O}{\|}}{C}-C_{17}H_{35} \\ | \\ CH_2-O-\underset{\underset{\displaystyle O}{\|}}{C}-C_{17}H_{35} \end{array} + \underset{\text{Sodium hydroxide}}{3NaOH} \longrightarrow \underset{\text{Sodium stearate (soap)}}{3C_{17}H_{35}COONa} + \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}}$$

Glyceryl ester of stearic acid (Fat)

Thus, the source of this excess alkali (which irritates skin) is the alkali left unused when the soap is prepared by hydrolysis of fat.

45. Explain why some times foaming is seen in river water near the place where sewage water is poured after treatment?

Ans. Slow degradation of detergents leads to their accumulation. Effluents containing such detergents reach the rivers, ponds, etc. These persist in water even after sewage treatment and cause foaming in rivers, ponds and streams and their water gets polluted.

46. Which category of the synthetic detergents is used in toothpaste?

Ans. Anionic detergents are used in toothpastes. The anionic part of the molecule is involved in the cleansing action. Sodium salts of alkylbenzenesulphonates are an important class of anionic detergents. They are mostly used for household work.

47. Hair shampoos belong to which class of synthetic detergent?

Ans. Cationic detergents are used in shampoos. Cationic part possess a long hydrocarbon chain and a positive charge on nitrogen atom. Hence, these are called cationic detergents. Etyltrimethylammonium bromide is a popular cationic detergent and is used in hair conditioners.

48. Dishwashing soaps are synthetic detergents. What is their chemical nature?

Ans. Liquid dishwashing detergents are non-ionic type. Mechanism of cleansing action of this type of detergents is the same as that of soaps.

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These also remove grease and oil by micelle formation.

49. Draw the diagram showing micelle formation by the following detergent.
$CH_3(CH_2)_{10}CH_2OSO_3Na$

Ans. Sodium lauryl sulphate, $CH_3(CH_2)_{10}CH_2OSO_3Na$ is an example of anionic detergent.

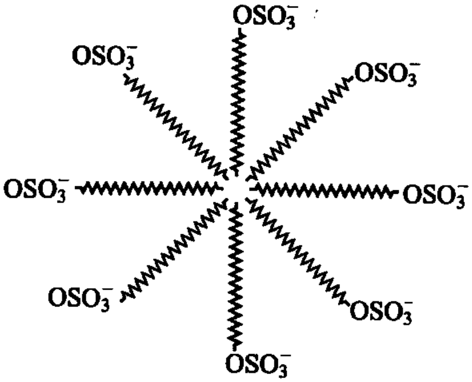
When added to water, it dissociates as follows:

$$CH_3-(CH_2)_{10}-CH_2OS\overset{-}{O}_3\overset{+}{Na} \xrightarrow{H_2O} CH_3-(CH_2)_{10}CH_2-OSO_3^- + \overset{+}{Na}$$

These anions are present on the surface with their $-OSO_3^-$ groups in water and hydrocarbon part staying away from it and remain at the surface.

At higher concentration, these anions are pulled into the bulk of the solution and form an aggregate of spherical shape with their hydrocarbon part pointing towards the centre and OSO_3^- part outwards on the surface of the sphere.

An aggregate thus formed is known as micelle.



Micelle

50. How does the branching of hydrocarbon chain of synthetic detergents affect their biodegradability?

Ans. Highly branched hydrocarbon chains cannot be degraded by bacteria easily. Slow degradation of detergents leads to their accumulation. Effluents containing such detergents reach the rivers, ponds, etc. These persist in water even after sewage treatment and cause foaming in rivers, ponds and streams and their water gets polluted. Less branching leads to easy biodegradability.

51. Why is it safer to use soap from the environmental point of view?

Ans. Unbranched chains can be biodegraded more easily and hence pollution is prevented. Therefore, soap is preferred more than detergent.

52. What are analgesics?

Ans. Analgesics reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system.

53. What is the scientific explanation for the feeling of depression?

Ans. Noradrenaline is one of the neurotransmitters that plays a role in mood changes. If the level of noradrenaline is low for some reason, then the signal-sending activity becomes low, and the person suffers from depression. In such situations, antidepressant drugs are required.

54. What is the basic difference between antiseptics and disinfectants?

Ans. Antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces. Whereas, disinfectants are applied to inanimate objects such as floors, drainage system, instruments, etc. Same substances can act as an antiseptic as well as disinfectant by varying the concentration. For example, 0.2 per cent solution of phenol is an antiseptic while its one percent solution is disinfectant.

55. Between sodiumhydrogencarbonate and magnesium hydroxide which is a better antacid and why?

Ans. Excessive hydrogencarbonate can make the stomach alkaline and trigger the production of even more acid. Metal hydroxides are better alternatives because of being insoluble, these do not increase the pH above neutrality.

56. Which analgesics are called opiates?

Ans. Morphine narcotics are sometimes referred to as opiates, since they are obtained from the opium poppy. Morphine and many of its homologues, when administered in medicinal doses, relieve pain and produce sleep. In poisonous doses, these produce stupor, coma, convulsions and ultimately death.

57. What is the medicinal use of narcotic drugs?

Ans. These analgesics are chiefly used for the relief of postoperative pain, cardiac pain and pains of terminal cancer, and in child birth.

58. What are antagonistic drugs?

Ans. Drugs that bind to the receptor site and inhibit its natural function are called antagonists. These are useful when blocking of message is required.

59. What is the mode of action of antimicrobial drugs?

Ans. An antimicrobial tends to destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal agents), virus (antiviral agents), or other parasites (antiparasitic drugs) selectively.

60. What is the side product of soap industry? Give reactions showing soap formation.

Ans. Soaps are the detergents used since long. Soaps used for cleaning purpose are sodium or potassium salts of long chain fatty acids, e.g., stearic, oleic and palmitic acids. Soaps containing sodium salts are formed by heating fat (i.e., glyceryl ester of fatty acid) with aqueous sodium hydroxide solution.

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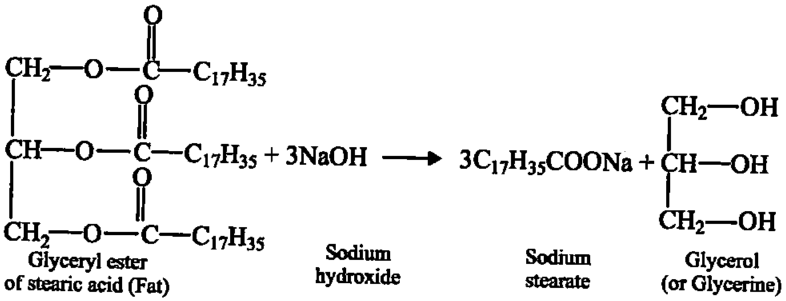

$$CH_2(OCOC_{17}H_{35})-CH(OCOC_{17}H_{35})-CH_2(OCOC_{17}H_{35}) + 3NaOH \longrightarrow 3C_{17}H_{35}COONa + CH_2(OH)-CH(OH)-CH_2(OH)$$

61. What is the difference between bathing soap and washing soaps?

Ans. Only sodium and potassium soaps are soluble in water and are used for cleaning purposes. Generally potassium soaps are soft to the skin than sodium soaps. These can be prepared by using potassium hydroxide solution in place of sodium hydroxide.

Bathing soaps are potassium salts of long chain fatty acids while washing soaps are sodium salts of long chain fatty acids.

62. How are transparent soaps manufactured?

Ans. Transparent soaps are made by dissolving the soap in ethanol and then evaporating the excess solvent.

63. What is the advantage of using antihistamines over antacids in the treatment of acidity?

Ans. Antacids control only symptoms, and not the cause. Therefore, with these metal salts, the patients cannot be treated easily. In advanced stages, ulcers become life threatening and its only treatment is removal of the affected part of the stomach. Whereas, antihistamines in the treatment of hyperacidity came through the discovery according to which a chemical, histamine, stimulates the secretion of pepsin and hydrochloric acid in the stomach. The drug cimetidine was designed to prevent the interaction of histamine with the receptors present in the stomach wall. This resulted in release of lesser amount of acid.

64. What are the functions performed by histamine in the body?

Ans. Histamine is a potent vasodilator. It has various functions. It contracts the smooth muscles in the bronchi and gut and relaxes other muscles, such as those in the walls of fine blood vessels. Histamine is also responsible for the nasal congestion associated with common cold and allergic response to pollen.

65. With the help of an example explain how do tranquilizers control the feeling of depression?

Ans. Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases. These relieve anxiety, stress, irritability or excitement by inducing a sense of well-being. For example, noradrenaline is one of the neurotransmitters that plays

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a role in mood changes. If the level of noradrenaline is low for some reason, then the signal-sending activity becomes low, and the person suffers from depression.

66. Why are certain drugs called enzyme inhibitors?

Ans. This can block the binding site of the enzyme and prevent the binding of substrate, or can inhibit the catalytic activity of the enzyme. Such drugs are called enzyme inhibitors.

67. What are fillers and what role these fillers play in soap?

Ans. Some substances are added to soap to affect the properties in order to make it useful for a particular application. Example, glycerol is added in shaving soaps to prevent it from drying. A gum called, rosin is added to soaps while making them. It forms sodium rosinate which lathers well. Laundry soaps contain fillers like sodium rosinate, sodium silicate, borax and sodium carbonate.

68. Sugar is the main source of energy as it produces energy on metabolic decomposition. But these days low calorie drinks are more popular, why?

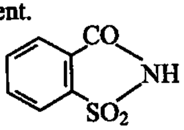
Ans. Natural sweeteners, e.g., sucrose add to calorie intake and therefore many people prefer to use artificial sweeteners. These artificial sweetening agents do not metabolise and hence do not produce any energy. Ortho-sulphobenzimide, also called saccharin, is the first popular artificial sweetening agent.

69. Pickles have a long shelf life and do not get spoiled for months, why?

Ans. Food preservatives prevent spoilage of food due to microbial growth. The most commonly used preservatives include table salt, sugar, vegetable oils and sodium benzoate, C_6H_5COONa. Plenty of salt and cover of oil act as preservative. These do not allow bacteria to thrive on them.

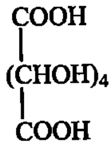
70. What is the difference between saccharin and saccharic acid?

Ans. Ortho-sulphobenzimide, also called saccharin, is the first popular artificial sweetening agent.



Saccharin
[Artificial sweetener]

Where as saccharic acid is obtained from oxidation of glucose by concentrated HNO_3.



$$\begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array}$$

Saccharic acid

71. Name an artificial sweetener which is derivative of sucrose.

Ans. Sucrolose is trichloro derivative of sucrose. Its appearance and taste are like sugar. It is stable at cooking temperature. It does not provide calories.

72. Name two α-amino acids which form a dipeptide which is 100 times more sweet than cane sugar?

Ans. Aspartame is the most successful and widely used artificial sweetener. It is roughly 100 times as sweet as cane sugar. It is methyl ester of dipeptide formed from aspartic acid and phenylalanine.

73. Aspartame is unstable at cooking temperature, where would you suggest aspartame to be used for sweetening?

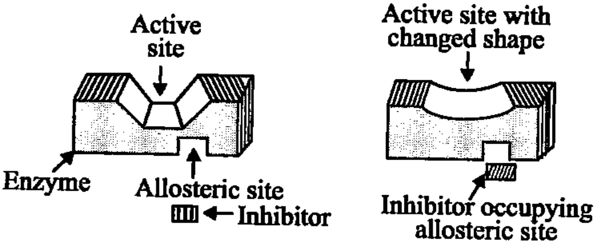
Ans. Cold foods and soft drinks because it is unstable at cooking temperature.

74. Sodium salts of some acids are very useful as food preservatives. Suggest a few such acids.

Ans. Food preservatives prevent spoilage of food due to microbial growth. Sodium salts of benzoic acid, sorbic acid and propanoic acid can be used as preservatives.

75. Explain the role of allosteric site in enzyme inhibition?

Ans. Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site. This binding of inhibitor at allosteric site changes the shape of the active site in such a way that substrate cannot recognise it.



76. How are receptor proteins located in the cell membrane?

Ans. Receptor proteins are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.

77. What happens when the bond formed between an enzyme and an inhibitor is a strong covalent bond?

Ans. If the bond formed between an enzyme and an inhibitor is a strong covalent bond and cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesises the new enzyme.

IV. MATCHING TYPE

Note: Match the items given in Column I with the items given in Column II.

78. Match the medicines given in Column I with their use given in Column II.

Column I	Column II
(*i*) Ranitidine	(*a*) Tranquilizer
(*ii*) Furacine	(*b*) Antibiotic
(*iii*) Phenelzine	(*c*) Antihistamine
(*iv*) Chloramphenicol	(*d*) Antiseptic
	(*e*) Antifertility drug

Ans. (*i*) → (*c*) (*ii*) → (*d*) (*iii*) → (*a*)
(*iv*) → (*b*)

Explanation:

Column I	Column II
(*i*) Ranitidine	Ranitidine was designed to prevent the interaction of histamine with the receptors present in the stomach wall.
(*ii*) Furacine	Furacine is applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces.
(*iii*) Phenelzine	Phenelzine is an important neuro-transmitter. It is slowly metabolized and can activate its receptor for longer periods of time, thus counteracting the effect of depression.
(*iv*) Chloramphenicol	Chloramphenicol, isolated in 1947, is a broad spectrum antibiotic.

79. Match the soaps given in Column I with items given in Column II.

Column I	Column II
(*i*) Soap chips	(*a*) dried miniature soap bubbles
(*ii*) Soap granules	(*b*) small broken pieces of soap formed from melted soaps
(*iii*) Soap powder	(*c*) soap powder + abrasives + builders (Na_2CO_3, Na_3PO_4)
(*iv*) Scouring soap	(*d*) soap powder + builders like Na_2CO_3 and Na_3PO_4

Ans. (*i*) → (*b*) (*ii*) → (*a*) (*iii*) → (*d*) (*iv*) → (*c*)

Explanation:

Column I	Column II
(*i*) Soap chips	Soap chips are made by running a thin sheet of melted soap onto a cool cylinder and scraping off the soaps in small broken pieces

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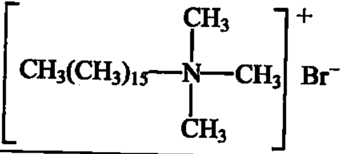
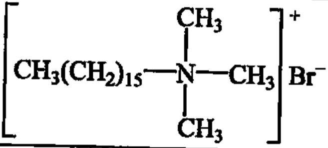
(*ii*) Soap granules	Soap granules are dried miniature soap bubbles.
(*iii*) Soap powder	Soap powders contain some soap, and builders like sodium carbonate and trisodium phosphate.
(*iv*) Scouring soap	Scouring soaps contain some soap, a scouring agent (abrasive) such as powdered pumice or finely divided sand, and builders like sodium carbonate and trisodium phosphate.

80. Match structures given in Column I with the type of detergents given in Column II.

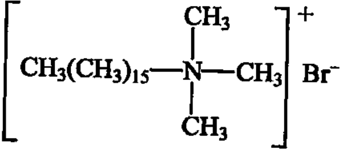
Column I	Column II
(*i*) $CH_3(CH_2)_{16}COO(CH_2CH_2O)_n CH_2CH_2OH$	(*a*) Cationic detergent
(*ii*) $C_{17}H_{35}COO^-Na^+$	(*b*) Anionic detergent
(*iii*) $CH_3—(CH_2)_{10}CH_2SO_3^-Na^+$	(*c*) Nonionic detergent
(*iv*)  $\left[CH_3(CH_3)_{15}—\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{N}}—CH_3\right]^+ Br^-$	(*d*) Soap

Ans. (*i*) → (*c*) (*ii*) → (*d*) (*iii*) → (*b*) (*iv*) → (*a*)

Explanation:

Column I	Column II
(*i*) Nonionic detergent	$CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$
(*ii*) Soap	$C_{17}H_{35}COO^-Na^+$
(*iii*) Anionic detergent	$CH_3—(CH_2)_{10}CH_2SO_3^-Na^+$
(*iv*) Cationic detergent	 $\left[CH_3(CH_2)_{15}—\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{N}}—CH_3\right]^+ Br^-$

81. Match the detergents given in Column I with their uses given in Column II.

Column I	Column II
(*i*)  $\left[CH_3(CH_3)_{15}—\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{N}}—CH_3\right]^+ Br^-$	(*a*) Dishwashing powder

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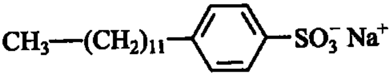
(*ii*) 	(*b*) Laundry soap
(*iii*) $C_{17}H_{35}CO\overset{-}{O}\overset{+}{N}a + Na_2CO_3 +$ Rosin	(*c*) Hair conditioners
(*iv*) $CH_3(CH_2)_{16}COO(CH_2CH_2O)_n$ CH_2CH_2OH	(*d*) Toothpaste

Ans. (*i*) → (*c*) (*ii*) → (*d*) (*iii*) → (*b*) (*iv*) → (*a*)

82. Match the class of compounds given in Column I with their functions given in Column II.

Column I	Column II
(*i*) Antagonists	(*a*) Communicate message between two neurons and that between neurons to muscles.
(*ii*) Agonists	(*b*) Bind to the receptor site and inhibit its natural function
(*iii*) Chemical messenger.	(*c*) Crucial to body's communication process
(*iv*) Inhibitors	(*d*) Mimic the natural messenger
(*v*) Receptors	(*e*) Inhibit activities of enzymes.

Ans. (*i*) → (*b*) (*ii*) → (*d*) (*iii*) → (*a*) (*iv*) → (*e*) (*v*)→ (*c*)

Explanation:

Column I	Column II
(*i*) Antagonists	Drugs that bind to the receptor site and inhibit its natural function are called antagonists. These are useful when blocking of message is required.
(*ii*) Agonists	Compounds that mimic the natural messenger by switching on the receptor, these are called agonists.
(*iii*) Chemical mesengers	Chemical messengers are received at the binding sites of receptor proteins. To accommodate a messenger, shape of the receptor site changes. This brings about the transfer of message into the cell. Thus, chemical messenger gives message to the cell without entering the cell.

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(*iv*) Inhibitors	These can block the binding site of the enzyme and prevent the binding of substrate, or can inhibit the catalytic activity of the enzyme.
(*v*) Receptors	Receptors are proteins that are crucial to body's communication process.

83. Match the classes of drugs given in Column I with their action given in Column II.

Column I	Column II
(*i*) Analgesics	(*a*) Inhibit the growth of microorganisms can be given orally.
(*ii*) Antiseptics	(*b*) Treatment of stress
(*iii*) Antihistamines	(*c*) Applied to inanimate objects
(*iv*) Antacids	(*d*) Prevents the interaction of histamine with its receptor
(*v*) Tranquilizers	(*e*) Pain killing effect
(*vi*) Antibiotics	(*f*) Applied to diseased skin surfaces
(*vii*) Disinfectants	(*g*) Treatment of acidity

Ans. (*i*) → (*e*) (*ii*) → (*f*) (*iii*) → (*d*) (*iv*) → (*g*) (*v*) → (*b*)
(*vi*) → (*a*) (*vii*) → (*c*)

Explanation:

Column I	Column II
(*i*) Analgesics	Analgesics reduce or abolish pain without causing impairment of consciousness, mental confusion, in coordination or paralysis or some other disturbances of nervous system.
(*ii*) Antiseptics	Antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces.
(*iii*) Antihistamines	to prevent the interaction of histamine with the receptors present in the stomach wall.
(*iv*) Antacids	treatment for acidity was administration of antacids.
(*v*) Tranquilizers	Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases.

(*vi*) Antibiotics	Antibiotics were classified as chemical substances produced by microorganisms that inhibit the growth or even destroy microorganisms.
(*vii*) Disinfectants	Disinfectants are applied to inanimate objects such as floors, drainage system, instruments, etc.

V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are correct statement but reason does not explain assertion.

(*ii*) Assertion and reason both are correct and reason explains the assertion.

(*iii*) Both assertion and reason are wrong statement.

(*iv*) Assertion is correct statement reason is wrong statement.

(*v*) Assertion is wrong statement reason is correct statement.

84. Assertion : Penicillin (G) is an antihistamine.

Reason : Penicillin (G) is effective against gram positive as well as gram negative bacteria.

Ans. (*iii*)

Explanation: Penicillin G is a antibiotic and it has a narrow spectrum.

85. Assertion : Sulpha drug contain sulphonamide group.

Reason : Salvarsan is a sulpha drug.

Ans. (*iv*)

Explanation: Salvarsan is antibacterial.

86. Assertion : Receptors are crucial to body's communication process.

Reason : Receptors are proteins.

Ans. (*i*)

Explanation: Receptors are proteins that are crucial to body's communication process. Message between two neurons and that between neurons to muscles is communicated through certain chemicals. These chemicals, known as chemical messengers are received at the binding sites of receptor proteins.

87. Assertion : Enzymes have active sites that hold substrate molecule for a chemical reaction.

Reason : Drugs compete with natural substrate by attaching covalently to the active site of enzyme.

Ans. (*iv*)

Explanation: Substrates bind to the active site of the enzyme through a variety of interactions such as ionic bonding, hydrogen bonding, van der Waals interaction or dipole-dipole interaction.

88. Assertion : Chemical messengers are chemicals that enable communication of message between two neurons or between neurons and muscles.

Reason : Chemicals enter the cell through receptor.

Ans. (*iv*)

Explanation: Binding sites of receptor proteins. To accommodate a messenger, shape of the receptor site changes. This brings about the transfer of message into the cell.

89. Assertion : Transparent soaps are made by dissolving soaps in ethanol.

Reason : Ethanol makes things invisible.

Ans. (*iv*)

Explanation: Ethanol helps scattering the light as it removes air and moisture.

90. Assertion : Sodium chloride is added to precipitate soap after saponification.

Reason : Hydrolysis of esters of long chain fatty acids by alkali produces soaps in colloidal form.

Ans. (*ii*)

91. Assertion : Competitive inhibitors compete with natural substrate for their attachment on the active sites of enzymes.

Reason : In competitive inhibition, inhibitor binds to the allosteric site of the enzyme.

Ans. (*iv*)

Explanation: In competitive inhibition, inhibitor binds to the active sites of the enzymes.

92. Assertion : Non-competitive inhibitor inhibits the catalyic activity of enzyme by binding with its active site.

Reason : Non-competitive inhibitor changes the shape of the active site in such a way that substrate can't recognise it.

Ans. (*v*)

Explanation: This binding of inhibitor at allosteric site changes the shape of the active site.

93. Assertion : Chemical messenger gives message to the cell without entering the cell.

Reason : Chemical messenger is received at the binding site of receptor proteins.

Ans. (*ii*)

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94. Assertion : Receptor proteins show selectivity for one chemical messenger over the other.

Reason : Chemical messenger binds to the receptor site and inhibits its natural fuction.

Ans. (*iv*)

Explanation: Chemical Messenger bind receptors and gives message to the cell without entering the cell.

95. Assertion : All chemicals added to food items are called food preservatives.

Reason : All these chemicals increase the nutritive value of the food.

Ans. (*iii*)

Explanation: These are added to increase the shelf life of stored food and they do not add nutritive value to food.

96. Assertion : Preservative are added to food items.

Reason : Preservatives inhibit the growth of microorganisms.

Ans. (*ii*)

97. Assertion : Artificial sweeteners are added to the food to control the intake of calories.

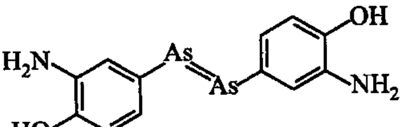
Reason : Most of the artificial sweeteners are inert and do not metabolise in the body.

Ans. (*ii*)

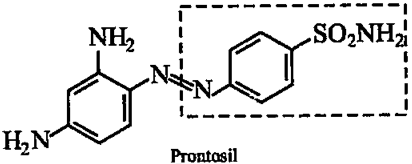
VI. LONG ANSWER TYPE

98. In what respect do prontosil and salvarsan resemble. Is there any resemblance between azo dye and prontosil? Explain.

Ans. Prontosil, which resembles in structure to the compound, salvarsan. Soon it was discovered that in the body prontosil is converted to a compound called sulphanilamide, which is the real active compound.

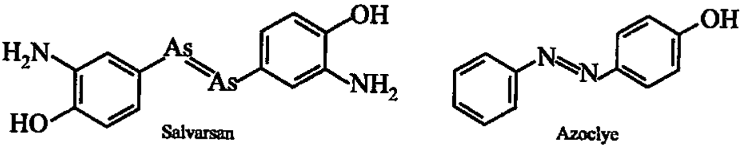


Salvarsan



Prontosil

There is similarity in structures of salvarsan and azodyes. The –As = As– linkage present in arsphenamine resembles the –N = N – linkage present in azodyes in the sense that arsenic atom is present in place of nitrogen.

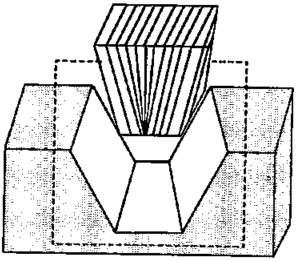


99. How do enzymes catalyse a chemical reaction in the living system? Explain drug target interaction taking the example of enzyme as target.

Ans. In their catalytic activity, enzymes perform two major functions:

(*i*) The first function of an enzyme is to hold the substrate for a chemical reaction. Active sites of enzymes hold the substrate molecule in a suitable position, so that it can be attacked by the reagent effectively.

Substrates bind to the active site of the enzyme through a variety of interactions such as ionic bonding, hydrogen bonding, van der Waals interaction or dipole-dipole.



Enzymes holding substrate

(*ii*) The second function of an enzyme is to provide functional groups that will attack the substrate and carry out chemical reaction.

100. Synthetic detergents have advantage over usual soaps as far as cleansing power is concerned. But use of synthetic detergents over a long time creates environmental pollution. How can the pollution caused by synthetic detergents be minimised? Classify the detergents according to their chemical nature.

Ans. Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap.Synthetic detergents are mainly classified into three categories:

(*i*) Anionic detergents (*ii*) Cationic detergents and (*iii*) Non-ionic Detergents.

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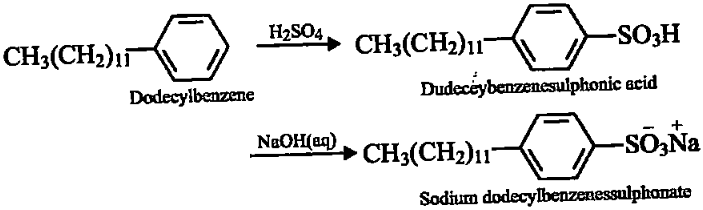
(*i*) **Anionic detergents:** Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. Alkyl hydrogensulphates formed by treating long chain alcohols with concentrated sulphuric acid are neutralised with alkali to form anionic detergents.

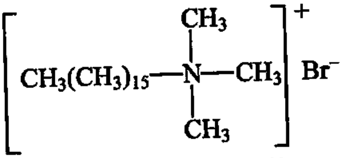
$$\underset{\text{Lauryl alcohol}}{CH_3(CH_3)_{10}CH_2OH} \xrightarrow{H_2SO_4} \underset{\text{Lauryl hydrogensulphate}}{CH_3(CH_3)_{10}CH_2OSO_3H}$$

$$\xrightarrow{NaOH(aq)} \underset{\substack{\text{Sodium laurylsulphate}\\ \text{(Anionic detergent)}}}{CH_3(CH_2)_{10}CH_2OS\overset{-}{O}_3\overset{+}{Na}}$$



In anionic detergents, the anionic part of the molecule is involved in the cleansing action. They are mostly used for household work. Anionic detergents are also used in toothpastes.

(*ii*) **Cationic detergents:** Cationic detergents are quarternary ammonium salts of amines with acetates, chlorides or bromides as anions. Cationic part possess a long hydrocarbon chain and a positive charge on nitrogen atom. Hence, these are called cationic detergents.



$$\left[CH_3(CH_3)_{15}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3 \right]^+ Br^-$$

Cetyltrimethyl ammonium bromide

Cationic detergents have germicidal properties and are expensive, therefore, these are of limited use.

(*iii*) **Non-ionic Detergents:** Non-ionic detergents do not contain any ion in their constitution. One such detergent is formed when stearic acid reacts with polyethyleneglycol.

$$\underset{\text{Stearic acid}}{CH_3(CH_3)_{10}COOH} + \underset{\text{Polyethyleneglycol}}{HO(CH_2CH_3O)_{10}CH_2CH_2OH} \xrightarrow{-H_2O} CH_3(CH_3)_{10}COO(CH_2CH_3O)_{10}CH_2CH_2OH$$

Liquid dishwashing detergents are non-ionic type.

Main problem that appears in the use of detergents is that if their hydrocarbon chain is highly branched, then bacteria cannot degrade

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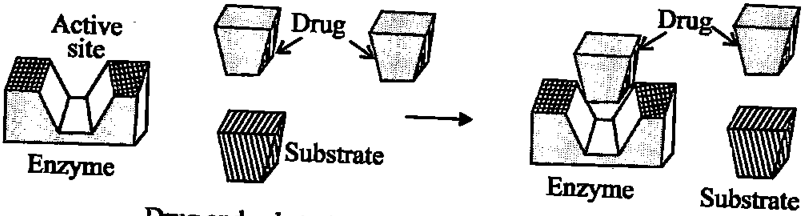
this easily. Slow degradation of detergents leads to their accumulation. These persist in water even after sewage treatment and cause foaming in rivers, ponds and streams and their water gets polluted.

These days the branching of the hydrocarbon chain is controlled and kept to the minimum. Unbranched chains can be biodegraded more easily and hence pollution is prevented.

101. What are enzyme inhibitors? Classify them on the basis of their mode of attachments on the active site of enzymes. With the help of diagrams explain how do inhibitors inhibit the enzymatic activity.

Ans. These can block the binding site of the enzyme and prevent the binding of substrate, or can inhibit the catalytic activity of the enzyme. Such drugs are called enzyme inhibitors. Drugs inhibit the attachment of substrate on active site of enzymes in two different ways;

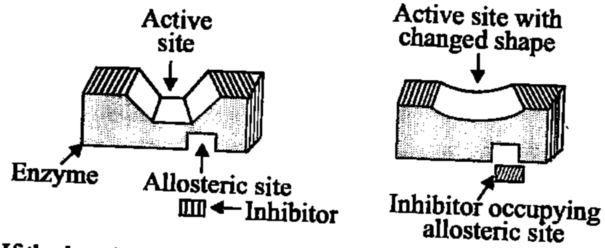
(*i*) Drugs compete with the natural substrate for their attachment on the active sites of enzymes. Such drugs are called competitive inhibitors.



Drug and substrate competing for active site of enzyme

Drug blocks the active site of enzyme

(*ii*) Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site. This binding of inhibitor at allosteric site changes the shape of the active site in such a way that substrate cannot recognise it.



If the bond formed between an enzyme and an inhibitor is a strong covalent bond and cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesises the new enzyme.

❑❑❑